Tetragonal copper ferrite obtained by self-propagating combustion

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Abstract

The nanosized copper ferrite with tetragonal structure was obtained by combustion-reaction of ureate precursors, so called self-propagating synthesis. The ureate complex compounds–precursors were characterized by chemical and physico-chemical measurements. The copper ferrites were investigated by: X-ray diffractometer (XRD), scanning electron microscopy (SEM), IR microscopy and magnetic measurements.
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1. Introduction

Copper ferrite, $CuFe_2O_4$, receives considerable attention not only from theoretical point of view, but, also, for its high electronic conductivity, high thermal stability and high catalytic activity for O_2 evolution from alumina–cryolite system used for aluminium production [1,2].

Copper ferrite crystallizes either in tetragonal (T) or cubic (C) symmetry depending on the cation distribution in the spinel structure. The tetragonal phase is stable at the room temperature and it is an inverse spinel. The Fe^{3+} ions occupy both the tetrahedral A and octahedral B-sites in almost equal amount. The Cu^{2+} ions occupy only the B-sites and this causes the tetragonal distortion due to the cooperative Jahn–Teller effect [1]. The cubic phase is stable at temperatures higher than $360\,^{\circ}C$, but it is obtained as a metastable phase at room temperature, by quenching from high temperatures.

It is known that the synthesis route plays a very important role in determining the chemical, structural and magnetic properties of the ultrafine, nanosized spinel ferrites. For this reason, the traditional methods (ceramic method, etc.) are replaced by the wet chemistry methods: hydro/solvothermal synthesis, microemulsion, sol–gel and complexation tehnique [3–9]. A new and very promising method is the self-propagating combustion [10–15]. The combustion reaction depends on the type of the fuel, the fuel to oxidizer ratio, the ignition temperature, etc. The combustion synthesis may be: solid state combustion and solution combustion [10]. In the solid state combustion (SSC), initial reactants, intermediates and final products are all in the solid state. The systems used in the solution combustion (SC) are: metal nitrate (oxidizer) and urea, hydrazides and derivatives of hydrazide, glycine or citric acid like fuels. The spinel ferrites obtained by this method are homogeneous, of high purity and high surface area.

In this paper, the solution combustion of the system:

$$2Fe(NO_3)_3 : Cu(NO_3)_2 : nCO(NH_2)_2$$

where $n = 7$; 16 is investigated in order to obtain $CuFe_2O_4$ powder.

2. Experimental

2.1. Synthesis of the ureate precursors

All chemicals: $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and urea ($CO(NH_2)_2$) are of reagent quality (Merck.). Copper and iron nitrates in the 1:2 ratio of cations are mixed with urea, in two different proportions:

$$2Fe(NO_3)_3 : 1Cu(NO_3)_2 : 7CO(NH_2)_2$$
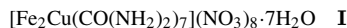
and

$$2Fe(NO_3)_3 : 1Cu(NO_3)_2 : 16CO(NH_2)_2$$
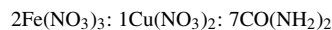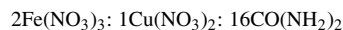
in the agate mortar. The nitrates and urea are solved in the hydration water of the salts. The mixing is kept on till homogenous brownish-green compounds are obtained. These compounds are dried on P_4O_{10}.
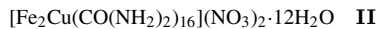
Elemental chemical analysis was consistent with the formula:

$[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$ **I**

(Calcd. : Fe% : 9.20; Cu% : 5.21; C% : 6.90; N% : 25.29;

found : Fe% : 9.14; Cu% : 5.18; C% : 7.02; N% : 25.18);

$[Fe_2Cu(CO(NH_2)_2)_{16}](NO_3)_2 \cdot 12H_2O$ **II**

(Calcd. : Fe% : 6.06; Cu% : 3.44; C% : 8.02; N% : 30.31;

found : Fe% : 5.95; Cu% : 3.38; C% : 8.12; N% : 30.50).

2.2. Physical measurements

In order to obtain information about the coordination of urea in the ureate precursors and also to confirm the formation of the copper ferrite, the IR spectra (KBr pellets) of the compounds and of the oxides were recorded on a Bio-Rad FTS-135 spectrophotometer, in the 400–4000 cm^{-1} region.

Data about the stereochemistry of the metal ions were obtained from the UV–vis spectra (diffuse reflectance technique) recorded with a Specord M40 spectrophotometer, in the range 400–1000 nm.

The crystalline phases of the powders were identified by XRD powder method using a Rigaku-Multiflex X-ray diffractometer, with CuKα radiation. For quantitative analysis, a step scanning technique was applied, in the 2θ range 20–80 with a step of 2 °/min.

Morphological analysis of samples was performed by scanning electron transmission (SEM) using electron microscope HITACHI S2600N (image analysis with secondary electron detector (SE)).

The magnetic measurements were carried out using a magnetometer based on Extraction Method with 10^{-4} emu resolution, accesible 1.5–300 K, maximum magnetic field 10 T, increment 10 Oe.

3. Results and discussion

The copper ferrite is obtained by solution-combustion of the ureate compounds. The combustion synthesis is based on the thermochemical concepts used in the propellant chemistry [11]. We used $Cu(NO_3)_2 \cdot 3H_2O$ as a Cu source (total valencies (−10)), $Fe(NO_3)_3 \cdot 9H_2O$ as a Fe source (total valencies (−15)) and urea $CO(NH_2)_2$ (total valencies (+6)).

The first system studied was:

$$2Fe(NO_3)_3 \cdot 9H_2O : Cu(NO_3)_2 \cdot 3H_2O : 7CO(NH_2)_2$$
$$\underset{(-30)}{} \qquad \underset{(-10)}{} \qquad \underset{7x(+6)=(+42)}{}$$
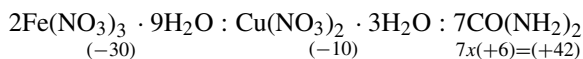
The nitrate salts are preferred as "raw materials" because they serve as a water-soluble room temperature nitrogen source for the synthesis. Urea has the lowest reducing power (+6), produces the smallest volume of gases and is very cheap. The combustion reaction of urea is exothermal and provides the heat needed for the $CuFe_2O_4$ synthesis reaction [13].

The second system chosen was:

$$2Fe(NO_3)_3 \cdot 9H_2O : 1Cu(NO_3)_2 \cdot 3H_2O : 16CO(NH_2)_2$$
$$\underset{(-30)}{} \qquad \underset{(-10)}{} \qquad \underset{16x(+6)=(+96)}{}$$

In this system the fuel (urea) is in excess. We try to investigate the influence of the excess of the fuel on the characteristics of the copper ferrite.

To better understand the solution-combustion synthesis route, we characterized the complex compounds obtained from these systems. We started from the idea that the homogeneous mix-

Table 1
IR frequencies (cm^{-1}) of the compounds **I** and **II**

Urea	I	II	Assignment
3448 vs	3422 s	3450 s	νNH
3343 s	3357 s	3349 s	$\nu_{sym}NH_2$
3256 sh	3236 sh	3228 sh	$\nu_{sym}NH_2$
	1709 m		
1678 vs	1646 s	1633 vs	νCO + δNH
1609 vs	1568 m	1556 s	
	1505 w	1501 m	
1466 vs			νC–N + δNH
	1382 vs	1355 vs	νNO$_3^-$
	1316 m		
1153 m	1147 w	1154 m	ρNH$_2$ (in plane)
1055 w	901 w	1030 m	
	822 w	828 w	ρNO$_3^-$
787 w		761 w	νNH$_2$ (out of plane) + ΦCN
718 w		612 m	
551 s	534 w	542 m	
486 s		428 m	νM–O

I: $[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$, **II**: $[Fe_2Cu(CO(NH_2)_2)_{16}](NO_3)_8 \cdot 12H_2O$. m = medium, vs = very strong, s = strong, w = weak and sh = shoulder.
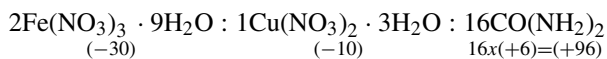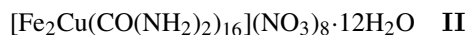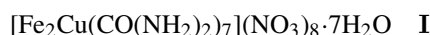
Table 2
Absorption bands in the electronic spectra

Transition	Compound	
	$[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$ **I** (nm)	$[Fe_2Cu(CO(NH_2)_2)_{16}](NO_3)_2 \cdot 12H_2O$ **II** (nm)
CT	∼320	∼320
$^6A_{1g} \rightarrow {}^4E_g(G)$	∼490	∼480
$d_{z^2} \rightarrow d_{x^2-y^2}$	∼820	∼750–800

ture, obtained in the mortar, is the result of the reaction between nitrates and urea, in a high concentrated solution.

The ureate compounds **I** and **II** are characterized by elemental chemical analysis, IR and UV–vis spectra:

$$[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O \quad \textbf{I}$$

$$[Fe_2Cu(CO(NH_2)_2)_{16}](NO_3)_8 \cdot 12H_2O \quad \textbf{II}$$

The IR spectra of the compounds **I** and **II** are recorded in the 400–4000 cm^{-1} range and they are compared with the spectrum of urea (Table 1). The IR spectra of the compounds suggested that urea acts as a monodentate ligand by the oxygen atom. The band assigned to ν_{CO} vibration present in the spectrum of urea at $\sim$1678 cm^{-1} is shifted at lower frequencies in the spectra of the compounds ($\sim$1646 cm^{-1} for **I**, $\sim$1633 cm^{-1} for **II**). The bands assigned to the vibrations of the –NH_2 groups remained unmodified. The spectra of the compounds also revealed the presence of the bands characteristic to the NO_3^- ion ($\nu NO_3^- \sim$ 1380–1355 cm^{-1}; $\rho NO_3^- \sim$ 822–828 cm^{-1}).

The reflectance spectra of these compounds revealed the presence of the weak forbidden transition band in an octahedral high spin configuration of the $Fe^{3+}(d^5)$ ions $^6A_{1g} \rightarrow {}^4E_g(G)$ (480–490 nm) and the characteristic band of the pseudotetrahedral environment of $Cu^{2+}(d^9)$ ions $d_{z^2} \rightarrow d_{x^2-y^2}$ ($\sim$750–800 nm), also, at 320 nm appeared a band assigned CT of urea ligand (Table 2).

In order to obtain the copper ferrite by the combustion reaction of these compounds, they are placed on a heater and they are maintained at around 250–300 °C. Initially, they melted and underwent dehydration, followed by the decomposition with evolution of a big amount of gases and heat. Then, they frothed and swelled forming foam which ruptured with a flame and finally gave foamy powders of copper ferrites. *In situ*, the temperature can be $\sim$1000 °C in a few minutes.

The XRD patterns of the samples resulting, treated 1h/800 °C showed the formation of the single-phase $CuFe_2O_4$ with tetragonal structure for the compound **I** and the formation of the same phase, but, with α-Fe_2O_3 traces for the compound **II** (Fig. 1a
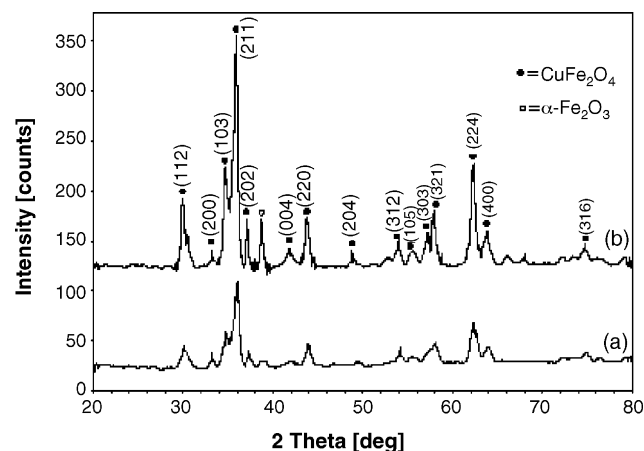

Fig. 1. XRD patterns of $CuFe_2O_4$ obtained by thermal decomposition of the compounds: (a) $[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$ (**I**) and (b) $[Fe_2Cu(CO(NH_2)_2)_{16}](NO_3)_8 \cdot 12H_2O$ (**II**).

and b). The crystallite sizes of the samples were: 15–25 nm for the first and 17–36 nm for the later.

To confirm the formation of the copper ferrite phases, the IR spectra were recorded in the range 400–4000 cm^{-1} (Fig. 2). These spectra indicated the presence of two intense absorption bands at $\sim$560–570 cm^{-1} (v_1^*) and at $\sim$400–429 cm^{-1} (v_2^*). The first band (v_1^*) is attributed to the stretching vibration of Fe^{3+}–O^{2-} in the tetrahedral complexes and the second band (v_2^*) to that of Cu^{2+}–O^{2-} in the octahedral one, in the structure of an inverse spinel ferrite like $CuFe_2O_4$.

The morphological features of these ferrites are shown in Fig. 3. The morphology of these samples revealed the presence of the agglomerates wherein the nanoparticles are almost spherical, with a large distribution. The SEM of the second sample evidenced a more uniform dimensional spectrum of the crystallites probably due to the excess of the fuel in the combustion reaction.

The magnetization decreases from 28.3 A m^2/kg at 4.5 K to 24.8 A m^2/kg at 300 K for the $CuFe_2O_4$ obtained from precursor **I**. The decrease of magnetization with temperature is
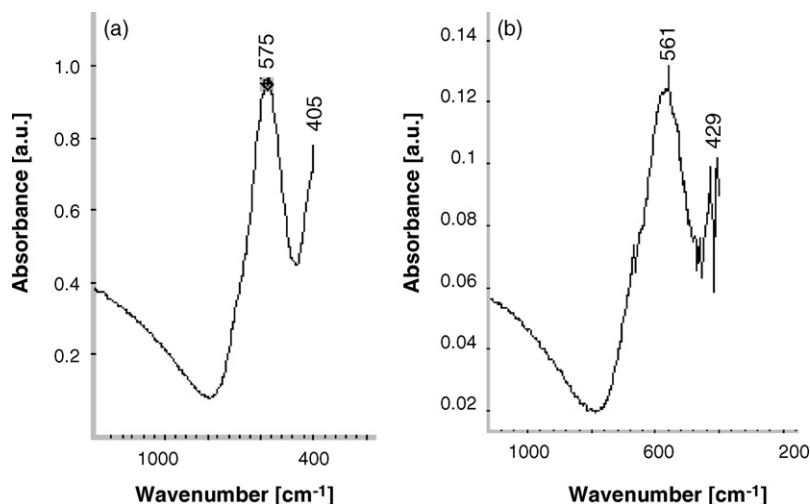

Fig. 2. IR spectra of $CuFe_2O_4$ obtained by thermal decomposition of the compounds: (a) $[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$ (**I**) and (b) $[Fe_2Cu(CO(NH_2)_2)_{16}](NO_3)_8$ 12H_2O (**II**).
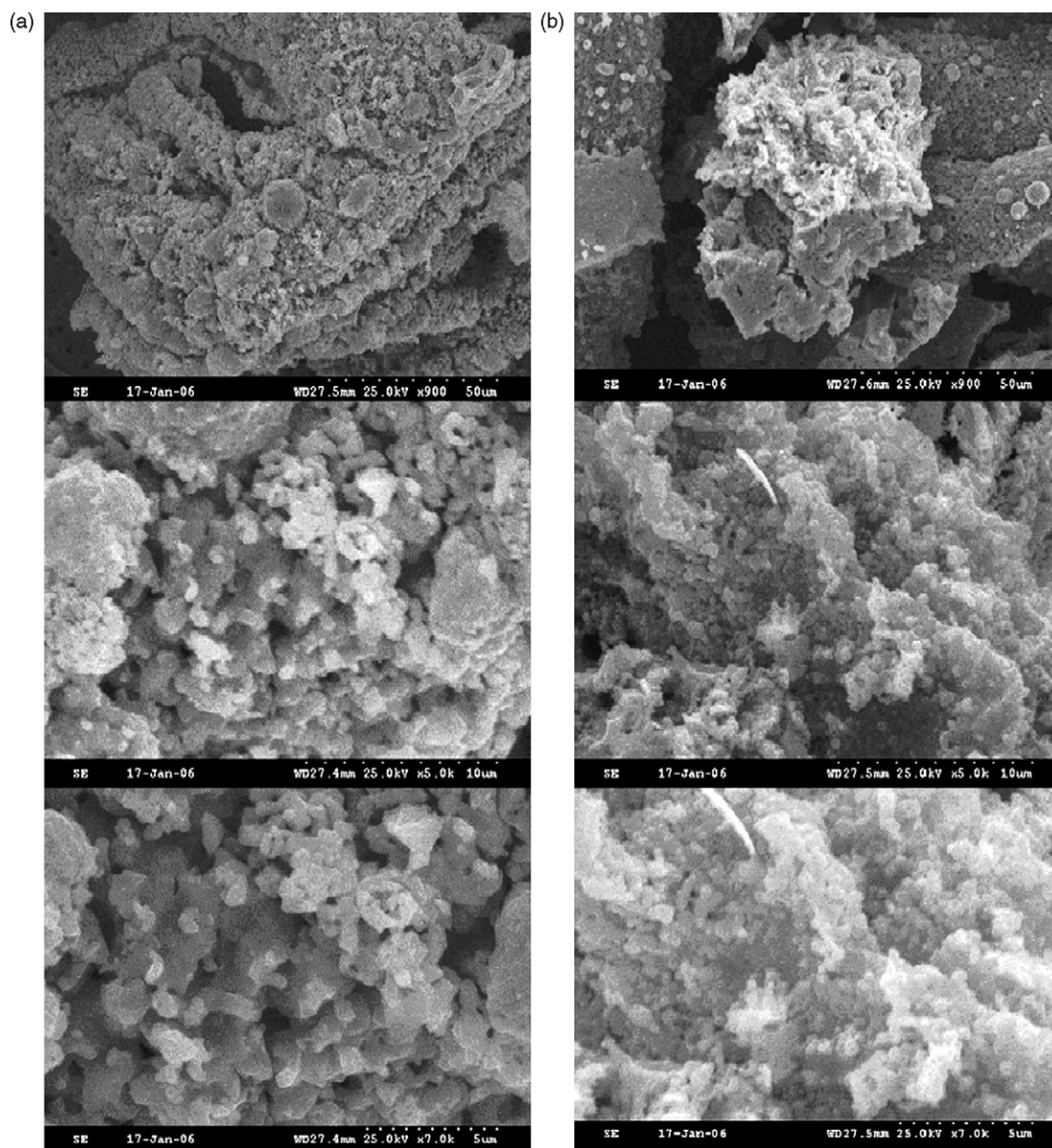
Fig. 3. SEM images, at different resolutions, of $CuFe_2O_4$ obtained by thermal decomposition of the compounds: (a) $[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$ (**I**) and (b) $[Fe_2Cu(CO(NH_2)_2)_{16}](NO_3)_8 \cdot 12H_2O$ (**II**).
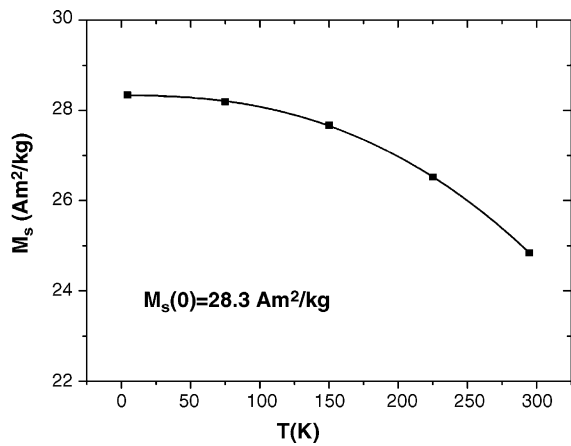

Fig. 4. Saturation magnetization M_S (A m^2/kg) *vs.* T(K) of $CuFe_2O_4$ obtained by thermal decomposition of the compound $[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$ (**I**).
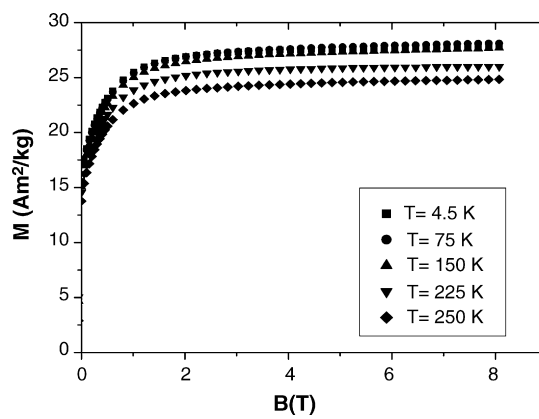
Fig. 5. The magnetization curves, at different temperatures, of $CuFe_2O_4$ obtained by thermal decomposition of the compound **I**: $[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$.
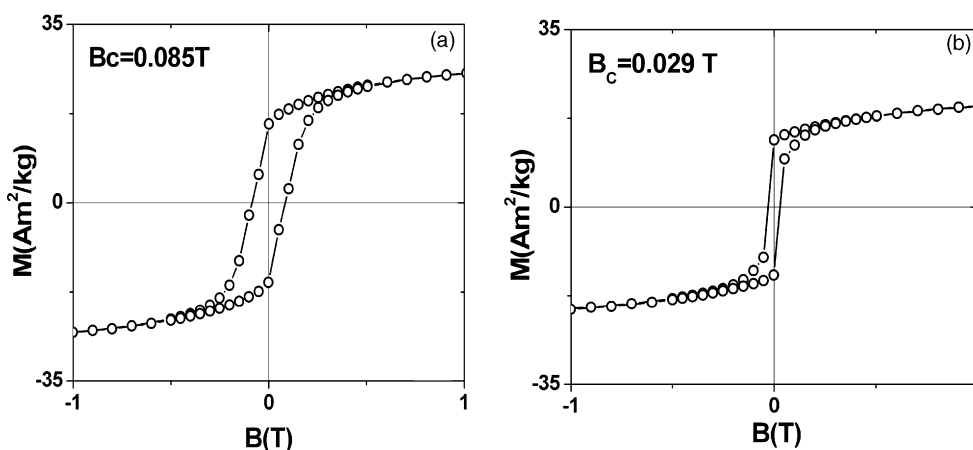
Fig. 6. The magnetization curves of $CuFe_2O_4$ obtained from compound $[Fe_2Cu(CO(NH_2)_2)_7](NO_3)_8 \cdot 7H_2O$ (**I**) at 75 K (a) and 225 K (b).

monotonous (Fig. 4). Such a result is expected for the nanosized particles. Fig. 5 shows the *M versus B(T)* curves for $CuFe_2O_4$ obtained by combustion of the precursor **I**. The values obtained for $CuFe_2O_4$ obtained from precursor **II** are smaller due probably to the presence of α-Fe_2O_3 traces, but the behaviour of the magnetization is the same. It decreases monotonous with the temperature from 26 A m^2/kg at 4.5 K to 21.4 A m^2/kg at 300 K. The hysteresis curves for the first $CuFe_2O_4$, at two different temperatures, are shown in Fig. 6.

4. Conclusion

The copper ferrites with tetragonal structure are obtained by combustion-reaction of ureate precursors. The ureate precursors were characterized by chemical analysis, IR and UV–vis spectra.

We tried to investigate the influence of the excess of the urea (fuel) on the structure of copper ferrites. Thus, the XRD pattern of the copper ferrite obtained by decomposition of the first compound **I** showed the single phase $CuFe_2O_4$ with tetragonal structure; the XRD pattern of the copper ferrite obtained from the second precursor **II** showed the same face with α-Fe_2O_3 traces. However, the SEM of this sample evidenced a more uniform dimensional spectrum of the crystallite probably due to excess of fuel.

We consider the combustion reaction of the ureate precursors a very simple and efficient way for the preparation of the single ferrites.

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