Complex oxides of the system Cu-Ni-Fe-O: synthesis parameters, phase formation and properties

DISSERTATION

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>A- sites</td>
<td>Tetrahedral sites</td>
</tr>
<tr>
<td>B- sites</td>
<td>Octahedral sites</td>
</tr>
<tr>
<td>□</td>
<td>Cation vacancy</td>
</tr>
<tr>
<td>pm</td>
<td>Picometer (=10(^{-12})m)</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom (=100 pm=10(^{-10})m)</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>PDF</td>
<td>Powder Diffraction File</td>
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<tr>
<td>cps</td>
<td>Counts per second</td>
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<td>Absolute intensity</td>
</tr>
<tr>
<td>I(_{rel})</td>
<td>Relative intensity</td>
</tr>
<tr>
<td>TA</td>
<td>Thermal analysis</td>
</tr>
<tr>
<td>C(_o)</td>
<td>Initial concentration of a solution</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential thermal analysis</td>
</tr>
<tr>
<td>DTG</td>
<td>Derivative thermogravimetry</td>
</tr>
<tr>
<td>TG</td>
<td>Thermogravimetry</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>p(O(_2))</td>
<td>Oxygen (O(_2)) partial pressure</td>
</tr>
<tr>
<td>p(H(_2))</td>
<td>Hydrogen (H(_2)) partial pressure</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Atmosphere</td>
</tr>
<tr>
<td>Ar 4.6</td>
<td>Argon 99.996 %vol. (purity)</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon 99.996 %vol. (purity)</td>
</tr>
<tr>
<td>2% H(_2)/Ar</td>
<td>Gas mixture containing 2%H(_2) in argon 4.6</td>
</tr>
<tr>
<td>tSp</td>
<td>Tetragonal spinel</td>
</tr>
<tr>
<td>cSp</td>
<td>Cubic spinel (Cuprospinel)</td>
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1. Introduction

1.1. Focus of the work

Ferrites of general formula $\text{MFe}_2\text{O}_4$ (where $\text{M}$ denotes a divalent cation) are technologically important materials. Their physical properties such as high magnetic permeability and high electrical resistance make them useful for applications in magnetic storage devices, microwave and electronic devices [1-3]. Apart from their technological importance as magnetic materials, ferrites also have well-established catalytic properties for many reactions such as oxidative dehydrogenation of hydrocarbons, decomposition of alcohols as well as good gas sensing properties [4-6]. All these properties strongly depend on their exact chemical composition and their microscopic physical structure. In fact, when these ferrites are used for magnetic or electrical applications, high-density materials are prepared by high temperature solid state reactions between the finely dispersed and the well ground constituent powders. On the other hand, like the application of materials for gas sensors, lower density and higher surface area materials are preferred. Thus, optimal methods that are supposed to prepare these materials have been for very long a major priority of researchers of this community. The large number of methods that have been accordingly developed shows an ever increased interest in this topic [7-10].

Ferrites are usually prepared by the ceramic method which involves reacting oxides, carbonates or other compounds of the component metals with repeated grinding and heating. Since the particle sizes of these starting materials can vary and the mixing operation may reach different degrees of “well mixing”, the calcination temperature is relatively high. Powders obtained are generally coarse-grained with eventually additional mineral phases. Moreover, when heated to high temperatures, the process of evaporation of certain elements (such as lithium (Li)) leads to the formation of chemical inhomogeneous materials [7]. Another inconvenient is the large particle size and the low surface area of the product [8]. In order to overcome the limitations of this ceramic method, new alternatives have been developed. Their common feature is that the mixing of components takes place at the atomic or molecular scale. In most cases, starting materials are finely divided and allow the improvement of the reactivity in comparison with the powder prepared by conventional ceramic method. In one group of these techniques, a solution is formed with cation stoichiometry of the desired ferrite; coprecipitation (with controlled conditions such as the pH and the concentration of the starting solutions) leads to a mixture of very small particles
containing the cations in the right proportion, for instance in the form of hydroxides. In another group, the precipitation occurs by the removal of the solvent either by evaporation (spray-drying) or solidification and sublimation (freeze-drying) or by the addition of a different solvent (sol-gel). In the case of molecular precursors, the technique is based on the preparation of a chemical compound (metal-organic molecule) containing the cations of the ferrite in the desired proportions (polynuclear coordination compounds) [1, 9, 11, 12]. Using these methods, ferrite particles are obtained at relatively low temperatures [1, 9, 10]. Particularly for the precursor method, the major advantages are: (i) the control of stoichiometry in the powder, (ii) the chemical homogeneity on atomic scale, (iii) the high chemical purity and strain free without grinding, (iv) the uniformity of oxide nanoparticles with high surface area commonly exhibiting many unusual and interesting properties [10, 13-15].

Current investigations on spinel ferrites are not confined to the simple formulae “MFe$_2$O$_4$”. Various substitutions have been incorporated to achieve desired electrical and magnetic properties. For instance, the attention of several researchers has been focused on copper ferrites and copper containing ferrites because of their interesting electrical, magnetic properties and crystal changes due to the heat treatment [16-19]. In fact, copper ferrite is distinguished among other spinel ferrites by the fact that it undergoes a structural phase transition accompanied by a reduction in the crystal symmetry to tetragonal due to the Jan-Teller effect [16, 20].

1.2. Outline and scope of the work

It is widely known that a great variety of oxides that possess interesting properties can be synthesized. Among them, those occurring within the system Cu-Ni-Fe-O were chosen because they have been proven as suitable materials for several applications [19, 21-23]. These compounds have been investigated for over fifty years, with emphasis not only on their properties but also and mostly on new synthesis methods that are currently under development. For this reason, the main aim of the present work is to develop promising methods enabling the preparation of oxide phases at relatively low temperatures (T ≤ 700°C). In general a great part of ferrite materials exhibits some degree of oxygen non-stoichiometry and their composition is controlled by the oxygen partial pressure and the temperature [24]. The effect is by far the most pronounced in manganese spinel oxides as well as copper spinel oxides and their derivatives [25-27]. Consequently, another main point of the present work is
to supply the information missing from the literature on the conditions of existence of copper nickel ferrites and their phase transformations during annealing under different atmospheres. These investigations may provide more insights into the influence of the synthesis method and the preparation conditions (\(T, p(O_2)\)) on the composition and properties of oxide materials occurring within the Cu-Ni-Fe-O system. Three synthesis routes have been employed, namely (i) the preparation and the thermal decomposition of freeze-dried carboxylate precursors, (ii) the preparation and the oxidation of intermetallic phases and (iii) the preparation and the heat treatment of mixed oxide/metallic powders. The motivation of the choice of the starting powders comes from the following main points:

(1) it has been generally recognized that the decomposition of carboxylate compounds occurs at lower temperatures (\(T \leq 400^\circ C\)) [9, 28, 29]. To this end, metal carboxylates (oxalate and formate) should be suitable as starting materials for the innovation of the freeze-drying method on the synthesis of oxide powders in the Cu-Ni-Fe-O system. Note that the advantage of this method over the other chemical methods is its reproducibility;

(2) according to the thermodynamic data [30, 31], the composition of the products obtained from the decomposition of simple and complex metal carboxylate compounds depends on the conditions of the experiment (oxygen partial pressure (\(p(O_2)\)), temperature (T)). The inclusion of these experimental conditions may help to find out a new route to intermetallic phases. One expects these intermetallic phases to behave as reactive phases since organic precursors are known as starting powders which allow the formation of homogeneous powders in a nanocrystalline state. On the same footing, an electrochemical route developed by Sartale and coworkers [32] has been successfully used for the conversion at room temperature of electrodeposited alloys MFe_2, with M = Cu, Ni and Co, into MFe_2O_4 thin films;

(3) the common ceramic method, using mixed oxide/metallic powders as starting material, was performed in order to find the most probable course of the solid state reaction occurring through the synthesis ways (i) and (ii) above. Ferrites of similar composition differ in their properties depending on the preparation technique. Due to this fact, the determination of the magnetic and electrical properties of selected compounds should be carried out.

After this introduction (Chapter 1), the rest of work is organised as follows. Chapter 2 presents basic structures and properties of some phases of the Cu-Ni-Fe-O system. Synthesis of simple and complex oxide materials in Cu-Fe-O and Ni-Fe-O systems are then detailed in Chapter 3 and 4. For this purpose, four different starting materials were used, namely oxalate as well as formate freeze-dried precursors, intermetallic phases, mixture of oxides
(CuO, $\alpha$-Fe$_2$O$_3$ as well as NiO, $\alpha$-Fe$_2$O$_3$) and mixture of metals (Cu-Fe/Ni-Fe). The preparation of intermetallic phases was performed by heat treatment under hydrogen atmosphere of metal carboxylate precursors and oxide phases prepared from the three other starting materials. Furthermore, the reactivity of the synthesized intermetallic phases was deduced from their thermal behaviour in air. Depending on the heat treatment conditions, copper and iron can be stabilized in two valences Cu$^+/\text{Cu}^{2+}$ and Fe$^{2+}/\text{Fe}^{3+}$, respectively. This indicates that the phase formation in the Cu-Fe-O system is influenced by the composition of the surrounding atmosphere. Moreover, in Chapter 3, an extensive study is performed in this area between 800 and 1200°C for the oxygen pressure ranging from 10$^{-5}$ to 0.209 atm. The electrical conductivity and/or magnetic properties of some synthesized copper- and nickel ferrites are given in Chapters 3 and 4, respectively. Chapter 5 describes the thermal studies on solid solutions of mixed Cu-Ni formate complexes synthesized by the freeze-drying method. In Chapter 6, the ferrites Cu$_{1-x}$Ni$_x$Fe$_2$O$_4$ (0 < x < 1) are synthesized by thermal decomposition of solid solution formates and the magnetic properties of some of them are determined. Moreover, other single spinel phases in the field Cu$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$-Cu$_{0.9}$Fe$_{2.1}$O$_4$-Cu$_{0.5}$Fe$_{2.5}$O$_4$ are prepared under special p(O$_2$)/T-conditions. Finally, the Chapter 7 provides concluding remarks on this work.
2. **Systems within Cu-Ni-Fe-O: structures and properties**

In the past, binary and ternary systems including copper, iron, nickel and oxygen have been investigated in order to improve on the properties of alloy and oxide phases formed within them. Traditionally, the preparation of oxide materials is carried out by means of a high-temperature reaction between finely milled oxide powders. The raw materials are usually iron oxide ($\alpha$-$\text{Fe}_2\text{O}_3$) and the metal oxide (MO, $M = \text{Cu, Ni} \ldots$) of the other cations in the desired ferrite. From Figure 2.1, one clearly sees that metallic or alloy phases can also be used as starting materials. Based on this observation, one of our objectives is to draw up a relationship between the nature of metallic/alloy phases and their oxidation processes. For this interest, the purpose of this chapter is to present an overview of the binary systems Cu-Fe and Ni-Fe. After that, a brief description of the spinel oxides (structure and properties) will be given as well as some characteristics of NiO-CuO solid solutions.

![Figure 2.1: Quaternary system Cu-Ni-Fe-O (only the important compounds for the present overview are shown).](image)

*Figure 2.1:* Quaternary system Cu-Ni-Fe-O (only the important compounds for the present overview are shown).
2.1. Metallic Systems

The transitions elements iron (Fe), copper (Cu) and nickel (Ni) have long been used in a wide variety of applications because of their desirable properties, such as their conductivity of electricity and heat, magnetic properties, their malleability and ductility. Copper and nickel crystallize with a face-centred cubic structure (fcc) while, iron exists in three different forms: the ordinary iron or $\alpha$Fe with a body centred cubic (bcc) structure, the $\gamma$Fe with a face centred cubic (fcc) structure and the $\delta$Fe with a bcc structure. The transitions from $\alpha$Fe to $\gamma$Fe and from $\gamma$Fe to $\delta$Fe occur at about 1179 and 1674K, respectively [2, 33]. These metallic elements readily form alloys with other elements (e.g. a copper-tin alloy is used for mirrors; brass is a copper-zinc alloy…). From such combinations, the properties of the resulting material can be enhanced compared to those of pure metals. This is the case for Fe-based alloys (Fe-Si alloys, Fe-Al alloys, Ni-Fe alloys…) [2, 34].

Fe-Cu system

The phase diagram of the system Fe-Cu indicates a nearly immiscibility between Cu and Fe in the equilibrium solid state [35, 36]. This behaviour is in accordance with the positive value of the calculated heat of mixing between Cu and Fe [37]. However, by using special techniques such as vapour deposition [38, 39], thermal evaporation [40], sputter deposition [41] or mechanical alloying [42-47], the solid solubility can be extended and metastable Cu-Fe solid solutions can be formed over the composition range 0-100%. In general, a single phase bcc structure is obtained for small x (in the Fe rich region) whereas for large x (in the Cu-rich side) an fcc structure is obtained. Besides, the phase boundaries to the coexistence region of fcc and bcc phase depend on the method of preparation. Using the mechanical-alloying [43] and the thermal evaporation methods [40], this coexistence region was found to be $0.6 \leq x \leq 0.8$ and $0.4 \leq x \leq 0.6$, respectively. The thermal treatment at elevated temperatures, 300°C to 600°C [38], gives rise to the decomposition of metastable Cu$_x$Fe$_{1-x}$ alloys followed by a Fe-Cu segregation. An overall increase in the mean diameter of the original particles is observed [45-47].
The phase diagram of the Fe-Ni system is rather complex and strongly temperature-dependent [36]. The equilibrium phases of the Ni-Fe system are: (1) the liquid; (2) the (δFe) solid solution based on the high temperature bcc Fe; (3) the fcc Fe-Ni solid solution called taenite (γFe,Ni) based on the fcc Fe and Ni; (4) the bcc Fe-Ni solid solution called kamacite (αFe) which is a nickel poor phase based on the low-temperature bcc Fe; and (5) the FeNi₃ intermetallic compound (awaruite), which is formed below 790K and has an extended range of solid solubility. The metastable ordered structures Fe₃Ni and FeNi have been proposed by several authors [55, 56]. Table 2.1 presents the composition and crystal structure data of the known phases of the Fe-Ni system.

**Table 2.1:** Composition and crystal structure of known phases of the Fe-Ni system [36, 55, 56]

<table>
<thead>
<tr>
<th>Phase</th>
<th>(δFe)</th>
<th>(γFe,Ni)</th>
<th>(αFe)</th>
<th>FeNi₃</th>
<th>Fe₃Ni</th>
<th>FeNi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition at. % Ni</td>
<td>0 to 3.5</td>
<td>0 to 100</td>
<td>0 to 5.5</td>
<td>63 to 85</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>Space group</td>
<td>Im 3m</td>
<td>Fm 3m</td>
<td>Im 3m</td>
<td>Pm 3m</td>
<td>Pm 3m</td>
<td>P4/mmm</td>
</tr>
</tbody>
</table>

At temperatures lower than 800ºC, the α + γ field in the Fe-Ni system is relatively broad and the attainment of equilibrium involves considerable diffusion. Diffusion rates at these lower temperatures are low, and then very long times are required to establish the equilibrium state. In order to reduce the time required to attain the phase equilibrium, distinct methods have been employed: the mechanical alloying [48, 49, 51], the electrodeposition [34, 52, 53] and the chemical reduction method [54]. Using these methods, an extension of the concentration ranges of the single-phase solid solution of Fe-Ni alloys is observed. Samples with low nickel concentrations have a bcc structure, while those with high nickel concentrations have a fcc one. Using the electodeposition [34] and the mechanical alloying [49] methods, the phase coexistence region of the bcc and the fcc phases is observed for nickel concentrations in the range 30-50 wt% Ni and 22-28 at% Ni, respectively. Moreover, it has been established that the existence of the fcc Ni-Fe alloy can be extended on a very wide concentration range 22-100 % at Ni, when the mechanical alloying process is followed by an annealing of samples at 650ºC in argon atmosphere [48, 49].
2.2. Oxide systems

2.2.a. Oxide spinels

Structures

Ferrites with the spinel-type structure may be described by the general formula MeFe₂O₄, where Me are divalent cations (Cu²⁺, Ni²⁺, Cd²⁺...). The space group of ferrites is Fd³m and the lattice parameters are typically ~ 8.5Å. The oxygen anions are arranged in a face-centered cubic (fcc) lattice. Each unit cell contains 8 formula units with O²⁻ anions in the 32(e) sites, and metal cations reside on 8 of 64 tetrahedral sites (A- sites) and 16 of the 32 octahedral sites (B- sites) [1, 58]. A whole range of possible cation distributions is observed. Therefore, in order to fully characterize the spinel structure, the parameter δ describing the degree of inversion is needed. The chemical formula of spinel ferrites can be represented in general by (Me⁺²Fe⁺³)₄[Me⁺²Fe⁺³₂]O₄²⁻, where the cations in ( ) are on tetrahedral sites and those in [  ] are on octahedral sites. According to the value of δ there are several types of ferrospinels:

(i) **normal spinel structure**: all Me²⁺ ions occupy the A- sites (δ = 0). The structural formula of such ferrites is Me²⁺[Fe³⁺₂]O₄²⁻. This type of cations distribution takes place in the zinc ferrite, Zn²⁺[Fe³⁺Fe⁺³]O₄²⁻, for example.

(ii) **inverse spinel structure**: all Me²⁺ are in the B- positions and all Fe³⁺ ions are equally distributed between the A- and B- sites (δ = 1). The structural formula of these ferrites is Fe³⁺[Me⁺²Fe⁺³]O₄²⁻. For example, NiFe₂O₄ and CoFe₂O₄ have this structure.

(iii) **mixed spinel structure**: Me²⁺ and Fe³⁺ cations occupy both the A- and the B-positions. The value of δ describing the fraction of Me ions on the octahedral sites is situated between zero and one. Copper ferrite represents this type of structure and has an inversion degree which is affected remarkably by the temperature. In fact, the lowering of the annealing temperature leads to an increase of the Cu²⁺ ions concentration on the B-sites. The tetragonality of copper ferrite is a result of sufficient concentration of copper ions on the B-sites. The value of δ should exceed 0.66-0.8 [59-61]. When the concentration of the Cu²⁺ cations in octahedral sites is less than these critical values, the symmetry is cubic. In some cases the cubic and the tetragonal phase coexist.

The literature review indicates that a well-known characteristic of the iron oxide family is the variety of possible conversions between the different phases: FeO, Fe₃O₄ and Fe₂O₃ (γ-Fe₂O₃, α-Fe₂O₃) [62-64], to name a few. Both magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) are
spinels whereas hematite (α-Fe2O3) crystallizes in the corundum structure (space group \( R \bar{3}c \)). The basic structure of \( \gamma \)-Fe2O3 is closely related to that of the inverse spinel Fe3O4 \( \text{“(Fe}^{3+})[\text{Fe}^{3+}\text{Fe}^{2+}]\text{O}_4” \) but differs from the latter by the presence of vacancies distributed on the cation sublattice. Its formula can be written \( (\text{Fe}^{3+})[\text{Fe}^{3+}\frac{1}{2}\text{Fe}^{2+}\frac{1}{2}]\text{O}_4 \), where \( \Box \) represents the lattice vacancies. The ordering of these vacancies within the octahedral positions can give rise to several crystal symmetries [65-68]. The varieties characterized by a totally random, a partly ordered and a totally ordered vacancy distribution have a face-centred cubic, a primitive cubic and a tetragonal structure, respectively. The respective space groups are Fd\( \bar{3}m \), P4\( _{1}32 \) and P4\( _{2}2_{1}2_{1} \).

Properties

Magnetic properties

Spinels represent a classical example of a crystal structure allowing a special type of magnetic order called ferrimagnetism [2, 57, 69]. This property results from the antiferromagnetic coupling between the magnetic moments of the ions on the tetrahedral and octahedral sublattices, which are crystallographically non equivalent. Consequently, the net magnetization moment of spinel oxides at a temperature \( T \) below the Curie temperature \( T_c \) is given by the relation,

\[
M(T) = M_B(T) - M_A(T)
\]

where \( M_B(T) \) and \( M_A(T) \) are the magnetization of octahedral and tetrahedral sublattices, respectively. The spontaneous magnetization occurring at 0 K can be estimated on the basis of composition, cation distribution and relative strength of possible interactions. In the inverse ferrites, one half of Fe\(^{3+}\) is placed on the A- sites and another half on the B- sites. Their magnetic moments are mutually compensated and the resulting moment of the ferrite is due to the magnetic moments of bivalent cations Me\(^{2+}\) on the B- positions. For instance at 0 K, the total magnetic moment per formula unit of nickel ferrite \((\text{Fe}^{3+})[\text{Ni}^{2+}\text{Fe}^{3+}]\text{O}_4 \) can be written: \( M(0K) = (5 + 2) - (5) = 2 \, \mu_B \). The experimental value is 2.3 \( \mu_B \). For the inverse copper ferrite \( “(\text{Fe}^{3+})[\text{Cu}^{2+}\text{Fe}^{3+}]\text{O}_4” \), the theoretical and experimental values of \( M(0 \, K) \) are 1 and 1.3 \( \mu_B \), respectively [1, 40]. For 85% inverse CuFe\(_2\)O\(_4\), the value of the saturation magnetization moment per formula unit measured is 2.2 \( \mu_B \) [17]. Small deviations are observed between experimental and theoretical results. This discrepancy is usually attributed to the fact that for theoretical calculations, some parameters such as the small orbital contribution are neglected.
Additionally, the established cation distribution may not be the same experimentally. For instance Cu$_{0.5}$Fe$_{2.5}$O$_4$ should exhibit ideally a net saturation magnetic moment of 7.5µ$_B$ at 0K. However, the site distribution of copper ions over the available sites in the spinel is complicated by the multivalent nature of the copper ions. It turns out that the measured moment of Cu$_{0.5}$Fe$_{2.5}$O$_4$ varied from 4.05 to 5.40 µ$_B$ [70-72].

It is generally found that ferrites of similar composition differ in their magnetic properties depending on the preparation technique (synthesis method, quenching as well cooling rates). One reason for such behaviour is the differences in the particle sizes. In fact, the decrease in the particle sizes leads to the increase of the magnetic order on the particle surface. For instance zinc ferrite “ZnFe$_2$O$_4$”, which is assumed to be a normal spinel, is a standard example of antiferromagnetic materials with a Neel temperature at 10K. However, ultrafine ZnFe$_2$O$_4$ have been reported to be exhibiting a net magnetic moment at room temperature [74]. The magnetization (M$_s$) is defined as the magnetic moment per unit volume:

$$\mathbf{M}_s = \frac{8n\mu_B}{V}$$  \hspace{1cm} (2)

where $n$ is the number of magnetic moments per formula unit MFe$_2$O$_4$, $8$ is the number of formula units per cell and $V$ is the volume of the unit cell [2]. The specific saturation or magnetization per gram ($\sigma_s$) [75] is expressed by the relation:

$$\sigma_s = \frac{M_s}{d} = \frac{n \mu_B N 10^3}{M} \left( \frac{d}{g/cm^3} \right) = \frac{8 M}{N V}$$  \hspace{1cm} (3)

where $d$ is the density of the ferrite, $N = 6.022045 \times 10^{23} \text{ mol}^{-1}$ (Avogadro’s number), 1 emu = 10$^3$ A. m$^2$, $\mu_B = 9.274078 \times 10^{-24}$ A.m$^2$ and $M$ is the molecular weight of the ferrite. Furthermore, $\sigma_s$ can also been expressed as follows [76]:

$$\sigma_s = \frac{M_s}{d} = \frac{\left(4\pi M_s \right)}{4\pi d} \left( \text{emu} \cdot \text{g}^{-1} \right) \left( \text{Gauges} \right)$$  \hspace{1cm} (4)

As the temperature increases, the ferromagnetic materials undergo a transition from an ordered ferromagnetic phase for $T < T_C$ to a disordered paramagnetic phase at $T > T_C$ [3]. The spinel family that offers the most promise for increased $4\pi M$ values at 300K is the generic cation system Fe$_{3-x}$A$_{x}$[B$^{1+}$$_{0.5-x}$Fe$_{3+}$$_{1.5+x}$]O$_4$, where A$^{1+}$ and B$^{1+}$ represent Li$^{1+}$, Na$^{1+}$ or Cu$^{1+}$. In general, the optimum thermomagnetization properties in ferrites result from (i) maximizing the octahedral B- sublattice magnetic moment and (ii) selecting the optimum compromise
between the reduction of the tetrahedral A- sublattice moment and the maximization of the number of $\text{Fe}_A^{3+} \leftrightarrow \text{Fe}_B^{3+}$ exchange couplings [57, 77].

**Electrical properties**

Both semiconductors and magnetic materials exhibit interesting properties that could be used in electronic devices. This is the case of ferrites which are ferrimagnetic semiconductors. The electrical conductivity of ferrites varying between $10^{-11}$ and $10^2 \Omega^{-1}.\text{cm}^{-1}$ is low compared to those of other semiconductor materials ($10^{-5} - 10^2 \Omega^{-1}.\text{cm}^{-1}$). In fact the conduction mechanism in ferrites is quite different from that in other semiconductors. For instance, in ferrites the temperature dependence of the mobility affects the conductivity and the carrier concentrations is almost unaffected by temperature variation. Unlike in semiconductors wherein the charge carriers occupy states in wide energy bands, the charge carriers in ferrites are localized at the magnetic atoms. The measurement of the conductivity ($\sigma$) of solids can be done either by a two-probe or four-probe method. In the two-probe technique, the resistance is measured across the sample with an ohmmeter. The main disadvantage of this method is that the contact resistance is included as a part of the sample resistance, introducing serious errors in the results. For the four-probe method two probes are used to pass current through the sample and two other probes are connected to a voltmeter which has a high input impedance. The advantage of this method is that the high impedance voltmeter “sees” only the sample and not the current contacts. Therefore, errors due to contact resistance are eliminated. After the measurement of the resistance of a solid, the conductivity ($\sigma$) is given as:

$$\sigma = \frac{\ell}{R \times A}$$

where $\ell$ is the length of the sample (cm), A is the cross-section area (cm$^2$) and R is the resistance (Ω). In ferrite materials, a considerable increase of $\sigma$ is connected usually with the combined effect of disorder and the presence of cations able to change easily their valency states or actually coexisting with different valencies in the material. Typical examples are bivalent and trivalent Fe or Co in the B- positions. The charge transfer may then be carried out by hopping of electrons or holes between equivalent ions (valency exchange). The sign of the Seebeck coefficient (thermopower) is often helpful in clarifying the nature of the dominating charge carriers and the mechanism of their motion. For the CuFe$_2$O$_4$ spinel phase, the Seebeck coefficient data show the p-type and n-type conductions at room temperature and
at high temperatures, respectively [78, 79]. The temperature dependence of the electrical conductivity is given by the relationship:

\[ \sigma = \sigma_0 \exp \left[ - \frac{E_\delta}{kT} \right] \]  

(k is the Boltzmann constant, \(E_\delta\) is the activation energy in the conduction process and \(\sigma_0\) is a constant). In many ferrite systems it is observed that the slope of the \(\ln \sigma = f(1/T)\) curves changes at the Curie point. The activation energy increases as the ferromagnetic changes to the paramagnetic region [3]. This anomaly strongly supports the influence of the magnetic ordering upon the conduction process in ferrites.

### 2.2.b. CuO-NiO system

Copper and nickel form a substitutional solid-solution without miscibility gap but their oxides Cu$_2$O, CuO and NiO, exhibit small mutual solubilities [80]. Whereas the monoclinic CuO dissolves only approximately 5\% of NiO in its network, an appreciable solubility from 20 to 30\% of CuO in NiO is observed towards 900°C [81, 82]. Above this temperature, the solid solutions (CuO)$_x$(NiO)$_{1-x}$ with higher copper content \((x > 0.25)\) show a tetragonal distortion from the cubic symmetry. There have been some discrepancies in the interpretation of this distortion. Some authors [81-83] found that it is due to the cation ordering whereas the others pointed out the existence of the Jan-Teller effect which becomes cooperative above a critical concentration of Cu$^{2+}$ ions \((x > x_c \approx 0.25)\) [84-86].
3. System Cu-Fe-O

Depending on the cation distribution among the interstitial sites of the spinel structure, copper ferrite crystallizes either in a tetragonal or cubic symmetry [59, 87]. The tetragonal phase which is stable at low temperatures is a mixed spinel phase; the Fe$^{3+}$ ions occupy both the tetrahedral A- and the octahedral B- sites in about equal amount. The cubic phase is stable at temperatures higher than 360°C, but is obtained also as a metastable phase at room temperature by quenching from high temperatures. In such case, more Cu$^{2+}$ ions occupy the A-sites and the tetragonal distortion diminishes. Prince and Treuting [20] carried out a neutron diffraction study on the copper ferrite powder. They found that the most probable space group for the tetragonal phase is I4$_1$/amd with $a = 5.81\,\text{Å}$ and $c = 8.71\,\text{Å}$ (four formula units). This correlates with the $c/a$ value of 1.06 of the larger unit cell, $a_0 = 8.22\,\text{Å}$ and $c_0 = 8.71\,\text{Å}$, with eight formula units. Besides, the cubic phase is assumed to possess the space group of the ideal cubic spinels (Fd$\bar{3}$m). The XRD patterns of the two crystallographic structures of CuFe$_2$O$_4$ are shown on Figures A1 and A2 (Section 11.1). The cuprous ferrite “CuFeO$_2$” belonging to the space group R$\bar{3}$m is one of the typical stable compound in the Cu-Fe-O ternary system exhibiting the so-called delafossite structure. Under reduced atmosphere, it is generally identified as being the principal product of decomposition of copper ferrite powders.

3.1. Literature review on the synthesis of copper ferrite

Yund and coworkers [88] have investigated for the first time the extensive phase diagram on the Cu-Fe-O system. In addition to the stable phases observed in binary systems Cu-O and Fe-O, they found two ternary phases such as delafossite “CuFeO$_2$” and cupric ferrite “CuFe$_2$O$_4$”. No solid solution between CuFe$_2$O$_4$ and Fe$_3$O$_4$ was identified at temperatures below 800°C. Another investigation focusing again on the phase relation of Cu-Fe-O was carried out as function of the temperature and the oxygen partial pressure ranging from 800 to 1500°C and from 0.21 to 1 atm, respectively [89]. The authors were able to demonstrate the existence of a region of continuous solid solution between CuFe$_2$O$_4$ and Fe$_3$O$_4$. Further investigations performed by several other authors [90-92] confirmed this result. In general, the attention of researchers has been mostly paid on CuFe$_2$O$_4$ and Cu$_{0.5}$Fe$_{2.5}$O$_4$ [25, 27, 59, 94-97]. The main result that comes out regarding copper ferrite is that a pure phase “CuFe$_2$O$_4$” can not be synthesized using the conventional ceramic method [59, 94, 95, 97].
For instance, Mexmain [94] shows that the formation of that pure phase in air is prevented by the reduction of $\text{Cu}^{2+}$ to $\text{Cu}^{+}$ taking place at the beginning of the solid state reaction between $\text{CuO}$ and $\alpha\text{-Fe}_2\text{O}_3$ ($T = 800^\circ\text{C}$). Following the same method, Brabers and Klerk [95] have prepared a number of polycrystalline samples $\text{Cu}_x\text{Fe}_{3-x}\text{O}_{4+\lambda}$ (with $x = 0.84, 0.88, 0.92, 0.96$ and $1$). From this investigation, the formation of monovalent copper “$\text{Cu}^{+}$” is confirmed while in samples prepared in oxygen atmosphere at $920^\circ\text{C}$, the spinel phase has the composition $\text{Cu}_{0.96}\text{Fe}_{2.04}\text{O}_{4+\lambda}$. Moreover, this spinel phase is found [25, 94, 97] to be a solid solution of $\text{CuFe}_2\text{O}_4$ and $\text{CuFe}_5\text{O}_8$ with $\lambda$ which depends on the working conditions (temperature, atmosphere, cooling temperature…). Besides, $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$ is commonly found to be thermodynamically stable only under the synthesis conditions (in air above $1200^\circ\text{C}$). In fact, below $1200^\circ\text{C}$, this compound leads to hematite ($\alpha\text{-Fe}_2\text{O}_3$) and delafossite (CuFeO$_2$) [27, 96]. It is worth to recall that different chemical methods have been also used for the synthesis of copper ferrite; the co-precipitation [23, 98-106], the sol-gel [23], the citrate process [107] and the combustion synthesis method [108]. From some of these studies the authors found that a synthesis temperature above $700^\circ\text{C}$ is required for the preparation of copper ferrite [98-103]. When the synthesis is possible below $400^\circ\text{C}$, the resulting spinel phase is metastable. In most cases the product contains some impurities namely traces of oxide phases ($\text{CuO}$ or $\alpha\text{-Fe}_2\text{O}_3$) [103, 109] or amorphous phases [110].

In the literature, the aforementioned methods have been commonly found to be suitable for the synthesis of transition metal oxides. However with regard to the synthesis of the copper ferrite some failures are observed. Nevertheless, one notes a lack of information on the influencing parameters. Moreover, investigations on the compounds having the composition $\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_{4+\lambda}$ ($0 < x < 0.5$) are uncommon and up to now, no work has been carried out on synthesis of copper ferrite starting from the freeze-dried precursors. The following part of this chapter is based on a review of the synthesis of copper ferrite using the ceramic method. It represents a reference investigation which may help to get insights on the phase formation according to the preparation conditions. The next two parts are mainly based on the elucidation of chemical processes that take place during the synthesis of copper ferrite from freeze-dried oxalate and from freeze-dried formate. We then explore the possibility of using metallic phases as starting material for the synthesis of single spinel phase of $\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_{4+\lambda}$ ($0 \leq x \leq 0.5$). Finally in the last part, the influence of the temperature ($T$) and the oxygen partial pressure $p(O_2)$ on the phase formation and stability is studied.
3.2. Solid state reaction - for comparison

Intimate mixtures of pure oxides CuO and $\alpha$-Fe$_2$O$_3$ with the final composition Cu$_{1-x}$Fe$_{2+x}$O$_{4+z}$ ($x = 0, 0.1$ and $0.5$) were obtained by using the mechanical milling method (Section 8.1). Afterwards, they were heated in air at $700^\circ$C, $800^\circ$C and $1000^\circ$C during 24 hours then removed from the furnace and cooled down to RT inside a dessicator. The as-prepared samples were then ground to the fine particle size and characterized using the XRD method. Figure 3.2.1 illustrates the obtained XRD patterns. After annealing at $700^\circ$C which ever the value of $x$, the indexed peaks correspond to CuO and $\alpha$-Fe$_2$O$_3$ phases. At $800^\circ$C, copper ferrite “CuFe$_2$O$_4$” is formed as main phase whereas CuO and $\alpha$-Fe$_2$O$_3$ become the second phases. By further increase of the calcination temperature up to $1000^\circ$C, it is found that the composition of end products depends on $x$: (1) for $x = 0$ (Fig. 3.2.1(a)), the diffraction peaks of $\alpha$-Fe$_2$O$_3$ disappear completely but a small amount of CuO remains as second phase beside the tetragonal copper ferrite ; (2) for $x = 0.1$ (Fig. 3.2.1(b)), a single phase of tetragonal copper ferrite with lattice parameters of $a = 585.2$ pm and $c = 859.0$ pm is identified and (3) for $x = 0.5$ (Fig. 3.2.1(c)), $\alpha$-Fe$_2$O$_3$ is the second phase beside a tetragonal distorted spinel phase.

Partial conclusion

From the above, it turns out that the solid interaction between CuO and $\alpha$-Fe$_2$O$_3$, leading to the formation of copper ferrite, begins only above $700^\circ$C. Up to $1000^\circ$C, a single spinel phase is formed for the sample with $x=0.1$ “Cu$_{0.9}$Fe$_{2.1}$O$_4$”. For the composition CuFe$_2$O$_4$ ($x = 0$) free CuO is present in the product. This is due to the partial reduction of some Cu(II) to Cu(I), taking place around $800^\circ$C. In accordance with several authors, one may expect that the spinel phase CuFe$_2$O$_4$ prepared by the ceramic method is composed of a copper poor spinel phase and a small amount of CuO [59, 94, 95]. When the synthesis of CuFe$_2$O$_4$ is performed in oxygen [95], Cu$_{0.96}$Fe$_{2.04}$O$_4$ is formed. On synthesis in air “Cu$_{0.9}$Fe$_{2.1}$O$_4$” should be the spinel with the maximum copper content. When the iron content in the sample increases, temperatures above $1000^\circ$C should be required for the synthesis of single spinel phases “Cu$_{1-x}$Fe$_{2+x}$O$_{4+z}$” with $0.1 < x \leq 0.5$. With regards to the synthesis of a pure CuFe$_2$O$_4$, a low synthesis temperature ($T < 800^\circ$C) seems to be suitable.
Figure 3.2.1: XRD patterns of CuFe$_2$O$_4$ (a), Cu$_{0.9}$Fe$_{2.1}$O$_4$ (b), Cu$_{0.5}$Fe$_{2.5}$O$_4$ (c) obtained after annealing of CuO and α-Fe$_2$O$_3$ mixtures at different temperatures (24 hours). Atm.: air.

From preceding works, a synthesis made on the basis of carboxylate compounds should be more recommended because of the characteristics (low temperature of decomposition) of very fine particles of these powders [9, 111]. As a consequence, the thermal decomposition of oxalate precursors deserves to be carefully studied.
3.3. **Synthesis of copper ferrite from the freeze-dried oxalate precursors**

The thermal decomposition of oxalates yields oxides or metals which are suitable for enhancing solid state reactions. Therefore, various mechanisms of decomposition have been proposed focusing on their thermal behaviour.

Several authors have investigated the thermal decomposition of ferrous, ferric and complexes of iron oxalate [112-118]. Dollimore et al [112] found that the decomposition of iron(II) oxalate in inert atmosphere leads to the formation of a metal oxide and a gaseous mixture of CO and CO₂. This result was confirmed in later works performed by several authors [113-115]. Using Mössbauer investigations, Gallagher and coworkers [116] found that during the thermal decomposition of iron(III) oxalate, the valency change of iron(III) to iron(II) occurs at 250°C. In air as well as in nitrogen, the decomposition temperatures of iron(III)- and of iron(II) oxalate differ but the end products are similar [117]. In the same footing iron(III) tris oxalato ferrate(III) tetrahydrate “Fe[Fe(C₂O₄)₃].4H₂O” and iron(III)-oxalate “Fe₂(C₂O₄)₃.5.3H₂O” decompose in air through different decomposition processes but lead to the same product “Fe₂O₃” [118]. The thermal decomposition of the ammonium tris oxalato ferrate(III) trihydrate “(NH₄)₃Fe(C₂O₄)₃.3H₂O” was also studied [117]. In [117] no elucidation was given on the behaviour of the gaseous decomposition products.

As copper oxalate is concerned, its thermal decomposition differs substantially from that of the other transition metal oxalates. In fact in nitrogen, copper oxalate exhibits a strongly exothermic decomposition reaction whereas other transition metal oxalates show one or more endothermic processes. There is a common agreement that the final solid product of CuC₂O₄ decomposition is Cu when the reaction proceeds in inert atmosphere or CuO when the reaction proceeds in air [98, 112, 114, 119]. However it is also reported that Cu₂O can be a final product of CuC₂O₄ decomposition in nitrogen [120]. More recently, Prasad [121] has investigated the thermal decomposition of the complex precursor “Cu(NH₃)₂C₂O₄”. This author found that after the endothermic release of ammonia in nitrogen, the following process corresponding to the decomposition of copper oxalate occurs also endothermically. This finding apparently disagrees with the aforementioned works. Moreover, Hsu and coworkers [120] claimed that, the decomposition of copper oxalate in argon leads to the formation of CuO which is then reduced by CO to a lower oxide (Cu₂O) or to Cu.

Several works have been devoted on the synthesis of copper ferrite from oxalate precursors. The chemical routes commonly used are the hydrolytic decomposition method [99, 100] and
the coprecipitation method [98, 101-104]. Among these works is that of Coetzee et al. [98] that has investigated the thermal decomposition of the co-precipitated mixed oxalate “FeCu(C2O4)2 x 3H2O”. The authors found that in nitrogen gas stream, at a heating rate of 20K/min, the decomposition process takes place between 200 and 400°C and leads to the formation of FeO and Cu2O with the release of CO and CO2. In oxygen atmosphere, the decomposition occurs between 200 and 340°C. The end products are γ-Fe2O3 and CuO. Nanoscaled oxide “CuFe3-xO4” particles were prepared by a “chimie douce” method via decomposition of mixed oxalate Cu(x/3)Fe(3-x/3)C2O4 x 2H2O precursors [101, 102]. The oxalic precursors were first decomposed at 600°C under air flow. After this treatment, spinel particles with x < 0.5 were obtained by further treatments at lower temperatures (T ≤ 290°C) in N2/H2/H2O. For the preparation of thin films of CuFe2O4, Despax et al. [103] used the same synthesis method. XRD studies indicate that, the thermal decomposition followed by an annealing up to 750°C leads to the formation of a product containing a tetragonal copper ferrite and a low quantity of CuO. The thermal decomposition of [Fe(III)2Cu(C2O4)2(ОН)4(H2O)2] obtained by the hydrolytic decomposition of “FeC2O4.2H2O-Cu(CH3COO)2.H2O” was investigated [99, 100]. From the thermal study in air, the authors show that the decomposition takes place in the range 20-300°C. The main processes are the formation and the decomposition of a carbonate complex which are responsible of the release of CO, H2O and CO2. From the XRD studies, the formed product was a poor crystalline spinel phase crystallizing on further heating at higher temperatures. Marinescu and coworkers [105] found that contrarily to other Cu-Fe oxalate compounds, the specific architecture of the coprecipitated trinuclear coordination compound “[Fe2Cu(C2O4)2(ОН)4] x 4H2O” allows the direct synthesis of CuFe2O4 at a relatively low temperature. In this work, one notes however that no research has been carried out in the range 400-600°C, where takes place the transformation of γ-Fe2O3 to α-Fe2O3. This means that the direct formation above 400°C of a pure crystalline spinel phase is not guaranteed by using the coprecipitated trinuclear coordination compound “[Fe2Cu(C2O4)2(ОН)4] x 4H2O”. From another investigation also performed in presence of air [106] the same authors established that during the decomposition of oxalate compounds, the metal-metal connections influence more than the ligand content. Furthermore, they claimed that oxalic coordination compounds obtained in different manners show different decomposition pathways. Tao et al. [23] have employed a hydroxide precursor obtained using the co-precipitation method. After the decomposition of the dried precipitate at 600°C, the authors pointed out the formation of a
pure copper ferrite “CuFe₂O₄”. However, a scrutiny analysis of the XRD pattern presented in this work shows the presence of CuO beside the spinel phase.

From this literature review, we note that thermal analysis studies can provide primary informations regarding the nature and the temperature range of oxide formation. Some parameters such as the structure of oxalate compounds and the kind of atmosphere used during the decomposition may affect the temperature ranges of particular steps, the composition of the gaseous and even the solid products. With regards to the works carried out on mixed Cu-Fe oxalates it is observed that, the attention of researchers has been mostly paid on the study of thermal behaviour in air environment. Besides, less works have been performed in argon. Note however that such investigations are necessary for the elucidation of the solid-state pathway of mixed oxides formation. Apart from the work of Marinescu et al. [105] one sees that high synthesis temperatures (T > 700°C) are commonly required for the synthesis of copper ferrite from oxalate compounds [99-103]. Since it is known that the nature of the precursor influences the characteristics of the final oxides, the subsequent part of the work is going to focus on the study of the thermal decomposition of individual and mixed copper-iron oxalate compounds obtained using the freeze-drying method. The goal of this investigation is the determination of the decomposition process in air and in argon 4.6 of the freeze-dried ammonium Cu₁₋ₓFe₂₊ₓ oxalate precursors (with 0 ≤ x ≤ 0.5) and the exploration of the possibility of using these precursors like starting powders for the direct synthesis of copper ferrite at low temperatures (T ≤ 700°C).

3.3.1. Preparation and characterization of the freeze-dried oxalate precursors

For the synthesis of Cu-ferrites with the composition “Cu₁₋ₓFe₂₊ₓO₄” (0 ≤ x ≤ 0.5), the freeze-dried oxalate powders were prepared as described in Section 8.2. Initial complex oxalate solutions having a low concentration of metal ions, called C₀, as well as those having a larger metal ions concentration (C₀’) were first prepared. The concentration of Cu²⁺ and Fe³⁺ ions in the low concentrated solution (C₀) was determined titrimetrically to be 0.08M and 0.16M. In the more concentrated solution (C₀’), the Cu²⁺ and Fe³⁺ ions concentration were 0.13M and 0.23M, respectively. The starting solutions were mixed in the requested stoichiometric Cu : Fe ratio, namely 1 : 2, 0.9 : 2.1, 0.8 : 2.2, 0.7 : 2.3, 0.5 : 2.5, and then quickly frozen in liquid nitrogen and dried from -40°C to 25°C in a vacuum chamber of a freeze-drying apparatus (alpha 2-4, Christ) under a pressure of about 1Pa.
In the Figure 3.3.1, the XRD patterns of some complex metal oxalate precursors are compared with those of simple metal oxalates from which they were prepared. One sees that the pattern of the ammonium CuFe$_2$ oxalate prepared from the slightly concentrated solution ($C_0$) (Fig. 3.3.1(b)) is somewhat a superposition of the patterns of individual salts (Fig. 3.3.1(a), (e)). For the same precursor, but prepared starting from the more concentrated solution ($C_0'$), the main peak of Cu(II) oxalate appearing at $\sim$$2\theta = 11.6^\circ$ disappears completely (Fig. 3.3.1(c)).

This later remark is also valid for a precursor with weak copper contents “ammonium Cu$_{0.5}$Fe$_{2.5}$ oxalate” (Fig. 3.3.1(d)). From a general point of view, the diffraction peaks of mixed metal oxalate powders (Fig. 3.3.1(b), (c), (d)) are very close to those obtained for the ammonium iron(III) oxalate precursor (Fig. 3.3.1(a)). This fact suggests that, during the freeze-drying process an interaction occurs between the single metal oxalates. In the literature, the possible intrusion of Cu(II) ions in the iron oxalate lattice is well established [100]. Taking into account the former interpretation, it turns out that inside the freeze-dried ammonium Cu(II)-Fe(III) oxalate precursors the interaction between individual salts increases with the concentration of metal ions in the starting solution. It can thus be concluded that the homogeneous state of the freeze-dried precursors ammonium Cu(II)-Fe(III) oxalate is relatively a function of the concentration of the starting solutions used for their preparation.

Figure 3.3.1: XRD patterns of some freeze-dried precursors: (a) ammonium Fe(III) oxalate; (b) ammonium CuFe$_2$ oxalate (from $C_0$); (c) ammonium CuFe$_2$ oxalate (from $C_0'$); (d) ammonium Cu$_{0.5}$Fe$_{2.5}$ oxalate (from $C_0$); (e) ammonium Cu(II) oxalate.

Among the prepared oxalate precursors, those used for thermal analysis (TA) investigations were quantitatively characterized by complexometric titration and elemental analysis.
(Section 9). From the obtained results, their composition is described approximately by the following formulas:

Ammonium copper(II) oxalate: \((\text{NH}_4)_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 1.03(\text{NH}_4)_2\text{C}_2\text{O}_4 \times 1.5\text{H}_2\text{O}\)

Ammonium iron(III) oxalate: \((\text{NH}_4)_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 0.42(\text{NH}_4)_2\text{C}_2\text{O}_4 \times 1.5\text{H}_2\text{O}\)

Ammonium iron(III) oxalate: \((\text{NH}_4)_3\text{Fe}(\text{C}_2\text{O}_4)_3 \times 2.5\text{H}_2\text{O}\) (commercial)

Ammonium copper(II)-iron(III) oxalate: 

\[\text{[CuC}_2\text{O}_4.2(\text{NH}_4)_3\text{Fe}(\text{C}_2\text{O}_4)_3.2.6(\text{NH}_4)_2\text{C}_2\text{O}_4 \times 3.5\text{H}_2\text{O}]\]

The freeze-dried ammonium copper(II)-iron(III) oxalate selected for the thermal analysis (TA) investigations is the one which was prepared from the low concentrated solution \((\text{C}_0)\) containing a Cu:Fe ratio of 1:2.

### 3.3.2. Thermal decomposition of the freeze-dried oxalate precursors

The examination of the thermal behaviour of the freeze-dried oxalate powders was conducted using TA and the mass spectrometry (MS) analysis methods. The X-ray diffraction (XRD) analysis method was used for the identification of the phase composition.

#### 3.3.2.a. Thermal decomposition of ammonium iron(III) oxalate

Figure 3.3.2 illustrates the TA curves (TG and DTA) obtained in air during the decomposition of the freeze-dried and the commercial ammonium iron(III) oxalate.

![Figure 3.3.2: TG curves of (a) the freeze-dried and (b) the commercial ammonium iron(III) oxalate; (c) DTA curve of the commercial sample. Atm.: air; heating rate: 5K/min.](image)
One sees that, the decomposition begins below 100°C by an endothermic release of water. For the freeze-dried sample, the calculated mass loss ($\Delta m_{\text{cal}} = -6.0\%$) corresponding to the loss of 1.5 moles of water for each mole of the precursor is very close to the mass loss ($\Delta m_{\text{exp}} = -5.8\%$) observed from the TG curve. With regards to the commercial sample, the calculated mass loss ($\Delta m_{\text{cal}} = -10.7\%$) corresponding to the elimination of 2.5 moles of H$_2$O per mole of the sample is also close to the experimental value of 10.6%. According to the TG curve, the decomposition of the anhydrous compounds occurs in one step in the range 180-300°C. The simultaneous oxidation of the gaseous decomposition product CO results in the formation of CO$_2$ and, consequently the decomposition process is strongly exothermic. The slight exothermic peak occurring between 480 and 540°C is connected with the oxidation of some pyrolytic carbon (C + O$_2$ → CO$_2$) and/or crystallization processes (Fig. 3.3.2(c)). Up to 800°C, the total mass losses of 82.2 and 80.9 % are registered from the decomposition of the freeze-dried and the commercial sample, respectively. When the solid residue is assumed to be $\alpha$-Fe$_2$O$_3$, these mass losses correlate with the theoretical values of 82.4 and 80.9%, respectively.

For the elucidation of the decomposition processes occurring during the thermal treatment of ammonium iron(III) oxalate, further investigations under inert atmosphere are required. Figure 3.3.3 shows the TA curves obtained in argon. For the freeze-dried sample “(NH$_4$)$_3$Fe(C$_2$O$_4$)$_3$ .0.42(NH$_4$)$_2$C$_2$O$_4$ x 1.5H$_2$O”, the TG curve shows that the loss of water ends at 100°C and the anhydrous sample starts to decompose only above 180°C. With regards to the commercial sample “(NH$_4$)$_3$Fe(C$_2$O$_4$)$_3$ x 2.5H$_2$O”, the dehydration process ends at 120°C and the anhydrous compound becomes stable up to 220°C. The differences observed during this first step should be caused by the different H$_2$O content and the excess of (NH$_4$)$_2$C$_2$O$_4$ of the freeze-dried sample. Note that for both samples the mass loss associated to the dehydration step corresponds to the value obtained in presence of air (Fig. 3.3.2). During subsequent heating, the anhydrous compounds decompose endothermically in three more or less superimposed steps. For the freeze-dried sample two endothermic peaks appear at 240 and 280°C during the first and the second step, respectively. The endothermic process of the third step is not clearly defined, but is materialized on the TG curve by a marked inflexion in the range 300-410°C. This last process is assumed to be related to the decomposition of Fe(II) oxalate formed during the former steps [122]. For the commercial sample, the decomposition ends at 420°C. The first decomposition step of the anhydrous compound is characterized by a sharp endothermic peak with two close maxima appearing at 255 and
275°C. During the second and the third steps, two distinguishable peaks appear at 310 and 390°C, respectively. For both samples under investigations, a very slight gain of mass by the products is observed. The total mass loss including the slight gain of mass, observed at the end of the decomposition, is about 82.8% for the freeze-dried sample and 81.1% for the commercial sample (Fig. 3.3.3, Tables A3 and A4 of the Section 11.2). The observed difference is also caused by the excess of (NH₄)₂C₂O₄ of the freeze-dried sample and the different H₂O content.

![Graph](image)

**Figure 3.3.3:** Thermal analysis (TA) of ammonium iron(III) oxalate (a) freeze-dried sample (b) commercial sample. Atm.: Ar; heating rate: 5K/min.

To elucidate the mechanism of decomposition in argon, the gaseous products occurring were analyzed by the MS analysis method. Moreover, the thermal decomposition of the crystalline ammonium oxalate ((NH₄)₂C₂O₄.H₂O) was studied. Concerning the decomposition of (NH₄)₂C₂O₄.H₂O it was found that the dehydration process occurs below 200°C. Afterwards
the anhydrous compound $\text{(NH}_4\text{)}_2\text{C}_2\text{O}_4$ becomes stable and then decomposes endothermically in the range 200-300°C. For the freeze-dried and the commercial ammonium iron(III) oxalate the MS results are plotted in Figure 3.3.4 and recorded in Tables A3 and A4 (Section 11.2).

\[ \text{(NH}_4\text{)}_2\text{C}_2\text{O}_4 \rightarrow 2\text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2 + \text{CO} \quad (2a) \]

\[ \text{Fe(III)}_2(\text{C}_2\text{O}_4)_3 \rightarrow 2\text{Fe(II)}(\text{C}_2\text{O}_4) + 2\text{CO}_2 \quad (2b) \]
Synthesis of copper ferrite from the freeze-dried oxalate precursors

\[
\begin{align*}
\left(\text{NH}_4\right)_2\text{C}_2\text{O}_4 & \rightarrow \text{H}_2\text{N} - \text{CO} - \text{CO} - \text{NH}_2 + 2\text{H}_2\text{O} \\
\text{H}_2\text{N} - \text{CO} - \text{CO} - \text{NH}_2 & \rightarrow \text{HCN} + \text{NH}_3 + \text{CO}_2
\end{align*}
\] (2c)

As the temperature increases above 300°C, CO and CO$_2$ are the only gaseous decomposition products (process 3). The process (3a) or (3b) should occur when the ratio CO/CO$_2$ is greater than one. On the other hand, the process (3c) is expected when CO and CO$_2$ are released in the same amount.

\[
\begin{align*}
\text{Fe(II)(C}_2\text{O}_4) & \rightarrow 1/2\gamma\text{-Fe}_2\text{O}_3 + 0.5\text{CO}_2 + 1.5\text{CO} \quad (3a) \\
\text{Fe(II)(C}_2\text{O}_4) & \rightarrow 1/3\text{Fe}_3\text{O}_4 + 2/3\text{CO}_2 + 4/3\text{CO} \quad (3b) \\
\text{Fe(C}_2\text{O}_4) & \rightarrow \text{“FeO” + CO}_2 + \text{CO} + \text{(+ traces of O}_2\text{ in argon)} \rightarrow 1/2\gamma\text{-Fe}_2\text{O}_3,\delta \quad (3c)
\end{align*}
\]

For the elucidation of the TA behaviours taking place above 300°C, various thermal treatments were carried out in the range 300-425°C. After reaching the desired temperature, the samples were quenched rapidly to RT under the same atmosphere. Their characterization was done using the XRD analysis method (Figs. 3.3.5 and 3.3.6). For both samples, the diffraction peaks of the product obtained at 300°C match very well with the pattern of the crystalline Fe(II) oxalate (PDF 14-807). Particularly for the freeze-dried sample (Fig. 3.3.5(1)), the partial decomposition of Fe(II) oxalate leads to the formation of an amorphous material (iron oxide phase) which crystallizes with the increase of the temperature.

This is in accordance with the identification of the spinel phase at 380°C. Up to 400°C, the black color of the product confirms the presence of Fe$_3$O$_4$. Due to the broadness of the diffraction peaks appearing around $2\theta = 36°, 43.0°$ and $63.0°$, the presence of some wüstite phase “FeO” is expected. As a consequence of its low stability, FeO is extremely sensitive to small changes in the reaction conditions. This is illustrated by the difference observed at 400°C on the ratio Fe$_3$O$_4$ / FeO of the investigated samples. At 425°C (Fig. 3.3.6), FeO disappears completely while the intensity of the diffraction peaks of the spinel phase increases and correlates very well with that of the spinel phase $\gamma$-Fe$_2$O$_3$ (PDF 25-1402). This indicates that the main reaction occurring up to 425°C is the oxidation of FeO and Fe$_3$O$_4$ to $\gamma$-Fe$_2$O$_3$ by the traces of oxygen present in argon. By heating for 2 hours at 425°C, the oxidation of Fe$_3$O$_4$ is finished and the transition $\gamma$-Fe$_2$O$_3 \rightarrow \alpha$-Fe$_2$O$_3$ leads to the identification of sharp defined peaks of $\alpha$-Fe$_2$O$_3$. 

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Figure 3.3.5: XRD patterns of the decomposition products of ammonium iron(III) oxalate quenched after annealing up to 300°C (a), 350°C (b), 380°C (c), 400°C (d).

(1) freeze-dried sample, (2) commercial sample. Atm.: Ar; heating rate: 5K/min.

Figure 3.3.6: XRD patterns of the decomposition products of the freeze-dried ammonium Fe(III) oxalate quenched after annealing up to 425°C (a) and slowly cooled after annealing at 425°C for 2 hours (b). Atm.: Ar; heating rate: 5K/min.
For the freeze-dried ammonium iron(III) oxalate the main decomposition steps in argon 4.6 can be summarized as follows:

**Scheme 3.3.1:** Main decomposition steps of the freeze-dried ammonium iron(III) oxalate

```
(NH₄)₃Fe(C₂O₄)₃ .0.42(NH₄)₂C₂O₄ x 1.5H₂O

30°C - 100°C (1)

(NH₄)₃Fe(C₂O₄)₃ .0.42(NH₄)₂C₂O₄

180°C - 300°C (2a), (2b), (2c)

Fe(C₂O₄)₂

300°C - 410°C (3a), (3b), (3c)

1/2 "γ-Fe₂O₃"

1/3 "Fe³⁺₂FeⅡO₄"

“FeO”

T > 410°C (oxidation)

1/2 (γ-Fe₂O₃, α-Fe₂O₃)
```

**Partial conclusion**

On the basis of various TA investigations, it is proposed that in argon or in air, the thermal decomposition of the commercial and the freeze-dried iron(III) ammonium oxalate occurs in three main superimposed steps: (i) the dehydration of the precursor, (ii) the decomposition of ammonium oxalate which leads to the reduction of the anhydrous complex to iron(II) oxalate, (iii) the decomposition of the iron(II) oxalate which yields Fe₃O₄ and FeO in argon or γ-Fe₂O₃ in air. Above the decomposition temperature, the oxidation of Fe₃O₄ and FeO to γ-Fe₂O₃ takes place. Afterwards, transition of the metastable phase γ-Fe₂O₃ into the thermodynamically stable one “α-Fe₂O₃” occurs. By means of the TA and the MS results, the exact assignment of
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the decomposition processes occurring during the different steps is complicated due to their superimposition. From the XRD results (Fig. 3.3.5) it turns out that under argon, the thermal decomposition of commercial sample leads to the direct formation of Fe$_3$O$_4$ and FeO at 400°C. However, for the freeze-dried sample, the same products are formed via the intermediate formation of an amorphous phase.

3.3.2.b. Thermal decomposition of ammonium copper(II) oxalate

In argon and in air, the thermal decomposition of the freeze-dried ammonium copper(II) oxalate “(NH$_4$)$_2$Cu(C$_2$O$_4$)$_2$.1.03(NH$_4$)$_2$C$_2$O$_4$ x 1.5H$_2$O” begins as soon as the heating starts (Fig. 3.3.7). The TG curves show about 6.3 % mass loss upon heating up to 100°C. This mass loss which is accompanied by one endothermic peak in the DTA curve corresponds to the elimination of 1.5 moles of water for each mole of the precursor (process 1). Between 100 and 180°C, the anhydrous compound is stable. By further heating, its decomposition takes place in function of the atmosphere conditions.

![Figure 3.3.7: TA curves of the freeze-dried ammonium copper(II) oxalate. (a) DTA curve in argon; (b) TG curve in air and (c) TG curve in argon. Heating rate: 5K/min.](image)

In argon, three more or less superimposed steps occur in the range 180-340°C. The first and the second step are two successive endothermic processes appearing at 220 and 265°C, respectively. In accordance with the decomposition of ammonium Fe(III) oxalate (Section 3.3.2.a), it follows that these two endothermic processes materialize the decomposition of ammonium oxalate which leads to the formation of copper oxalate “CuC$_2$O$_4$” (processes (2a) and (2c)). This interpretation agrees with the XRD pattern of the sample annealed up to 280°C.
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(Fig. 3.3.8(b)). Note that the copper oxalate was identified using the PDF [21-297] of the hydrate compound “CuC₂O₄·H₂O”. This is due to the fact that, the structure of copper oxalate is maintained up to the beginning of the decomposition of the oxalate. The calculated mass loss ($\Delta m_{cal} = -58.5\%$) corresponding to the formation of copper oxalate is found to be lower than the experimental value ($\Delta m_{exp.} = -61.0\%$). This suggests that the decomposition of copper oxalate begins a little bit before 280°C. The associated gaseous products are CO, CO₂, H₂O, NH₃ and some HCN (Fig. 3.3.9).

**Figure 3.3.8:** XRD patterns of (a) the freeze-dried ammonium copper(II) oxalate and (b) of the decomposition product quenched after annealing up to 280°C (x-offset = 10°). Heating rate: 5K/min; atm.: Ar.

**Figure 3.3.9:** MS characterization of some gaseous occurring during the decomposition of the freeze-dried ammonium copper(II) oxalate. Atm.: Ar; heating rate: 5K/min.
The decomposition of copper oxalate takes place during the last step (~280-340°C). According to [121], the exothermic effect associated to this process should rather be endothermic. This discrepancy is due to the fact that copper metal newly formed oxidizes slowly into Cu₂O by the traces of oxygen in argon gas stream. It turns out that, the exothermic oxidation of Cu into Cu₂O dominates the endothermic decomposition of copper oxalate. Because of the partial decomposition of Cu(C₂O₄) up to 280°C, the mass loss associated to this step (Δm_{exp.} = -16.9%) is lower than the theoretical value corresponding to the formation of Cu₂O (Δm_{cal} = -18.6 %, (4a)) and Cu (Δm_{cal} = -20.5%, (4b)). But, the overall mass loss of 84.2% up to 340°C correlates very well with the formation of Cu₂O and Cu.

\[
\begin{align*}
\text{Cu(C}_2\text{O}_4 \rightarrow 1/2\text{Cu}_2\text{O} + 1.5\text{CO}_2 + 0.5\text{CO} & \quad (4a) \\
\text{Cu(C}_2\text{O}_4 \rightarrow \text{Cu} + 2\text{CO}_2 & \quad (4b)
\end{align*}
\]

The occurrence of the reaction (4a) is confirmed once more by the identification of CO in the gaseous decomposition products (Fig. 3.3.9). Additionally, after annealing at 320°C, the solid product contains Cu and Cu₂O (Fig. 3.3.10(a)). The increase of the amount of Cu₂O with the temperature (Fig. 3.3.10(a), (b)) shows that its formation is controlled kinetically.

**Figure 3.3.10:** XRD patterns of the decomposition products of the freeze-dried ammonium copper(II) oxalate quenched after annealing up to 320°C (a), 350°C (b), 400°C (c) and 500°C (d). Heating rate: 5K/min; atm.: Ar.
Above 340°C, a slight gain of mass (\(\Delta m_{\text{exp}} = +1.5\%\)) assigned to the oxidation of Cu and \(\text{Cu}_2\text{O}\) occurs as confirmed by the XRD patterns obtained at 350-500°C (Fig. 3.3.10(c), (d)). This finally leads to the end product \(\text{CuO}\) (reactions (5a) and (5b)).

\[
\begin{align*}
\frac{1}{2}\text{Cu}_2\text{O} + \frac{1}{4}\text{O}_2 & \to \text{CuO} \quad (5a) \\
\text{Cu} + \frac{1}{2}\text{O}_2 & \to \text{CuO} \quad (5b)
\end{align*}
\]

As already observed during the thermal decomposition carried out in argon, the TA results show that, the decomposition of the anhydrous ammonium copper(II) oxalate in air starts with the endothermic decomposition of \((\text{NH}_4)_2\text{C}_2\text{O}_4\) in the range 180-270°C. During the following step (270°C-320°C), the decomposition of copper oxalate takes place exothermically, because of the simultaneous formation and oxidation of copper metal. The observed mass loss (\(\Delta m_{\text{exp}} = -16.8\%\)) is close to the value calculated (\(\Delta m_{\text{cal}} = -16.7\%\)) for the formation of \(\text{CuO}\) (Fig. 3.3.7(b)). The main decomposition steps of the freeze-dried ammonium copper(II) oxalate in argon 4.6 can be established as follows:

\[
\begin{align*}
\text{“(NH}_4)_2\text{Cu(C}_2\text{O}_4)_2 \cdot 1.03(\text{NH}_4)_2\text{C}_2\text{O}_4 \times 1.5\text{H}_2\text{O”}
\end{align*}
\]

\[30°C - 100°C \rightarrow (1)\]
\[(\text{NH}_4)_2\text{Cu(C}_2\text{O}_4)_2 \cdot 1.03(\text{NH}_4)_2\text{C}_2\text{O}_4 \rightarrow \text{Cu(C}_2\text{O}_4)_2 \rightarrow (2a), (2b), (2c)\]
\[180°C - 280°C \rightarrow \text{Cu(C}_2\text{O}_4)_2 \rightarrow \text{Cu}_2\text{O}, \text{Cu} \rightarrow (4a), (4b)\]
\[280°C - 340°C \rightarrow \text{Cu}_2\text{O}, \text{Cu} \rightarrow \text{CuO} \rightarrow \text{CuO} \rightarrow T > 340°C \rightarrow \text{CuO} \rightarrow (5a), (5b)\]

\[\text{Scheme 3.3.2: Main decomposition steps of the freeze-dried ammonium copper(II) oxalate “(NH}_4)_2\text{Cu(C}_2\text{O}_4)_2 \cdot 1.03(\text{NH}_4)_2\text{C}_2\text{O}_4 \times 1.5\text{H}_2\text{O”} \rightarrow \text{CuO} \text{ (argon 4.6).}\]
Partial conclusion

The thermal decomposition of the freeze-dried ammonium copper(II) oxalate was studied in air and in argon. The TA and the XRD show that the main steps of decomposition are analogous to those established during the decomposition of the freeze-dried ammonium iron(III) oxalate. In fact, after the elimination of H₂O (T ≤ 100°C), the anhydrous sample is stable up to 180°C. Between 180 and 280°C, the endothermic decomposition of (NH₄)₂C₂O₄ takes place and the solid product is copper oxalate. By subsequent heating above 280°C, copper oxalate decomposes and the simultaneous oxidation of the product leads to the occurrence of an exothermic effect. In argon 4.6, the decomposition process ends at 340°C and leads to a product containing Cu₂O and Cu (Cu₂O >>> Cu) whereas in air, the oxidation of Cu₂O and Cu to CuO is complete at the end of the decomposition (T = 320°C).

3.3.2.c. Thermal decomposition of ammonium copper(II)-iron(III) oxalate

For the synthesis of Cu₁₋ₓFeₓO₄ (0 ≤ x ≤ 0.5) ferrite powders, the thermal decomposition behaviour of freeze-dried ammonium Cu(II)-Fe(III) oxalate precursors was investigated. From the TA and the MS results, all the investigated precursors decompose in a similar way in presence of argon as well as in air atmosphere. From that, any of these samples can be employed for the determination of their decomposition processes. In what follows, the precursor “CuC₂O₄.2(NH₄)₃Fe(C₂O₄)₃.2.6(NH₄)₂C₂O₄ x 3.5H₂O”, with the Cu:Fe ratio of 1:2, is studied throughout.

![Figure 3.3.11: TA curves of the freeze-dried ammonium CuFe₂ oxalate. (a) DTA curve in argon; (b) TG curve in argon, (c) TG curve in air ; (d) TG curve in argon of the freeze-dried ammonium Fe(III) oxalate, (e) TG curve in argon of the freeze-dried ammonium Cu(II) oxalate. Heating rate: 5K/min.](image-url)
In argon the decomposition proceeds in three more or less overlapped steps (Fig. 3.3.11). The first step corresponds to the endothermic elimination of water (30-100°C, process (1)). Between 100 and 180°C, the anhydrous sample is stable and then decomposes gradually between 180 and 400°C. The end temperature value of 400°C is located between that of ammonium copper(II) oxalate (340°C) and close to that of the ammonium iron(III) oxalate (410°C). This shows that only a slight interaction takes place between the components of the freeze-dried product. During the first decomposition step of the anhydrous sample (200-300°C), a sharp endothermic peak with two close maxima appears. According to the results of the decomposition of single metal oxalates (sections 3.3.2.a and 3.3.2.b), this step is due to the decomposition of (NH₄)₂C₂O₄ which leads to the reduction of the anhydrous complex to the iron(II) state (processes 2(a)-2(c)). The schematic main decomposition steps established for the freeze-dried ammonium copper(II) oxalate (Scheme 3.3.2) show that the thermal decomposition of CuC₂O₄ should finish at 340°C, during the decomposition of Fe(II) oxalate (Scheme 3.3.1). However for a good correlation of the calculated and the experimental mass losses occurring in the range 200-300°C, one must consider that the decomposition of copper(II) oxalate is nearly finished already at 300°C (Table A5, Section 11.2). In this case, the calculated mass loss due to the simultaneous occurrence of the processes (2a)-(2c), (4a) and/or (4b) is situated between -67.2% and -67.8%. This interval of values is very close to the experimental result (Δm_{exp} = -66.6%). The earlier decomposition of copper(II) oxalate should be caused by the presence of an excess of (NH₄)₂C₂O₄ inside the ammonium CuFe₂ oxalate precursor, which decomposes into the reducing gas CO.

Figure 3.3.12: MS characterization of the gaseous products occurring during the decomposition of the freeze-dried ammonium CuFe₂ oxalate. Atm.: Ar., heating rate: 5K/min.
The other gaseous products such as CO₂, H₂O, NH₃ and HCN (small amount) are also eliminated during the decomposition of (NH₄)₂C₂O₄ (Fig. 3.3.12). Between 300 and 400°C, the third step which is related to the decomposition of the last part of copper(II) oxalate and the decomposition of iron(II) oxalate takes place exothermically. This means that the endothermic decomposition of Fe(II)(C₂O₄) is dominated by exothermic crystallization processes taking place simultaneously.

For further elucidation of the TA results, various thermal treatments were carried out in argon in the range 200-500°C. At the end of each treatment the product was quenched under the same atmosphere. Afterwards the characterization was done using the XRD analysis method (Fig. 3.3.13).

Figure 3.3.13: XRD pattern of the decomposition products of the freeze-dried ammonium CuFe₂ oxalate quenched after annealing up to 280°C (a), 300°C (b), 350°C (c), 450°C (d) and (e) after decomposition at 500°C and annealing for 3 hours. Atm.: Ar., heating rate: 5K/min.
At 280°C (Fig. 3.3.13(a)), the product is an amorphous phase containing some characteristic reflexes of iron(II) oxalate (PDF 14-807). When the annealing temperature increases up to 300°C (Fig. 3.3.13(b)), the product becomes more amorphous. The decomposition ends around 350°C and leads to the formation of a spinel phase and copper metal (Fig. 3.3.13(c)). Above 350°C, the spinel phase reacts progressively with CuO resulting from the oxidation of Cu by the traces of oxygen in argon atmosphere (processes (5a), (5b) and (6a)). The increase of the diffraction peaks of the spinel phase with the temperature materializes the formation of a more stable spinel (Fig. 3.3.13(d)). The presence of $\alpha$-Fe$_2$O$_3$ at 500ºC (Fig. 3.3.13(e)) confirms the occurrence of the process (6c) beside the process (6b).

\[
\gamma$-Fe$_2$O$_3 + (1-x)CuO \rightarrow Cu_{1-x}Fe_2O_{4-y} \quad (6a)
\]
\[
Cu_{1-x}Fe_2O_{4-y} + xCuO \rightarrow CuFe_2O_4 \quad (6b)
\]
\[
Cu_{1-x}Fe_2O_4 + xCuO \rightarrow \alpha$-Fe$_2$O$_3 + CuO \quad (6c)
\]

In air, the decomposition of the anhydrous precursor takes place in the temperature range 200-310°C. The observation of a single step in the TG curve (Fig. 3.3.11(c)) indicates that the steps (2) and (3) are completely superimposed. Due to the fact that the thermal treatment is performed in presence of air, the oxidation of CO to CO$_2$ takes place following a strongly exothermic reaction. The local heat generated by this process initiates an earlier decomposition of iron(II) oxalate. Consequently, the complete decomposition of the freeze-dried precursor ammonium CuFe$_2$ oxalate takes place in air at a temperature (310°C) lower than the one observed in argon (400°C). The oxidation of the solid products (Cu$_2$O / Cu and FeO) begins before the end of the decomposition process. After a heat treatment in air at 400°C the product contains three phases namely, a cubic spinel phase, $\alpha$-Fe$_2$O$_3$ and CuO.

**Partial conclusion**

The thermal decomposition of the freeze-dried ammonium CuFe$_2$ oxalate has been studied in air and in argon. This decomposition occurs in three more or less overlapped steps that end at a lower temperature in air (T~310°C) than in argon (400°C). The nearly independent decomposition of copper(II) and of iron(III) oxalate inhibit the direct synthesis of copper ferrite below 600°C. In fact in air with the formation of $\alpha$-Fe$_2$O$_3$ at 400°C, the synthesis of the copper ferrite should be performed only at high temperature by a conventional solid state reaction. In argon, the ferritization process can not end up at 400°C because the oxide phases
γ-Fe₂O₃ and CuO which are supposed to react together are obtained at different temperatures; and since the transition γ-Fe₂O₃ → α-Fe₂O₃ is performed in argon between 400 and 600°C, the increase of the temperature beyond 400°C does not enhance the total reaction but leads rather to the formation of a third phase called hematite “α-Fe₂O₃”. Having regards to this conclusion, some annealing processes were done between 400 and 1000°C.

From the results obtained above, the decomposition pathways of ammonium CuFe₂ oxalate in argon can be established as follows:

Scheme 3.3.3: Main decomposition steps of the freeze-dried precursor ammonium CuFe₂ oxalate “CuC₂O₄·2(NH₄)₃Fe(C₂O₄)₃·2.6(NH₄)₂C₂O₄ · 3.5H₂O” in argon 4.6.
3.3.3. Phase formation from the freeze-dried ammonium copper(II)-iron(III) oxalate precursors

The synthesis of copper ferrite powders is investigated by the heat treatment in air of freeze-dried ammonium Cu$_{1-x}$Fe$_{2+x}$ oxalates ($0 \leq x \leq 0.5$) at 400°C, 600°C, 800°C and 1000°C. Additional investigations are performed in oxygen, at 800°C, for the optimization of the synthesis conditions of a pure copper ferrite “CuFe$_2$O$_4$”. In order to avoid the overheating during the decomposition of the oxalate, a heating rate of 5K/min was used for the annealing temperature equal 400°C. Above 400°C, a heating rate of 10K/min was applied. After three hours of the thermal treatment at 400°C, irrespectively to the initial concentration of the solution of the precursor and of the value of x, the oxalate powders are converted into the products containing hematite ($\alpha$-Fe$_2$O$_3$), tenorite (CuO) and a partially crystalline spinel phase. At 600°C (Fig. 3.3.14), a significant increase of the intensity of the diffraction peaks of $\alpha$-Fe$_2$O$_3$ and CuO is observed. Moreover, the diffraction peaks of the spinel phase are completely absent on the patterns obtained from the slightly concentrated precursor solution (Fig. 3.3.14(a1), (b)-(e)). Only some traces of this phase are identified in the product resulting from the concentrated solution (Fig. 3.3.14(a2)).

(a1) and (a2) slightly and most concentrated precursor solution with x = 0. (b), (c), (d) and (e) slightly concentrated precursor solutions with x = 0.1, 0.2, 0.3, 0.5, respectively.

Figure 3.3.14: XRD patterns of the decomposition products of freeze-dried ammonium Cu$_{1-x}$Fe$_{2+x}$ oxalates annealed at 400°C (3 hours) followed by the heating at 600°C (24 hours). Atm.: air, heating rate: 10K/min
Due to the formation of single oxide phases at 600°C, the synthesis of the copper ferrite powders should be performed only at higher temperatures (T > 800°C) by a conventional solid state reaction. The increase of the heat treatment temperature to 800°C (Fig. 3.3.15) leads to the appearance of the diffraction peaks of a well crystalline spinel phase “CuFe$_2$O$_4$” with a tetragonal structure. Moreover, one notes that the pattern of the sample with x = 0 exhibits a peak around 37.8° indicating the presence of unreacted CuO while for $0 < x \leq 0.5$, α-Fe$_2$O$_3$ is the impurity phase. The intensity of the diffraction peaks of α-Fe$_2$O$_3$ increases when the value of x increases (content of iron) (Fig. 3.3.15).

**Figure 3.3.15:** XRD patterns of the decomposition products of freeze-dried ammonium Cu$_{1-x}$Fe$_{2+x}$ oxalates annealed at 400°C (3 hours) followed by the heating at 800°C (24 hours). Atm.: air; heating rate: 10K/min.

Up to 1000°C (Fig. 3.3.16), the composition of the product depends on x. As already observed using the conventional ceramic method (Section 3.2), there are in addition to the spinel phase small amounts of simple oxides identified by the less intense peaks at $2\theta = 37.8°$ which can be assigned to CuO for x = 0, and at $2\theta = 33.2°$ which can be assigned to α-Fe$_2$O$_3$ for $0.2 < x \leq 0.5$. The single phase is obtained only for x = 0.1 and x = 0.2. For x = 0.1, the pattern is indexed to a tetragonal copper ferrite with the following lattice parameters $a = 826.8$ pm and $c = 858.9$ pm. For x = 0.2, a cubic spinel phase ($a = 826.8$ pm) is indexed as major phase beside a tetragonal copper ferrite (traces). The decrease of the tetragonal...
Synthesis of copper ferrite from the freeze-dried oxalate precursors

distortion in the last sample is ascribed to the decrease of the concentration of Cu$^{2+}$ ions inside
the B- sites [59].

Investigations in oxygen were performed on the precursor with x = 0. After 3 hours of
decomposition at 500°C in argon, the product contains a partial crystalline spinel phase, a
small amount of $\alpha$-Fe$_2$O$_3$ and some traces of CuO (Fig. 3.3.13(e)). The annealing of this
sample in air or in oxygen during 24 hours at 800°C leads to the formation of some tenorite
(CuO) beside a well crystallized copper ferrite with a tetragonal structure (Fig. 3.3.17(a), (b)).
By further annealing in oxygen during 40-50 hours, one notes a progressive decrease of the
amount of free CuO (Fig. 3.3.17(c), (d)). Up to 70 hours, the end product is almost a pure
phase (Fig. 3.3.17(e)). The lattice parameters of these samples, determined from X-ray data
with an accuracy of $\pm$ 0.002, are shown on the Table 3.3.1. For this purpose the WinXpow
program [P1] was used. It is observed that when the synthesis is performed in oxygen, the
tetragonal distortion of CuFe$_2$O$_4$ increases.
This is mainly due to the decrease of the oxygen deficiency inside the spinel phase. In fact,
the formation of Cu$^+$ ions is limited or avoided under oxidizing atmosphere. As a

Figure 3.3.16: XRD patterns of the decomposition products of freeze-dried ammonium Cu$_{1-x}$Fe$_{2+x}$
oxalates annealed at 400°C (3 hours) followed by the heating at 1000°C (24 hours).
Atm.: air; heating rate: 10K/min.
consequence, the distribution of Cu$^{2+}$ ions responsible of the tetragonal distortion is no longer influenced. Furthermore, the absence of any variation of the c/a’ values with the annealing time reassures the formation of the stoichiometric copper ferrite.

Figure 3.3.17: XRD patterns of the decomposition product of the freeze-dried ammonium CuFe$_2$oxalate decomposed at 500°C for 3 hours in argon followed by the heating at 800°C in air during (a) 24 hours and in oxygen during (b) 24 hours, (c) 40 hours (d) 50 hours and (e) 70 hours. Heating rate: 5K/min.

<table>
<thead>
<tr>
<th>time (hours)</th>
<th>atmosphere</th>
<th>a(pm)</th>
<th>a'(pm)</th>
<th>c(pm)</th>
<th>c/a’(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>air</td>
<td>583.40</td>
<td>825.05</td>
<td>860.93</td>
<td>~1.04</td>
</tr>
<tr>
<td>24</td>
<td>oxygen</td>
<td>580.92</td>
<td>821.55</td>
<td>871.20</td>
<td>~1.06</td>
</tr>
<tr>
<td>40</td>
<td>oxygen</td>
<td>581.10</td>
<td>821.80</td>
<td>871.40</td>
<td>~1.06</td>
</tr>
<tr>
<td>50</td>
<td>oxygen</td>
<td>580.64</td>
<td>821.15</td>
<td>870.21</td>
<td>~1.06</td>
</tr>
<tr>
<td>70</td>
<td>oxygen</td>
<td>580.64</td>
<td>822.22</td>
<td>872.20</td>
<td>~1.06</td>
</tr>
</tbody>
</table>

(*' the tetragonal distortion is expressed as c/a’ where a’ = a$\sqrt{2}$, thus referring to the face-centered cubic unit cell constructed along the diagonal of the tetragonal one.).
3.4. Synthesis of copper ferrite from the freeze-dried formate precursors

Many studies have been performed on the thermal decomposition of formate precursors [9, 124-126]. Koleva et al. [124] have used copper-manganese formate solid solutions as precursors for copper manganese oxides. Polla et al. [125, 126] have synthesized Cu-Ca- and Cu-Sr-oxides by thermal decomposition of appropriate mixed formates. Note that investigations carried out in [124-126] preferentially aimed at the formation of oxide phases and, the decomposition processes were discussed only on the basis of summarizing schematic equations. More recently, it has been shown [9] that the preparation of manganese ferrite with the freeze-dried precursor manganese iron formate “MnFe₂O(CHOO)₆(H₂O)₃” occurs at a low temperature (T=600°C). In this part of the work, we attempt to use copper(II)-iron(III) formate as a precursor for the direct synthesis of pure copper ferrite. Specifically, we aim to enlighten relationships between the thermal decomposition of freeze-dried copper-iron formates and the formation of solid copper-iron oxide phases. Thus, the thermal decomposition of Cu(II)-Fe(III) formate is compared to that of individual metal formates and the effect of the calcination temperature on the phase formation is studied. Besides, it is worth to emphasize once more that the thermal analysis coupled with MS is a promising method to investigate the decomposition behaviour [9].

3.4.1. Preparation and characterization of the freeze-dried formate precursors

For the freeze-drying process, the preparation of Cu-Fe formate solutions was first required. In order to proceed, the starting materials copper(II)- and iron(II) formate were synthesized and used for the preparation of Cu(II)-, Fe(III)- and Cu(II)-Fe(III)- formate solutions (Section 8.3). The solutions were then quickly frozen in liquid nitrogen and dried from -40°C to 25°C in a vacuum chamber of a freeze-drying apparatus (Alpha 2-4, Christ). After 72 hours, the drying process was complete and very slight powders were obtained. In order to study the influence of the degree of dilution of starting solutions on the homogeneity of the freeze-dried Cu(II)-Fe(III) formate powders, two precursors with different metal ions concentration were prepared as described in Section 8.3.2. From the XRD analysis, the freeze-dried iron(III) formate (Fig. 3.4.1(a)) is amorphous. The analysis of the IR spectra of the freeze-dried amorphous Fe(III) formate shows that at least partially complex trinuclearµ-oxo-formate species are present in the amorphous phase. Such complexes are well known for crystalline iron carboxylates [127]. The pattern of the freeze-dried copper(II) formate (Fig. 3.4.1(d)) is in
agreement with that of the dihydrated crystalline copper(II) formate (PDF 32-331) which has a monoclinic structure. However, the presence of some non-indexed peaks may be due to the partial dehydrated state of the freeze-dried powders. For the Cu(II)-Fe(III) formate precursors (Fig. 3.4.1(b), (c)), the diffraction peak of copper(II) formate appearing around $2\theta = 16.9^\circ$ is identified beside the amorphous phase. This fact suggests the formation of a partially homogeneous precursor and shows that a partial segregation of copper formate has taken place during the freeze-drying process. Moreover, one notes that the intensity of the mentioned peak increases with the degree of dilution of the reactant solution. This observation justifies the fact that the non-diluted solution leads to the more homogeneous precursor (Fig. 3.4.1(b)).

The quantitative analysis of the investigated precursors was done by complexometric titration and elemental analysis. From the obtained results, their composition can be described approximately by the following formulas:

- Iron(III) formate: $[\text{Fe}_3\text{O}(\text{HCOO})_6]^+ \cdot \text{HCOO}^- \times 3.8\text{H}_2\text{O}$;
- Copper(II) formate: Cu(\text{HCOO})$_2$ $\times 0.1\text{H}_2\text{O}$ ;
- Copper(II)-iron(III) formate: CuFe$_2$O$_{2/3}$(HCOO)$_{6.67}$ $\times 2.5\text{H}_2\text{O}$ (diluted solution (C$_0$)).

**Figure 3.4.1:** XRD patterns of the freeze-dried formate precursors
The complex copper(II)-iron(III) formate contains less coordinated water than copper(II) formate and iron(III) formate. This observation is in agreement with the fact that the water content in a freeze-dried precursor depends on the intensity of the drying process [9].

3.4.2. Thermal decomposition of the freeze-dried formate precursors

3.4.2.a. Thermal decomposition of iron(III) formate

The thermal decomposition of the freeze-dried precursor iron(III) formate in argon is illustrated in Figure 3.4.2. The decomposition starts with an endothermic process corresponding to about 13% mass loss in the TG curve. This step is superimposed by the beginning of a weakly exothermic process occurring between 200 and 290°C and characterized by two substeps on the DTG. The last process is an endothermic one with a maximum at about 325°C. Above 330°C, a small gain of mass by the products is observed. The total mass loss including the small gain of mass is ~57% (Table 3.4.1). To elucidate the mechanism of decomposition, the gaseous decomposition products were analyzed by MS. The results of this measurement are plotted in Figure 3.4.3 and recorded in Table 3.4.1. The MS analysis of gaseous products permits to conclude that at least five parallel and/or consecutive reactions occur during the four decomposition steps identified on the DTA and the DTG curves (Table 3.4.1).

Figure 3.4.2: TA curves of the freeze-dried Fe(III) formate. (1) DTG curve; (2) DTA curve; (3) TG curve. Atm.: Ar; heating rate: 5K/min.
Synthesis of copper ferrite from the freeze-dried formate precursors

**Figure 3.4.3:** MS characterization of the gaseous decomposition products occurring during the decomposition of the freeze-dried Fe(III) formate precursor. Atm.: Ar; heating rate: 5K/min.

**Table 3.4.1:** Main primary gaseous decomposition products of the freeze-dried precursor [Fe$_3$O(HCOO)$_6$]$^+$ HCOO$^-$ x 3.8H$_2$O

<table>
<thead>
<tr>
<th>Process/ (equation)</th>
<th>Temperature range (°C), roughly</th>
<th>Main primary gaseous decomposition products</th>
<th>$\Delta m$ (calc.) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\Delta m$/step $\Delta m$/total</td>
</tr>
<tr>
<td>1</td>
<td>30 - 220</td>
<td>3.8H$_2$O</td>
<td>- 12.1 - 12.1</td>
</tr>
<tr>
<td>2a</td>
<td>200 - 260</td>
<td>0.5HCOOH ; 0.5CO$_2$</td>
<td>- 7.9 - 20.0</td>
</tr>
<tr>
<td>2b</td>
<td>240 - 290</td>
<td>HCOOH ; CO$_2$</td>
<td>- 15.9 - 35.9</td>
</tr>
<tr>
<td>3</td>
<td>280 - 330</td>
<td>2HCOOH ; 2CO</td>
<td>- 26.1 - 62.0</td>
</tr>
<tr>
<td>4</td>
<td>280 - 330</td>
<td>2H$_2$CO ; 2CO$_2$</td>
<td>- 26.1 - 62.0</td>
</tr>
<tr>
<td></td>
<td>330 - 520</td>
<td>(oxidation)</td>
<td>+ 4.2 - 57.8</td>
</tr>
</tbody>
</table>
One sees that the decomposition starts with the elimination of H₂O (process (1)). The calculated mass loss (12.1%) corresponding to the loss of 3.8 moles of water per mole of precursor is found to be lower than the experimental value (about 13%). This suggests that the formation of HCOOH and CO₂ (process (2a)) should be superimposed to (1).

\[
[\text{Fe}_3\text{O(HCOO)}_6]^+ \text{HCOO}^- \times 3.8\text{H}_2\text{O} \rightarrow [\text{Fe}_3\text{O(HCOO)}_6]^+ \text{HCOO}^- + 3.8\text{H}_2\text{O} \quad (1)
\]

\[
[\text{Fe(III)}_3\text{O(HCOO)}_6]^+ \text{HCOO}^- \rightarrow [\text{Fe(III)}_2\text{Fe(II)}\text{O(HCOO)}_6] + 0.5\text{HCOOH} + 0.5\text{CO}_2 \quad (2a)
\]

\[
[\text{Fe(III)}_2\text{Fe(II)}\text{O(HCOO)}_6] \rightarrow [\text{Fe(II)}_3\text{O(HCOO)}_4] + \text{HCOOH} + \text{CO}_2 \quad (2b)
\]

HCOOH and CO₂ result from an electron transfer from the formate anion to Fe(III) and from the reaction of two HCOO- moieties via an H-transfer from one to the other. The decomposition proceeds with the process (2b). In this process which is analogous to (2a), a further reductive elimination with the delivery of HCOOH and CO₂ takes place. As the temperature increases, the competitive processes (3) and (4) become more and more important. Contrary to the processes (2a) and (2b), they occur without alteration of the oxidation number of iron.

\[
[\text{Fe(II)}_3\text{O(HCOO)}_4] \rightarrow 3 \text{“FeO”} + 2\text{HCOOH} + 2\text{CO} \quad (3)
\]

\[
[\text{Fe(II)}_3\text{O(HCOO)}_4] \rightarrow 3 \text{“FeO”} + 2\text{H}_2\text{CO} + 2\text{CO}_2 \quad (4)
\]

The formation of HCOOH and CO, or H₂CO and CO₂ can be explained by the breaking of Fe-O- and O-C- bonds in the trinuclear molecular units according to the schematic equations (5) and (6) and by H-transfer reactions between the resulting HCOO- and HCO- radicals.

\[
(\text{R})\text{Fe-O(CO)}\text{H} \rightarrow (\text{R})\text{Fe-O• + HC•O} \quad (5)
\]

\[
(\text{R})\text{Fe-O(CO)}\text{H} \rightarrow (\text{R})\text{Fe• + HCOO•} \quad (6)
\]

From the reaction between the simultaneously formed (R)Fe-O• and (R)Fe• species Fe-O-Fe-links arise. This should result in the formation of wüstite, “FeO”, as a final solid product. At about 300°C, wüstite is a metastable iron oxide in relation to a Fe / Fe₃O₄ mixture. But, its formation by decomposition of a Fe(II)-compound at relatively low temperature is not unusual. Analogous decomposition processes were also identified during the decomposition in argon of the freeze-dried precursor Mn-Fe formate [9].

The small gain of mass between 330 and 520°C is caused by the reoxidation of Fe(II), formed during the decomposition, by traces of oxygen in the argon gas stream (see below). After
finishing the thermal analysis at about 800°C, hematite ($\alpha$-Fe$_2$O$_3$) is formed as a solid product. During all the decomposition processes a delivery of H$_2$O is observed. Beside this, H$_2$ is detected above 300°C. This fact can be explained by the decomposition processes according to the equations (7), (8) and (9).

\[
\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO} \quad (7)
\]

\[
\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2 \quad (8)
\]

\[
\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO} \quad (9)
\]

The reactions (8) and (9) become important above 300°C, whereas the reaction (7) had already taken place above 200°C. Because of the simultaneous presence of CO, CO$_2$, H$_2$O and H$_2$ in the reaction system, the existence of further equilibria like (10) and (11) are expected.

\[
\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad (10)
\]

\[
2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C} \quad (11)
\]

Reaction (10) has been discussed by Maciejewski et al. as H$_2$ forming process during the decomposition of Co(C$_2$O$_4$) x 2H$_2$O [128]. The Boudouard reaction (11) could explain the presence of traces of carbon in the solid decomposition product up to about 700°C.

According to Dollimore and Tonge [129], there are two main routes for the decomposition of anhydrous metal formates M(OOCH)$_2$ to metal oxides MO at temperatures $\vartheta > 400$°C: the formation of a) 2CO, H$_2$O and b) CO, CO$_2$, H$_2$ in addition to MO. Peshev et al. [130] have investigated the thermal dissociation of a crystalline complex trinuclear iron(III) formate in inert atmosphere by gas-chromatographic analysis between 340 and 350°C. They have characterized H$_2$O, CO, CO$_2$ and H$_2$ as gaseous decomposition products. Our results are fully in agreement with those of [129] and [130]. However, a careful investigation as a function of the temperature with MS detection of products allows some further conclusions concerning the single processes and their primary gaseous products. To confirm the TA results, various thermal treatments were performed in the range 30-800°C. The resulting solid products were characterized using the XRD method. In order to proceed, defined amounts (100-150mg) of Fe(III) formate were decomposed under argon. After reaching the desired temperature, the samples were quenched rapidly to RT under the same temperature. From the examination of the XRD profiles obtained at selected temperatures (260°C, 300°C, and 340°C), one can note that the thermal reactions defined from the TA (DTA, TG) and MS results, are approved (Fig. 3.4.4). After annealing up to 260°C (step (2a)), a less crystalline iron formate is formed from the amorphous freeze-dried precursor (Fig. 3.4.4(a)). This should be the reason for the
small exothermic effect at about 260°C (Fig. 3.4.2). After further reduction of iron during the annealing process up to 300°C (step 2b) another crystalline formate is formed. The most intensive peak, at about 2θ = 14.5°, coincides with the two most intensive nearly neighboring peaks of iron(II) formate (PDF 20-0514) (Fig. 3.4.4(b)).

![XRD patterns](image)

**Figure 3.4.4:** XRD patterns of the decomposition products of the freeze-dried Fe(III) formate quenched after annealing up to 260°C (a), 300°C (b), 340°C (c). Atm.: Ar, heating rate: 5K/min.

Obviously, the crystallization processes are related to the exothermic peaks at about 260 and 290°C in the DTA curve (Fig. 3.4.2). Moreover, we observed that the crystallization of iron oxides begins at 300°C. The metastable wüstite “FeO” and the magnetite “Fe₃O₄” are formed at the end of the decomposition process (340°C) (Fig. 3.4.4(c)). There are two possible reasons for the appearance of magnetite beside wüstite: a) before the interruption of the decomposition process at 340°C, a partial reoxidation of wüstite has already passed off or b) more probable, in competition and superimposed to the processes (2b) (between 240 and 290°C) (3) and (4) (between 280 and 330°C) a further decomposition without further reduction of Fe(III) takes place according to the parallel reactions (12a), (13a) and (12b), (13b), respectively.

\[
\text{[Fe(III)₂Fe(II)O(HCOO)₆]} \rightarrow \text{[Fe(III)₂Fe(II)O₂(HCOO)₄]} + \text{HCOOH} + \text{CO} \quad (12a) \\
\text{[Fe(III)₂Fe(II)O(HCOO)₆]} \rightarrow \text{[Fe(III)₂Fe(II)O₂(HCOO)₄]} + \text{H₂CO} + \text{CO₂} \quad (13a) \\
\text{[Fe(III)₂Fe(II)O₂(HCOO)₄]} \rightarrow \text{Fe₃O₄} + 2\text{HCOOH} + 2\text{CO} \quad (12b) \\
\text{[Fe(III)₂Fe(II)O₂(HCOO)₄]} \rightarrow \text{Fe₃O₄} + 2\text{H₂CO} + 2\text{CO₂} \quad (13b)
\]
The raw reaction given in the Scheme 3.4.1 summarizes the results of TG / DTA / MS in argon. Because of the large number of different superimposed primary and secondary processes and the large number of different products and their MS fragments, exact conclusions concerning the single processes are not possible. The actual yield in each reaction product is very sensitive to the experimental conditions.

Scheme 3.4.1: Schematic main decomposition steps of “[Fe₃O(HCOO)₆]⁺ HCOO⁻ x 3.8H₂O” in inert atmosphere (argon 4.6)
The decomposition of the iron(III) formate in air occurs in only two observable steps. The decomposition also starts with the endothermic release of coordinated water (process 1, between 30-220°C). All the further processes are superimposed by the oxidation of the primary decomposition products. This results in an altogether exothermic process in a narrow temperature range (maximum of the DTA curve at 273°C). From the XRD pattern obtained after decomposition up to 290°C, the resulting solid phase is maghemite, $\gamma$-Fe$_2$O$_3$. The primary formation of magnetite and its reaction to $\gamma$-Fe$_2$O$_3$ is also expected. At temperatures above 400°C, the metastable maghemite is transformed to the thermodynamically stable hematite, $\alpha$-Fe$_2$O$_3$. The same result was obtained from the decomposition of ammonium iron (III) oxalate in air (Section 3.3.2.a).

**3.4.2.b. Thermal decomposition of copper(II) formate**

In argon and in air (Fig. 3.4.5(a)-(c)), the TG curves show about 1.2% mass loss upon heating up to ~180°C. This mass loss which is accompanied by two less intensive endothermic peaks in the DTA curve (Fig. 3.4.5(a)) is due to the dehydration of copper(II) formate. Between 190 and 220°C, the total decomposition of the formate takes place.

![Figure 3.4.5](image_url)

**Figure 3.4.5:** TA curves of the freeze-dried Cu(II) formate. (a) DTA curve in argon; (b) TG curve in argon; (c) TG curve in air and (d) TG curve in argon of a precipitated Cu(II) formate. Heating rate: 5K/min.

For the decomposition in argon, the total mass loss at 215°C correlates with the formation of copper metal ($\Delta m_{\text{calc.}} = -59.1\%$). This agrees with the XRD pattern of the sample annealed up
to 220°C. Copper metal is formed as the main crystalline substance (Fig. 3.4.6(b)). The gain of mass above 220°C is caused by the reoxidation of copper metal by traces of oxygen in the argon atmosphere (Δm_{calc} = +10.3%). From the experimental gain of mass observed between 230 and 750°C it turns out that up to 750°C, the total oxidation of copper is not yet occurred. The resulting product is constituted of Cu₂O and a remaining amount of Cu (Fig. 3.4.6(c)). The broad exothermic peak in the DTA curve above 250°C should result from the slow oxidation of Cu and crystallization of Cu₂O. Because of several different processes between 200 and 250°C (decomposition and crystallization processes) the DTA peaks in this region do not allow any further detailed discussion. In air, indicated by the maximum mass loss of only 57%, the reoxidation begins before the full decomposition and ends at about 400°C. The altogether mass loss is in agreement with the calculated value of Δm_{calc} = -48.8 % (Fig. 3.4.5(c)).

The main gaseous decomposition products in argon are CO₂, H₂O, CO, H₂ and HCOOH (Fig. 3.4.7). As in the reductive decomposition of iron(III) formate ((2a) and (2b)), the primary process in the decomposition of the dehydrated copper(II) formate should be the formation of HCOOH and CO₂ (14). The decomposition of HCOOH results in the formation of H₂O and CO (7) or H₂ and CO₂ (8). Unlike the decomposition of the freeze-dried iron(III)
formate, H₂ is already formed at about 200°C. The reaction (7) is probably enhanced kinetically. Including a catalytic activity of a fine grained copper metal, formed during the decomposition of copper(II) formate, the reaction (8) can already be important at a much lower temperature. The detection of minor amounts of H₂CO (M/z = 30) should be the result of the reaction HCOOH + CO \xrightleftharpoons{} CO + CO₂ or the result of a side reaction without reduction, analogous to the reaction (4).

\[
\text{Cu(HCOO)₂} \rightarrow \text{Cu} + \text{HCOOH} + \text{CO}_2 \quad (14)
\]

An orthorhombic copper(II) formate (PDF 32-332) obtained by a special preparation was decomposed [131]. Already at 110°C, the authors observed the formation of a Cu(I)-compound. From the above, one found that the decomposition of the freeze-dried copper(II) formate with the monoclinic structure (PDF 32-331) does not lead to the same result. This shows the different decomposition behaviour of different crystalline forms of copper(II) formate.

![Figure 3.4.7: MS characterization of the gaseous decomposition products occurring during the decomposition of the freeze-dried Cu(II) formate. Atm.: Ar; heating rate: 5K/min.](image)

The thermal decomposition of the copper(II) formate prepared using the precipitation method was also studied. Under argon, as observed during the decomposition of the freeze-dried sample its decomposition occurs in two main steps (Figure 3.4.5(d)). The first step occurring below 100°C corresponds to the dehydration process. The associated mass loss
(\Delta m_{\text{exp.}} = -19.4\%) is close to the theoretical value (\Delta m_{\text{exp.}} = -19.0\%) due to the presence of two moles of water per mole of Cu(II) formate. During the second step, the decomposition of the anhydrous sample leads to the direct formation of copper metal. As already observed for the freeze-dried sample one notes that above \sim 220^\circ C, a continuous gain of mass occurs due to the oxidation of copper metal.

3.4.2.c. Thermal decomposition of copper(II)-iron(III) formate

The thermal decomposition of the freeze-dried copper(II)-iron(III) formate occurs in argon in three more or less superimposed steps in the range 30-290°C (Fig. 3.4.8(b)). The decomposition starts with an endothermic delivery of water (30-220°C) (process 1). One notes that the initial and the final temperatures of further decomposition are located between those of the single formates. This reflects interactions between the components of the freeze-dried product.

![TA curves of the freeze-dried Cu(II)-Fe(III) formate precursor: (a) DTG curve in Ar; (b) TG curve in Ar, (c) TG curve in air; (d) TG curve in Ar of the freeze-dried Fe(III) formate, (e) TG curve in Ar of the freeze-dried Cu(II) formate. Heating rate: 5K/min.](image)

According to the decomposition of Fe(III) formate (Section 3.4.2.a) and Cu(II) formate (3.4.2.b), the second step (210-250°C) overall exothermic is related to the superposition of three processes: the reduction of Cu\(^{2+}\) to Cu yielding to the release of HCOOH and CO\(_2\).
Synthesis of copper ferrite from the freeze-dried formate precursors

(equation 14), the reduction of Fe(III) to Fe(II) also leading to the release of HCOOH and CO$_2$ (equation 2a) and the further decomposition of the iron component without reduction, forming HCOOH and CO (equation 12a) or H$_2$CO and CO$_2$ (equation 13a). The superimposed third step (250-290°C), overall endothermic, characterizes the total decomposition of Fe(II/III) formate nearly without a further reduction of Fe(III). In this step, the competition processes described by the equations (12b) and (13b) occur simultaneously (Table 3.4.2). Analogous to the decomposition of single formates, the intensities of the MS peaks of the primary decomposition products HCOOH and H$_2$CO are much lower than the intensities of the peaks of secondary products (Fig. A3, Section 11.2). But, unlike the decomposition of the iron(III) formate precursor, the development of H$_2$ begins at about 220°C. That means in the case of the complex formate, the consecutive reactions (8) and (9) are important at this temperature. This should be caused by the catalytic activity of the metallic copper. The altogether mass loss of about 60% at 290°C correlates very well with the expectation for “2/3 Fe$_3$O$_4$ + Cu”. Above 290°C, the product is progressively oxidized by the traces of oxygen in argon atmosphere.

Table 3.4.2: Main primary gaseous decomposition products of the freeze-dried precursor [2/3 ([Fe$_3$O(HCOO)$_6$]+ HCOO$^-$), Cu(HCOO)$_2$ x 2.5 H$_2$O]

<table>
<thead>
<tr>
<th>Process/ (equation)</th>
<th>Temperature range (°C), roughly</th>
<th>Main primary gaseous decomposition products</th>
<th>$\Delta m$ (calc.)/%</th>
<th>$\Delta m$/step</th>
<th>$\Delta m$/total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30-220</td>
<td>2.5H$_2$O</td>
<td>- 8.5</td>
<td>- 8.5</td>
<td>- 8.5</td>
</tr>
<tr>
<td>14</td>
<td>210-250</td>
<td>HCOOH ; CO$_2$</td>
<td>- 17.0</td>
<td>- 25.5</td>
<td>- 25.5</td>
</tr>
<tr>
<td>2a</td>
<td>210-250</td>
<td>2/3(0.5HCOOH; 0.5CO$_2$)</td>
<td>- 5.7</td>
<td>- 31.2</td>
<td>- 31.2</td>
</tr>
<tr>
<td>12a</td>
<td>210-250</td>
<td>2/3(HCOOH; CO)</td>
<td>- 9.3</td>
<td>- 40.5</td>
<td>- 40.5</td>
</tr>
<tr>
<td>13a</td>
<td>210-250</td>
<td>2/3(H$_2$CO;CO$_2$)</td>
<td>- 9.3</td>
<td>- 40.5</td>
<td>- 40.5</td>
</tr>
<tr>
<td>12b</td>
<td>250-290</td>
<td>2/3(2HCOOH; 2CO)</td>
<td>- 18.6</td>
<td>- 59.1</td>
<td>- 59.1</td>
</tr>
<tr>
<td>13b</td>
<td>250-290</td>
<td>2/3(2H$_2$CO; 2CO$_2$) (oxidation)</td>
<td>- 18.6</td>
<td>- 59.1</td>
<td>- 59.1</td>
</tr>
<tr>
<td></td>
<td>290-600</td>
<td></td>
<td>+ 2.5</td>
<td>- 56.6</td>
<td></td>
</tr>
</tbody>
</table>

Because of the numerous strongly superimposed processes, summarized in Table 3.4.2, no reaction scheme is given. The decomposition behaviour reflects the characteristics of the decomposition of the single compounds. Because of the “dilution” of the copper component, their decomposition begins at a somewhat higher temperature, and the catalytic influence of the arising copper metal induces a favorable decomposition of the iron formate component.
According to the XRD analysis (Fig. 3.4.9), the results obtained from the TG / MS are clearly approved. After annealing up to 240°C, crystalline \( \text{“Cu”} \) is present beside the amorphous iron component (Fig. 3.4.9(a)). Further annealing up to 320°C leads to the additional formation of the spinel phase \( \text{Fe}_3\text{O}_4 \) (Fig. 3.4.9(b)). Contrarily to the decomposition of the single iron(III) formate, no wüstite phase is detectable. The continuation of the annealing process results in the slow oxidation of copper (\( \text{Cu} \rightarrow \text{Cu}_2\text{O} \rightarrow \text{CuO} \)) and magnetite (\( \text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3 \)) by traces of oxygen in the argon (Fig. 3.4.9(c)). After 24 hours of thermal treatment at 400°C, the metastable spinel compound \( \gamma\text{-Fe}_2\text{O}_3 \) is transformed partially to \( \alpha\text{-Fe}_2\text{O}_3 \) (Fig. 3.4.9(d)). The formation of some copper poor spinel phase (\( \text{Cu}_{1-x}\text{Fe}_2\text{O}_4-\lambda \)) beside the aforementioned phases is expected.

Figure 3.4.9: XRD patterns of the decomposition products of the freeze-dried \( \text{CuFe}_2 \) formate quenched after annealing up to 240°C (a), 320°C (b), 400°C (c) and slowly cooled after annealing at 400°C during 24 hours (d). Atm.: Ar; heating rate: 5K/min.

In air, the thermal decomposition of the freeze-dried \( \text{Cu(II)-Fe(III)} \) formate also starts with the endothermic delivery of water (Fig. 3.4.8(c)). The decomposition of the anhydrous formate takes place between 200 and 260°C. The simultaneous oxidation of the gaseous products results in the formation of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) and, altogether, the decomposition process is strongly exothermic. The small gain of mass above 260°C indicates that the reoxidation of copper metal and iron(II) begins during the decomposition process.
3.4.3. Phases formation in air from the freeze-dried copper(II)-iron(III) formate

The two precursors under investigation (the diluted and the non-diluted (Section 8.3.2)) were quenched after annealing at 260°C and 400°C and furthermore, heat treated in air for 24 hours at 400°C, 600°C, 800°C and 1000°C. From the XRD patterns of resulting products it was found that, at each temperature the same phases are formed in approximately the same amount. The patterns obtained from the non-diluted precursor are shown on Figure 3.4.10.

**Figure 3.4.10:** XRD patterns of the decomposition products of the freeze-dried CuFe₂ formate quenched after annealing up to 260°C (a), 400°C (b) and slowly cooled after annealing during 24 hours at 400°C (c), 600°C (d), 800°C (e), 1000°C (f).

Atm.: air; heating rate: 5K/min.
At 260°C (Fig. 3.4.10(a)), the solid product contains a less crystalline cubic spinel compound (copper poor spinel phase Cu$_{1-x}$Fe$_2$O$_{4-\lambda}$, and/or $\gamma$-Fe$_2$O$_3$), copper metal (small amount) and cuprite (Cu$_2$O). After annealing up to 400°C (Fig. 3.4.10(b)), Cu and Cu$_2$O are fully oxidized to CuO. The separation of $\alpha$-Fe$_2$O$_3$ begins during the annealing at 400°C (Fig. 3.4.10(c)). This separation is continued up to 600°C. Upon annealing at 600°C (Fig. 3.4.10(d)), the solid state reaction between $\alpha$-Fe$_2$O$_3$ and CuO starts and ends at 800°C (Fig. 3.4.10(e)). From this reaction a tetragonal copper ferrite is formed after a slow cooling process. Due to the partial reduction of Cu(II) to Cu(I) that takes place in the range 800-1000°C, the product contains an iron rich spinel phase Cu$_{1-x}$Fe$_{2+x}$O$_4$ and a small amount of CuO (Fig. 3.4.10(e), (f)).

The results obtained above are in agreement with those of our investigations concerning the synthesis of copper ferrites by oxidation of metallic precursors (Section 3.6.2) or by thermal decomposition of freeze-dried ammonium Cu(II)-Fe(III) oxalate precursors (Section 3.3.3). In the same footing, a single spinel phase is obtained at 1000°C from a freeze-dried formate precursor with the composition Cu$_{0.9}$Fe$_{2.1}$ formate.

**Partial conclusion**

The thermal decomposition of freeze-dried iron(III) formate, copper(II) formate and copper(II)-iron(III) formate includes an intermediate reduction of the metal ions. Regarding copper(II)-iron(III) formate, the resulting product of decomposition in argon contains copper metal and an iron oxide with spinel structure Fe$^{3+}_{(8/3-2x)}$Fe$^{2+}_{1/3-x}$O$_{4}$. The value of x depends on the scale of oxidation by traces of oxygen after decomposition (x=0 for maghemite and x = 1/3 for magnetite). In air, the reoxidation begins during the decomposition process. After decomposition up to 400°C, the solid product contains a poor crystalline spinel beside CuO (Fig. 3.4.10(b)). A raw calculation of the lattice constant of the spinel phase gives $a_0 = 836$ pm. This value is situated between the lattice constants of $\gamma$-Fe$_2$O$_3$ ($a_0 = 834$ pm) and that of CuFe$_2$O$_4$ ($a_0 = 837$ pm). It follows that the poor crystalline spinel phase contains some copper. Analogously to the maghemite-hematite transformation, the thermal treatment in the range 400-600°C leads to the separation of hematite. Due to this fact, the synthesis of copper ferrite from the freeze-dried Cu(II)-Fe(III) formate should be performed only at a high temperature (T > 700°C) by a conventional ceramic method. The chance to form copper ferrite directly in a decomposition reaction is expected to be higher for heteronuclear Cu-Fe$_2$-complex compounds with an ideal homogeneity on the molecular level and (if possible) without reducing components.
3.5. Comparison of the behaviour under heating of ammonium copper(II)-iron(III) oxalate and copper(II)-iron(III) formate

The freeze-dried oxalate and formate precursors were prepared for the direct synthesis of copper ferrites $\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4 \pm \lambda$ ($0 \leq x \leq 0.5$) at low temperatures ($T \leq 700^\circ\text{C}$). From the XRD results, the freeze-dried ammonium copper(II)-iron(III) oxalate was characterized as a mixture of crystalline iron(III) and copper(II) oxalate components (Fig. 3.3.1) whereas the freeze-dried copper(II)-iron(III) formate was identified as a mixture of an amorphous iron(III) formate component and a small amount of crystalline copper(II) formate (Fig. 3.4.1). However, additional observations point out the existence of an interaction between the single metal components of these complex carboxylate precursors. In comparison to the patterns of single metal components, the complex carboxylate precursors have a lower crystallinity than the copper components and, their diffraction peaks are very close to those obtained for the iron components. Moreover, the thermal decomposition of the complex carboxylate precursors ends at temperatures relatively lower than that of the single metal components.

During the decomposition of the freeze-dried ammonium Cu(II)-Fe(III) oxalate precursors, the presence of CO in the gaseous products favours the partial reduction of Fe$^{3+}$ to Fe$^{2+}$, Cu$^{2+}$ to Cu$^{+}$ and Cu$^{2+}$ to Cu. Starting from the freeze-dried Cu(II)-Fe(III) formate precursors, the intermediate reduction of metal ions occurs due to the release of HCOOH and CO$_2$. Consequently, the properties of the reactive homogeneous precursors are affected and the synthesis of single phase copper iron oxides requires an annealing temperature close to that of a mixed oxide method. That means the advantage of the reactive homogeneous precursor can not lead to a low synthesis temperature of the complex oxides. This should also be a problem for other copper ferrite precursors which are likely to release reducing components during the decomposition.

The preparation of well-crystallized copper ferrite “CuFe$_2$O$_4$” from the freeze-dried oxalate and formate precursors requires a synthesis temperature greater than 700°C. In fact up to 700°C, the main phases are copper oxide (CuO) and iron oxide ($\alpha$-Fe$_2$O$_3$). The same conclusion is also valid for other compositions $\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4 \pm \lambda$ with $0.1 \leq x \leq 0.5$.

In the framework of the following part, the synthesis of copper ferrite powders is performed starting from metallic mixtures of Cu and Fe. The two main parts of this investigation are the following:
Comparison of the thermal behaviour of oxalate and formate precursors

- Synthesis of Cu-Fe phases
Due to the positive enthalpy of mixing within the system Cu-Fe [37], the synthesis of Cu-Fe alloys is prevented during the conventional heat treatment method. In the present work, Cu-Fe phases are prepared using a reduction method. For that, two different approaches are used. In the first one, freeze-dried ammonium Cu(II)-Fe(III) oxalate precursors are decomposed directly under hydrogen atmosphere and in the second one, oxide phases are generated from oxalate precursors before their heat treatment in hydrogen. The principal goal of this investigation is to see if the interdiffusion between copper and iron can take place during the reduction process.

- Oxidation of the synthesized Cu-Fe phases
For the synthesis of copper ferrite powders, the samples prepared using the reduction method are heated in air under controlling heating rates.
For the establishment of the relations between the kind of the starting powders and the oxidation processes, a reference investigation is also carried out. It is based on the synthesis of the copper ferrite by oxidation of the mixtures of iron and copper metal obtained using the mechanical milling method.
3.6. **Synthesis of copper ferrite from the metallic powders “Cu$_{1-x}$Fe$_{2+x}$” ($0 \leq x \leq 0.5$)**

3.6.1. **Synthesis of the metallic powders from the freeze-dried oxalate precursors**

It is well known that the reduction of Cu-Fe oxides proceeds rapidly under a pure hydrogen (H$_2$) atmosphere. Thus a reducing atmosphere of 2% H$_2$ in Ar (2%H$_2$/Ar) was chosen for the identification of the intermediate steps occurring during the reduction of freeze-dried ammonium Cu(II)-Fe(III) oxalate precursors.

The thermal decomposition under 2%H$_2$/Ar was studied using the TA (DTA, TG) and the MS methods. Under H$_2$, experiments were realized in a tubular furnace. For each trial, a defined amount of the starting powder (20-30 mg) was introduced in a quartz crucible and firstly purged during 20 minutes with the hydrogen. Thereafter, the sample was heated at a constant rate of 5-20 K/min up to a specific temperature in the range 400-600°C and then annealed during a specific time (3hours, 6 hours). The gas flow rate of ~10 l/h was maintained. When the reduction time was complete, the product was cooled down to RT under the same gas flow. The cooling rate of 20 K/min was used.

3.6.1.a. **Synthesis under 2%H$_2$ in argon**

The TA results show that under 2%H$_2$/Ar, the main decomposition steps of freeze-dried ammonium Cu$_x$Fe$_{2-x}$ oxalate precursors ($0 \leq x \leq 0.5$) are similar to those already observed under argon (Section 3.3.2.c). However, the third step due to the decomposition of iron(II) oxalate occurs endothermically under 2%H$_2$/Ar, while under argon an exothermic peak is observed (Section 3.3.2.c). This observation results from the fact that under 2%H$_2$/Ar, the exothermic crystallization of Cu/Cu$_2$O obtained from the second step is inhibited. Beside the previous difference, one observes that under 2%H$_2$/Ar, the decomposition temperature of the freeze-dried ammonium Cu$_x$Fe$_{2-x}$ oxalate precursors (~420°C) is almost 20°C above the temperature observed under argon (~400°C). At the end of the TA measurements performed up to 450°C, magnetite “Fe$_3$O$_4$” and copper metal “Cu” are formed. The absence of iron metal shows that the reduction of “Fe$_3$O$_4$” has not yet started. Many works performed on the reducibility of $\alpha$-Fe$_2$O$_3$ under low H$_2$ partial pressure were used for the determination of the reduction temperature of Fe$_3$O$_4$ into Fe. Because of the differences in the heating rate and in the composition of the reducing atmosphere employed by several authors, the temperatures
reported for the decomposition of $\text{Fe}_3\text{O}_4$ to Fe are different. For instance, under 5\%H$_2$/N$_2$ [132] and under 15\%H$_2$/Ar [133] atmospheres, the reduction temperature of $\text{Fe}_3\text{O}_4$ to Fe was found to be 497°C and 470°C, respectively. These data confirm once more the very slow reduction of $\text{Fe}_3\text{O}_4$ under a low H$_2$ partial pressure. Consequently the TA results obtained under 2\%H$_2$/Ar, which are quite similar to those obtained under argon, can be helpfully used for the determination of the primary gas-solid reactions taking place in presence of hydrogen. This implies thus that, the individual behaviour of the single metal oxalates taking place during the decomposition in argon (Section 3.3.2.c) occurs also under H$_2$ partial pressure.

### 3.6.1.b. Synthesis under hydrogen atmosphere

The XRD patterns of the products obtained after the reduction at 400°C (for 3 hours) of some freeze-dried ammonium Cu$_{1-x}$Fe$_{2+x}$ oxalates ($x = 0, 0.4, 0.5$) are shown in Figure 3.6.1. The different patterns show the diffraction peaks of iron carbide (Fe$_3$C), copper metal (Cu) and magnetite (Fe$_3$O$_4$). The amounts of Cu and Fe$_3$C varie according to the value of $x$. Regarding the spinel phase Fe$_3$O$_4$, only one of its most intensive peaks appearing at $2\theta = 35.4^\circ$ is used for its identification. This means that Fe$_3$O$_4$ was formed in small quantity or it is still amorph. For an annealing carried out at 450°C, the principal process that takes place is the increase of the amount of iron carbide "Fe$_3$C". The amount of copper remains constant and no important change is observed on the crystallinity and the amount of the Fe$_3$O$_4$ phase. It is then obvious that, the slight increase of the reduction temperature/time enhances the formation of Fe$_3$C.

**Figure 3.6.1:** XRD patterns of the products obtained after the reduction under H$_2$ of the freeze-dried ammonium Cu$_{1-x}$Fe$_{2+x}$ oxalate precursors at 400°C for 3hours. Heating rate: 5K/min.
Synthesis of copper ferrite from the metallic powders “Cu_{1-x}Fe_{2+x}” (0 \leq x \leq 0.5)

In accordance with Carles and coworkers [134], the main reactions taking place are the following:

\[
\text{FeC}_2\text{O}_4 \rightarrow \text{FeO} + \text{CO} + \text{CO}_2 \quad (1a)
\]

\[
4\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe} \quad (1b)
\]

The iron Fe formed from the reaction (1b) is not stable and is quickly converted into iron carbide (Fe$_3$C) by the action of CO/ H$_2$ [134]. The possible reactions are:

\[
3\text{Fe} + 2\text{CO} \rightarrow \text{Fe}_3\text{C} + \text{CO}_2 \quad (2a)
\]

\[
3\text{Fe} + \text{CO} + \text{H}_2 \rightarrow \text{Fe}_3\text{C} + \text{H}_2\text{O} \quad (2b)
\]

On the basis of the processes (2a) and (2b), it turns out that the increase of the amount of CO in the gaseous decomposition products enhances the formation of the iron carbide “Fe$_3$C”. After 3 hours of reduction at 600°C under H$_2$, the product contains iron (Fe) and copper (Cu) metal as main phases. This indicates that the decomposition of Fe$_3$C and Fe$_3$O$_4$, formed according to the processes (1a), (1b) and (2a), (2b), takes place between 450 and 600°C. The main reactions responsible for the reduction of Fe$_3$O$_4$ to Fe can be formulated as follows [134]:

\[
\text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2\text{O} \quad (3)
\]

\[
\text{Fe}_3\text{C} + 2\text{H}_2 \rightarrow 3\text{Fe} + \text{CH}_4 \quad (4)
\]

\[
\text{Fe}_3\text{O}_4 + \text{H}_2 \rightarrow 3\text{FeO} + \text{H}_2\text{O} \quad (5a)
\]

\[
\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O} \quad (5b)
\]

The reaction (3) is the combination of the reactions (5a) and (5b). Using the thermodynamic data, the stability of Fe$_3$C and Fe$_3$O$_4$ under hydrogen stream can readily be predicted. In fact at a given temperature, the change of the standard free enthalpy of a reaction can be calculated using the following relation:

\[
\Delta G^\circ_T = \sum G^\circ_T(\text{products}) - \sum G^\circ_T(\text{reactants}) = -RT \ln K \quad (i)
\]

where \(\sum G^\circ_T(\text{reactants})\) and \(\sum G^\circ_T(\text{products})\) are the free enthalpy of formation of reactants and products, respectively; R is the gas constant, T is the temperature and K is the equilibrium constant. When the standard free enthalpy of the system is negative, K is greater than one (K > 1) and the reaction can occur in the written direction. On the other hand, a positive value of the standard free enthalpy shows that the reaction can be realized more in the opposite
Synthesis of copper ferrite from the metallic powders “Cu_{1-x}Fe_{2+x}^{0.5}” (0 ≤ x ≤ 0.5)

direction (K < 1). At a defined temperature, the equilibrium constant of a reaction is given by
the following relation:

\[ \text{lg } K = \sum \text{lg } K (\text{products}) - \sum \text{lg } K (\text{reactants}) \]  

(ii)

where \( \sum \text{lg } K (\text{reactants}) \) and \( \sum \text{lg } K (\text{products}) \) are the equilibrium constant of the reactants and the products, respectively. From the obtained data, \( \text{lg } K \) versus T may then be plotted and used for the direct evaluation of the reaction equilibria as the temperature increases.

\[ \begin{align*}
(3) & \quad \text{Fe}_3\text{O}_4 + 4\text{H}_2 \rightarrow 3\text{Fe} + 4\text{H}_2 \\
(4) & \quad \text{Fe}_3\text{C} + 2\text{H}_2 \rightarrow 3\text{Fe} + \text{CH}_4
\end{align*} \]

Figure 3.6.2: \( \text{lg } K \) versus T for the reactions (3) and (4) (calculated using the thermodynamic data given in [30]).

In Figure 3.6.2, the plots \( \text{lg } K \) versus T are shown for the reactions (3) and (4). The equilibrium constant of the reaction (4) is found to be greater than one only for temperatures lower or equal to 450°C. However, the equilibrium constant of the reaction (3) is lower than one. From the explanations given above, it turns out that below 450°C the direct reduction of \( \text{Fe}_3\text{O}_4 \) in Fe (3) is not favorable whereas that of \( \text{Fe}_3\text{C} \) in Fe (4) is. Moreover, one observes that when the reduction temperature increases, the equilibrium constant value of the reaction (3) tends towards one whereas that of the reaction (4) decreases continuously. It follows that above 450°C, the reduction of \( \text{Fe}_3\text{C} \) in Fe requires a continuous increase of the hydrogen partial pressure (p(H2)) in the working atmosphere while the reduction of \( \text{Fe}_3\text{O}_4 \) in Fe should occur more and more and also at weaker p(H2). In recent works, the reduction of \( \text{CuFe}_2\text{O}_4 \) was studied under low partial pressure of hydrogen [133, 135]. It was observed that under atmosphere of 5%H2/Ar, the reduction occurs gradually up to 800°C and led to a
Synthesis of copper ferrite from the metallic powders “$\text{Cu}_{1-x}\text{Fe}_{2+x}$” ($0 \leq x \leq 0.5$)

product containing FeO, Cu and Fe [135]. Under a more reducing atmosphere (15%H$_2$/85% Ar), a product containing copper and iron metal was formed at the end of the reduction process (440°C) [133]. With the aim of further investigating the synthesis of the phases Cu-Fe using the reduction method, Cu-Fe oxides obtained from the decomposition in air of freeze-dried ammonium Cu(II)-Fe(III) oxalate precursors were also subjected to several heat treatments in H$_2$. After the decomposition of oxalate precursors at 400°C (3 hours) under argon, the resulting products containing a partially crystalline spinel phase and a small amount of $\alpha$-Fe$_2$O$_3$ were reduced at 450°C (3 hours) under H$_2$. On the XRD patterns of the products, copper (Cu) and iron metal (Fe) were identified as main phases. In addition, a small amount of magnetite “Fe$_3$O$_4$” was indexed as secondary phase. For further investigations, the aforementioned partially crystalline powder obtained at 400°C under argon was also calcined at 1000°C during 24 hours in presence of air. From this treatment, the formation of well crystalline copper ferrite powders was confirmed on the resulting XRD patterns. Using the thermogravimetry method, the as-prepared powders were reduced completely in H$_2$ atmosphere at 800°C. For around 1.1-1.5g of oxide a reduction time of 24-30 hours was necessary for the formation of a product containing only the diffraction peaks of copper (Cu) and iron (Fe) metal.

By taking in consideration the results obtained in 2%H$_2$/Ar (Section 3.6.1.a.) it turns out that, the decomposition of freeze-dried ammonium Cu(II)-Fe(III) oxalates in H$_2$ is characterized by the individual decomposition of copper and iron oxalate. Copper oxalate decomposes below 400°C with the formation of copper metal (Cu). Regarding the iron oxalate, a temperature of at least 450°C is required and leads to a product containing Fe$_3$O$_4$ and Fe$_3$C. Thereafter, thermal treatments above 450°C are necessary for the formation of iron metal (Fe). On the other hand, oxide phases obtained from the decomposition of the mentioned precursors are also reduced in two main steps leading to the formation of copper and iron metal without an interaction between them.

To summarize, we have studied the reduction in H$_2$ atmosphere of freeze-dried ammonium Cu(II)-Fe(III) oxalates as well as that of their products of decomposition obtained in air. XRD and TA results indicate that these precursors loose their homogeneous state during the reduction under an atmosphere of H$_2$. Consequently, the copper components (oxide and oxalate) are reduced before the iron phase. Moreover, an additional factor having eventually an influence on the interaction between copper and iron should be the instability of Cu-Fe alloy in the temperature range 300-600°C [45 - 47].

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3.6.2. Oxidation of the metallic powders

3.6.2.a. Oxidation of reduced freeze-dried ammonium Cu(II)-Fe(III) oxalates

The mixtures of copper-iron metal obtained from the reduction of freeze-dried ammonium Cu(II)-Fe(III) oxalates under H₂ at 450°C/6 hours were oxidized in presence of air. Figure 3.6.3 shows an example of the XRD patterns of the products obtained after 3-24 hours of heat treatment at different temperatures.

One sees that after 3 hours of heat treatment at 400°C, the total oxidation of the metallic powder occurs. The product contains a partially crystalline spinel phase (γ-Fe₂O₃ and/or Fe₃O₄), hematite (α-Fe₂O₃) and tenorite (CuO). When the sample preheated at 400°C is annealed at 600°C for 24 hours, only the oxide phases α-Fe₂O₃ and CuO are identified. The disappearance of the less crystalline spinel phase, formed at 400°C, suggests that the transition γ-Fe₂O₃ → α-Fe₂O₃ has taken place in the range 400-600°C. Having regards to this fact, the synthesis of the copper ferrite should be performed only at a high temperature by a conventional solid state reaction. Up to 1000°C, it is clearly seen that the oxidation of the mixture 0.9Cu:2.1Fe leads to the formation of a single spinel phase. A similar result was obtained during the synthesis of copper ferrite from carboxylate precursors (Sections 3.3.3 and 3.4.3).
3.6.2.b. oxidation of mechanical milled Cu-Fe mixtures

The mixtures of copper and iron investigated in this part result from the mechanical milling during 3 hours of defined amounts of copper and iron metal (Section 8.4). A short-time of milling was selected since extended milling introduces significant quantities of impurities into the powder. The XRD patterns of the mixtures (1-x)Cu:(2+x)Fe, with the compositions varying from \(x = 0\) to \(x = 0.5\), obtained from the ball mill process show the individual peaks of copper and iron metal. Figure 3.6.4 presents the XRD patterns of the products obtained from the oxidation at different temperatures of the sample with \(x = 0.1\).

Contrary to the results obtained at 400°C during the oxidation of the reduction products of ammonium Cu(II)-Fe(III) oxalate precursors (Fig. 3.6.3), it is found that after an annealing time of 3 hours in air, the oxidation of the metal phase is not complete (Fig. 3.6.4). The product is constituted of copper metal, iron metal, a spinel phase (\(\gamma\)-Fe\(_2\)O\(_3\) and/or copper containing \(\gamma\)-Fe\(_2\)O\(_3\)) and single oxide (Cu\(_2\)O, CuO, \(\alpha\)-Fe\(_2\)O\(_3\)) phases. Further annealing up to 600°C enhances the total oxidation of the metals and the resulting product is constituted \(\alpha\)-Fe\(_2\)O\(_3\) and CuO. The diffraction peaks due to the presence of the spinel phase are not indexed. By increasing the temperature of treatment up to 800°C, a new crystalline spinel phase “CuFe\(_2\)O\(_4\)” is formed as a result of solid-solid interaction between \(\alpha\)-Fe\(_2\)O\(_3\) and CuO. For all mixtures, copper ferrite is detected as major phase beside \(\alpha\)-Fe\(_2\)O\(_3\) (increasing amount
with $x$) and CuO (decreasing amount with $x$). When the treatment temperature is further increased up to 1000°C, after slow cooling, the pattern of the sample with $x = 0.1$ can be indexed to a single phase of tetragonal copper ferrite with lattice parameters of $a_0 = 584.7$ pm and $c_0 = 858.9$ pm. From the Figure 3.6.5, one clearly sees that the phase composition of the product after annealing in air at 1000°C strongly depends on $x$. For the mixture 1Cu:2Fe, the diffraction lines of $\alpha$-Fe$_2$O$_3$ disappear completely, but a small amount of CuO is detected as a second phase beside the tetragonal copper ferrite. According to several authors [59, 94, 95], the presence of free CuO is due to the partial reduction of Cu$^{2+}$ to Cu$^+$. For $x = 0.2$, the sample contains a cubic spinel phase (major phase) and a tetragonal copper ferrite (minor phase). The decrease of the tetragonal distortion can be ascribed to the decrease of the amount of Cu$^{2+}$ ions inside the octahedral sites [59]. When $0.2 < x \leq 0.5$, the decrease of the copper content is associated with a gradual increase of the amount of $\alpha$-Fe$_2$O$_3$ present beside the cubic and the tetragonal spinel phase.

![Figure 3.6.5: XRD patterns of the mixtures 1Cu:2Fe (x=0), 0.9Cu:2.1Fe (x=0.1), 0.8Cu:2.2Fe (x=0.2), 0.67Cu:2.33Fe (x=0.33), 0.6Cu:2.4Fe (x=0.4) and 0.5Cu:2.5Fe (x=0.5) preheated at 400°C (3h, air) and calcined at 1000°C during 24 hours in air, slow cooling.](image)

From these results it seems to be possible that, when the synthesis is performed at 1000°C in air, (a) the composition of the spinel phase is around Cu$_{0.9}$Fe$_{2.1}$O$_4$ inside the sample containing copper and iron in the ratio of 1:2, and (b) for samples with $0.2 < x \leq 0.5$, the
composition of the spinel phase is about Cu_{0.8}Fe_{2.2}O_4. After rapid cooling all samples contain only the cubic spinel beside some CuO (x = 0), or beside α-Fe_2O_3 (0.2 < x ≤ 0.5), or as a single phase (x = 0.1, 0.2). According to Kim et al. [136], 20% replacement of copper by iron in the copper ferrite “CuFe_2O_4” transforms the crystal structure from tetragonal to cubic. Based on our observations, the results of Kim et al. [136] must be relativated: with the increase of the iron content in the ferrite, the Cu^+-content increases and the temperature of transformation from tetragonal to cubic decreases. The higher the temperature of transformation, the higher the cooling rate must be to freeze the cubic form at room temperature.

It is found that, under the same working conditions, the oxidation rate of Cu-Fe mixtures resulting from the reduction of Cu-Fe oxalate precursors is significantly higher than that of mixtures of pure copper and iron. The reason for the increase in the oxidation rate with respect to the mixture of pure Cu-Fe is the high reactivity of metallic phases resulting from the decomposition of carboxylate precursors. At 600°C, copper oxide (CuO) and hematite (α-Fe_2O_3) are the main phases in the product of both starting powders. According to the results of the sections 3.3 and 3.4, it turns out that the synthesis of copper ferrite from the investigated metallic powders also requires a minimal temperature of 1000°C.
3.7. **Comparison between the unconventional “freeze-drying method” and the ceramic method**

The above sections 3.2-3.6 were based on the study of the chemical reactions that lead to the formation of copper ferrite \( \text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_{4+\lambda} \) with \( 0 \leq x \leq 0.5 \) using the ceramic and the non-conventional method. As already mentioned in the introduction, the interest of the freeze-drying method laid on the study of the thermal decomposition of single and mixed metal carboxylates under different atmospheres and also, on the determination of the influence of organic ligands (\( \text{C}_2\text{O}_4^{2-} \) and HCOO\(^-\)) on the phase formation. Furthermore, the ceramic method was performed in order to establish the influence of starting materials on the final synthesis temperature of oxide phases. For the ceramic method, the starting materials were the mixtures of oxides (\( \text{CuO} \) and \( \alpha\)-\( \text{Fe}_2\text{O}_3 \)) and metals (\( \text{Cu} \) and \( \text{Fe} \)). For the non-conventional method, the precursors were the freeze-dried Cu-Fe oxalate and formate powders.

In contrast to the prediction of some authors [94, 95], we found that a pure \( \text{CuFe}_2\text{O}_4 \) cannot be obtained by the conventional ceramic method at a temperature lower or equal to 800°C. To bypass this drawback, we have investigated the thermal decomposition of reactive Cu-Fe carboxylate precursors of appropriate composition (Sections 3.3 and 3.4). The thermal decomposition already finishes at about 400°C. Nevertheless, a single phase copper ferrite is not obtained because of the intermediate reduction of \( \text{Cu}^{2+} \) to \( \text{Cu} \) by the carboxylate. This results in a phase separation and the full reaction to the complex oxide also needs a temperature higher than 800°C. It follows that the advantage of using non-conventional methods is lost. When the treatment temperature is further increased up to 1000°C, the composition of the products obtained using the non-conventional method are identical to those obtained using the ceramic method. However, the amount of simple oxide phases (\( \text{CuO} \) and \( \alpha\)-\( \text{Fe}_2\text{O}_3 \)) is more important inside the product obtained using the ceramic method.

For all the investigated samples \( \text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_{4+\lambda} \) \( (0 \leq x \leq 0.5) \), the products which are formed at 800°C are constituted of a mixture of simple (\( \text{CuO} \), \( \alpha\)-\( \text{Fe}_2\text{O}_3 \)) and mixed oxide phases. Furthermore, only the compositions \( \text{Cu}_{0.9}\text{Fe}_{2.1}\text{O}_4 \) and \( \text{Cu}_{0.8}\text{Fe}_{2.2}\text{O}_4 \) can be prepared as single spinel phase in presence of air at 1000°C.
3.8. Synthesis of $\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_{4+\lambda}$ $(0 \leq x \leq 0.5)$: Influence of the temperature and the oxygen partial pressure on the phase formation and composition

Thermodynamic calculations provide information about the behaviour of a system at various temperatures and concentrations of species. If the Gibbs free energy of formation of all components of the system are known, they can be used for predicting the equilibrium composition and to indicate whether a particular reaction can proceed or not. For the Cu-Fe-O system the thermodynamic data of binary (FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, CuO, Cu$_2$O) and ternary (CuFe$_2$O$_4$ and CuFeO$_2$) phases are well known [30, 31]. Using the relation (i), with the help of the free energy values from Barin [30] calculated for different temperatures, coexistence equilibria between different oxide phases under the conditions of experiments can be predicted and the stability of the aforementioned oxide phases can be derived for any pressure of oxygen present (Section 11.3).

$$\lg p(O_2) = f(\Delta G^+, T)$$

(i)

The Figure 3.8.1 shows the plot $\lg p(O_2)$ versus $(1000/T)$ of Cu-O and Fe-O systems. One sees that depending on the heat treatment conditions copper and iron can be stabilized in two valences Cu$^+$/Cu$^{2+}$ and Fe$^{2+}$/Fe$^{3+}$, respectively.

![Figure 3.8.1: $\lg p(O_2)$ versus $(1000/T)$ diagram of Cu-O and Fe-O systems (calculated using the thermodynamic data given in [30]).](image)
In general it is known that, for a given system a phase transformation to the lower valence oxide occurs if the p(O\textsubscript{2}) falls below the equilibrium value at constant temperature or if the temperature exceeds a critical value at constant oxygen pressure. This implies that in air, up to 1000°C, the reduction of Cu\textsuperscript{2+} to Cu\textsuperscript{+} is the main reaction taking place in the Cu-Fe-O system (Fig. 3.8.1). Under the same atmosphere, the reduction of Fe\textsuperscript{3+} to Fe\textsuperscript{2+}, leading primarily to the decomposition of α-Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4} will occur above 1000°C. According to these thermodynamic results, the formation and the stabilisation of oxide materials in the Cu-Fe-O system should suffer from chemical changes when subjected to heat treatments. Furthermore, extensive works available in the literature point out the influence of the temperature and the p(O\textsubscript{2}) on the phase formation in the system under consideration [70, 89, 91, 92]. Schaeffer et al. [91] have identified nine coexistence regions for different complex and simple oxides under p(O\textsubscript{2}) from 10\textsuperscript{-4} to 5.10\textsuperscript{-1} atm and temperatures from 900 to 977°C. From the XRD analysis, in agreement with the chemical analysis, these authors found that copper ferrite exists only as solid solution with a Fe:Cu ratio greater than two. Another investigation of the phase relation was carried out by Jacob et al. [92].

Figure 3.8.2: Phase diagram of the Cu-Fe-O system at 1000°C (Jacob and coworkers [92]).
They used the thermodynamic informations and a computational program to calculate and establish the effect of the temperatures below 1600°C on the phase formation in the Cu$_2$O-CuO-Fe$_2$O$_3$ system, at p(O$_2$) equal 1 and 10$^{-4}$ atm. They found that delafossite “CuFeO$_2$” is unstable at 1 atm, while both CuFeO$_2$ and CuFe$_2$O$_4$ (solid-solution) phases are stable at 10$^{-4}$ atm. The same authors have proposed a schematic representation of phase equilibrium in the system Cu-Fe-O as a function of the p(O$_2$) at 1000°C (Fig. 3.8.2). From this diagram, they conclude that the spinel solid solutions Cu$_x$Fe$_{3-x}$O$_4$ (0 ≤ x ≤ 1) have a large range of stability for the p(O$_2$) ranging from 10$^{-12.7}$ atm (for Fe$_3$O$_4$) to 1 atm (for compositions with x about 1) and furthermore that the “Cu$_x$Fe$_{3-x}$O$_4$” spinel phase field is extremely narrow in the range 10$^{-2.5}$ atm to 10$^{-4}$ atm.

This review clearly shows the influence of the temperature (T) and the oxygen partial pressure (p(O$_2$)) on the phase formation in the Cu-Fe-O system. However, it is noted that in this system, the phase equilibrium as well as the extent of the spinel solid solution field were extensively studied only in the interval of temperature 900-1000°C. The main purpose of the present part is to (1) determine the phase composition in the Cu$_{1-x}$Fe$_{2+x}$O$_{4+\lambda}$ (0 ≤ x ≤ 0.5) system, for different temperatures (800-1200°C) and p(O$_2$) ranging from 10$^{-3}$ to 0.209 atm and (2) to find out the conditions (T, p(O$_2$)) required for the synthesis of single Cu$_{1-x}$Fe$_{2+x}$O$_{4+\lambda}$ (0 ≤ x ≤ 0.5) spinel phases. Our attention is also focused on the study of the consequences resulting from the oxygen exchange between the oxide powders and the gaseous phase. This last investigation is performed under more reduced atmosphere p(O$_2$) in the range 10$^{-5}$-10$^{-4}$ atm at 800°C, 900°C and 1000°C.

### 3.8.1. Phase formation as a function of temperature at constant oxygen partial pressure

From the above, it is followed that the formation of single Cu$_{1-x}$Fe$_{2+x}$O$_{4+\lambda}$ (0 ≤ x ≤ 0.5) spinel phases requires a high temperature and eventually the control of the working atmosphere; this confirms the predictions already mentioned in Sections 3.3 and 3.4. Given that, under these conditions, the diffusion rate of reactants is mostly controlled by the temperature; the nature of starting materials should not have a great influence on the course of the ferritization process (formation of the ferrite phase). Thus, we explore in this part the possibility of using mixtures of fine grained metals as starting materials. In this way, contrary to the thermal decomposition of reactive carboxylate precursors (sections 3.3 and 3.4), the synthesis conditions are independent of the influence of carbon containing impurities on the p(O$_2$) during synthesis.
Synthesis of Cu_{1-x}Fe_{2+x}O_{4+\lambda} \ (0 \leq x \leq 0.5) : Influence of T and p(O_2)

Experimental

The complex oxide samples obtained in air at 1000°C, from intimate mixtures of copper and iron metal, were used as starting powders. The details on the preparation and the compositions of these samples are given in Section 3.6 (Fig. 3.6.5). For the present experiments, the powders were weighed (0.3-0.5g) into a quartz or alumina crucible and heated at a defined temperature during 6-24 hours. The working temperatures (800-1200°C) were reached with a heating rate of 10K/min and the desired oxygen partial pressures were achieved using different gas mixtures prepared from oxygen or air combined with argon, using a pump (Digamix Pump type 5KA, Wösthoff GmbH) (Table A6, Section 11.4). Furthermore, the oxygen partial pressure in the gas flow was controlled with a solid electrolyte cell device. The oxygen stoichiometry in different single spinel phases was determined by thermogravimetry, during total reduction in a stream of hydrogen at 800°C (Section 9.2.1). The obtained results were close to the theoretical value of 4.0.

To maintain the phases formed above 1000°C or under a low oxygen partial pressure (p(O_2) < 0.212 x 10^5 Pa), it was necessary to quench the material. This observation is consistent with the literature [70]. Consequently, the samples prepared in air were quenched in water. However, those treated under a gas stream with low oxygen content (argon + 0.1% O_2, argon + 1% O_2, argon + 1% air) were quenched by pulling the quartz boat from the hot to the cold zone of the tube (“rapid cooling”). Particularly for the samples prepared in air at 800°C in an alumina boat, the cooling process was done inside a desiccator. With regard to the synthesis of a single phase CuFe_2O_4, several synthesis processes were done in oxygen atmosphere at relatively low temperatures (700°C and 800°C). The phase composition was determined by XRD analysis method.

3.8.1.a. Heat treatment in air

Figures 3.8.3 - 3.8.6 illustrate the effect of the annealing temperature on the phase formation in air. Comparing the XRD patterns obtained after annealing at 800°C (Fig. 3.8.3) with those of the starting materials (Fig. 3.6.5), one observes that all samples contain the tetragonal spinel; for x = 0.1 or 0.2, hematite is formed as a second phase, for the samples with 0.33 \leq x \leq 0.5, the portion of hematite is increased and for the composition with x = 0, the tenorite (CuO) portion is somewhat lower. From these results, it is clear that the ferrite samples obtained in air at 1000°C are unstable at lower temperatures. The lower oxygen coexistence pressure of the samples at 800°C is due to the gain of the oxygen followed by the
release of iron from the ferrite lattice in the form of $\alpha$-Fe$_2$O$_3$. This should enhance the
formation of a copper(II)-rich spinel phase following the reactions (1) and (2).

$$
(1-x+y)Cu_{1-x}Fe_{2+x}O_4 + \frac{y}{4}O_2 \rightarrow (1-x)Cu_{1-x+y}Fe_{2+2y}O_4 + \frac{3y}{2}Fe_2O_3
$$

(1)

$$
(2+x-y)Cu_{1-x}Fe_{2+x}O_4 + 3yCuO + \frac{y}{2}O_2 \rightarrow (2+x)Cu_{1-x+y}Fe_{2+2y}O_4
$$

(2)

(with $0 \leq x \leq 0.5 ; y \leq x$)

The increase of the amount of free $\alpha$-Fe$_2$O$_3$ with increasing iron content (Fig. 3.8.3) demonstrates clearly that inside all samples obtained at 800°C, a nearly fixed composition of the spinel phase is present in addition to small amount of a second phase of $\alpha$-Fe$_2$O$_3$ ($x \geq 0.1$) or CuO ($x = 0$).

Figure 3.8.3: XRD patterns of Cu$_{1-x}$Fe$_{2+x}$O$_4$ ($0 \leq x \leq 0.5$) prepared in air at 1000°C and annealed 24 hours at 800°C. Slow cooling.

Figure 3.8.4 shows the XRD patterns for the sample with $x = 0$ after annealing in air at 1050°C and 1100°C. In comparison with the pattern obtained at 1000°C (Fig. 3.8.4(a)) it is observed that after annealing at 1050°C the product contains a cubic phase and some delafossite (CuFeO$_2$) (Fig. 3.8.4(b)). However after annealing at 1100°C, cuprite (Cu$_2$O) is
formed as a second phase (Fig. 3.8.4(c)). For a sample with \( x = 0.4 \), the \( \alpha \)-Fe\(_2\)O\(_3\) content decreases when the annealing temperature increases. After annealing that sample at 1150°C, a single phase cubic spinel is obtained (Fig. 3.8.5(d)).

**Figure 3.8.4:** XRD patterns of CuFe\(_2\)O\(_4\) prepared in air at (a) 1000°C and annealed at (b) 1050°C and (c) 1100°C (air). Rapid cooling

**Figure 3.8.5:** XRD patterns of Cu\(_{0.6}\)Fe\(_{2.4}\)O\(_4\) prepared in air at (a) 1000°C and annealed at (b) 800°C, (c) 1100°C and (d) 1150°C (air). Rapid cooling
Synthesis of Cu$_{1-x}$Fe$_{2+x}$O$_{4+\lambda}$ ($0 \leq x \leq 0.5$): Influence of T and p(O$_2$)

The results of X-ray phase analysis of all Cu$_{1-x}$Fe$_{2+x}$O$_4$ samples annealed in air are summarized in Figure 3.8.6. It turns out that above 1000°C in air, the stability of the ferrite samples “Cu$_{1-x}$Fe$_{2+x}$O$_4$” with $0 < x < 0.2$ decreases as the temperature increases while, for $0.2 < x \leq 0.5$, the presence of α-Fe$_2$O$_3$ in the primary product results in the formation of more ferrite (rich in iron). With regard to the synthesis of single phase copper ferrite spinels, it is noted that the heat treatment temperature must be increased as the content of iron increases.

The oxygen coexistence pressures of the binary metal oxides in the system Cu-Fe-O plotted as function of the temperature are presented in Figure 3.8.1. By extrapolation one sees that, above 1000°C, the reduction of Cu$^{2+}$ to Cu$^{+}$ should be the principal reaction taking place in air. This means that the formation of monovalent copper leads, for $0 < x < 0.2$, to the partial decomposition of the spinel (following the reactions (3) or (4)) and, for $0.2 < x \leq 0.5$, to the increase of the ferritization process (formation of the ferrite following reaction (1) in reversed order). The latter is materialized on the XRD patterns by the decrease of the intensity of the characteristic peaks of α-Fe$_2$O$_3$ with the increase of the temperature.

\[
(1 + 2x + 2y)\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4 \rightarrow (1 + 2x)\text{Cu}_{1-x-y}\text{Fe}_{2+x+y}\text{O}_4 + 3y\text{CuFeO}_2 + y\text{O}_2 \quad (3)
\]
Synthesis of Cu$_{1-x}$Fe$_{2+x}$O$_{4+y}$ (0 ≤ x ≤ 0.5): Influence of T and p(O$_2$)

\[(2 + x + y)\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4 \rightarrow (2 + x)\text{Cu}_{1-x-y}\text{Fe}_{2+x+y}\text{O}_4 + \frac{3y}{2}\text{Cu}_2\text{O} + \frac{5y}{4}\text{O}_2\] (4)

(with 0 ≤ x ≤ 0.5 ; y ≤ 0.5 - x)

At a critical temperature (\(\theta_{cr}\)) a single spinel phase is formed. An increase of \(\theta_{cr}\) with the iron content is observed. In fact for the composition with x = 0.33, a single spinel phase is formed at about 1100°C while for x = 0.5 a temperature of 1250°C is required [70].

3.8.1.b. Heat treatment under a reducing atmosphere

Figure 3.8.7 illustrates the relation between the composition parameter x and phase formation on annealing at 1000°C under a constant oxygen partial pressure p(O$_2$) = 1.013 x 10$^3$ Pa.

As x increases, three regions of phase stability are defined namely, cuprospinel + delafossite (x = 0…0.1), a single spinel phase (x = 0.2), and cuprospinel + hematite (0.2 < x ≤ 0.5).

It can be concluded from Figures 3.8.8 - 3.8.10 that, this result can be generalized for other temperatures and other p(O$_2$). The stability field of CuFeO$_2$ (beside spinel) increases with the temperature, while that of \(\alpha\)-Fe$_2$O$_3$ (beside spinel) decreases. Under the investigated p(O$_2$), the existence domain of a single spinel phase is narrow. This tightness becomes more
predominant when the $p(O_2)$ in the surrounding atmosphere decreases until $p(O_2) = 1.013 \times 10^2$ Pa.

Figure 3.8.8: Phase stability in the system Cu-Fe-O at $1.013 \times 10^3$ Pa (argon + 1% $O_2$).

Figure 3.8.9: Phase stability in the system Cu-Fe-O at $3.2 \times 10^2$ Pa (argon + 1% air).
Synthesis of Cu$_{1-x}$Fe$_{2+x}$O$_{4+\lambda}$ ($0 \leq x \leq 0.5$): Influence of $T$ and $p$(O$_2$)

Figure 3.8.10: Phase stability in the system Cu-Fe-O at 1.013 x 10$^2$ Pa (argon + 0.1% O$_2$).

At a given temperature, while decreasing the copper content, the peaks intensity of delafossite decreases (coexistence equilibrium according to (3)). Then, up to a critical value of $x$ labelled “$x_{cr}$”, a single cubic spinel phase is formed. For the composition with $x$ greater than $x_{cr}$, hematite is identified as a second phase beside the spinel phase (coexistence equilibrium according to (1)). The increase of the temperature or the decrease of the oxygen partial pressure displaces the value of $x_{cr}$ to a higher value of $x$. At $p$(O$_2$) < 1.013 x 10$^2$ Pa and $\vartheta \geq 1000$°C Fe$^{2+}$-containing cuprospinels with $x < 0.5$ are formed (Section 3.8.2). At about 1000°C and low oxygen partial pressure, a disproportionation of cuprospinels with the formation of delafossite and hematite takes place following the reaction (5). This result is in agreement with investigations reported in [92, 93].

$$
Cu_{1-x}Fe_{2+x}O_4 \rightarrow (1-x)CuFeO_2 + \frac{1+2x}{2}Fe_2O_3 + \frac{0.5-x}{2}O_2
$$

(5)

Partial conclusion

The results discussed above show that the oxidation of copper-iron mixtures is a suitable method for preparing single phase copper ferrites Cu$_{1-x}$Fe$_{2+x}$O$_4$ with $0.1 \leq x \leq 0.5$. Because of
the different content of \( \text{Cu}^{1+} \) as function of \( x \), each composition requires a defined \( p(\text{O}_2) \)-temperature regime for synthesis. When the working temperature increases, the oxygen coexistence pressure of the sample increases as well as the reduction of \( \text{Cu}^{2+} \) to \( \text{Cu}^+ \). The synthesis of a pure \( \text{CuFe}_2\text{O}_4 \) (\( x = 0 \)) is prevented at higher temperatures (\( \vartheta \geq 1000^\circ \text{C} \)) by the reduction of some \( \text{Cu}^{2+} \) to \( \text{Cu}^+ \). For the compositions with \( x \) belonging to the interval \( 0.1 \leq x \leq 0.5 \), single phases are obtained under the conditions defined above. The increase of \( x \) requires an increase of the reaction temperature and/or a decrease of the \( p(\text{O}_2) \) in the reaction gas stream. In air, with the increase of the iron content, the annealing temperature must be increased from 1000°C for \( x = 0.1 \) and \( x = 0.2 \) to about 1250°C for \( x=0.5 \). Under reduced atmosphere (\( 1.013 \times 10^3 < p(\text{O}_2) \) (Pa) < \( 1.013 \times 10^3 \)) the firing temperature must vary from 800°C for \( x = 0.1 \) to 1110°C for \( x = 0.5 \). We showed that, the narrowness of the spinel field, in the \( p(\text{O}_2) \) ranging from \( 10^{-2.5} \) to \( 10^{-4.5} \) atm (\( 3.2 \times 10^2 \) to \( 3.2 \) Pa), observed at 1000°C by Jacob et al. [92] is maintained up to 1200°C. The \( p(\text{O}_2) \)-temperature conditions required for the synthesis of single spinel phases \( \text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4 \) are summarized in Figure 3.8.11.

---

**Figure 3.8.11**: Conditions required for the synthesis of single spinel phases \( \text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4 \)

\((0.1 \leq x \leq 0.5)\)
3.8.1.c. Heat treatment in oxygen: attempts for the synthesis of a pure copper ferrite

“CuFe_2O_4” (x = 0)

According to Jacob et al. [92] a stoichiometric copper ferrite CuFe_2O_4 should exist at p(O_2) equal 1.013 x 10^5 Pa only below 800°C. Following the equation \( \Delta G^\circ = (17150-17.99 \ T) \pm 300 \ J \), the authors determined a decomposition temperature of 680°C. However a value of 400°C was calculated from thermodynamic data for CuO, Fe_2O_3 and CuFe_2O_4, given in [30]. Despite the observed discrepancy one notes that, the synthesis of CuFe_2O_4 should be possible only in a very small temperature interval. Due to the fact that the solid state reaction between CuO and \( \alpha \)-Fe_2O_3 ends only at about 1000°C (Section 3.2), further investigations for the synthesis of a pure “CuFe_2O_4” (x = 0) were performed using as starting material the product obtained at 1000°C/air. In order to proceed, the sample prepared in air at 1000°C (Fig. 3.6.5) was annealed in oxygen atmosphere at 700°C and 800°C. Figure 3.8.12 presents the XRD analysis results.

**Figure 3.8.12:** XRD patterns of CuFe_2O_4 prepared at (a) 1000°C, annealed in O_2 at 700°C (b) during 24 hours and at 800°C during (c) 50 hours and (d) 100 hours.
After synthesis at 1000°C/air, CuFe$_2$O$_4$ contains a tetragonal copper ferrite (as predominant phase) and a small amount of CuO (Fig. 3.8.12(a)). The annealing of this sample under oxygen atmosphere at 700°C during 24 hours leads to the additional formation of some α-Fe$_2$O$_3$ beside the spinel phase and CuO (Fig. 3.8.12(b)). This means, the Cu/Fe ratio in the spinel is somewhat increased. Since at 700°C the solid state reaction between CuO and α-Fe$_2$O$_3$ is negligible [94], 800°C was chosen as working temperature for further investigations. The XRD patterns obtained after annealing at 800°C are shown on Figure 3.8.12(c) and (d). After 50 hours (Fig. 3.8.12(c)), one sees that the amount of free CuO and Fe$_2$O$_3$ decreases a little bit. Up to 100 hours (Fig. 3.8.12(d)) of heat treatment, the remaining “small” amounts of CuO and α-Fe$_2$O$_3$ do not vary much. They act as inactive phases.

Partial conclusion

From the above it turns out that, under oxygen atmosphere at 700 and 800°C, the oxidation of the Cu$^+$ formed during the sintering process at 1000°C leads to the loss of some iron in the form of α-Fe$_2$O$_3$ from the ferrite lattice. The solid state reaction between CuO and α-Fe$_2$O$_3$ takes place simultaneously and is aborted when the maximum composition of the spinel phase Cu$_{1-\eta}$Fe$_{2+\eta}$O$_4$ (with $\eta \geq 0$) is reached. This implies that the synthesis of a pure copper ferrite “CuFe$_2$O$_4$” at lower temperatures ($\theta \leq 800$°C) is prevented by the formation of some inactive copper oxide occurring during the synthesis process and that, a fixed composition of the spinel phase is present inside the tetragonal copper ferrite “CuFe$_2$O$_4$”. However, when the reactive freeze-dried ammonium CuFe$_2$ oxalate precursor is the starting powder, no inactive CuO is formed (Section 3.3.3). Consequently, the decomposition of the oxalate precursor (at 500°C) followed by a heat treatment at 800°C under O$_2$ atmosphere, during 70 hours, allows the formation of a pure CuFe$_2$O$_4$ phase.

3.8.2. Oxygen exchange between oxide powders and the gaseous phase

The composition of a non-stoichiometric spinel phase can be denoted as AB$_2$O$_{4+\lambda}$. This implies that the spinel phase can exist in a slightly oxygen deficient (-λ) or oxygen excess (+λ) form. However in the case of large changes in the oxygen content, the spinel can form few distinctive different phases. This indicates that the study of the interaction of ferrites with the gas phase is crucial for the understanding of the nature of the oxide materials. Copper ferrite “CuFe$_2$O$_4$” prepared above 800°C under low oxygen partial pressure contains some
oxygen vacancies which lead to the partial reduction of Fe$^{3+}$ to Fe$^{2+}$ as well as that of Cu$^{2+}$ to Cu$^{+}$. Consequently, the phase composition which is important for the comprehension of the properties of oxides is modified. However in the literature, only few investigations have been carried out so far on the oxide phases occurring within the system Cu-Fe-O [96, 137]. The objective of the present section is to evaluate the stability of the sample Cu$_{0.9}$Fe$_{2.1}$O$_{4\pm\lambda}$ at $p$(O$_2$) between $10^{-5}$ and $10^{-4}$ atm in the temperature range 800-1000°C. This investigation is mainly based on the determination of the amount of oxygen exchanged between the sample and the gas flow at a given T and $p$(O$_2$). In addition, detailed informations are provided on the phase transitions. The method used is the solid-electrolyte technique employing a PC-controlled device OXYLYT (SensoTech Magdeburg, Germany) (Section 9.2.2.a) [138].

**Experimental**

The starting powder Cu$_{0.9}$Fe$_{2.1}$O$_{4\pm\lambda}$ was synthesized in air at 1000°C using fine grained metals. From the XRD analysis, Cu$_{0.9}$Fe$_{2.1}$O$_{4\pm\lambda}$ is a single tetragonal spinel phase (Fig. 3.6.5). The initial oxygen stoichiometry of Cu$_{0.9}$Fe$_{2.1}$O$_{4\pm\lambda}$ determined by the total reduction in H$_2$ atmosphere was 4.02 (Section 9.2.1). That means the spinel should contain some cation vacancies. The oxygen release of oxides were measured on powders (50mg-100mg) placed in a quartz container within the furnace of the solid electrolyte device OXYLYT (Fig. 3.8.13).

![Figure 3.8.13: Schematic view of the experimental arrangement with solid electrolyte cells.](image)

I = pumping current; $U_1$, $U_2$, = voltages of the cells; $R$ = resistance of the sample.

A regular flow of argon was controlled and sensored by cell 1. In this cell, the $p$(O$_2$) of the gas flow was fixed to a defined oxygen partial pressure by pumping of oxygen into (or out of) the flow (current $I_1$ of the cell1). The corresponding $p$(O$_2$) values were determined by a solid electrolyte potentiometric cell ($U_1$ of cell 1). From that, a gas of controlled $p$(O$_2$) flowed
through the reactor containing the sample. The investigated \( p(O_2) \) were prepared from argon/oxygen mixtures. During the heating process, the deviation of the oxygen content from the initial content was registered continuously in the downstream cell (cell 2) by potentiometric measurements. The Figure A4 (Section 11.5) shows the data recorded at 900°C. Using these recorded data, the calculation of the oxygen exchange between the oxide and the gaseous phase was performed (Section 9.2.2.b).

**Results and discussions**

The \( p(O_2) \) and \( T \) dependencies of the total oxygen content of the sample \( \text{Cu}_{0.9}\text{Fe}_{2.1}\text{O}_{4.02} \) is presented in Table A7 (Section 11.5) and in Figure 3.8.14. One sees that under the investigated \( p(O_2) \), the sample \( \text{Cu}_{0.9}\text{Fe}_{2.1}\text{O}_{4.02} \) is characterized by a drastic decrease of the oxygen content with the increase of the temperature. In the temperature range 800-1000°C, three main stability domains are identified. In the first domain, the cubic phase is in equilibrium with delafossite. In the second one, delafossite and hematite are in equilibrium and in the third one a cubic phase with a composition close to \( \text{Fe}_3\text{O}_4 \) is in equilibrium with delafossite. When the oxygen content is close to a boundary between two domains the drastic non-stoichiometry variation slows down the process to reach the equilibrium state.

![Figure 3.8.14](image)

Figure 3.8.14: Total oxygen content in \( \text{Cu}_{0.9}\text{Fe}_{2.1}\text{O}_{4.02} \) as a function of \( p(O_2) \) and \( T \).
From the analysis of the XRD patterns obtained after achievement of the equilibrium state (Fig. 3.8.15), the observed behaviours should be attributed to the decomposition of the spinel phase. At 800°C, the phases in the product are a cubic spinel phase and delafossite. This means that the surrounding atmosphere is reducing; thereby the reduction of Cu$^{2+}$ to Cu$^{+}$ enhances the formation of cuprous ferrites. Comparing this result with the one obtained under oxidizing atmosphere (Section 3.8.1.a) it turns out that the reaction (3) which takes place above 1000°C in air should occur under the current conditions. For x equal to 0.1, the relation (3) becomes:

\[
(1.2 + 2y)\text{Cu}_{0.9}\text{Fe}_{2.1}O_4 \xrightarrow{800°C} 1.2\text{Cu}_{0.9-y}\text{Fe}_{2.1+y}O_4 + 3y\text{CuFeO}_2 + yO_2
\]  
\(y \leq 0.4\)  

At 900°C, delafossite and hematite are the main phases in the product. This means that the reduction process becomes more important and consequently the total dissociation of the cubic phase occurs following the reaction (7):

\[
\text{Cu}_{0.9}\text{Fe}_{2.1}O_4 \xrightarrow{900°C} 0.9\text{CuFeO}_2 + 0.6\text{Fe}_2O_3 + 0.2O_2
\]  

\[\text{Fig. } 3.8.15: \text{ XRD patterns of } \text{Cu}_{0.9}\text{Fe}_{2.1}O_{4.02} \text{ after synthesis at } 1000°C \text{ in air and after annealing under Ar/O}_2.\]
In the literature, it is shown that the same behaviour (reaction 7) takes place below 980°C for the composition Cu_{0.5}Fe_{2.5}O_4 [92]. Above 900°C, under investigated p(O_2), the reduction of α-Fe_2O_3 into Fe_3O_4 occurs already (Fig. 3.8.1). The delafossite phase becomes unstable and its partial decomposition leads to the formation of Cu_2O which reacts progressively with Fe_3O_4. From this last process, a copper poor spinel phase (Cu_{0.9-y,Fe_{2.1+y}}O_{4-y}) is formed according to the reaction (8). The difference with the reaction (6) is that the value of “y” becomes larger (y > 0.4).

\[(1.2 + 2y)\text{Cu}_{0.9}\text{Fe}_{2.1}\text{O}_4 \xrightarrow{1000°C} 1.2\text{Cu}_{0.9-y}\text{Fe}_{2.1+y}\text{O}_4 + 3y\text{CuFeO}_2 + y\text{O}_2\]  
\[(y > 0.4)\]

From the above mentioned it turns out that, under the defined conditions (p(O_2) range 10^{-5}-10^{-4} atm and temperatures from 800 to 1000°C), the tetragonal copper ferrite phase Cu_{0.9}Fe_{2.1}O_{4.02} is unstable. For a fixed metal ion ratio, the non stoichiometry \(\lambda\) should be only about ± 0.02. Significant changes in the oxygen content lead to the separation in different phases.
3.9. **Electrical and magnetic properties of \( \text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_{4+\lambda} \) \((0.1 \leq x \leq 0.5)\)**

3.9.1 **Experimental**

Single spinel phases \( \text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4 \) \((x = 0.1, 0.2, 0.33, 0.4, 0.5)\) used were prepared under specific conditions \((T, p(O_2))\), from intimate mixtures of copper and iron metals. The details of preparation given in Section 3.8.1 are presented in Table 3.9.1. In order to prepare pellets, powders were pressed into bars of specific sizes \((a \times b \times c)\) together with four platinum wires \((0.1 \text{ mm diameter})\) and sintered during 24 hours under conditions \((T, p(O_2))\) which are identical to those used for their preparation (Table 3.9.1).

**Table 3.9.1:** Sinterization of ceramic shapes of \( \text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4 \)

<table>
<thead>
<tr>
<th>Composition</th>
<th>Temperature</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}<em>{0.9}\text{Fe}</em>{2.1}\text{O}_4 )</td>
<td>1000°C</td>
<td>air</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.8}\text{Fe}</em>{2.2}\text{O}_4 )</td>
<td>1000°C</td>
<td>air</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.67}\text{Fe}</em>{2.33}\text{O}_4 )</td>
<td>1100°C</td>
<td>argon + 1% ( O_2 )</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.6}\text{Fe}</em>{2.4}\text{O}_4 )</td>
<td>1100°C</td>
<td>argon + 1% ( O_2 )</td>
</tr>
<tr>
<td>( \text{Cu}<em>{0.5}\text{Fe}</em>{2.5}\text{O}_4 )</td>
<td>1110°C</td>
<td>argon</td>
</tr>
</tbody>
</table>

The electrical conductivity was measured by means of a DC four-point method (Section 9.5). These measurements were carried out in air flow for the samples \( \text{Cu}_{0.9}\text{Fe}_{2.1}\text{O}_4 \) and \( \text{Cu}_{0.8}\text{Fe}_{2.2}\text{O}_4 \) and in \( \text{Ar}/\text{O}_2 \) gas flow for the samples \( \text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4 \), \( \text{Cu}_{0.6}\text{Fe}_{2.4}\text{O}_4 \) and \( \text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4 \). The heating and the cooling processes were carried out between RT and 1223K with a rate of 5K/min. At 1223K, the equilibrium state values of the conductivity were achieved after 3-6 hours. The knowledge of the exact geometry of the sample was necessary to calculate the conductivity from the resistance. From the recorded data, plots of the conductivity versus \( 1000/T \) were constructed.

The magnetization measurements were carried out using a vibrating sample magnetometer (Compagny Oxford) with nickel as a calibration substance (Section 9.6). The magnetization curves obtained at \( T = 5K \) were used for the determination of the value of the saturation magnetic moments \((n_B)\). This was performed by applying the relation (3) of the Section 2.2.a. An example of magnetization curve at 5K is shown in Figure A5 (Section 11.6).
3.9.2 Results and discussions

Figure 3.9.1 shows the XRD patterns of sintered powders. All powders are identified as single spinel phases, which are tetragonal and/or cubic depending on the value of x. For the compositions with x = 0.1 and x = 0.2, reflexes of a tetragonal and a cubic phase are indexed. From Figure 1, one sees clearly additional peaks of the tetragonal phase. For x = 0.1, the major phase is the tetragonal copper ferrite, while the cubic spinel phase is the main phase when x = 0.2. For the compositions with x = 0.33, x = 0.4 and x = 0.5, only the cubic copper ferrite reflexes are indexed. The differences observed on the crystalline structure of these samples were attributed to the synthesis conditions (T, p(O2) and cooling rate) used during their preparation (Section 3.8).

Figure 3.9.1: XRD patterns of the sintered spinel phases Cu_{1-x}Fe_{2+x}O_4 prepared as described in Table 3.9.1.
For Cu$_{0.9}$Fe$_{2.1}$O$_4$ ($x=0.1$) and Cu$_{0.8}$Fe$_{2.2}$O$_4$ ($x=0.2$), the variation of the conductivity ($\sigma$) with the temperature is displayed in Figure 3.9.2. Both heating and cooling plots are shown.

![Figure 3.9.2: lg (\(\sigma\)) versus (1000/T) of the samples Cu$_{0.9}$Fe$_{2.1}$O$_4$ (a) and Cu$_{0.8}$Fe$_{2.2}$O$_4$ (b). Heating and cooling rates: 5K/min; atm.: air.](image)

Each heating curve is characterized by two distinguishable regions of different slopes. Initially, for $x=0.1$, the conductivity ($\sigma$) increases gradually with the temperature up to 733K where a local broad maximum is observed (Fig. 3.9.2(a)). This anomaly, ascribed to the phase transition from tetragonal to cubic, varies sensitively with the concentration of B- site Cu$^{2+}$ ions, which changes with the heat treatment via two factors:
Electrical and magnetic properties of Cu$_{1-x}$Fe$_{2+x}$O$_{4+\lambda}$ ($0.1 \leq x \leq 0.5$)

(a) the excitation of Cu$^{2+}$ ions from B- to A- sites and (b) the loss of oxygen [59]. It has been found that for the samples CuFe$_2$O$_4$ ($x=0$) and Cu$_{0.96}$Fe$_{2.4}$O$_4$ ($x=0.96$), these anomalies happen at 633-673K and 688K, respectively [59, 95, 139, 140]. Then further increasing the temperature ($T > 673K$, for CuFe$_2$O$_4$), the number of ions Fe$^{3+}$ which migrate from A- to B-sites is equivalent to that of Cu$^{2+}$ ions, migrating from B- to A- sites [59, 139, 141]. The transition from ordered (ferrimagnetic) to disordered (paramagnetic) states occurs in the range 722-768K [17, 142, 143]. It turns out that the migration of cations is responsible for the breaks (anomalies) observed for the samples Cu$_{0.9}$Fe$_{2.1}$O$_4$ and Cu$_{0.8}$Fe$_{2.2}$O$_4$. On the other hand, these anomalies are not noticeable in the cooling curves. Because heating and cooling curves are not identical, these anomalies are likely to be attributed to the thermal history of the sample rather than the change of the magnetic ordering in the ferrite lattice. Some authors [145] demonstrated that this irreversibility is due to the fact that the cation redistribution is not the same during the cooling process. Furthermore, one sees clearly that the anomaly observed in the variation of $\sigma$ in Cu$_{0.9}$Fe$_{2.1}$O$_4$ is less pronounced in Cu$_{0.8}$Fe$_{2.2}$O$_4$. One reason for such behaviour is the difference in the crystal structure of both samples. In fact before the conductivity measurement, Cu$_{0.9}$Fe$_{2.1}$O$_4$ ($x = 0.1$) is mostly tetragonal, whereas the sample Cu$_{0.8}$Fe$_{2.2}$O$_4$ ($x = 0.2$) is mostly cubic (Fig. 3.9.1).

![XRD patterns](image)

**Figure 3.9.3:** XRD patterns after the conductivity measurement on the pellets Cu$_{0.9}$Fe$_{2.1}$O$_4$ (a) and Cu$_{0.8}$Fe$_{2.2}$O$_4$ (b). Heating and cooling rates: 5K/min; atm.: air.
For the elucidation of the observed behaviours the pellets were characterized after conductivity measurements, using the XRD method (Fig. 3.9.3). Comparing these patterns with those of the sintered samples (Fig. 3.9.1), it turns out that the diffraction lines of the cubic phase disappear completely. The pattern of Cu$_{0.9}$Fe$_{2.1}$O$_4$ is indexed to a single phase of tetragonal copper ferrite with the lattice parameters of $a_0 = 583.0$ pm and $c_0 = 863.1$ pm (Fig. 3.9.3 (a)). For $x = 0.2$, $\alpha$-Fe$_2$O$_3$ is detected as a second phase beside the tetragonal copper ferrite (Fig. 3.9.3 (b)). From these results, it is clear that the tetragonal distortion of the spinel phase has increased inside the sample after the conductivity measurements. This observation suggests that during the cooling step, a migration of copper from the tetrahedral towards the octahedral sites occurs. Such behaviour materializes a redistribution of cations in the spinel lattice. The change in Cu$_{0.9}$Fe$_{2.2}$O$_4$ was attributed to the oxidation of the Cu$^{1+}$ ions formed during its synthesis (Section 3.8.1).

For the ferrite samples, it is well established that the temperature affects the mobility of the charge carriers but not their concentration. However in the case of copper ferrite samples, one notes that a great number of processes occurring with the variation in the temperature can affect the number of charge carriers. The most common processes are the change of the composition of copper ferrite as function of the temperature and the change of the distribution of cation according to the cooling and heating rates. These principal processes which have an effect on conductivity of the samples Cu$_{0.9}$Fe$_{2.1}$O$_4$ and Cu$_{0.8}$Fe$_{2.2}$O$_4$ affect also the conductivity of the samples Cu$_{0.67}$Fe$_{2.33}$O$_4$, Cu$_{0.5}$Fe$_{2.4}$O$_4$ and Cu$_{0.5}$Fe$_{2.5}$O$_4$.

Figure 3.9.4 presents the data recorded during the measurement of the conductivity of the samples Cu$_{0.67}$Fe$_{2.33}$O$_4$, Cu$_{0.6}$Fe$_{2.4}$O$_4$ and Cu$_{0.5}$Fe$_{2.5}$O$_4$ in Ar/O$_2$ atmosphere. In the range 400-1223K, Cu$_{0.67}$Fe$_{2.33}$O$_4$ and Cu$_{0.6}$Fe$_{2.4}$O$_4$ show a non-linear variation of the conductivity ($\sigma$) with the temperature (Figure 3.9.4 (a), (b)). After exposition at 1223 K, the decomposition of the spinel phase induces the decrease of the conductivity. For the sample Cu$_{0.5}$Fe$_{2.5}$O$_4$, the “high” conductivity value of ~12.5 S.cm$^{-1}$ registered at 720K falls suddenly to 0.13 S.cm$^{-1}$ at 843K (Fig. 3.9.4 (c)). For the determination of the process responsible for these phenomena, the XRD patterns of the slowly cooled pellets were registered after conductivity measurements (Fig. 3.9.5).
Electrical and magnetic properties of $Cu_{1-x}Fe_{2+x}O_{4+\lambda}$ ($0.1 \leq x \leq 0.5$)

Figure 3.9.4: $\lg (\sigma)$ versus $(1000/T)$ of the samples $Cu_{0.67}Fe_{2.33}O_4$ (a), $Cu_{0.6}Fe_{2.4}O_4$ (b) and $Cu_{0.5}Fe_{2.5}O_4$ (c). Heating and cooling rates: 5K/min; atm.: Ar/O$_2$.

(cSp = cubic spinel ; D = delafossite “CuFeO$_2$”; H = hematite)
The analysis of the obtained patterns shows that for all samples, delafossite (CuFeO$_2$) and hematite ($\alpha$-Fe$_2$O$_3$) are the main phases in the product. This result confirms the assumption according to which Cu$_{0.67}$Fe$_{2.33}$O$_4$, Cu$_{0.6}$Fe$_{2.4}$O$_4$ and Cu$_{0.5}$Fe$_{2.5}$O$_4$ are unstable under the conditions chosen for conductivity measurements i.e in Ar/O$_2$ atmosphere for $T \leq 1223$K (Section 3.8.1). For Cu$_{0.6}$Fe$_{2.4}$O$_4$ (Fig. 3.9.5 (b)), the presence of a remaining amount of the spinel phase is observed due to the incomplete decomposition. This implies that for Cu$_{0.5}$Fe$_{2.5}$O$_4$, the equilibrium state value of the conductivity has not been attained at 1223K.

After the first cycle of the conductivity measurement (Fig. 3.9.4), the Cu$_{0.5}$Fe$_{2.5}$O$_4$ pellet containing CuFeO$_2$ and $\alpha$-Fe$_2$O$_3$, was submitted to a second cycle. After a measurement of the conductivity (second cycle, Fig. 3.9.6(a)) carried up to 1123K, the XRD pattern shows that the pellet retains the same phase composition i.e. CuFeO$_2$ and $\alpha$-Fe$_2$O$_3$. For a third cycle of the conductivity measurement, the pellet obtained from the second cycle was heated again at 1110°C during 24 hours under argon gas flow. After this treatment, the formation of a single spinel phase with a cubic structure was confirmed by XRD analysis method. At the end of the conductivity measurement on this last sample (third cycle, Fig. 3.9.6 (b)), the decomposition of Cu$_{0.5}$Fe$_{2.5}$O$_4$ into CuFeO$_2$ and $\alpha$-Fe$_2$O$_3$ was found to be reproducible. A second pellet with the composition Cu$_{0.5}$Fe$_{2.5}$O$_4$ (pure cubic spinel phase) was sintered. After the measurement carried out from RT up to 823K, the XRD pattern shows that the decomposition of the single spinel phase into CuFeO$_2$ and $\alpha$-Fe$_2$O$_3$ had already taken place.
Electrical and magnetic properties of Cu$_{1-x}$Fe$_{2+x}$O$_{4\pm\lambda}$ ($0.1 \leq x \leq 0.5$)

(a) Second cycle of the measurement on the pellet Cu$_{0.5}$Fe$_{2.5}$O$_4$ (performed after the first cycle, Fig. 3.9.4(c)). Composition of the pellet: $\alpha$-Fe$_2$O$_3$ (H) + CuFeO$_2$ (D).

(b) Third cycle of the measurement on the pellet Cu$_{0.5}$Fe$_{2.5}$O$_4$ (after the 2$^{nd}$ cycle, Fig. 3.9.6(a), the pellet is heated again for the formation of a single spinel phase).

Figure 3.9.6: $\lg(\sigma)$ versus (1000/T) of Cu$_{0.5}$Fe$_{2.5}$O$_4$ plotted with the data recorded during (a) the second and (b) the third cycle of conductivity measurements, performed up to 1223K.
In accordance to the literature [27, 96], it follows that the decomposition of the spinel phase is the phenomenon responsible of the break occurring on the conductivity curves of $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$, $\text{Cu}_{0.6}\text{Fe}_{2.4}\text{O}_4$ and $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$.

From the above, one sees that in the temperature range where the spinel phase is maintained, $T < 1223K$ for $x = 0.33$, $x = 0.4$ and $T < 723K$ for $x = 0.5$, the conductivity of the materials increases with the iron content. Furthermore, one notes that the conductivity values of $\text{Cu}_{0.67}\text{Fe}_{2.33}\text{O}_4$, $\text{Cu}_{0.6}\text{Fe}_{2.4}\text{O}_4$ and $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_4$ are higher than that of the $\text{Cu}_{0.9}\text{Fe}_{2.1}\text{O}_4$ and $\text{Cu}_{0.8}\text{Fe}_{2.2}\text{O}_4$, measured in air (Fig. 3.9.2). It is well known that the conduction mechanism in ferrites is the hopping of charge carriers between ions having different oxidation states on the octahedral sites [78, 146, 147]. From this point of view, the increase of the conduction with the iron content $(x)$ may be a consequence of the reduction of the spinel phase which enables the change of some $\text{Cu}^{2+}$ and $\text{Fe}^{3+}$ ions to $\text{Cu}^+$ and $\text{Fe}^{2+}$, respectively. However, from the thermodynamic data, it is well established that $\text{Cu}^{2+}$ and $\text{Fe}^{2+}$ should not coexist. Consequently, when copper and iron are present in different oxidation states ($\text{Cu}^{2+}$, $\text{Fe}^{3+}$, $\text{Cu}^+$, $\text{Fe}^{2+}$) the equilibrium (i) which is established moves favorably according to the direction (2).

\[
\text{Fe}^{3+} + \text{Cu}^+ \overset{(1)}{\longrightarrow} \text{Fe}^{2+} + \text{Cu}^{2+} \\
\text{Fe}^{2+} + \text{Cu}^{2+} \overset{(2)}{\longrightarrow} \text{Fe}^{3+} + \text{Cu}^+ 
\]

Therefore, the electronic conductivity taking place due to the exchange of electron between $\text{Fe}^{3+}$ and $\text{Fe}^{2+}$ ions in octahedral positions will not be very important. Thus, additional processes mentioned previously, namely (a) the change of the composition of copper ferrite as function of the temperature and (b) the change of the distribution of cation according to the cooling and the heating rate should also have their main contribution on the resulting value of the conductivity.

For further investigations, the magnetic properties of copper ferrite samples “$\text{Cu}_{1-x}\text{Fe}_{2+x}\text{O}_4$ with $x = 0.1, 0.2, 0.33, 0.4$ and $0.5$” which also depend on the thermal history of the material were determined. From the data presented in the Table 3.9.2, it follows that at $5K$, the value of $\sigma_S$ increases with the iron content $x$. The outer electron-shell of $\text{Cu}^+$ “d-shell” is saturated, thereby leading to the magnetic saturation moment of zero. On the other hand, it has been established from a number of investigators that $\text{Cu}^+$ ions have a strong preference for tetrahedral sites. From these two main remarks, the increase of $\text{Cu}^+$ ions in the ferrite compound should enable the decrease of the magnetic moment of the tetrahedral sites. In this case, the increase of the magnetic properties of the ferrite requires the maximization of the
octahedral magnetic moment ($n_0$). For the samples under investigation, the lattice parameter “a” determined from the XRD patterns (Table 3.9.2) are higher than those of the samples obtained under more oxidizing atmospheres. This is understandable because Cu$^{2+}$ with the smaller ionic radius (87 pm) is being replaced by the larger Cu$^+$ radius (91 pm). It follows that the conditions defined (Table 3.9.1) for the synthesis of investigated samples enable the reduction of some Cu$^{2+}$ to Cu$^+$. From the details given above, it turns out that at 5K, the increase of $\sigma_S$ with the iron content $x$ is mainly a consequence of the increase of iron ions in the B- sites. However, the saturation magnetization values measured at 300K do not increase absolutely with the iron content. In fact, the saturation magnetization value $\sigma_S = 78.97$ emu/g obtained for the sample Cu$_{0.6}$Fe$_{2.4}$O$_4$ is close the value of 78.83 emu/g obtained for Cu$_{0.5}$Fe$_{2.5}$O$_4$. This observation can be attributed to the fact that the change of the spin ordering in the ferrite lattice from 5 to 300K is a function of the thermal history of the ferrite sample. Some other examples that bring insights into this feature are the following: at 300K, the $\sigma_S$ value of 38.5 emu/g is obtained for a CuFe$_2$O$_4$ sample, quenched from 1000°C [148]; for the iron rich spinel phase Cu$_{0.5}$Fe$_{2.1}$O$_4$ prepared at the same temperature but cooled more slowly, the value of $\sigma_S$ is equal 31.54 emu/g. On the other hand, $\sigma_S = 82.83$ emu/g is recorded for Cu$_{0.5}$Fe$_{2.5}$O$_4$ prepared at 1348°C in air and quenched in oil [70]. This last value is relatively higher than $\sigma_S = 78.83$ emu/g, obtained for a Cu$_{0.5}$Fe$_{2.5}$O$_4$ which is prepared from metal powders at 1110°C under argon atmosphere.

### Table 3.9.2: Magnetic properties and lattice parameters of copper ferrite samples

<table>
<thead>
<tr>
<th>Composition</th>
<th>Magnetization at 5K</th>
<th>Magnetization at 300K</th>
<th>Lattice parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_S$ (emu/g)</td>
<td>$n_0(\mu_0)$</td>
<td>$\sigma_S$ (emu/g)</td>
</tr>
<tr>
<td>Cu$<em>{0.9}$Fe$</em>{2.1}$O$_4$</td>
<td>49.80</td>
<td>2.13</td>
<td>31.54</td>
</tr>
<tr>
<td>Cu$<em>{0.8}$Fe$</em>{2.2}$O$_4$</td>
<td>70.93</td>
<td>3.02</td>
<td>-</td>
</tr>
<tr>
<td>Cu$<em>{0.67}$Fe$</em>{2.33}$O$_4$</td>
<td>125.42</td>
<td>5.31</td>
<td>-</td>
</tr>
<tr>
<td>Cu$<em>{0.6}$Fe$</em>{2.4}$O$_4$</td>
<td>126.59</td>
<td>5.35</td>
<td>78.97</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Fe$</em>{2.5}$O$_4$</td>
<td>153.27</td>
<td>6.46</td>
<td>78.83</td>
</tr>
</tbody>
</table>
Partial conclusion

From the above it follows that for the copper ferrite samples “Cu$_{1-x}$Fe$_{2+x}$O$_4$ with x = 0.1, 0.2, 0.33, 0.4 and 0.5”, the change in the conductivity with the temperature is irreversible. Due to their thermal history, the deviation from the linearity of $\lg(\sigma)$ as a function of 1000/T is observed. For the samples with x = 0.1 and x = 0.2 investigated in air, the deviations take place due to the rearrangement of cations during heating. In reducing atmosphere, the conductivity deviations for the samples with x = 0.33, 0.4 and 0.5 occur due to the decomposition of the spinel phase into CuFeO$_2$ and $\alpha$-Fe$_2$O$_3$. At 5K, the saturation magnetic moment $n_B$ increases with the iron content. On the other hand, the saturation magnetization measured at 300K depends on the synthesis conditions of the sample. In accordance with other authors [144, 149], it can be concluded that the electrical and magnetic properties of copper ferrite samples depend on their chemical composition and preparation conditions.

From the results obtained in Section 3.8, it is obvious that copper ferrites release oxygen and are dissociated during the heating at higher temperatures and under reducing atmospheres. Therefore during the conductivity measurement under the mentioned conditions, the variation of $\sigma$ as a function of the temperature T is influenced additionally by the change of the oxygen-to-metal stoichiometry. Thus, the study of the temperature dependence of the conductivity at steady composition (O/M stoichiometry) of the material has to be measured under isostoichiometric conditions. That means each step of increasing temperature requires an adequate increase in oxygen partial pressure to suppress the release of oxygen and the thermal dissociation of the oxide. This investigation would allow the obtention of the pure temperature dependence of conductivity at constant oxygen-to-metal stoichiometry of the oxide.
4. System Ni-Fe-O

4.1. Literature review on the synthesis of nickel ferrite

Nickel ferrite is a well-known spinel magnetic material with a high Curie temperature value of ~585°C. Its preparation by classical solid state reaction requires a high calcination temperature (T>1100°C) and hence induces the sintering and aggregation of particles [150-152]. To produce nanosized ferrite particles, some techniques such as chemical coprecipitation [153-155], hydrothermal synthesis [156], sol-gel [6, 157], freeze-drying of metal carboxylate solution [158] have been developed. Yang and coworkers [155] prepared ultrafine nickel ferrite powders by the calcination at 400°C of gel powders of coprecipitated Ni and Fe tartrates. However, these ferrite powders are decomposed above 400°C forming α-Fe2O3 as second phase. We think that it can not be excluded that γ-Fe2O3 beside a fine grained NiO is primary formed. Therafter, when the temperature increases the transformation of the metastable spinel phase γ-Fe2O3 leads to the additional formation of α-Fe2O3. Using the hydrothermal method [156], nickel ferrite powders with high degree of crystallization and uniform morphologies have been prepared from α-FeOOH and amorphous Ni(OH)2. After characterization, the authors [156] found that the as-prepared powders possess a high saturation magnetization moment of 54.5 emu/g which is close to the value of 56 emu/g reported for NiFe2O4 [3]. Works available in the literature on the synthesis of the nickel ferrite (NiFe2O4) from mixed acetate complexes show that the complete decomposition of the acetate finishes below 400°C but, the composition of the oxide products depends considerably on the reaction conditions in the synthesis [159-161]. For instance, Elmasry and coworkers [159] found that the high rate of heating (above 10K/min) causes the elevation of the decomposition temperature and the metal ions in the products are partially reduced. In such cases it has generally been proven that the reoxidation of the product takes place during further heating and enables the segregation of α-Fe2O3 [9, 162]. Langbein and Eichhorn [160] revealed that slow heating during the decomposition of acetate precursors up to 300-400°C can avoid the crystallization of α-Fe2O3 beside the spinel phase. Moreover, one notes that nickel ferrite “NiFe2O4” was, more recently, successfully synthesized from the thermal decomposition of Ni-Fe-µ-oxo-acetates in air at 400°C [154, 158]. Although nickel ferrites have been synthesized and commercialized in high frequency application for a long time, they still have been attracting intense research interests due to
some new promising applications, such as ferrofluids [21], gas sensor [163], requiring the use of well crystalline nickel ferrite powders which have been synthesized at a relatively low temperature. From the great number of synthesis methods mentioned above, the properties of nickel ferrites have nevertheless been successfully optimized but, studies on the mechanism and the process of preparing these powders are seldom in the literature. In most works, the authors found commonly that during the calcination process, single metal salts behave individually in the mixed metal complex. However, it is proven that such behaviour has an influence on the composition of the oxide products.

The following section of this chapter is based on a review of the synthesis of nickel ferrite using the ceramic method. It represents a reference investigation which may help to get insights on the phase formation according to the preparation conditions. In the next section, we are interested in the preparation and thermal decomposition of freeze-dried nickel(II)-iron(III) formate precursors. This investigation aimed on the determination of a synthesis method which can enable the preparation of nickel ferrite powders with suitable properties. The last section is based on the synthesis and the characterization of Ni-Fe inter-metallic phases. The starting materials are nickel-iron oxide phases and freeze-dried precursors of nickel-iron formate. In this case, the synthesis is performed using the reduction method as described in Section 3.6. The reactivity of the prepared Ni-Fe alloy phases is deduced from their thermal behaviour in the presence of air.
4.2. **Solid state reaction - for comparison**

The mixture of NiO and α-Fe₂O₃, in the ratio 1:1, was prepared by mechanical milling (Section 8.1). Following each thermal treatment performed in air, the product was subjected to the powder XRD analysis for the phase identification. The pattern obtained at 600°C and 800°C show the characteristic peaks of NiO and α-Fe₂O₃. By increasing the temperature up to 1000°C, it is detected that a new crystalline phase “NiFe₂O₄” is formed as main phase and the remaining amount of α-Fe₂O₃ is small (Fig. 4.2.1). Besides, the presence of nickel oxide is not very well identified because the most intensive peaks of NiO (2θ = 37.3° and 2θ = 43.3°) are covered by those of the spinel phase. After 48 hours of annealing at 1000°C, a single spinel phase “NiFe₂O₄” with the lattice parameter a=833.4 pm is formed. Furthermore, the increase of the temperature up to 1100°C also leads to the formation of a single spinel phase with a = 834.3 pm.

![Figure 4.2.1: XRD patterns of the products obtained after annealing of the mixture NiO:Fe₂O₃ during 24 hours at 1000°C, 1100°C and during 48 hours at 1000°C(*) Atm.: air; heating rate: 10K/min.](image)

From the above it turns out that, for a heat treatment time of around 24 hours the formation of nickel ferrite from the mixture NiO:α-Fe₂O₃ starts only above 800°C and ends at 1100°C. When the annealing time equals 48 hours, the synthesis temperature of 1000°C is sufficient. Note however that, starting from the mixture of nickel(II) and iron(III) nitrates Elmasry and coworkers [150] found that a temperature of 1500°C was required for the synthesis of nickel ferrite. In what follows, freeze-dried nickel(II)-iron(III) formate precursors are used for the synthesis of nickel ferrite powders at a relatively low temperature.
4.3. **Synthesis of nickel ferrite from the freeze-dried formate precursors**

4.3.1. **Preparation and characterization of the freeze-dried formate precursors**

Raw materials iron(II) formate and nickel(II) formate used for the preparation of the Ni(II)-Fe(III) formate precursors were produced as described in sections 8.3.1 and 8.5.1, respectively. From these powders, solutions of Ni(II)-, Fe(III)- and Ni(II)-Fe(III) formate with an excess of formic acid were prepared (Section 8.5.2). In order to establish the optimal conditions required for the formation of a good homogeneous precursor, complex formate solutions of different ion concentrations were prepared. The concentration of nickel and iron ions range from 0.02 to 0.16M and from 0.04 to 0.32M, respectively. The prepared solutions were quickly frozen in liquid nitrogen and dried from -40°C to 25°C in a vacuum chamber of a freeze-drying apparatus (Alpha 2-4, Christ). After 72 hours, the drying process was complete and very slight powders were obtained.

Figure 4.3.1: XRD patterns of the freeze-dried precursors: (a) Fe(III) formate, (b) NiFe₂ formate ([Ni²⁺] ~0.125M) and (c) Ni(II) formate.

In Figure 4.3.1(b), the pattern of the freeze-dried Ni(II)-Fe(III) formate precursor prepared from the complex formate solution with nickel concentration of ~0.125M is shown. A comparison is made with the patterns of Fe(III) formate (Fig. 4.3.1(a)) and Ni(II) formate (Fig. 4.3.1(c)). One sees that Ni(II) formate is crystalline, while Fe(III)- and the complex Ni(II)-Fe(III) formate are amorphous. It turns out that the freeze-dried Ni(II)-Fe(III) formate is formed via the total intrusion of Ni(II) ions in the Fe(III) formate amorphous precursor. Besides, the pattern of the freeze-dried nickel(II) formate (Fig. 4.3.1(c)) is in agreement with that of the precipitated crystalline sample used for the freeze-drying and, with that of the
dihydrated nickel(II) formate (PDF 15-917). Compared to the precipitated sample, the diffraction peaks of the freeze-dried nickel(II) formate are not very intense because the freeze-dried sample consists of very fine grains. Among the prepared formate precursors, those used for thermal analysis (TA) investigations were quantitatively characterized by complexometric titration and elemental analysis (Section 9). From the obtained results, their composition is described approximately by the following formulas:

- Nickel(II) formate: \( \text{Ni(HCOO)}_2 \times 1.5\text{H}_2\text{O} \);
- Iron(III) formate: \([\text{Fe}_3\text{O(HCOO)}_6]^+ \cdot \text{HCOO}^- \times 3.8\text{H}_2\text{O}\);
- Nickel(II) formate: \( \text{Ni(HCOO)}_2 \times 2\text{H}_2\text{O} \) (prepared using the precipitation method);
- Nickel(II)-iron(III) formate: “\( \text{NiFe}_2\text{O}_{2/3} \)\text{(HCOO)}_6\text{.67} \times 3.2\text{H}_2\text{O} \)” (from the complex formate solution with the nickel ions concentration of around 0.125M).

The freeze-dried nickel formate contains less coordinated water than the precipitated one. This observation is due to the fact that the water content in the freeze-dried samples depends on the intensity of the drying process [9].

4.3.2. Thermal decomposition of the freeze-dried formate precursors

4.3.2.a. Thermal decomposition of nickel(II) formate

Figure 4.3.2 illustrates the TA curves obtained in air and in argon during the decomposition of the freeze-dried and the precipitated Ni(II) formate. In air, the thermal decomposition of the freeze-dried sample occurs in two steps in the temperature range 30-280°C (Fig. 4.3.2 (c)).

**Figure 4.3.2:** TA curves of the freeze-dried Ni(II) formate: (a) DTA curve in Ar, (b) TG curve in Ar and (c) TG curve in air; (d) TG curve in Ar of the precipitated Ni(II) formate.

Heating rate: 5K/min.
The first step (30-240°C) corresponds to the endothermic elimination of coordinated water. The calculated mass loss ($\Delta m_{\text{cal}} = -15.4\%$) corresponding to the loss of 1.5 moles of water per mole of the precursor is close to the experimental value ($\Delta m_{\text{exp}} = -15.7\%$). Due to the fact that the decomposition is performed in presence of air, the following process corresponding to the decomposition of the anhydrous sample is superimposed by the oxidation of the primary products. This leads to the appearance of an exothermic peak in the temperature range 240-280°C. The associated mass loss ($\Delta m_{\text{cal}} = -48.5\%$) is situated between the value corresponding to the formation of nickel oxide ($\Delta m_{\text{cal}} = -42.1\%$) and of that due to the formation of nickel metal ($\Delta m_{\text{cal}} = -51.2\%$). This proves that, at the end of the decomposition in air ($T = 280°C$), the product contains NiO and Ni. The oxidation of nickel metal takes place by further heat treatment in the range 280-400°C (Fig. 4.3.2(c)). On the other hand, the same main decomposition processes are also established for the nickel(II) formate obtained using the precipitation method. For the precipitated Ni(II) formate, the mass loss agrees with the formula Ni(HCOO)$_2$ x 2H$_2$O.

The TG curves obtained under argon (Fig. 4.3.2 (b), (d)) show that the decomposition of the precipitated and the freeze-dried nickel(II) formate occur also in two steps between 30 and 280°C. For the freeze-dried sample “Ni(HCOO)$_2$ x 1.5H$_2$O”, the mass loss ($\Delta m_{\text{exp}} = -14.8\%$) associated to the elimination of coordinated water is relatively lower than the value obtained in presence of air ($\Delta m_{\text{exp}} = -15.7\%$). This difference is due to the ambient temperature which heats the flow of argon, thereby inducing the elimination of some water from the sample during the calibration of the apparatus. The following process due to the decomposition of the anhydrous sample is materialized on the DTA curve by a sharp endothermic effect occurring in the range 235-280°C (Fig. 4.3.2(a)). The total mass loss observed in this step ($\Delta m_{\text{exp}} = -51.1\%$) correlates with the formation of nickel metal ($\Delta m_{\text{cal}} = -51.2\%$). The main gaseous decomposition products identified using the MS analysis method are CO, CO$_2$, H$_2$O and HCOOH. As in the reductive decomposition of copper(II) formate (Section 3.4.2.b), the primary process in the decomposition of the dehydrated nickel(II) formate should be the formation of HCOOH and CO$_2$. Analogous to the decomposition of copper(II) formate, the intensity of the MS peak of the primary product HCOOH is much lower than the peaks intensities of the secondary products formed by the consecutive reaction of HCOOH (reactions (7) and (8), Section 3.4.2.a). The XRD pattern of the freeze-dried sample annealed up to 280°C agrees very well with the formation of nickel metal at the end of the
Synthesis of nickel ferrite from the freeze-dried formate precursors

decomposition process (Fig. 4.3.3(b)). Nickel metal results from the reaction (15) taking as follows:

\[
\text{Ni(HCOO)}_2 \rightarrow \text{Ni} + \text{HCOOH} + \text{CO}_2 \tag{15}
\]

Between 280 and 750°C, its re-oxidation by the traces of oxygen in argon occurs. This is confirmed by the presence of some nickel oxide already inside the product which is formed at 350°C (Fig. 4.3.3(c)). Up to 750°C, only some traces of nickel metal remains beside the oxide phase NiO (Fig. 4.3.3(d)). On the other hand, the same main decomposition processes are also established for the nickel(II) formate obtained using the precipitation method (Fig. 4.3.2(d)).

Figure 4.3.3: XRD patterns of the freeze-dried Ni(II) formate (a) and of the decomposition products quenched after annealing up to 280°C (b), 350°C (c) and 750°C (d). Atm.: Ar; heating rate: 5K/min.

4.3.2.b. Thermal decomposition of nickel(II)-iron(III) formate

In argon, three more or less superimposed steps are observed in the range 40-300°C (Fig. 4.3.4(a)). By means of the TG results, the exact assignment of the decomposition steps is complicated because of the overlapping of the decomposition processes (Fig. 4.3.4(b)). However one sees that after the elimination of water, the end temperature of the following processes (T=300°C) is located between that of Ni(II)- and iron(III) formate (Fig. 4.3.4, comparison of (b) with (d) and (e)).
Synthesis of nickel ferrite from the freeze-dried formate precursors

Figure 4.3.4: TA curves of the freeze-dried Ni(II)-Fe(III) formate: (a) DTG curve in Ar, (b) TG curve in Ar, (c) TG curve in air and (d) TG curve in Ar of the freeze-dried Fe(III) formate, (e) TG curve in Ar of the freeze-dried Ni(II) formate (5K/min).

For further investigations, light is shed on the mechanism of the decomposition of the freeze-dried Ni(II)-Fe(III) formate precursors by the analysis of the gaseous decomposition products. The results of these measurements are shown in Figure 4.3.5 and summarized in Table 4.3.1. One sees that the elimination of coordinated water occurs in the range 40-200°C. The calculated mass loss of 10.7% corresponds to the release of 3.2 moles of water per mole of the precursor. The second step occurs in the range 200-270°C and leads to the release of HCOOH ($M/z=46$) and CO$_2$ ($M/z=44$). Analogous to the process (2a) (Section 3.4.2.a), the release of HCOOH and CO$_2$ enhance the partial reduction of Fe(III) to Fe(II). Moreover, according to the results of the thermal decomposition of the freeze-dried Ni(II) formate (Section 4.3.2.a) it turns out that, the partial reduction of Fe(III) to Fe(II) should be followed by the complete decomposition of nickel formate into nickel metal (process 15). But surprisingly, no traces of nickel are detected on the XRD pattern obtained up to 270°C (Fig. 4.3.6(b)). Two reasons may be responsible: the decomposition of nickel(II) formate and iron(III) formate take place simultaneously and inhibit the formation of nickel metal or nickel metal is present but in an amorphous state.
Table 4.3.1: Main primary gaseous products of the freeze-dried precursor

NiFe$_2$O$_{2/3}$(HCOO)$_{6.67}$$\times3.2$H$_2$O (Process / equation see sections 3.4.2.a and 4.3.2.a)

<table>
<thead>
<tr>
<th>Process/ (\text{equation})</th>
<th>Temperature range (^{\circ}\text{C},) roughly</th>
<th>Main primary gaseous decomposition products</th>
<th>(\Delta m) (calc. ) / %</th>
<th>(\Delta m/\text{step})</th>
<th>(\Delta m/\text{total})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40 - 200</td>
<td>3.2H$_2$O</td>
<td>-10.7</td>
<td>-10.7</td>
<td></td>
</tr>
<tr>
<td>2a, 15</td>
<td>200 - 270</td>
<td>4/3(HCOOH ; CO$_2$)</td>
<td>-22.3</td>
<td>-33.0</td>
<td></td>
</tr>
<tr>
<td>12a/12b</td>
<td>270 - 300</td>
<td>2(HCOOH ; CO)</td>
<td>-27.5</td>
<td>-60.5</td>
<td></td>
</tr>
<tr>
<td>13a/13b</td>
<td>270 - 300 T &gt; 300</td>
<td>2(HCOH ; CO$_2$) (oxidation)</td>
<td>-27.5</td>
<td>-60.5</td>
<td>+2.5</td>
</tr>
</tbody>
</table>

Figure 4.3.5: MS characterization of the main gaseous products occurring during the decomposition of the freeze-dried Ni(II)-Fe(III) formate. Atm.: Ar; heating rate: 5K/min.
Synthesis of nickel ferrite from the freeze-dried formate precursors

**Figure 4.3.6:** XRD patterns of the freeze-dried NiFe\(_2\) formate ([Ni\(^{2+}\) \~0.125M) (a); of the decomposition products quenched after annealing up to 270°C (b) and 300°C (c). Atm.: Ar; heating rate: 5K/min.

In the temperature range 270-300°C (third step), a further decomposition without further reduction of Fe(III) takes place according to the parallel reactions (12a), (13a) and (12b), (13b) described in the Section 3.4.2.a. The absence of wüstite “FeO” at the end of the decomposition process confirms the formation of magnetite (Fe\(_3\)O\(_4\)) at 300°C (Fig. 4.3.6(c)). Due to the gain of mass (\(\Delta m_{\text{exp}} = +2.5\%\)) observed above 300°C, it is then expected that the product should contain a mixture of Ni (amorph) and Fe\(_3\)O\(_4\) instead of a single spinel phase “NiFe\(_2\)O\(_4\)”. In this case, the calculated mass loss including the small gain of mass (58.0%) is close to the experimental value (57.1%). The main processes taking place above 300°C are the crystallization of Ni (amorph) into NiO followed by the reaction with Fe\(_3\)O\(_4\) (ferritization process).

In air, the thermal decomposition of the freeze-dried precursor nickel(II)-iron(III) formate occurs in two steps in the range 40-290°C (Fig. 4.3.4(c)). The decomposition starts with the delivery of water. In the temperature range 195-290°C, the decomposition of the anhydrous formate takes place. All further processes are superimposed by the oxidation of the primary decomposition products. At 290°C, for any metal ion concentration in the precursor solution used for the preparation of the Ni(II)-Fe(III) formate, the resulting product is a less crystalline spinel phase.
4.3.3. Phase formation from nickel(II)-iron(III) formate

The synthesis of nickel ferrite was investigated by the heat treatment of the freeze-dried Ni(II)-Fe(III) formate precursors in air in the range 400-1000°C. In order to avoid the overheating during the decomposition of the formate, the slow heating rate of 2.5K/min was applied during the decomposition at 400°C. Thereafter, the resulting product was used like the starting powder for the thermal treatments carried out above 400°C. In this last case, a heating rate of 10K/min was applied. The resulting products were examined by XRD method.

At 400°C (Fig. 4.3.7(a)), for any metal ion concentration in the precursor solution used for the preparation of the freeze-dried Ni(II)-Fe(III) formate, only the broad reflections of a spinel phase are indexed on the XRD pattern. The heat treatments carried out at temperatures above 400°C result to the increase of the intensity of the diffraction peaks. Such a behaviour shows that a crystallization process has taken place. Consequently, it is found that the phase composition of the end products varies as a function of the metal ions concentration in the precursor solution. At 600°C, the decomposition of the precursor resulting from the low concentrated solution ([Ni^{2+}] < 0.15M) leads to the formation of a product containing a spinel phase and some α-Fe₂O₃ (Fig. 4.3.7(1b)). The presence of the nickel oxide is not very well identified. The increase of the temperature up to 800°C leads to the increase of the diffraction peaks of α-Fe₂O₃ (Fig. 4.3.7(1c)). After three hours of annealing at 1000°C, a single spinel phase is formed (Fig. 4.3.7(1d)). Figure 4.3.7(2) shows the XRD patterns of the products resulting from the decomposition at 600°C, 800°C and 1000°C of the precursor of the concentrated solution. From the analysis of these patterns, one notes that the single phase formed at 400°C is maintained up to 1000°C. No intermediate formation of α-Fe₂O₃ is observed. From these results, it turns out that the homogeneity of the freeze-dried Ni(II)-Fe(III) formate depends on the concentration of the metal ions in the precursor solution. This means that according to the metal ions concentration in the precursor solution, the chemical composition of the freeze-dried powders can vary between the two extreme compositions namely: (a) \([\text{Fe}^{3+}\text{Ni}^{2+}\text{O}(\text{HCOO})_6]\) (for the concentrated solution) and,

\[(1)\quad 2/3[\text{Fe}^{3+}\text{O}(\text{HCOO})_6]\text{HCOO}^- + \text{Ni}(\text{HCOO})_2 \quad \leftrightarrow\quad [\text{Fe}^{3+}\text{Ni}^{2+}\text{O}(\text{HCOO})_6] + 2/3\text{HCOOH}\quad \text{(i)}\]

(b) \(2/3[\text{Fe}^{3+}\text{O}(\text{HCOO})_6]\text{HCOO}^- + \text{Ni}(\text{HCOO})_2\) (for the low concentrated solution)
For the concentrated solution, the equilibrium (i) is much more realized in the direction (1). The occurrence of the reaction (i) following the direction (2) enables the segregation of some nickel(II) formate. This is the main process taking place during the freeze-drying of the complex formate solutions with the nickel concentration below 0.15M.

**Figure 4.3.7:** XRD patterns of the decomposition products of the freeze-dried NiFe$_2$ formate precursors annealed at 400°C during 3 hours (a) followed by the heating at 600°C (b), 800°C (c) and 1000°C (d) during 3 hours. Atm.: air; heating rate: 2.5-10K/min.

1. Ni-Fe formate from the low concentrated precursor solution ([Ni$^{2+}$] = 0.125M),
2. Ni-Fe formate from the concentrated precursor solution ([Ni$^{2+}$] = 0.15M).
4.3.4. Characterization of nickel ferrite powders

Single spinel phases obtained from the decomposition of the freeze-dried Ni(II)-Fe(III) formate of the concentrated solution precursor are characterized. The XRD pattern of the product obtained at 400°C (Figure 4.3.7(2a)) exhibits a pronounced diffraction broadening which decreases as the heat treatment temperature increases. After a thermal treatment performed at 1000°C for 24 hours, the resulting product is obviously the more crystallized one. This is confirmed by the progressive increase of the lattice parameter with the calcination temperature (Table 4.3.2). On the other hand, the saturation magnetization value $\sigma_S$ increases also in the same way. The saturation magnetization ($\sigma_S$) value of $\sim$5.450 emu/g obtained for NiFe$_2$O$_4$ prepared at 400°C increases up to 43.6 emu/g when nickel ferrite is prepared at 1000°C. Moreover, the increase of $\sigma_S$ is noticeable when the annealing time used at 1000°C increases. The saturation magnetization value of 46.9 emu/g obtained for a sample which is prepared at 1000°C during 24 hours is close to 47-56 emu/g, obtained using the ceramic method [3, 143]. It is generally found that ferrites of similar composition differ in their magnetic properties depending on the preparation technique (synthesis method, quenching as well cooling rates). In this case, one of the reasons for which such a behaviour will be observed should be the differences in the temperature of synthesis. In fact using the conventional method, the preparation of nickel ferrite “NiFe$_2$O$_4$” requires a synthesis temperature greater or equal to 1100°C. However, a temperature of 600°C is sufficient when the freeze-fried Ni(II)-Fe(III) formate precursor is employed.

Table 4.3.2: Lattice parameters “a” and saturation magnetization “$\sigma_S$” (at RT) of NiFe$_2$O$_4$ obtained after decomposition of the freeze-dried Ni(II)-Fe(III) formate at different temperatures for 3 and 24 hours in presence of air.

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>synthesis time (hour)</th>
<th>a (pm)</th>
<th>$\sigma_S$ (emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>3</td>
<td>832.51 (1)</td>
<td>5.450</td>
</tr>
<tr>
<td>600</td>
<td>3</td>
<td>833.56 (1)</td>
<td>11.417</td>
</tr>
<tr>
<td>800</td>
<td>3</td>
<td>833.90 (1)</td>
<td>27.602</td>
</tr>
<tr>
<td>1000</td>
<td>3</td>
<td>834.13 (2)</td>
<td>43.600</td>
</tr>
<tr>
<td>1000</td>
<td>24</td>
<td>834.30 (2)</td>
<td>46.885</td>
</tr>
</tbody>
</table>
Partial conclusion

The synthesis of nickel ferrite by thermal decomposition of freeze-dried Ni(II)-Fe(III) formate precursors has been carried out. After the preparation and the characterization of the different formate precursors, it was found that the freeze-dried iron(III) formate is amorphous; the nickel(II) formate is crystalline while the nickel(II)-iron(III) formate is amorphous. This implies thus that inside the Ni(II)-Fe(III) formate precursors prepared using the freeze-drying method, nickel(II) and iron(III) formate are well mixed. The decomposition of the freeze-dried nickel formate corresponds widely to that of the well known nickel(II) formate prepared using the precipitation method. In argon, the decomposition ends at 280°C and nickel metal is obtained. In air, the product contains a mixture of nickel oxide and a small amount of nickel metal (Ni). Up to 400°C, the total oxidation of the latter occurs. As already observed during the decomposition of freeze-dried iron(III) formate (Section 3.4.2.a) it was found that after the dehydration, the decomposition of the anhydrous nickel(II)-iron(III) formate includes an intermediate reduction of the Fe(III) ion. On the other hand, an interaction occurs between nickel and iron formate. At the end of the decomposition process (300°C), a partially crystalline spinel phase is formed beside the nickel metal which is amorphous. The subsequent heat treatment carried out at 400°C enables the crystallisation of the nickel metal and the ferritization process. Note however that the concentration of nickel ions inside the solution used for the preparation of the Ni(II)-Fe(III) formate precursor has an influence on the solid-solid reactions occurring during the decomposition process. For the nickel ion concentration lower than ~0.15M in the precursor solution, the spinel powders obtained at 400°C are highly susceptible to the heat treatments performed at higher temperatures. Besides, for the nickel ion concentration higher or equal to 0.15M, well crystallized nickel ferrite powders can be prepared by the direct heat treatment at 600°C / 800°C. This result is a consequence of the homogeneous state of the freeze-dried Ni(II)-Fe(III) formate obtained from a concentrated precursor solution. For these powders, the saturation magnetization value $\sigma_S$ and the lattice parameter “a” increase progressively with the calcination temperature.

The subsequent part of the work is based on the synthesis and the characterization of Ni-Fe alloy phases. The starting materials used for the synthesis of Ni-Fe alloys are nickel-iron oxide phases and freeze-dried precursors of nickel(II)-iron(III) formate. The synthesis is performed using the reduction method as described in Section 3.6. The reactivity of the prepared Ni-Fe alloy phases is deduced from their thermal behaviour in presence of air. The phase identification of the samples is carried out using the XRD method.
4.4.  Synthesis of nickel ferrite from Ni-Fe alloy phases

4.4.1.  Synthesis of Ni-Fe alloy phases

For the determination of the intermediate phases occurring during the reduction of the freeze-dried Ni(II)-Fe(III) formate under hydrogen, preliminary investigations were made under 2%H₂ in argon (2%H₂/Ar). In order to proceed, the TA, the MS and the XRD methods were employed.

4.4.1.a.  Synthesis under 2%H₂ in argon

The decomposition of the freeze-dried Ni(II)-Fe(III) formate under 2% H₂ /Ar atmosphere is illustrated in Figure 4.4.1. A comparison is made with the decomposition under argon.

![Figure 4.4.1: TA curves of the freeze-dried NiFe₂ formate precursor recorded under argon and under 2%H₂/Ar. Heating rate: 5K/min.](image)

The decomposition behaviour under 2%H₂/Ar is similar to the already described decomposition in argon (Section 4.3.2.b). But at the end of the decomposition, the slight gain of mass resulting from the crystallization of the product in argon is absent under 2%H₂/Ar. As a consequence of this difference, one notes that the initial and the end of the decomposition processes appear at slightly lower temperatures under argon than under 2%H₂/Ar. The experimental mass loss observed up to 400°C is similar in presence of both atmospheres. Moreover, the same gaseous products are released approximately in the same proportions up to the end of the decomposition. In the temperature range 280-345°C, the main composition of the solid products occurring under 2%H₂/Ar was examined. In order to proceed, 100mg of
Synthesis of nickel ferrite from Ni-Fe alloy phases

precursor was introduced in a quartz crucible and placed within a tubular furnace. The decomposition was done at a heating rate of 5K/min. After reaching the temperature of 320°C, the sample was quenched rapidly to RT under the same atmosphere (2%H₂/Ar). The resulting product (Fig. 4.4.2(a)) contains a spinel phase and some nickel metal/awaruite (FeNi₃) (Table 2.1, Section 2.1). Because the characteristic peaks of nickel oxide and those of the spinel phase appear at the same values of 2θ, the identification of nickel oxide, whose peaks are smaller, is not obvious.

![XRD patterns of the decomposition products of the freeze-dried Ni-Fe formate ([Ni²⁺] ~0.125M) quenched after annealing up to 320°C (a), slowly cooled after the TA measurements up to 450°C (b).](image)

The pattern of the product obtained at the end of TA measurements shows that the amount of Ni/FeNi₃ and that of the spinel phase increase from 320 up to 450°C (Figure 4.4.2(b)). The intermediate formation of Ni or FeNi₃ (an alloy rich in Ni) materializes the nearly independent decomposition of Ni(II)- and Fe(III) formate. During the decomposition of Ni(II)-Fe(III) formate under 2%H₂/Ar, a crystalline nickel metal is formed. In the presence of argon, nickel metal is amorphous (Section 4.3.2.b). This result emphasizes once more the influence of the working atmosphere on the composition of the products resulting from the decomposition of metal complex carboxylate precursors.

For further investigations, other heat treatments were performed at 400 and 600°C during 3-6 hours. After 3 hours of reduction at 400°C (Fig. 4.4.3(a)), the spinel phase (Fe₃O₄) and taenite (γFe,Ni) become the main phases in the product. It turns out that under the defined conditions, the partial reduction of the spinel phase takes place and enables the formation of the Ni-Fe alloy phase named taenite (Table 2.1, Section 2.1). Upon subsequent annealing at
600°C for 3 hours (Fig. 4.4.3(b)), the diffraction peaks of the spinel phase disappear completely and a small amount of the Ni-Fe alloy phase named kamacite is indexed beside taenite. Under 2%H₂/Ar, a pure taenite phase should be obtained after more than 6 hours of heat treatment at 600°C (Fig. 4.4.3(c)).

![Graph](image)

**Figure 4.4.3:** XRD patterns of the decomposition products of the freeze-dried Ni(II)-Fe(III) formate quenched after annealing during 3 hours at 400°C (a), 600°C (b) and during 6 hours at 600°C (c). Atm.: 2%H₂ in Ar; heating rate: 5K/min.

As previously observed for freeze-dried ammonium Cu(II)-Fe(III) oxalates (Section 3.6.1.a), the reduction of the freeze-dried Ni(II)-Fe(III) formate occurs very slowly under 2%H₂/Ar and long annealing above 400°C is required for the formation of metallic phases. Due to this fact, further investigations under hydrogen atmosphere are more suitable for the synthesis of Ni-Fe alloy phases.

### 4.4.1.b. Synthesis under hydrogen atmosphere

Under hydrogen, the thermal decomposition was carried out between 400 and 800°C. The Table 4.4.1 presents the compositional details of the different starting powders S1, S2, S3, S4, S5 and S6. Apart from S6 which is also a single spinel phase like S4 and S5, the XRD patterns of S1 - S5 have been shown; in Figure 4.3.6(a) for S1; Figure 4.3.7(1, a, c, d) for S2, S3, S4 and in Figure 4.2.1 for S5. The Table 4.4.2 presents the name and the composition of the Ni-Fe alloys which are formed during the present investigation. Figures 4.4.4 and 4.4.5 show the phase composition of some reduction products obtained using the XRD analysis method.
Table 4.4.1: Starting powders used for the reduction under H₂

<table>
<thead>
<tr>
<th>Sample N°</th>
<th>samples</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Freeze-dried Ni-Fe formate precursor</td>
<td>Amorphous phase</td>
</tr>
<tr>
<td>S2</td>
<td>Ni-Fe₂ formate heated at 400°C</td>
<td>(γ-Fe₂O₃, NiO), NiO and Fe₂O₃</td>
</tr>
<tr>
<td>S3</td>
<td>Ni-Fe₂ formate heated at 800°C</td>
<td>NiFe₂O₄, NiO and Fe₂O₃</td>
</tr>
<tr>
<td>S4</td>
<td>Ni-Fe₂ formate heated at 1000°C</td>
<td>NiFe₂O₄ (trevorite)</td>
</tr>
<tr>
<td>S5</td>
<td>mixture (NiO:Fe₂O₃) heated at 400°C and annealed at 1100°C (air)</td>
<td>NiFe₂O₄ (trevorite)</td>
</tr>
<tr>
<td>S6</td>
<td>mixture (Ni:2Fe) heated at 400°C and annealed at 1100°C (air)</td>
<td>NiFe₂O₄ (trevorite)</td>
</tr>
</tbody>
</table>

Table 4.4.2: Name and composition of some Fe-Ni alloy phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>(γFe,Ni)</th>
<th>(αFe,Ni)</th>
<th>FeNi₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Taenite</td>
<td>Kamacite</td>
<td>Awaruite (alloy rich in iron)</td>
</tr>
<tr>
<td>Composition at. % Ni</td>
<td>0 to 100</td>
<td>0 to 5.5</td>
<td>63 to 85</td>
</tr>
</tbody>
</table>

The XRD patterns obtained from the heat treatment under H₂ of the freeze-dried NiFe₂ formate (S1) are shown in Figure 4.4.4. It is found that after 3 hours of heat treatment at 400°C, (γFe,Ni) and (αFe,Ni) phases are formed. Note however that the diffraction peaks of the (αFe,Ni) (nickel-poor intermetallic phase) and that of the iron metal (αFe) appear at the same position. It is thus not easy to distinguish both phases using the XRD analysis method. The increase of the reduction temperature from 400 up to 600°C leads to an important decrease of the amount of the (αFe,Ni) phase and to the increase of the amount of the (γFe,Ni) phase. Up to 800°C, several hours of heat treatment are required to attain the equilibrium state leading to the formation of a product containing only the taenite phase (γFe,Ni). Figure 4.4.5 shows the XRD patterns obtained when the starting powder which is submitted to the reduction process is constituted of nickel and iron oxides (S2, S3 and S4). At 400°C, the phases of (γFe,Ni) and (αFe,Ni) are also formed (Fig. 4.4.5(a)). An important decrease of the amount of the (αFe,Ni) phase is observed after 3 hours of reduction at 600°C (Fig. 4.4.5(b)). The resulting product contains the (γFe,Ni) phase and some traces of (αFe,Ni). On the other
hand, it is found that the reduction of a pure spinel phase NiFe$_2$O$_4$ (S4) under the same conditions (i.e. at 600°C for 3 hours in H$_2$) results to the direct formation of a product containing only the taenite phase ($\gamma$Fe,Ni) (Fig. 4.4.5(c)).

**Figure 4.4.4:**
XRD patterns of the reduction products of the freeze-dried Ni(II)-Fe(III) formate (S1) quenched after annealing at 400°C, 600°C and 800°C for 3-12 hours. Atm.: H$_2$, Heating rate: 5K/min.

**Figure 4.4.5:**
XRD patterns of quenched products obtained after the reduction of S2 at 400°C (a); S3 (b) and S4 (c) at 600°C. Atm.: H$_2$; reduction time: 3hours, heating rate: 5K/min.
From the above it turns out that at 600°C, a short annealing time (3 hours) is sufficient to obtain the single phase ($\gamma$Fe,Ni) by reducing NiFe$_2$O$_4$ under hydrogen. On the other hand under the same conditions, the inhomogeneous reduction of the freeze-dried Ni-Fe formate as well as that of the mixtures of Ni-Fe oxide results to the formation of a product containing some nickel poor kamacite phase ($\alpha$Fe,Ni) beside the taenite phase ($\gamma$Fe,Ni). In this case, the synthesis of the single phase ($\gamma$Fe,Ni) requires a long annealing time or the increase of the temperature of the reduction (up to $\sim$800°C). Therefore, the process of reduction which leads to the formation of a pure taenite phase ($\gamma$Fe,Ni) occurs more quickly when the starting sample is a single spinel phase NiFe$_2$O$_4$ than when the starting samples used are the homogeneous freeze-dried Ni(II)-Fe(III) formate precursors or the mixture of oxide phases.

**4.4.2. Oxidation of Ni-Fe alloy phases**

*Experimental*

The starting powders are ($\gamma$Fe,Ni) alloy phases M4, M5 and M6 obtained from the reduction of S4, S5 and S6 under H$_2$ at 600°C/3hours, respectively (Table 4.4.1). The oxidation of the different ($\gamma$Fe,Ni) alloy phases was performed under controlled heating rate. In fact after several investigations, it was found that the heating rates greater than 5K/min affect the formation of the pure spinel phase NiFe$_2$O$_4$. The annealing time varied from 3 to 24 hours and the heat temperature from 400 up to 1000°C. Following each treatment, the product was removed from the furnace and cooled down to RT inside the desiccator. Its characterization was done using the XRD analysis method. In what follows the abbreviations P4(T), P5(T) and P6(T), where T is the oxidation temperature are used for the identification of the products resulting from the oxidation of ($\gamma$Fe,Ni) alloy phases named M4, M5 and M6, respectively.

*Oxidation of the reduced NiFe$_2$O$_4$ powders*

Figures 4.4.6 and 4.4.7 show the XRD patterns obtained after the oxidation of the several ($\gamma$Fe,Ni) phases, prepared differently. At 400°C for the annealing times lower or equal to 48 hours, the complete oxidation of the metallic powder does not occur (Fig. 4.4.6). For each sample M4, M5 and M6, the resulting phases in the product are a spinel phase, hematite ($\alpha$-Fe$_2$O$_3$), taenite ($\gamma$Fe,Ni) and awaruite (FeNi$_3$). The presence of FeNi$_3$ in the product shows that ($\gamma$Fe,Ni) is a metastable phase which is decomposed already at low temperatures ($T \leq 400°C$). The same point of view has commonly been pointed out in several works.
devoted in the study of the phase formation in the system Ni-Fe [36]. The samples P4(400), P5(400) and P6(400) contain the same phases but in different amounts. The low amount of taenite inside P4(400) and P5(400) is materialized by a relative large amount of hematite and spinel compounds (Fig. 4.4.6).

![XRD patterns of oxide products obtained from the oxidation at 400°C of (γFe,Ni) alloys. Atm.: air; heating rate: 5K/min, annealing time: 48 hours.](image)

Figure 4.4.6: XRD patterns of oxide products obtained from the oxidation at 400°C of (γFe,Ni) alloys. Atm.: air; heating rate: 5K/min, annealing time: 48 hours.

It turns out that, the oxidation rate of (γFe,Ni) phases varied slightly as function of the starting powders used for their preparation. The taenite sample “M4” obtained from the decomposition followed by the reduction of the homogeneous freeze-dried Ni(II)-Fe(III) formate precursor should be more porous and fine grained thus, more reactive. On the other hand, the low reactivity of the samples “M5” and “M6” should be due to the fact that the starting materials used for their synthesis were prepared at 1100°C. In fact the powders obtained using the ceramic method have large particle sizes and low surface areas. A subsequent heating at 600°C results to the total oxidation of (γFe,Ni) and FeNi₃. The phases in the products are a spinel phase, NiO and α-Fe₂O₃. The amount of α-Fe₂O₃ in the products P4(600), P5(600) and P6(600) is still significant after 48 hours of heat treatment, showing that a pure spinel phase (NiFe₂O₄) can not be obtained at 600°C. Upon further heating at 800°C for 24 hours, the pure ferrite “NiFe₂O₄” is the only phase present on the XRD patterns of P4(800), P5(800) and P6(800) (Fig. 4.4.7). Besides, it was also found that the heating of (γFe,Ni) in air from RT up to 800°C, followed by an annealing during 24hours at the same temperature, leads to the direct formation of the single spinel phase NiFe₂O₄.
Synthesis of nickel ferrite from Ni-Fe alloy phases

Discussion and conclusions

The synthesis and the oxidation of the alloy phase ($\gamma$Fe,Ni) have been carried out. The single phase ($\gamma$Fe,Ni) was accordingly formed from the reduction of nickel ferrite under hydrogen at 600ºC. Furthermore, the complete oxidation of ($\gamma$Fe,Ni) is effective after 24 hours of heat treatment in air at 800ºC. From this last process, the spinel phase NiFe$_2$O$_4$ is regenerated. The reversibility phenomenon observed in the system Ni-Fe-O can be written as follows:

\[
\begin{align*}
\text{NiO} + \alpha - \text{Fe}_2\text{O}_3 &\xrightarrow{1000ºC \text{ (air, 48 hours) / 1100ºC (24 hours, air)}} \text{NiFe}_2\text{O}_4 \text{ (nickel ferrite)} \\
\text{Ni} + 2\text{Fe} &\xrightarrow{1000ºC \text{ (air, 48 hours) / 1100ºC (24 hours, air)}} \text{NiFe}_2\text{O}_4 \text{ (nickel ferrite)} \\
\text{NiFe}_2\text{O}_4 &\xrightarrow{\text{reduction under hydrogen at 600ºC (3 hours)}} (\gamma\text{Fe, Ni}) \text{ (taenite)} \\
(\gamma\text{Fe, Ni}) &\xrightarrow{\text{oxidation in air at 800ºC (24 hours)}} \text{NiFe}_2\text{O}_4 \text{ (nickel ferrite)}
\end{align*}
\]

For comparison, the metallic mixture Ni:2Fe prepared from mechanical milling (Section 8.1) was oxidized in presence of air. The oxidation at 600ºC generates the mixture NiO and $\alpha$-Fe$_2$O$_3$ (Fig. 4.4.8). At 800ºC, the resulting product contains only a small amount of nickel ferrite. This means that NiO and $\alpha$-Fe$_2$O$_3$ are still the main phases. After 24 hours of heat treatment at 1100ºC, a single spinel phase is formed. It turns out that using the conventional

Figure 4.4.7: XRD patterns of NiFe$_2$O$_4$, prepared from the oxidation at 800ºC of the ($\gamma$Fe,Ni) phases. Atm.: air; heating rate: 5K/min, annealing time: 24 hours.
ceramic method, the reaction between NiO and $\alpha$-Fe$_2$O$_3$ is not important at 800°C/24hours. Thus, during the oxidation of the taenite phase, the formation of nickel ferrite occurs as soon as the oxidation process takes place.

![Figure 4.4.8: XRD patterns of oxide products obtained from the oxidation of the metallic mixture (Ni, 2Fe). Atm.: air; heating rate: 5K/min.](image)

**Figure 4.4.8:** XRD patterns of oxide products obtained from the oxidation of the metallic mixture (Ni, 2Fe). Atm.: air; heating rate: 5K/min.

Foley [164] has studied the kinetic of oxidation of commercial Fe-Ni alloy samples. Investigations were performed in air and under controlled oxygen over the range 500-1100°C. For the Fe-Ni alloys containing 30-75% Ni, the first-formed film on alloys was an oxide of iron resulting from the selective oxidation. However, upon oxidation at time longer than one minute at 600°C, a spinel structure Ni$_x$Fe$_{3-x}$O$_4$ was formed. From these studies the author concluded that above 500°C, the reaction between the oxide phases is rapid in such a way that NiO and $\alpha$-Fe$_2$O$_3$ did not coexist, but reacted to form nickel ferrite “NiFe$_2$O$_4$. From a careful investigation performed under controlled heating rate we found that, during the oxidation of the intermetallic phase ($\gamma$Fe,Ni), the presence of $\alpha$-Fe$_2$O$_3$ up to 800°C can be avoided only when the oxidation process is performed under a controlled rate of heating (lower or equal 5K/min).

Thus we have shown that the synthesis of nickel ferrite from the oxide mixture (NiO:$\alpha$-Fe$_2$O$_3$) or from the metallic mixture (Ni:2Fe) requires a temperature of around 1000-1100°C while with the alloy phase ($\gamma$Fe,Ni), a single spinel phase “NiFe$_2$O$_4$” is formed at 800°C. This means that the ($\gamma$Fe,Ni) alloy phase is more reactive than the mixture of metallic powders Ni, Fe as well as the mixture NiO:$\alpha$-Fe$_2$O$_3$. 
4.5. **Comparison between the unconventional “freeze-drying method” and the ceramic method**

Nickel ferrite can be prepared by the thermal decomposition of the amorphous freeze-dried Ni(II)-Fe(III) formate. However, the homogeneous state of these precursors is affected by the concentration of metal ions in the precursor solution. This is caused by the following equilibrium which is established during the freeze-drying process.

\[
\frac{2}{3}[Fe_{3}^{3+}O(HCOO)_{6}]HCOO^- + Ni(HCOO)_{2} + \frac{1}{3}H_{2}O \xrightarrow{\text{eq}(1)} Fe_{3}^{3+}Ni^{2+}O(HCOO)_{6} + \frac{2}{3}HCOOH
\]

The higher the concentration of the nickel ions in the solution of precursor is, the stronger the homogeneous state of the freeze-dried powder becomes. In this case, the reaction (i) moves according to the direction (1). The decrease of the mixing state of nickel and iron formate leads to the displacement of the equilibrium (i) following the direction (2). During the decomposition of the resulting precursor, the individual crystallization of intermediate phases (\(\gamma\)-Fe\(_{2}\)O\(_{3}\)/Fe\(_{3}\)O\(_{4}\), Ni(amorph)) occurs. Consequently, the composition of the powders thus obtained is affected and the temperature required for the formation of nickel ferrite is above 600°C. Particularly for the precursor solution with a nickel ion concentration higher or equal to 0.15M, the intermediate formation of \(\alpha\)-Fe\(_{2}\)O\(_{3}\) is inhibited and well crystallized NiFe\(_{2}\)O\(_{4}\) powders can be prepared by the direct decomposition of the freeze-dried NiFe\(_{2}\)O\(_{4}\) formate precursor at 600°C/800°C. Compared to the conventional method, the synthesis of nickel ferrite using the freeze-dried formate precursor is a suitable method. In fact using the mixture NiO:\(\alpha\)-Fe\(_{2}\)O\(_{3}\), the required temperature is 1100°C. This means 300°C above the temperature which is used when the starting powder is the freeze-dried NiFe\(_{2}\) formate precursor. More particularly it is found that starting from the freeze-dried precursor NiFe\(_{2}\) formate, the synthesis of the well crystalline nickel ferrite is possible at a temperature lower than that of the one obtained from the thermolysis of oxalate/tartrate precursors (> 800°C) [153, 155]. Note however that when the time interval employed at 1000°C is longer (48 hours), the synthesis of nickel ferrite from the mixture NiO:\(\alpha\)-Fe\(_{2}\)O\(_{3}\) becomes possible. The variation in the working temperature required for the synthesis of a pure nickel ferrite may be due to the fact that the contact between nickel and iron atoms varies inside starting powders prepared differently. In most cases, the low diffusion rate may be due to the difference in the
positioning of the ions in the original lattices, which is also suggested by Lin [165]. In the 
\( \alpha\)-Fe\(_2\)O\(_3\), all the iron ions are located in octahedral sites and the oxygen ions form a nearly hexagonal close-packed structure. In NiO, all the nickel ions are also in octahedral sites and the oxygen ions form a close-packed structure. To form the inverse NiFe\(_2\)O\(_4\), repositioning of half of the iron ions into tetrahedral sites is needed plus a shift of the oxygen lattice of the hematite whereas the newly formed spinel lattice has an identical oxygen lattice as that of nickel oxide. Starting from the Ni-Fe alloy phase (\(\gamma\)Ni,Fe), the close contact between Ni and Fe ions enhances their ability to form nickel ferrite. Thus, well crystalline NiFe\(_2\)O\(_4\) powders are obtained from the oxidation of (\(\gamma\)Ni,Fe) alloy at 800°C (24 hours) in presence of air.
5. **System Cu-Ni-O**

5.1. **Literature review on the synthesis of solid solutions of the system Cu-Ni-O**

Up to now, solid solutions $(\text{CuO})_x(\text{NiO})_{1-x}$ have been extensively prepared and characterized by several authors [80-86]. What comes out is that the monoclinic CuO dissolves only approximately 5% of NiO in its network, while an appreciable solubility from 20 to 30% of CuO in NiO is observed towards 900°C [81, 82]. Above 900°C, the solid solutions $(\text{CuO})_x(\text{NiO})_{1-x}$ with higher copper content ($> 25\%$) show a tetragonal distortion from the cubic symmetry. The phase diagram established by Delorme [82] is the following.

![Diagram of states of the solid solutions $(\text{CuO})_x(\text{NiO})_{1-x}$ (according to [82]).](image)

- $S_0 =$ cubic solid solution, type NiO;
- $S_1 =$ quadratic structure $c/a < 1$;
- $S_2 =$ quadratic structure $c/a > 1$;
- $S_3 =$ monoclinic solid solution, type CuO.

For all the previous works, only the solid state reaction of simple oxides was used. With regards to the study of the influence of the synthesis method on the formation of $(\text{Cu}_x\text{Ni}_{1-x})\text{O}$ oxide phases, some compositions were prepared by the thermal decomposition of freeze-dried formate precursors.
5.2. Preparation and thermal decomposition of the freeze-dried Cu(II)-Ni(II) formate precursors

For the synthesis of \((\text{Cu}_x\text{Ni}_{1-x})\text{O}\) solid solutions with \(x = 0.25, 0.35, 0.5, 0.75\) and 0.9, the freeze-dried formate powders were prepared as described in Section 8.6. Figure 5.2.1(b) illustrates the XRD pattern obtained for the precursor \(\text{Cu}_{0.35}\text{Ni}_{0.65}\) formate which is used as an example. A comparison is made with the patterns of nickel(II) formate (Fig. 5.2.1(a)) and copper(II) formate (Fig. 5.2.1(c)).

![Figure 5.2.1: XRD patterns of freeze-dried precursors: (a) Ni(II) formate, (b) Cu_{0.35}Ni_{0.65} formate and (c) Cu(II) formate.]

Here all the mentioned precursors are crystalline. On the pattern of the mixture \(\text{Cu}_{0.35}\text{Ni}_{0.65}\) formate (Fig. 5.2.1(b)), one sees for instance that the characteristic peak of copper formate which appears at \(2\theta = 16.9^\circ\) is absent. From this observation, it is obvious that during the freeze-drying process, an interaction took place between nickel and copper formate. This behaviour points out the homogeneous state of the freeze-dried \(\text{Cu}_{0.35}\text{Ni}_{0.65}\) formate. A solid solution with the structure of nickel formate is probably formed.

Figure 5.2.2 shows the DTA- and the TG- plot obtained in argon for the precursor \(\text{Cu}_{0.35}\text{Ni}_{0.65}\) formate (Fig. 5.2.2(a), (d)). The TG curve of copper and nickel formate are also shown (Fig. 5.2.2(b), (c)). As observed during the decomposition of copper and nickel formate, it is found that the TG curve of \(\text{Cu}_{0.35}\text{Ni}_{0.65}\) formate exhibits two main superimposed mass loss steps. The first mass loss step occurs in the range 30-160\(^\circ\)C and corresponds to the elimination of the coordinated water. During the second one (160-240\(^\circ\)C), the decomposition of the formate takes place. The end temperature of about 240\(^\circ\)C is lower than that of nickel
formate (280°C) and almost the same with that of copper formate. The main gaseous decomposition products identified using the MS analysis method are H₂O, CO, CO₂ and HCOOH. According to the results of the decomposition of Cu(II) formate (Section 3.4.2.b) and Ni(II) formate (Section 4.3.2.a), the broad exothermic peak in the DTA curve above 240°C is the result of the slow oxidation of the end products (Cu and Ni) and the crystallization of Cu₂O / CuO and NiO.

Figure 5.2.2: TG curves of the freeze-dried Cu₀.₃₅Ni₀.₆₅ formate (a), Ni(II) formate (b), Cu(II) formate (c) and DTA curve of Cu₀.₃₅Ni₀.₆₅ formate (d). Atm.: Ar; heating rate: 5K/min.

5.3. Phase formation from the freeze-dried copper(II)-nickel(II) formate precursors

The freeze-dried precursors CuₓNi₁₋ₓ formate (x = 0.25, 0.35, 0.5, 0.75 and 0.9) were decomposed in air at a heating rate of 2.5K/min up to 400°C for one hour. After this treatment, the resulting powders were heated at 600°C, 800°C and 1000°C for 24 hours (heating rate 10K/min). The phase formation was investigated by XRD analysis method. After the thermal treatment performed at 400°C, all the samples present broad diffraction peaks. This should be due to the formation of fine grained products. The diffraction peaks in the product with x = 0.25 and 0.35 belong only to the rock-salt phase NiO. This result confirms the insertion of copper ions inside the lattice of nickel oxide and, thus the formation of cubic solid solution phases. For the sample with x = 0.5, the solid solution types CuO and NiO are formed approximately in the same amount. However, when x is greater than 0.5, the solid solution type CuO becomes the main phase inside the product. After annealing at 600-800°C, for every value of x, the indexed peaks correspond to the diffraction lines of well crystalline
Preparation and thermal decomposition of the freeze-dried Cu(II)-Ni(II) formates

solid solution types CuO and NiO. The amount of each phase is proportional to the value of x. At 1000°C, the reaction between these intermediate phases is important, thereby a single and well crystallized (Cu_{0.25}Ni_{0.75})O phase is formed (Figure 5.3.1). The patterns of the samples with x = 0.35, 0.5, 0.75, 0.9 exhibit a peak around 35.5°, indicating the formation of a nickel poor solid solution phase beside the nickel rich oxide phase. The amount of the nickel poor solid solution phase is negligible for x = 0.35 but becomes important for x = 0.5, 0.75 and 0.9. Moreover for the samples with x = 0.35, 0.5, 0.75, 0.9, the characteristic peak of the nickel rich oxide phase which appears at 2θ = 43.3° is broad (Fig. 5.3.1). This means that above x = 0.25, the concentration of Cu^{2+} ions inside the lattice of NiO is sufficient for the distorsion of its symmetry. This result is in agreement with the phase diagram established in Figure 5.1.1. The single solid solution phase (Cu_{0.25}Ni_{0.75})O obtained at 1000°C was annealed at 700°C for 16 hours. After this treatment, the product contains a Ni-poor solid solution (small amount) beside a Ni-rich solid solution (main phase). From this result, it is clear that the oxide phase (Cu_{0.25}Ni_{0.75})O obtained in air at 1000°C is unstable at lower temperatures.

![XRD patterns of the decomposition products of the freeze-dried Cu_{x}Ni_{1-x} formate annealed at 400°C and followed by the heating at 1000°C. Atm.: air; Heating rate: 10K/min, heating time: 24 hours, cooling rate: slow (dessiccator), (x-offset = 5°).](image)

**Figure 5.3.1:** XRD patterns of the decomposition products of the freeze-dried Cu_{x}Ni_{1-x} formate annealed at 400°C and followed by the heating at 1000°C. Atm.: air; Heating rate: 10K/min, heating time: 24 hours, cooling rate: slow (dessiccator), (x-offset = 5°).

Particularly for x = 0.35, further investigations were performed above 1000°C (Fig. 5.3.2). The thermal treatment at 1000°C (for 52 hours) and at 1050°C (for 24 hours) followed by the slow cooling of the resulting products lead to the formation of the single phase (Cu_{0.35}Ni_{0.65})O with a partially distorted cubic structure. By further thermal treatment performed at 1100°C,
the decomposition of the solid solution \((\text{Cu}_{0.35}\text{Ni}_{0.65})\text{O}\) occurs. Consequently, a nickel poor solid solution phase is indexed as the second phase. This implies that at higher temperatures, the synthesis field of \((\text{Cu}_{0.35}\text{Ni}_{0.65})\text{O}\) extends from 1000°C to a temperature higher than 1050°C but lower than 1100°C. For further investigations, the sample with \(x = 0.35\) was annealed at 1050°C (for 24 hours) and quenched in water (Fig. 5.3.3). The XRD pattern of the product was indexed using the tetragonal phase \(\text{Ni}_2\text{CuO}_3\) (PDF 40-959).

**Figure 5.3.2:** XRD patterns of the decomposition products of the freeze-dried \(\text{Ni}_{0.65}\text{Cu}_{0.35}\) formate annealed at 400°C and followed by the heating at 1000°C (52 hours) 1050°C (24 hours) and (c) 1100°C (24 hours). Atm.: air; heating rate: 10K/min, cooling rate: slow (dessiccator), (x-offset = 5°).

**Figure 5.3.3:** XRD pattern of the decomposition product of the freeze-dried \(\text{Cu}_{0.35}\text{Ni}_{0.65}\) formate annealed at 400°C, followed by the heating at 1050°C (24 hours). Atm.: air; heating rate: 10K/min, cooling rate: rapid (in water).
The lattice parameters determined with the help of the WinXpow program ([P1]) are \(a = b = 424.30(1)\text{pm}\) and \(c = 412.68(1)\text{pm}\). The reported data are \(a = b = 413.56(7)\text{pm}\) and \(c = 433.36(7)\text{pm}\) [85]. According to Davies [86], the composition of \(\text{Ni}_2\text{CuO}_3\) is closely equivalent to \((\text{Cu}_{0.35}\text{Ni}_{0.65})\text{O}\).

**Partial conclusion**

The thermal decomposition in air of appropriate freeze-dried Cu(II)-Ni(II) formate precursors allows the direct formation at about 400°C of partially crystalline solid solutions \((\text{Cu}_{0.25}\text{Ni}_{0.75})\text{O}\) and \((\text{Cu}_{0.35}\text{Ni}_{0.65})\text{O}\). The increase of the amount of copper “\(x\)” in the formate precursor induces the additional formation of a Ni-poor solid solution phase in the product. The partially crystalline products obtained at 400°C crystallize in the temperature range 600-800°C. For every value of \(x\), the product which is formed at 800°C contains a mixture solid solution types CuO and NiO. The amount of each phase is proportional to the value of \(x\). By subsequent annealing at 1000°C, well crystalline solid solutions \((\text{Cu}_{0.25}\text{Ni}_{0.75})\text{O}\) and \((\text{Cu}_{0.35}\text{Ni}_{0.65})\text{O}\) are formed, whereas for the composition \((\text{Cu}_{x}\text{Ni}_{1-x})\text{O}\) with \(x = 0.50, 0.75\) and 0.90 a Ni-poor solid solution is formed beside a Ni-rich solid solution with a distorted structure. According to several authors [81, 82], this last observation is due to the fact that, only few amounts of NiO dissolve in the CuO network. At 1000°C, the oxide phase \((\text{Cu}_{0.25}\text{Ni}_{0.75})\text{O}\) is cubic while the composition \((\text{Cu}_{0.35}\text{Ni}_{0.65})\text{O}\) has a partially distorted one. The complete conversion of \((\text{Cu}_{0.35}\text{Ni}_{0.65})\text{O}\) to the tetragonal structure requires an annealing at 1000-1050°C followed by the quenching of the resulting product in water. According to Delorme (Fig. 5.1.1) the solid solution \((\text{Cu}_{0.25}\text{Ni}_{0.75})\text{O}\) prepared at 1000°C is a thermodynamically stable phase. This prediction is only correct for the synthesis temperature of 1000°C. In fact we found that \((\text{Cu}_{0.25}\text{Ni}_{0.75})\text{O}\) decomposes below 1000°C into two phases: a Ni-poor solid solution (small amount) and a Ni-rich solid solution (main phase). Starting from the homogeneous freeze-dried Cu(II)-Ni(II) formate precursor, the intermediate phases occurring during the formation of the solid solutions \((\text{Cu}_{0.25}\text{Ni}_{0.75})\text{O}\) and \((\text{Cu}_{0.35}\text{Ni}_{0.65})\text{O}\) are sufficient for the prediction of their metastable state. However when the oxide mixture CuO-NiO, commonly used in the reported investigations, is the starting powder this prediction is not possible. In fact using this last method, the phases formation begins only above 800°C.
6. **System Cu-Ni-Fe-O**

6.1. **Literature review on the synthesis of nickel-copper mixed ferrites**

The interest put on the preparation of substituted ferrite is generated by the fact that such materials have particular physical properties leading to various applications in magnetic and electronic devices. Amongst them, copper containing ferrites have shown interesting properties [17, 166, 167]. Their behaviour is explained on the basis of cation migration of Cu$^{2+}$ and tetragonal distortion.

Copper-nickel ferrites were first studied by Van Uitert [19]. One important finding of the author is that copper ferrite CuFe$_2$O$_4$ shows a tetragonal structure but with the addition of nickel, the tetragonality disappears and the copper-nickel ferrite samples exhibit a cubic structure. Since then, there has been remarkable other contributions such as Mössbauer studies [168, 169], cations distribution [143], electrical and magnetic properties [140, 143].

In these previous works, the conventional ceramic method, requiring a working temperature above 1000°C was commonly used as the synthesis method. No synthesis using the unconventional method has been reported. Unlike the conventional method, the unconventional one allows the production of single spinel phase at a relatively low temperature [9, 125]. Moreover, one notes that the previous works were based only on the spinel solid-solution formed between NiFe$_2$O$_4$ and CuFe$_2$O$_4$ [19, 143, 168, 169]. Other regions of the spinel solid-solutions in the Cu-Ni-Fe-O system have been inadequately studied.

In what follows, we intend to use the freeze-dried precursors Cu(II)-Ni(II)-Fe(III) formate as starting powders for the synthesis of the spinel solid-solution occurring between nickel ferrite “NiFe$_2$O$_4$” and copper ferrite “CuFe$_2$O$_4$”. Furthermore, our attention is also paid on the determination of the working conditions (T/p(O$_2$)) required for the synthesis of some single spinel phases in the phase triangle Cu$_{0.5}$Fe$_2$O$_4$-Cu$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$-Cu$_{0.9}$Fe$_{2.1}$O$_4$. From the data existing in the literature, we establish the relation between the synthesis method and the physical properties of Cu-Ni ferrite materials.
6.2. Synthesis of nickel-copper mixed ferrites from the freeze-dried formate precursors

6.2.1. Preparation and characterization of the formate precursors

The starting powders iron(II) formate, nickel(II) formate and copper(II) formate were obtained as described in Section 8. From these powders, solutions of Ni(II) and Cu(II) formate with excess of formic acid were prepared. According to the composition of the ferrite samples $\text{Cu}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ($0 < x < 1$), adequate volumes of Cu(II) and Ni(II) formate solutions were mixed and the required mass of Fe(II) formate was added. The following preparation procedures are identical to the one employed for the preparation of freeze-dried Cu(II)-Fe(III) formate precursors (Section 8.7). The characterization of the loose powders obtained from the freeze-drying process was performed using the XRD analysis method (Fig. 6.2.1).

![XRD patterns of the freeze-dried Cu$_x$Ni$_{1-x}$Fe$_2$ formate precursors with (a) $x$ = 0.3, (b) $x$ = 0.5 and (c) $x$ = 0.9.](image)

Figure 6.2.1: XRD patterns of the freeze-dried Cu$_x$Ni$_{1-x}$Fe$_2$ formate precursors with (a) $x$ = 0.3, (b) $x$ = 0.5 and (c) $x$ = 0.9.

From Figure 6.2.1, one notes that the amorphous state of the freeze-dried precursors Cu$_x$Ni$_{1-x}$Fe$_2$ formate becomes considerably lower as the copper content “$x$” increases. In fact, when $x$ is equal to 0.3, the precursor does not show any diffraction peak accounting for an amorphous state (Fig. 6.2.1(a)). For $x$ equal to 0.5 and to 0.9, the crystalline phase “Cu(HCOO)$_2$” is indexed beside the amorphous phase (Fig. 6.2.1(b), (c)). The increase of the peaks intensity of the copper formate with the value of $x$ is observed. From that, it could be concluded that the segregation of some copper formate took place during the freeze-drying
Synthesis of nickel-copper mixed ferrites from the freeze-dried formate precursors

process. This behaviour becomes more important as the copper content increases in the freeze-dried Cu(II)-Ni(II)-Fe(III) formate precursor.

6.2.2. Thermal decomposition of the formate precursors

The thermal decomposition of the freeze-dried Cu(II)-Fe(III)- and Ni(II)-Fe(III) formate precursors were investigated in sections 3.4.2.c and 4.3.2.b, respectively. On the basis of the results of these previous studies, the evaluation of the thermal decomposition of the freeze-dried Cu$_x$Ni$_{1-x}$Fe$_2$ formate (0 < x < 1) precursors is performed. Figure 6.2.2(c) shows the DTA- and TG- plots obtained in argon for the precursor Cu$_{0.5}$Ni$_{0.5}$Fe$_2$ formate, used as an example. These TA curves are compared with those of the freeze-dried Ni(II)-Fe(III) formate (Fig. 6.2.2(a)) and Cu(II)-Fe(III) formate (Fig. 6.2.2(b)). One notes that the TG profiles of the three precursors are rather similar (Fig. 6.2.2(1)). The decomposition of Cu$_{0.5}$Ni$_{0.5}$Fe$_2$ formate ends at 260°C whereas Cu(II)-Fe(III)- and Ni(II)-Fe(III) formate decompose completely at 290°C and 300°C, respectively. It turns out that, the maximum mass loss of the mixed Cu(II)-Ni(II)-Fe(III) formate precursor is reached at a temperature lower than for the freeze-dried Cu(II)-Fe(III)- and Ni(II)-Fe(III) formate precursors. This means that during the thermal decomposition, an interaction takes place between the components and results in a lower decomposition temperature of the freeze-dried Cu(II)-Ni(II)-Fe(III) formate.

Figure 6.2.2: TG- (1) and DTA- (2) plots of freeze-dried formate precursors. (a) NiFe$_2$ formate, (b) CuFe$_2$ formate and (c) Cu$_{0.5}$Ni$_{0.5}$Fe$_2$ formate. Atm.: Ar ; heating rate: 5K/min.
When the freeze-dried precursor Cu$_{0.5}$Ni$_{0.5}$Fe$_2$ formate is decomposed in presence of air, the simultaneous oxidation of the gaseous and the primary solid products by oxygen causes the decomposition of the anhydrous sample following a whole exothermic process. The decomposition process ends at 230°C. Figure 6.2.3 shows the XRD patterns of the intermediate products occurring during the decomposition of the freeze-dried Cu$_{0.5}$Ni$_{0.5}$Fe$_2$ formate in presence of argon. Up to 200°C (Fig. 6.2.3(a)), the precursor remains nearly amorphous. Beside the amorphous phase, a negligible amount of the crystalline copper formate remains. The characteristic peaks of copper metal Cu and cuprite Cu$_2$O with low resolved intensity are indexed. The diffraction peaks of nickel metal “Ni” are absent. The additional formation of the spinel phase (Fig. 6.2.3(b)) occurs by annealing up to 220°C. Moreover, the amount of the crystalline metallic copper Cu increases. Up to 250°C, the amount of the previous phases increases. Note however that no decomposition product of Ni component is indexed (Fig. 6.2.3(c)). A partially crystalline spinel phase is formed at 400°C (Fig. 6.2.3(d)).

**Figure 6.2.3:** XRD patterns of the decomposition products of the freeze-dried Cu$_{0.5}$Ni$_{0.5}$Fe$_2$ formate quenched after annealing up to 200°C (a), 220°C (b), 250°C (c) and 400°C (d).

Atm.: Ar; heating rate: 5K/min.

From this observation, it turns out that during the decomposition of the freeze-dried precursor Cu$_{0.5}$Ni$_{0.5}$Fe$_2$ formate, nickel formate and iron formate behave simultaneously whereas an independent behaviour of copper formate takes place. As already observed during the synthesis of copper ferrite from the formate precursors, it is expected that the intermediate formation of copper metal should prevent the direct formation of a single spinel phase at a low temperature.
6.3. Phase formation from freeze-dried copper(II)-nickel(II)-iron(III) formate precursors

The freeze-dried precursors Cu<sub>x</sub>Ni<sub>1-x</sub>Fe<sub>2</sub> formate with x = 0.3, 0.5, 0.6, 0.7 and 0.9 were decomposed in air at 400°C during three hours and heated at different temperatures for 24 hours. To maintain a single-phase spinel from 1000°C, it was necessary to quench the material. Figure 6.3.1 illustrates the XRD patterns of the samples with x = 0.3, 0.5 and 0.9. At 400°C, 3 hours, the decomposition product contains a partially crystalline spinel phase. Except the compositions with x = 0.3 and x = 0.5, a very negligible amount of copper oxide (CuO) is also identified for other compositions. At 600°C, the crystallization of the spinel phase occurs. For the sample with x = 0.3, a small amount of α-Fe<sub>2</sub>O<sub>3</sub> is formed whereas for other compositions both CuO and α-Fe<sub>2</sub>O<sub>3</sub> are identified as second phases. It is important to mention that the presence of nickel oxide is not very well identified because the most intensive peaks of NiO are covered by those of the spinel phase. Upon heating at 800°C, the amount of spinel phase increases due to the reaction occurring between the simple oxides (CuO/NiO and α-Fe<sub>2</sub>O<sub>3</sub>). For x = 0.3, 0.5, 0.6 and 0.7, the XRD patterns match with that of NiFe<sub>2</sub>O<sub>4</sub> (cubic phase) whereas reflections arising due to the tetragonal CuFe<sub>2</sub>O<sub>4</sub> are identified on the pattern of the sample with x = 0.9. For all the investigated samples, the formation of the cubic spinel phase at 1000°C is observed for any cooling process (slow or rapid). For the compositions with x = 0.7 and x = 0.9 (Fig.3.6.1(c)), some negligible traces of CuO are found in addition to the spinel phase. The lattice parameter “a” of Cu<sub>x</sub>Ni<sub>1-x</sub>Fe<sub>2</sub>O<sub>4</sub> ferrites (x = 0, 0.3, 0.5, 0.6, 0.7, 0.9) are shown in Table 6.3.1. These data reveal a slight increase of the parameter “a” with the value of x (copper content). This is due to the lower ionic radius of Ni<sup>2+</sup> (69 pm) compared to that of Cu<sup>2+</sup> ions (87 pm).

Table 6.3.1: Lattice parameter “a” of quenched nickel-copper mixed ferrites prepared at 1000°C from the freeze-dried Cu(II)-Ni(II)-Fe(III) formate precursors.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Lattice parameter “a” (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>834.13 (2)</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.3&lt;/sub&gt;Ni&lt;sub&gt;0.7&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>835.11 (1)</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.5&lt;/sub&gt;Ni&lt;sub&gt;0.5&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>835.70 (1)</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.6&lt;/sub&gt;Ni&lt;sub&gt;0.4&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>836.06 (1)</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.7&lt;/sub&gt;Ni&lt;sub&gt;0.3&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>837.10 (2)</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;0.9&lt;/sub&gt;Ni&lt;sub&gt;0.1&lt;/sub&gt;Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>838.00 (1)</td>
</tr>
</tbody>
</table>
Figure 6.3.1: XRD patterns of the decomposition products of Cu$_x$Ni$_{1-x}$Fe$_2$ formate annealed at 400°C and heated at different temperatures. (a) $x = 0.3$; (b) $x = 0.5$; (c) $x = 0.9$.

Atm.: air; heating rate 5-10K/min.
The synthesis of other single spinel phases in the phase triangle $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_{2}\text{O}_{4}$-$\text{Cu}_{0.9}\text{Fe}_{2.1}\text{O}_{4}$-$\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_{4}$ was investigated (Fig. 6.3.2).

In order to proceed, appropriate freeze-dried Cu(II)-Ni(II)-Fe(III) formate precursors were the starting powders. After the decomposition at 400°C (3 hours) followed by the annealing at 1000°C (24 hours) in air, the pure spinel phase is obtained for the composition $\text{Cu}_{0.81}\text{Ni}_{0.1}\text{Fe}_{2.09}\text{O}_{4}$. For the solid solutions existing between the compositions $\text{Cu}_{0.5}\text{Fe}_{2.5}\text{O}_{4}$ and $\text{Cu}_{0.5}\text{Ni}_{0.5}\text{Fe}_{2}\text{O}_{4}$, the synthesis temperatures higher than 1000°C are required. The Table 6.3.2 shows the synthesis conditions enabling the formation of the pure spinel phases $\text{Cu}_{0.8}\text{Ni}_{0.1}\text{Fe}_{2.2}\text{O}_{4}$ and $\text{Cu}_{0.5}\text{Ni}_{0.17}\text{Fe}_{2.33}\text{O}_{4}$. From a general point of view, it is found that the substitution of nickel in copper ferrite slightly affects the conditions of synthesis required for the formation of a pure spinel phase and also leads to the slight decrease of the lattice parameter “$a$” of the ferrite sample (Table 6.3.2).
The other spinel phases which are also mentioned on the Figure 6.3.2 were obtained from the appropriate formate precursors (Sections 3.4.3 and 4.3.3).

Table 6.3.2: Analysis of the XRD powder patterns of the nickel-copper mixed ferrites prepared from the decomposition of the freeze-dried formate precursors under special $p(O_2)/T$ conditions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Synt. Temp (°C), atm</th>
<th>Phases composition</th>
<th>a (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}_{0.9}\text{Fe}_2\text{O}_4$</td>
<td>1000, air</td>
<td>tetragonal</td>
<td>584.68 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(c = 858.90 (1))</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.81}\text{Ni}</em>{0.1}\text{Fe}_{2.09}\text{O}_4$</td>
<td>1000, air</td>
<td>cubic spinel</td>
<td>838.37 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.5}\text{Ni}</em>{0.3}\text{Fe}_{2.2}\text{O}_4$</td>
<td>1000, air</td>
<td>cubic spinel</td>
<td>838.32 (2)</td>
</tr>
<tr>
<td></td>
<td>1100, air</td>
<td>cubic spinel + $\alpha$-$\text{Fe}_2\text{O}_3$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1100, argon + 1% $O_2$</td>
<td>cubic spinel</td>
<td>838.31 (1)</td>
</tr>
<tr>
<td>$\text{Cu}_{0.8}\text{Fe}_2\text{O}_4$</td>
<td>1000, air</td>
<td>cubic spinel</td>
<td>839.47 (1)</td>
</tr>
<tr>
<td></td>
<td>1000, argon + 1% $O_2$</td>
<td>cubic spinel</td>
<td>840.00 (1)</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.5}\text{Ni}</em>{0.17}\text{Fe}_{2.33}\text{O}_4$</td>
<td>1000, air</td>
<td>cubic spinel + $\alpha$-$\text{Fe}_2\text{O}_3$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1100, argon + 1% $O_2$</td>
<td>cubic spinel</td>
<td>839.31 (2)</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.67}\text{Fe}</em>{2.33}\text{O}_4$</td>
<td>1000, air</td>
<td>cubic spinel + $\alpha$-$\text{Fe}_2\text{O}_3$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1100, argon + 1% $O_2$</td>
<td>cubic spinel</td>
<td>840.2 (2)</td>
</tr>
<tr>
<td>$\text{Cu}_{0.5}\text{Fe}_2\text{O}_4$</td>
<td>1110, argon</td>
<td>cubic spinel</td>
<td>841.10 (1)</td>
</tr>
</tbody>
</table>

(Synt. Temp (°C), atm: synthesis temperature, synthesis atmosphere)
6.4. Magnetic properties measurements

Since the publication of the first report on the preparation of copper-nickel ferrites, many physical properties of these materials have been studied. Among the magnetic properties, the saturation magnetic moment ($n_B$) has been the most extensively investigated. It has been commonly found that the value of $n_B$ increases with the nickel concentration. On the other hand, the Curie temperature ($T_C$) increases also with the substitution of nickel in copper ferrite. In the present section, the influence of the synthesis method on the magnetic properties of $\text{Cu}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ ferrites is investigated. In order to proceed, the present results are compared with the reported data.

**Experimental**

The magnetization measurements were carried out using a vibrating sample magnetometer (Compagny Oxford) with nickel as a calibration substance (Section 9.6). The samples used for this investigation are nickel-copper mixed ferrites prepared at 1000°C during 24 hours from freeze-dried $\text{Cu(II)}$-$\text{Ni(II)}$-$\text{Fe(III)}$ formate precursors (Section 6.3). The determination of the value of the saturation magnetic moments ($n_B$) was performed as described in Section 3.9.1. The results obtained from this investigation are compared to those of Kiran and coworkers [143]. The nickel copper ferrite powders were prepared from the respective oxides (ceramic method) [143]. After heating at 1050°C during 24 hours, the samples were also quenched to room temperature.

**Results and discussions**

The field dependence of the magnetization, measured at 5K and 300K, becomes constant with the field of 2kOe. The saturation magnetization ($\sigma_S$) at 5K, 300K and the magnetization number $n_B$ are summarized in Table 6.4.1. This table includes the results of Kiran and coworkers [143]. From our results, the magnetization number $n_B$ increases with the nickel concentration. However, from the data of [143], $n_B$ is almost invariable with the change of the composition. The difference observed may be due to the difference in the method of synthesis and to the different conditions of firing. Consequently for the same composition, the generated cations distribution should be different. Nickel ions have a strong preference for octahedral sites. As nickel-copper ferrite is an inverted spinel, $\text{Cu}^{2+}$ and $\text{Fe}^{3+}$ ions occupy both A- and B- sites. The cation distribution of nickel ferrite (mother compound) obtained from the magnetization data is close to $(\text{Fe})_A[\text{NiFe}]_B\text{O}_4$. From that, the substitution of some $\text{Ni}^{2+}$ by
Cu$^{2+}$ in the B-sites is accompanied by that of some Fe$^{3+}$ by the corresponding number of Cu$^{2+}$ ions. For the compositions Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ with 0 < x < 1, the proposed cations distribution is the following: (Cu$_y$Fe$_{1-y}$)$_A$[Ni$_{1-x}$Cu$_{x-y}$Fe$_{2+y}$]$_B$O$_4$. For a defined composition, the higher the value of y (amount of copper ions in the A-sites) is, the higher the magnetization number ($n_B$) becomes. In fact, the presence of the Cu$^{2+}$ ions in the A-sites displays the same amount of Fe$^{3+}$ ions towards the B-sites. Consequently the resultant magnetization number due to the interaction $Fe^{3+}_A \leftrightarrow Fe^{3+}_B$ increases. In parallel, the magnetization number of the ferrite compound increases as well. The presence of Cu$^+$ in these quenched samples cannot be ruled out. If it is present, it should go to the A-sites. However, its contribution becomes important only when the total amount of copper ions in the A-sites is important.

**Table 6.4.1:** Magnetic properties of quenched Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ ferrite samples with x = 0.3, 0.5, 0.6, 0.7 and 0.9 prepared from the decomposition of the freeze-dried formate precursors.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Magnetization at 5K</th>
<th>Magnetization at 300K</th>
<th>from [143]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_S$ (emu/g)</td>
<td>$n_B(\mu_B)$</td>
<td>$\sigma_S$ (emu/g)</td>
</tr>
<tr>
<td>Cu$<em>{0.3}$Ni$</em>{0.7}$Fe$_2$O$_4$</td>
<td>62.36</td>
<td>2.633</td>
<td>43.97</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Ni$</em>{0.5}$Fe$_2$O$_4$</td>
<td>60.89</td>
<td>2.582</td>
<td>43.45</td>
</tr>
<tr>
<td>Cu$<em>{0.6}$Ni$</em>{0.4}$Fe$_2$O$_4$</td>
<td>-</td>
<td>-</td>
<td>42.84</td>
</tr>
<tr>
<td>Cu$<em>{0.7}$Ni$</em>{0.3}$Fe$_2$O$_4$</td>
<td>58.07</td>
<td>2.472</td>
<td>46.48</td>
</tr>
<tr>
<td>Cu$<em>{0.9}$Ni$</em>{0.1}$Fe$_2$O$_4$</td>
<td>-</td>
<td>-</td>
<td>47.24</td>
</tr>
</tbody>
</table>

It turns out that the copper content in A-sites is more important inside the sample of the present work than observed in [143]. Despite the mentioned difference, the values of $\sigma_S$ at 300K obtained for this work are approximately of the same order of magnitude with the data of [143]. Some traces of CuO inside the samples Cu$_{0.7}$Ni$_{0.3}$Fe$_2$O$_4$ and Cu$_{0.9}$Ni$_{0.1}$Fe$_2$O$_4$ may have affected their values of $\sigma_S$. 
6.5. Partial conclusion

The thermal decomposition of freeze-dried formate precursors is a suitable method for preparing single phase ferrites Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ as well as other ferrites occurring in the phase triangle Cu$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$-Cu$_{0.9}$Fe$_{2.1}$O$_4$-Cu$_{0.5}$Fe$_{2.5}$O$_4$. In comparison with the conventional solid state reaction, the temperature necessary for the production of single phase compounds is much lower. Copper ferrite CuFe$_2$O$_4$ shows a tetragonal structure when slowly cooled from high temperature to room temperature. It has been found that by incorporating small amounts of nickel, the tetragonality disappears and all the investigated samples Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ with $x = 0.3, 0.5, 0.6, 0.7$ and $0.9$, prepared at 1000°C, exhibit a cubic structure. This is in agreement with the ceramic method employed previously [19]. Presumably, replacing Cu$^{2+}$ ions with Ni$^{2+}$ leads to the decrease of the distorting ions Cu$^{2+}$ on octahedral (B) sites. This reduces the tetragonal distortion of copper ferrite and brings it to a cubic structure. The lattice parameter “a” decreases from Cu-ferrite to Ni-ferrite is attributed to the ionic volume differences of Cu$^{2+}$ and Ni$^{2+}$. The relatively low synthesis temperature of 1000°C allows however the synthesis of oxide phases with a saturation magnetization close to that of oxide phases obtained at 1050°C using the ceramic method.
7. **General conclusion**

Freeze-drying of metal carboxylate solutions is a promising method for the preparation of precursors which by thermal treatment can be converted into single or mixed oxide powders. The decomposition of freeze-dried precursors into pure oxide phases requires the control of parameters such as the heating rate, the temperature and the oxygen partial pressure. In some cases, the synthesis conditions may be close to those required using the conventional ceramic method. Therefore, the use of reactive precursors is not the unique condition for a low temperature synthesis of complex oxides.

In the present work, copper-nickel ferrites and some solid-solutions copper-nickel oxides have been synthesized by the thermal decomposition of oxalate and/or formate precursors (unconventional method). Additionally, the conventional ceramic method has been used in order to get insights on the phase formation as a function of the preparation conditions. The electrical conductivity and the magnetic properties of selected compounds have been determined.

Using the freeze-drying method, ammonium copper(II)-iron(III) oxalate is crystalline, whereas copper(II)-iron(III) formate is amorphous with a small amount of crystalline copper(II) formate. The interaction between the components of these precursors is responsible of the slight decrease of their decomposition temperature, compared to that of the simple metal components. During the thermal decomposition process, these homogeneous precursors loose their reactivity because of the intermediate reduction of metal ions. Thus the synthesis of copper ferrites is performed only above 700°C by a conventional ceramic method. In the presence of air, the synthesis of a pure CuFe₂O₄ does not take place. However, 70 hours of heating at 800°C in the presence of the oxygen leads to the formation of a pure tetragonal copper ferrite phase with the ratio $c/a$ ratio equals 1.06. At 1000°C in the presence of air, the iron rich spinel phases Cu$_{0.9}$Fe$_{2.1}$O$_4$ and Cu$_{0.8}$Fe$_{2.2}$O$_4$ have been successfully prepared. For the compositions Cu$_{1-x}$Fe$_{2+x}$O$_4$ with $0.2 < x \leq 0.5$, the temperatures above 1000°C must be applied. Given that, at higher temperatures the nature of starting materials does not have a great influence on the course of the formation of the ferrite phase, the possibility of using mixtures of fine grained metals as starting materials has been explored. Under the same working conditions, the oxidation rate of Cu-Fe mixtures resulting from the reduction in H$_2$ of Cu-Fe oxalate precursors has been found to be significantly higher than that of the mixtures of
pure copper and iron. However, in both cases, the ferritization process took place via the intermediate formation of CuO and α-Fe2O3 occurring at 600°C. The oxidation of copper-iron mixtures has been found to be a suitable method for the synthesis of pure copper ferrite phases Cu1-xFe2+xO4 (0 < x ≤ 0.5). The synthesis conditions required have been defined in the temperature range 1000-1200°C and the p(O2) ranging from 10⁻³ to 0.209 atm.

The freeze-dried nickel(II)-iron(III) formate is amorphous. A well homogeneous nickel(II)-iron(III) formate precursor has been prepared upon a rigorous control of nickel ion concentration in the precursor solution. Its decomposition does not reflect only some aspects of the single formates, but also an interaction between the components which lowers the decomposition temperature. Crystalline nickel ferrite powders have been obtained at 600°C/800°C. This temperature is quite lower than 1100°C employed for the ceramic method.

The high crystalline nickel ferrite obtained at 1000°C has a saturation magnetization $\sigma_s$ of 46.9 emu/g. This value is close to 47-56 emu/g, reported for the sample obtained at 1100°C using the ceramic method. The taenite (γNi,Fe) phase has been synthesized through the reduction under hydrogen atmosphere of the freeze-dried Ni-Fe formate as well as that of their products of decomposition obtained in air. It has been established that the chemical environment of nickel and iron ions in the starting powder has a great influence on the speed of the reduction process. In fact, when nickel and iron constitute only one phase with a spinel structure “NiFe2O4”, the reduction is performed much more quickly than when they have a -C-O environment or when they are present in more than one phase. When the starting sample is a single spinel phase “NiFe2O4”, a short reduction time of 3 hours at 600°C is required for the formation of the taenite phase. In particular, we have shown that in the presence of air, the regeneration of nickel ferrite from the alloy phase (γNi,Fe) is accomplished at 800°C. This temperature is also 300°C below the temperature (T ≤ 1100°C) employed when the mixtures NiO:α-Fe2O3 or Ni:2Fe are the starting powders.

From a general point of view, the thermal decomposition of freeze-dried precursors Cu-Ni-Fe formate has been found to be a suitable method for preparing single phases of ferrites within the quaternary system Cu-Ni-Fe-O. In comparison with the conventional solid state reaction, the temperature necessary for the production of single phase compounds is much lower. Concerning the solid solution Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ (0 ≤ x ≤ 1), a single phase spinel is formed at 1000°C for x < 0.7; for 0.7 ≤ x ≤ 1 CuO is identified as second phase. In this latter range the formation of a pure phase required an increase of the iron content in the mixture. For example the composition Cu$_{0.81}$Ni$_{0.1}$Fe$_{2.09}$O$_4$ is a single phase at 1000°C/air. The other single spinel
phases in the phase triangle Cu$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$-Cu$_{0.9}$Fe$_{2.1}$O$_4$-Cu$_{0.5}$Fe$_{2.5}$O$_4$ have been synthesized under special synthesis p(O$_2$)/T-conditions.

The study of the consequences resulting from the oxygen exchange between the ferrite powders and a reducing gaseous phase has proven that the oxygen non-stoichiometry $\lambda$ and the stability of Cu$_{1-x}$Fe$_{2+x}$O$_4\pm\lambda$ ($0 < x \leq 0.5$) samples depend on the temperature and on the p(O$_2$) of the gaseous phase. For a fixed metal ion ratio, the non-stoichiometry $\lambda$ is only about $\pm 0.02$. Significant changes in the oxygen content lead to the separation in different phases. For the copper ferrites Cu$_{1-x}$Fe$_{2+x}$O$_4$ with $x = 0.1, 0.2, 0.33, 0.4$ and $0.5$, the change in the conductivity with the temperature is irreversible. The deviation from the linearity of the conductivity $\sigma$ as a function of the temperature occurs due to the thermal history of these samples. At 5K, the saturation magnetic moment $n_B$ increases with the iron content. On the other hand, the saturation magnetization measured at 300K depends on the synthesis conditions of the sample. For a fixed metal ion ratio, $n_B$ varies as a function of the synthesis conditions. When the synthesis is performed at a defined temperature, the value of $n_B$ decreases with the decrease of the oxygen partial pressure (p(O$_2$)), applied during the synthesis of the ferrite sample. Under a reducing oxygen partial pressure (p(O$_2$) < 0.209 atm), the saturation magnetization moment decreases with the increase of the synthesis temperature (Table A.8, Section 11.6). The saturation magnetic moment $n_B$ at 5K, of some synthesized Cu$_x$Ni$_{1-x}$Fe$_2$O$_4$ compounds has been determined. It has been found that $n_B$ increases with the nickel content in the ferrite sample.

The thermal decomposition in air of appropriate freeze-dried Cu(II)-Ni(II) formate precursors allows the direct formation at about 400°C of partially crystalline solid solutions (Cu$_{0.25}$Ni$_{0.75}$)O and (Cu$_{0.35}$Ni$_{0.65}$)O. The well crystalline phases are obtained only at 1000°C. The synthesis field of (Cu$_{0.35}$Ni$_{0.65}$)O extends from 1000°C to a temperature higher than 1050°C but lower than 1100°C. On the other hand, the solid solution (Cu$_{0.25}$Ni$_{0.75}$)O is thermodynamically stable only at about 1000°C.

Using different synthesis routes we have been able to establish the conditions of formation of single spinel phases within the quaternary system Cu-Ni-Fe-O. Attempts to synthesize copper-nickel ferrites below 700°C have been successful for the nickel ferrite “NiFe$_2$O$_4$”. Additionally, the effect of the thermal history of copper ferrites on their electrical and magnetic properties has been established. It would be interesting to carry out similar investigations on other important ferrite systems containing metal ions which like copper, can be stabilized in more than one valence state.
8. Preparation methods

8.1. Preparation of mixed oxide powders

According to the desired composition of Cu$_{1-x}$Fe$_{2+x}$O$_{4\pm\delta}$ ($x = 0$, $x = 0.1$, $x = 0.5$) ferrite samples, adequate amounts of reagent-grade copper oxide (CuO) and iron oxide ($\alpha$-Fe$_2$O$_3$) were put in a container with balls and milled in a planetary ball mill (Pulverisette 5, Fritsch) for 3 hours. The ball to powder mass ratio of 4:1 was chosen. Acetone was added to the containers in order to supply high particle mobility during milling. Following this process, the acetone was evaporated and afterwards the mixtures were dried at 100°C during 2 hours. The oxide mixture containing nickel oxide (NiO) and iron oxide ($\alpha$-Fe$_2$O$_3$) in the ratio 1:1 was prepared using the same protocol.

8.2. Preparation of the freeze-dried ammonium Cu(II)-Fe(III) oxalate precursors

For the freeze-drying process, oxalate solutions were first prepared. The starting materials were commercially available products: (NH$_4$)$_3$Fe(C$_2$O$_4$)$_3$.3H$_2$O (VEB Laborchemie Apolda), CuC$_2$O$_4$ (VEB Feinchemie Eisenach) and (NH$_4$)$_2$C$_2$O$_4$.H$_2$O (MERCK, Schuchardt). For the preparation of a 0.16M ammonium iron(III) oxalate solution, the appropriate quantity of (NH$_4$)$_3$Fe(C$_2$O$_4$)$_3$.3H$_2$O and 0.3 mole (NH$_4$)$_2$C$_2$O$_4$.H$_2$O per mole ammonium oxalato-ferrate were dissolved in water. On the other hand, a 0.08M ammonium oxalato-cuprate solution was prepared by dissolving in water two moles of ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$.H$_2$O) and one mole of copper oxalate (CuC$_2$O$_4$).

For the synthesis of Cu-ferrites with the composition “Cu$_{1-x}$Fe$_{2+x}$O$_4$” ($0 \leq x \leq 0.5$), these starting solutions were mixed in the requested stoichiometric ratio of the metal ions, namely 1 : 2, 0.9 : 2.1, 0.8 : 2.2, 0.7 : 2.3, 0.5 : 2.5, and vigorously stirred. Afterwards, these resulting mixed solutions (~50 - 250ml) as well as both pure Cu$^{2+}$ and Fe$^{3+}$ solutions were then quickly frozen in liquid nitrogen and dried from -40°C to 25°C in a vacuum chamber of a freeze-drying apparatus (alpha 2-4, Christ) under a pressure of about 1Pa.
8.3. Preparation of the freeze-dried Cu(II)-Fe(III) formate precursors

The starting materials copper(II) and iron(II) formate used for the preparation were produced as described below (Section 8.3.1). From these powders solutions of Cu(II)-, Fe(III)- and Cu(II)-Fe(III)- formate with an excess of formic acid were prepared. The solutions were then quickly frozen in liquid nitrogen and dried from -40°C to 25°C in a vacuum chamber of a freeze-drying apparatus (Alpha 2-4, Christ). After 72 hours, the drying process was complete and very slight powders were obtained.

8.3.1 Preparation of Fe(II)- and Cu(II) formate powders

*Fe(II) formate powders*
Iron powder (0.3mol) was mixed with formic acid (1.1mol) in H₂O (600ml). Under slow flow of nitrogen gas, the mixture was stirred and heated at reflux. After 2-3 hours, the reaction of iron metal was complete. The resulting light-green hot solution was filtered to remove any insoluble material. Using normal distillation, the solution was then concentrated under nitrogen atmosphere, up to the beginning of the crystallization of Fe(II) formate. After cooling, the obtained light-green solid “Fe(II) formate” was filtered off, washed three times with ethanol and dried during 2-3 hours under oil pump vacuum. Note that all operations were performed under nitrogen atmosphere in order to avoid the oxidation of Fe²⁺ to Fe³⁺ ions.

*Cu(II) formate powders*
Basic copper carbonate powders (22.11g) were introduced in water (100ml) and the resulting mixture was stirred gently. Under the heating at ~ 50°C, 20ml of concentrated formic acid in 20ml of water was slowly added until neutralization was complete. Thereafter, the resulting blue solution was cooled in a bath of ice. The endpoint was reached when no more blue crystals were formed on the walls of the beaker. Using a vacuum filtration, the blue crystals were separated and briefly washed with ethanol. At the end, the powders were dried under vacuum during 12hours.

8.3.2 Preparation of Cu(II)-Fe(III) formate solutions

Before the preparation of the different Cu(II)-Fe(III) formate solutions, the metal contents of the synthesized formate powders were determined by complexometric titration as described in the Section 9. The percentage of iron in the powder of Fe(II) formate was 31.52% and the concentration of copper in the solution of Cu(II) formate was 0.1507M/0.19M.
**Preparation methods**

*Preparation of single metal formate solutions*

**Solution of iron(III) formate:** The appropriate quantity of Fe(II) formate was dissolved in water and ~ 150ml of formic acid per mole iron was added. The resulting solution was stirred while a twofold excess of H₂O₂ was slowly added, for the oxidation of Fe²⁺ to Fe³⁺ ions. At the end a brown solution was formed.

The **solution of copper(II) formate** (0.15M-0.19M) was prepared by dissolving the appropriate quantity of Cu(II) formate in water.

* Diluted solution (C₀) of CuFe₂ formate

Around 1000ml of the CuFe₂ formate solution with the copper formate concentration of ~ 0.0904M and iron formate concentration of ~ 0.1808M was prepared as follows: to 600ml of Cu(II) formate solution (0.1507M), 32.04g of Fe(II) formate (0.1808mol of iron) and 27ml of formic acid were added. After that, the mixture was diluted to 900ml with deionised water. While stirring, 58 ml of H₂O₂ in 20ml of H₂O was slowly added. The addition of H₂O₂ caused a great deal of effervescence as some Fe²⁺ are oxidized to Fe³⁺ ions. At the end of the oxidation of Fe²⁺ ions a dusky-brown Cu-Fe formate solution was formed.

* Non-diluted solution (C₀’) of CuFe₂ formate

A small volume of around 130ml of CuFe₂ formate solution with the copper formate concentration of ~ 0.07M and iron formate concentration of ~ 0.14M was prepared from 48 ml of a copper formate solution 0.19M and 3.232g of Fe(II) formate (0.01824 mol of iron). The required volumes of HCOOH and of H₂O₂ were determined from those used for the preparation of the preceding solution (C₀).

8.4. **Preparation of mixed metallic powders**

Mixed metallic powders were prepared from copper and iron metal. The method used was identical to the one employed for the preparation of mixed oxide powders (Section 8.1).

8.5. **Preparation of the freeze-dried Ni(II)-Fe(III) formate precursors**

Raw materials nickel(II) formate and iron(II) formate used for the preparation of the different precursors were produced as described below (Section 8.5.1) and in Section 8.3.1, respectively. From these powders, solutions of Ni(II)-, Fe(III)- and Ni(II)-Fe(III) formate with an excess of formic acid were prepared, quickly frozen in liquid nitrogen and dried from
Preparation methods

-40°C to 25°C, in a vacuum chamber of a freeze-drying apparatus (Alpha 2-4, Christ). After 72 hours, the drying process was complete and very slight powders were obtained.

8.5.1. Preparation of Ni(II) formate powders

Basic nickel carbonate powder (15g) was introduced in water (~ 600ml). The resulting mixture was heated between 200 and 250°C under stirring while a slight excess of formic acid (11ml) was slowly added. After the complete dissolution of the basic nickel carbonate, the resulting green solution was then concentrated up to the beginning of the crystallization of Ni(II) formate. After cooling, the obtained light-green solid “Ni(II) formate” were filtered off, washed with ethanol and dried during 12 hours under vacuum.

8.5.2. Preparation of Ni(II)-Fe(III) formate solutions

For the preparation of the nickel(II) formate solution, 18.26g of nickel formate (0.0987 mol of Ni²⁺) was introduced in water (~ 600ml). The resulting mixture was heated (200°C-250°C) and stirred gently while 11 ml HCOOH in 10ml of H₂O (~ 45% excess) was slowly added. After 1-2 hours a clear solution was obtained.

The preparation of iron(III) formate solution was performed as described in Section 8.3.2. The method used for the preparation of the mixed Ni(II)-Fe(III) formate solutions was identical to the one employed for the preparation of mixed Cu(II)-Fe(III) formate solutions (Section 8.3.2.). Before the preparation of these solutions, the metal contents of the synthesized formate powders were determined by complexometric titration as described in the Section 9. The percentage of iron in the powder of Fe(II) formate was 31.28% and the concentration of nickel in the solution of Ni(II) formate was 0.18M.

The concentrations of nickel and iron ions inside the mixed Ni(II)-Fe(III) formate solutions were varied from 0.02 to 0.16M and from 0.04 to 0.32mol, respectively.

8.6. Preparation of the freeze-dried Ni(II)-Cu(II) formate precursors

The initial compounds nickel(II) formate (Ni(HCOO)₂ x 2H₂O) and copper(II) formate (Cu(HCOO)₂ x 2H₂O) were obtained as described in Sections 8.3.1. and 8.5.1. From these powders acid solutions of Ni(II) and Cu(II) formate with the concentration of 0.1M and 0.08M were prepared, respectively. According to the composition of the oxide samples (CuₓNi₁₋ₓ)O with x = 0.25, 0.35, 0.5, 0.75 and 0.9, adequate amounts of the formate solutions were mixed. The mixtures were frozen in liquid nitrogen and dried from -40°C to 25°C in the
vacuum chamber of a freeze-drying apparatus (Alpha 2-4, Christ). After 72 hours, the drying process was complete and very slight powders were obtained.

8.7. Preparation of the freeze-dried Cu(II)-Ni(II)-Fe(III) formate precursors

The initial compounds iron(II) formate (Fe(HCOO)₂ x 2H₂O), nickel(II) formate (Ni(HCOO)₂ x 2H₂O) and copper(II) formate (Cu(HCOO)₂·2H₂O) were obtained as described in Sections 8.3.1 and 8.5.1. From these powders, solutions of Ni(II) formate (0.19M) and Cu(II) formate (0.29M) with an excess of formic acid were prepared, respectively.

According to the composition of the ferrite samples (CuₓNi₁₋ₓFe₂O₄ (0 < x < 1)) adequate volume of Cu(II) and Ni(II) formate solutions were mixed and the required mass of Fe(II) formate was added. Following preparation procedures are identical to those employed for the preparation of mixed Cu(II)-Fe(III) formate solutions (Section 8.3.2). The resulting mixed solutions with the volume ranging from 200 to 250ml were then frozen in liquid nitrogen and dried from -40°C to 25°C in the vacuum chamber of a freeze-drying apparatus (Alpha 2-4, Christ). After 72 hours, the drying process was complete and very slight powders were obtained.
9. Analysis methods

9.1. Quantitative analysis of precursors

9.1.1. Elemental analysis
The quantitative elemental analysis for the determination of the carbon (C), nitrogen (N) and hydrogen (H) contents of the carboxylate precursors was done with the CHNS-O elemental analyzer, 3000, HEKA tech GmbH (Wegberg, Germany).

9.1.2. Complexometric titration of metal ions with EDTA
The metal contents of the oxalate and the formate precursors were determined by complexometric titration after decomposition of oxalates and formates with sodium peroxodisulfate (Na$_2$S$_2$O$_8$) and/or concentrated nitric acid (HNO$_3$). From an iron oxalate solution with the concentration of 0.16M, 7ml were introduced into a beaker and an excess (0.4 g) of sodium peroxodisulfate (Na$_2$S$_2$O$_8$) was added. The resulting solution was heated using a hot plate until all the liquid was evaporated. Thereafter, few milliliters of water were added to the residue. The resulting solution was heated again, evaporated down to 2-3 ml and cooled down to RT. The same process was repeated several times until a clear solution was obtained. This last solution was then transferred into a 100ml volumetric flask and diluted with deionised water up to the calibration mark.

For the preparation of other solutions destined to the titration, the same procedure was employed. For a copper oxalate solution, the destruction of oxalate ions was also effective by using the nitric acid (HNO$_3$) instead of sodium peroxodisulfate (Na$_2$S$_2$O$_8$).

For the complexometric titration, the concentration of the sample solution was around 0.01M i.e. ~ 0.001mole of metal ions in 100ml solution.

9.1.2.a. Back titration of Fe$^{3+}$
10 ml of an iron solution (~ 0.01M) are introduced into a conical flask. From a burette, a slight excess (20ml) of 0.01M EDTA solution is added; the pH (5-6) is adjusted by addition of Urotropin. Thereafter, the indicator Xylenolorange is added. The resulting solution is titrated with the standard 0.01M Pb(NO$_3$)$_2$ solution until the color change from yellow to orange-red.
9.1.2.b. Direct titration of Cu\(^{2+}\)

10 ml of a copper solution (~ 0.01M) are introduced into a conical flask and diluted to ~100 ml with deionised water. Thereafter, the indicator Murexide is added. Few millilitres of a 1M NH\(_3\) solution are used for the adjustment of the pH until about 7. The resulting solution, with yellow color, is titrated with a standard (0.01M) EDTA solution. When the end point is approached (greenish-yellow color), the solution is render strongly alkaline by the addition of some drops of a 1M NH\(_3\) solution. Thereafter, the titration continues until the endpoint which is marked by a change of the solution to a violet color.

9.1.2.c. Direct titration of Ni\(^{2+}\)

The process used is identical to the one employed for the titration of Cu\(^{2+}\) ions i.e. same indicator, at the end of the titration the coloration of the solution also changed from yellow to violet...). Note however that, the pH of the solution must be located between 7 and 8. Near the end point, the EDTA solution must be added dropwise because nickel complexes react rather slowly with EDTA.

9.2. Oxygen content measurements

9.2.1. Initial oxygen content (thermogravimetric measurements)

The oxygen content of synthesized compounds was measured by thermogravimetry during reduction in a stream of hydrogen. The powders were weighed (about 1.1-1.5g) into a quartz crucible and then heated during 6 hours at 800°C. The heating rate was 5K/min. After the cooling of the sample to RT under H\(_2\) gas flow, it was reweighed. This procedure was repeated until the reduced weight remained constant. Four heating (around 24hours) were necessary to reduce copper ferrite components to metals. The phase composition of the product obtained from this treatment was verified using the XRD method. Copper and iron metals were commonly the end products. After three trials, we found that this method indicates the initial oxygen stoichiometry with an accuracy of ± 0.01.

9.2.2. Change of oxygen content (potentiometric measurements)

9.2.2.a. Method of operation

The concept of combined coulometric-potentiometric arrangement for the investigation of solid-gas interactions in the carrier gas mode was described earlier in [138]. A carrier gas is so prepared that it has a definite gas pressure related to the chemical reaction. This gas with a
regular stream interacts with the solid in the furnace and is continually analyzed before and after this process. This analysis is performed with the help of a dosing and a measuring unit, which supplies the gas stream with defined amounts of oxygen and, at the same time measures the precise oxygen concentration (Fig. 9.2.1).

Figure 9.2.1: OXYLYT-Solid Electrolyte Cell with oxygen analysis and dosing units
(Senso Tech GmbH)

The OXYLYT analysis system contains two such cells. The oxygen concentration \( p(O_2) \) is measured by the potentiometric solid-electrolyte cell:

\[
\text{Pt, } p(O_2) \mid \text{Solid-electrolyte} \mid p(O_2)_{\text{ref}}, \text{Pt}
\]

The output voltage of the measuring unit follows the NERNST equation:

\[
U = \frac{RT}{4F} \ln \frac{p(O_2)}{p(O_2)_{\text{ref}}}
\]

(1)

The reference pressure is that of air \( (p(O_2)_{\text{ref}} = 0.209 \text{ atm}) \). The temperature of the sonde \( T = 700^\circ\text{C} \), \( F \) (Faraday-constant) = 96485 C. mol\(^{-1}\).

9.2.2.b. Determination of the oxygen non-stoichiometry

For the computation of the amount of oxygen exchanged between sample and gas, the oxygen pressures indicated from the fixed electrolytes cells 1 and 2 (Fig. 9.2.1) were used. This oxygen pressure change was referred to the pressure indicated by cell 2 when the voltage of the cell 2 becomes constant \( (U_0, \text{voltage at the equilibrium state}) \). With the help of the program “ORIGIN” [P2] and using the NERNST-equation (1), the exchanged oxygen quantity was computed as follows:
Analysis methods

\[ U = \frac{RT}{4F} \ln \frac{p(O_2)}{p(O_2)_{air}} \]  \(1\)  \(\Rightarrow\)  \[ \ln \left( \frac{p(O_2)}{p(O_2)_{air}} \right) = \frac{U}{0.0209} \]  \(U\) in volt

\[ \Rightarrow \frac{p(O_2)}{p(O_2)_{air}} = \exp \left( \frac{U}{0.0209} \right) = \exp(47.7086 \times U) \]  \(2\)

For the measurements, \(U\) was expressed in millivolt (mV) and counted negatively. The relation \(2\) becomes:

\[ p(O_2) = (p(O_2)_{air} \times \exp(-0.0477086 \times U)) \]  \(3\)

If \(p(O_2)_0\) is the oxygen partial pressure at the equilibrium state corresponding to the voltage \(U_0\) (voltage at the equilibrium state) and \(p(O_2)_2\) is the oxygen partial pressure of the downstream, from the relation \(3\) we will have the following equations:

\[ p(O_2)_0 = (\exp(-0.0477086 \times U_0) \times 0.209) \]  \(4\)

\[ p(O_2)_2 = (\exp(-0.0477086 \times U_2) \times 0.209) \]  \(5\)

The measurement occurred each 20 seconds and the gas flow was 5l/h. Taking into account this fact as well as of the relations \(4\) and \(5\), the exchanged oxygen content \((m_0)\) and the number of mole of oxygen corresponding to the mass \(m_0\) \((n_0)\) were calculated as follows:

\[ 5 \times 20 / 3600 = 0.02771 / 20s \]

\[ 0.0277 \times 32 \times 1000 / 22.4 = 39.68253 \text{ mg /20s} \]

\[ m_0 = (p(O_2)_0 - p(O_2)_2) \times 39.68253 \text{ mg} \]

\[ n_0 = m_0 \times M / 16 \times (E - m_0) \]

where \(M\) is the molar mass and \(E\) is the mass of the sample used for the measurement.

9.3. Thermal analysis and mass spectrometry

Thermal analysis (TG, DTA and DTG) were carried out by means of Netzsch Thermal Analyser STA 409, coupled with a capillary coupled mass spectrometer QMG 420 (Balzers). The decomposition of freeze-dried oxalates and formates was examined in argon, air, hydrogen or argon +2 %H2 at a heating rate of 5-10 K/min up to a maximum temperature of 500-800°C. Constant sample masses between 30mg and 50mg were used to minimize any possible influences of sample mass on instrument responses (peak shape and temperature maxima). Highly sintered \(\alpha\)-Al2O3 powder was employed as reference material.
9.4. **Structural studies**

The structural studies on the samples were carried out using the X-ray powder diffraction method. The XRD measurements were recorded at RT using a D5000 diffractometer (Siemens) with CuK$_\alpha$ radiation ($\lambda=1.5406$ Å). The data were collected in the 2$\theta$ range of 10°-80° with the step of 0.02° (the time was counted 1 second per step) or in the 2$\theta$ range of 20°-80° with the step of 0.01° (the time was counted 6 second per step).

The phase identification was performed by comparing the measured diffraction pattern with those listed in the JCPDS database of [P1]. The lattice parameters of compounds were estimated from the X-ray diffraction peak positions with [P3].

9.5. **Electrical conductivity measurements**

The electrical conductivity of ceramic samples was measured in gas atmospheres with defined oxygen partial pressures by a DC four-point method. The powders were pressed into bars together with 4 Pt wires (0.1 mm by diameter and 0.12mg). The figure 2 below shows a four point sample. During pressing, the shapes were equipped with four platinum wires (0.1 mm diameter). The inner wires were used to measure the voltage. The current was applied using the outer wires. The temperature was measured near to the sample using the thermocouple.

![Figure 9.5.2: Four point measurement.](image)

9.6. **Magnetic properties measurements**

Weighed quantities (~ 25 mg) of oxide powders were introduced into a cylindrical shape of 4 mm in diameter and 4 mm in height. The measurements were carried out at 5K and 300K by using a vibrating sample magnetometer (Compagny Oxford) with nickel as a calibration substance.
10. References


References


11. Appendix

11.1. Simulation of the X-ray diffraction patterns of copper ferrite

The Tables A1 and A2 show the structure parameters employed for the simulation of the XRD patterns which are shown on Figure A1 and A2, respectively. The computer program which was used is the Powder Cell 2.3 program [P3].

Table A1: Structure parameters for the cubic copper ferrite (ICSD code N° 37429)

<table>
<thead>
<tr>
<th>Atom</th>
<th>oxidation</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 1</td>
<td>+3</td>
<td>8 a</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe 2</td>
<td>+3</td>
<td>16 d</td>
<td>0.625</td>
<td>0.625</td>
<td>0.625</td>
</tr>
<tr>
<td>Cu</td>
<td>+2</td>
<td>16 d</td>
<td>0.625</td>
<td>0.625</td>
<td>0.625</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
<td>32 e</td>
<td>0.380</td>
<td>0.380</td>
<td>0.380</td>
</tr>
</tbody>
</table>

Table A2: Structure parameter for the tetragonal copper ferrite (ICSD code N° 16666)

<table>
<thead>
<tr>
<th>Atom</th>
<th>oxidation</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe 1</td>
<td>+3</td>
<td>4 a</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe 2</td>
<td>+3</td>
<td>8 d</td>
<td>0.5</td>
<td>0.25</td>
<td>0.125</td>
</tr>
<tr>
<td>Cu</td>
<td>+2</td>
<td>8 d</td>
<td>0.5</td>
<td>0.25</td>
<td>0.125</td>
</tr>
<tr>
<td>O</td>
<td>-2</td>
<td>16 h</td>
<td>0.000</td>
<td>0.266</td>
<td>0.375</td>
</tr>
</tbody>
</table>

Figure A1: XRD simulation of the cubic CuFe₂O₄ (a = 8.37 Å). Space group: Fd₃m
Figure A2: XRD simulation of the tetragonal distorted CuFe₂O₄ (a = 5.81 Å, c = 8.71 Å).

Space group: I 4₁ / amd

11.2. Gaseous decomposition products of some precursors

Table A3: Main primary gaseous decomposition products of the freeze-dried precursor (NH₄)₃Fe(C₂O₄)₃ · 0.42(NH₄)₂C₂O₄ x 1.5H₂O

<table>
<thead>
<tr>
<th>Process/ (equation)</th>
<th>Temperature range (°C), roughly</th>
<th>Main primary gaseous decomposition products</th>
<th>Δm (calc.) / %</th>
<th>Δm/step</th>
<th>Δm/total</th>
<th>Δm (exp.) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1</td>
<td>30 - 100</td>
<td>1.5H₂O</td>
<td>-6.0</td>
<td>-6.0</td>
<td>-6.0</td>
<td>-6.0</td>
</tr>
<tr>
<td>2 2a 2b 2c</td>
<td>180 - 300</td>
<td>1.92(2NH₃, H₂O, CO₂, CO)</td>
<td>-52.6</td>
<td>-58.6</td>
<td>-68.3</td>
<td>-67.7</td>
</tr>
<tr>
<td>3 3a 3b 3c</td>
<td>300 - 410</td>
<td>0.5CO₂, 1.5CO</td>
<td>-14.1</td>
<td>-82.4</td>
<td>-83.6</td>
<td>-83.6</td>
</tr>
<tr>
<td></td>
<td>410 - 800 (oxidation)</td>
<td></td>
<td>-410 - 800 (oxidation)</td>
<td>-</td>
<td>-82.8</td>
<td>-82.8</td>
</tr>
</tbody>
</table>

Table A4: Main primary gaseous decomposition products of the commercial sample (NH₄)₃Fe(C₂O₄)₃ x 2.5H₂O

<table>
<thead>
<tr>
<th>Process/ (equation)</th>
<th>Temperature range (°C), roughly</th>
<th>Main primary gaseous decomposition products</th>
<th>Δm (calc.) / %</th>
<th>Δm/step</th>
<th>Δm/total</th>
<th>Δm (exp.) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1</td>
<td>30 - 100</td>
<td>2.5H₂O</td>
<td>-10.7</td>
<td>-10.7</td>
<td>-10.4</td>
<td>-10.4</td>
</tr>
<tr>
<td>2 2a 2b 2c</td>
<td>180 - 300</td>
<td>1.5(2NH₃, H₂O, CO₂, CO)</td>
<td>-44.4</td>
<td>-55.1</td>
<td>-65.6</td>
<td>-65.0</td>
</tr>
<tr>
<td></td>
<td>300 - 420</td>
<td>0.5CO₂, 1.5CO</td>
<td>-15.3</td>
<td>-80.9</td>
<td>-81.2</td>
<td>-81.2</td>
</tr>
<tr>
<td></td>
<td>&gt; 420 (oxidation)</td>
<td></td>
<td>-17.2</td>
<td>-82.8</td>
<td>-81.1</td>
<td>-81.1</td>
</tr>
</tbody>
</table>
Appendix

Table A5: Main primary gaseous decomposition products of the selected freeze-dried ammonium CuFe oxalate “[CuC2O4.2(NH4)2Fe(C2O4)3.2.6(NH4)2C2O4, 3.5H2O]”

<table>
<thead>
<tr>
<th>Process/ (equation)</th>
<th>Temperature range (°C), roughly</th>
<th>Main primary gaseous decomposition products</th>
<th>∆m (calc.) / %</th>
<th>∆m (exp.) / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>∆m/step</td>
<td>∆m/total</td>
</tr>
<tr>
<td>1</td>
<td>30 - 100</td>
<td>3.5H2O</td>
<td>-4.9</td>
<td>-4.9</td>
</tr>
<tr>
<td>2</td>
<td>2a 2c 2b,4a 2b,4b 200 - 300</td>
<td>5.6 (2NH3, H2O, CO2, CO)</td>
<td>-54.1</td>
<td>-59.0</td>
</tr>
<tr>
<td></td>
<td>5.6 (HCN, NH3, CO2, 2H2O)</td>
<td>-54.1</td>
<td>-59.0</td>
<td>-54.1</td>
</tr>
<tr>
<td></td>
<td>200 - 300</td>
<td>3.5CO2, 0.5CO</td>
<td>-13.1</td>
<td>-72.1</td>
</tr>
<tr>
<td></td>
<td>300 - 400</td>
<td>4CO2</td>
<td>-13.7</td>
<td>-72.7</td>
</tr>
<tr>
<td>3</td>
<td>3c 2CO2, 2CO</td>
<td>-11.2</td>
<td>-83.3</td>
<td>-11.4</td>
</tr>
<tr>
<td></td>
<td>&gt; 400</td>
<td>2CO2, 2CO</td>
<td>-11.2</td>
<td>-83.9</td>
</tr>
<tr>
<td></td>
<td>(oxidation)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+2.0</td>
<td>-80.6</td>
<td></td>
</tr>
</tbody>
</table>

Figure A3: MS characterization of the gaseous decomposition products occurring during the decomposition of the freeze-dried Cu-Fe formate “CuFe2O2.5(HCOO)6.67 x 2.5H2O”. Atm.: argon; heating rate: 5K/min. M / z = 2 (H2); M / z = 18 (H2O) and M / z = 45 (HCOO fragment), M / z = 28 (CO); M / z = 30 (HCOH) and M / z = 44 (CO2).
11.3. Thermodynamic calculations

**Chemical equilibrium**

The stabilities of metal oxides at various oxygen partial pressures can be readily predicted from the thermodynamic data. The expression relating the free energy change for a reaction under arbitrary conditions ($\Delta G_R$) to the standard free energy is given by the relation:

$$\Delta G_R = \Delta G_R^\circ + RT \ln Q$$

(1)

Where $Q$ is the reaction quotient, $R$ is the gas constant and $T$ is the temperature in Kelvin. At the equilibrium, when the chemical reaction occurs reversibly, $\Delta G_R = 0$. Furthermore, the pressures (or concentrations) of all reactants and products must be equilibrium values so, $Q = K_{eq}$ ($K_{eq}$ = equilibrium constant). Making these substitutions in (1) gives the relation:

$$\Delta G_R^\circ = -RT \ln K_{eq}$$

(2)

For a system such as

$$6Fe_2O_3 \rightarrow 4Fe_3O_4 + O_2$$

The change in the free energy is given by

$$\Delta G^\circ = -RT \ln \frac{a_{Fe_3O_4}^4 \times p(O_2)}{a_{Fe_2O_3}^6}$$

$(a_{Fe_3O_4} = a_{Fe_2O_3} = 1)$ thus,

$$\Delta G^\circ = -RT \ln p(O_2) \Rightarrow \ln p(O_2) = -\frac{\Delta G^\circ}{RT} \quad \text{or} \quad \log p(O_2) = -\frac{\Delta G^\circ}{2.3RT}$$

Thus in $\log[p(O_2)]/(1/T)$ space the equilibria can be shown as essential straight lines (Fig. 3.8.1).

11.4. Oxygen partial pressure of the gas mixtures

The desired oxygen partial pressures were achieved using different gas mixtures prepared from oxygen or air combined with argon, using a pump (Digamix Pump type 5KA). Furthermore, the oxygen partial pressure in the gas flow was controlled with a solid electrolyte coulorimetric (SEC) device.

**Table A6:** Oxygen partial pressure obtained under different atmospheres

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Air</th>
<th>Argon + 0.1%O₂</th>
<th>Argon+1%O₂</th>
<th>Argon +1%air</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p(O_2)$ (atm)</td>
<td>~ 0.21</td>
<td>$10^{-1}$</td>
<td>$10^{-2}$</td>
<td>$3.16 \times 10^{-3}$</td>
</tr>
<tr>
<td>$p(O_2)$ (Pa)</td>
<td>$0.212 \times 10^5$ Pa</td>
<td>$1.013 \times 10^2$ Pa</td>
<td>$1.013 \times 10^1$ Pa</td>
<td>$3.2 \times 10^5$ Pa</td>
</tr>
</tbody>
</table>
11.5 Determination of the oxygen non-stoichiometry

Potentiometric measurement
As an example, the data recorded at 900°C for sample (S1) Cu$_{0.9}$Fe$_{2.1}$O$_{4.02}$ are shown on Figure A4. For the computation of the amount oxygen exchanged between sample and gas, the relations established in Section 9.2.2.b were employed. The results obtained from these calculations are presented in Table A7.

Table A7: Oxygen deficiencies “δ” of the sample Cu$_{0.9}$Fe$_{2.1}$O$_{4.02}$ as function of the p(O$_2$) in the temperature range 800-1000°C

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>lg[p(O$_2$)/(atm)]</th>
<th>lg[p(O$_2$)/(Pa)]</th>
<th>n$_{0'}$</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>-4.10</td>
<td>0.91</td>
<td>3.81</td>
<td>0.21</td>
</tr>
<tr>
<td>900</td>
<td>-4.55</td>
<td>0.46</td>
<td>3.61</td>
<td>0.41</td>
</tr>
<tr>
<td>1000</td>
<td>-4.32</td>
<td>0.69</td>
<td>3.50</td>
<td>0.52</td>
</tr>
</tbody>
</table>

δ = n$_{0'}$ - n$_{0''}$ (δ = variation of the oxygen stoichiometry; n$_{0'}$ and n$_{0''}$ are oxygen stoichiometry of the sample before and after annealing under Ar/O$_2$, respectively. n$_{0'}$ is equal 4.02).

Figure A4: Potentiometric measurement with the solid electrolyte cells. Sample Cu$_{0.9}$Fe$_{2.1}$O$_{4.02}$; atm.: Ar/O$_2$, T = 900°C.
11.6. Some magnetization results at 5K

Figure A5: Magnetization curve of Cu$_{0.7}$Ni$_{0.3}$Fe$_2$O$_4$ at 5K. The inset shows the low fields regions. (m = 24.4mg)

Table A.8: Magnetic properties of some copper ferrite samples prepared under different condition from copper-iron mixtures.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Synthesis conditions (*)</th>
<th>Magnetization at 5K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>Atmosphere (p(O$_2$), atm)</td>
</tr>
<tr>
<td>Cu$<em>{0.8}$Fe$</em>{2.2}$O$_4$</td>
<td>1000</td>
<td>Air (0.209)</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>Air (0.209)</td>
</tr>
<tr>
<td>Cu$<em>{0.67}$Fe$</em>{2.33}$O$_4$</td>
<td>1150</td>
<td>Air (0.209)</td>
</tr>
<tr>
<td></td>
<td>1150</td>
<td>Ar+1%O$_2$ (10$^{-2}$)</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Fe$</em>{2.5}$O$_4$</td>
<td>1110</td>
<td>Argon 4.6 (10$^{-3}$)</td>
</tr>
<tr>
<td></td>
<td>1115</td>
<td>Argon 4.6 (10$^{-3}$)</td>
</tr>
</tbody>
</table>

(*) After the heating process, all samples were quenched rapidly from the high temperature to room temperature as described in Section 3.8.1.
11.7. Computer programs used


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I would like to express my deep gratitude to my supervisor Prof. Dr. Hubert Langbein for giving me the opportunity to perform this interesting work in the Inorganic Chemistry Institute of the TU Dresden, and for his scientific support during its completion.

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Special thanks go to Dr. M. Al Daroukh, who performed all the measurements on the OXYLYT-Solid Electrolyte apparatus, and helped with many experimental details.

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I would like also to thank Christian Wende who, during his stay in the Goa University (India), measured the saturation magnetization at 300K of some nickel and copper ferrite samples.

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Conferences and Publications


3) GDCh-Jahrestagung Chemie Oktober 2003, München.
   Thema: „Investigation on the formation of copper-nickel ferrites by thermal decomposition of solid-solution formates“

   Thema: „Synthese und Zersetzung von Spinellen Cu_{1-x}Fe_{2+x}O_{4+δ} in Abhängigkeit von Temperatur und p(O_2)“
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2001 - 2004 Scientific Assistant, Institute of Inorganic Chemistry, Faculty of
Mathematics and Natural Sciences, Dresden University of
Technology, Germany.
**Versicherung**

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher oder ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

Die vorliegende Arbeit wurde am Institut für Anorganische Chemie der Technischen Universität Dresden unter wissenschaftlichen Betreuung von Herrn Prof. Dr. Hubert Langbein im Zeitraum von Oktober 2000 bis Oktober 2004 angefertigt.

Es haben keine früheren erfolglosen Promotionsverfahren stattgefunden.

Hiermit erkenne ich die Promotionsordnung der Fakultät Mathematik und Naturwissenschaften der Technischen Universität Dresden vom 16 April 2003 an.

Dresden, den 14. 10. 2004

F. Kenfack