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# Structural characterization and magnetic properties of $(Li_{0.5}Fe_{0.5})_{1-x}Cu_xFe_2O_4$ ferrites

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The structural and magnetic properties of the ferrites $(Li_{0.5}Fe_{0.5})_{1-x}Cu_xFe_2O_4$ (where x=1, 0.5 and 0.1) have been investigated by means of X-ray diffraction (XRD), IR spectroscopy, scanning electron microscopy (SEM) and magnetic measurements. The experimental results show the possibility of obtaining the mixed lithium-copper ferrites with cubic structure at room temperature. The size of the crystallites ranges between 30-60 nm.

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## 1. Introduction

The ferrites represent an active field of research and development. Among the ferrites, copper ferrite and copper mixed ferrite have been the focus of continuous interest in recent years.

Copper ferrite crystallizes either in tetragonal (T) or cubic (C) symmetry depending on the distribution of the cation in the spinel structure. The tetragonal phase is stable at room temperature and it is an invers spinel. The $Fe^{3+}$ ions occupy both the tetrahedral A and octahedral B-sites in approximately equal amount. The $Cu^{2+}$ ions occupy only the B-sites and due to the cooperative Jahn-Teller effect this causes tetragonal distortion [1]. The cubic phase is stable at temperatures higher than

360 ºC, but it is obtained as a metastable phase at room temperature, by quenching from high temperatures.

$CuFe_2O_4$ can be obtained by many methods, such as: coprecipitation [2], solvothermal method [3], sol-gel method [4,5], reverse micelle method [6], self-propagating combustion [7,8], complexation method [8-11].

Various researchers studied the changes in the properties of the copper ferrite due to the substitution of $Cu^{2+}/Fe^{3+}$ with various ions.

Diamagnetic substitution in simple and mixed ferrites has received special attention. The effect of iron substitution by tetravalent ions $Ge^{4+}$and $Ti^{4+}$ on the magnetic properties of Cu-ferrites was investigated [12].

Gabal *et al.* [13] studied the role of the cadmium content on the structural, electrical and magnetic properties of Cu-Cd mixed ferrites.

Other authors studied the magnetic and electrical properties of rare earth substituted Cu-Cd ferrites [14] and Cu-Zn ferrites [15]. It was found that rare earth substitution leads to the redistribution of cations and this causes changes in the structural, electrical and magnetic properties.

Small amounts of $Ga^{3+}$ and $La^{3+}$ ions substituted for iron in Cu-Mg ferrite [16] can have different effects on the structure, density and electric resistivity of ferrite. The Cu – Mg doped with $Ga^{3+}$ can be a promising material for use in humidity sensors.

Li-Cu ferrites have been studied less extensively. The Li-Cu ferrites have shown interesting electrical and magnetic properties [17-21].

The aim of this work was to investigate the possibility of obtaining the mixed lithium-copper ferrite with cubic structure at room temperature. In other words, we tried to determine what amount of Li(I) makes the copper ferrite with tetragonal structure change into a ferrite with cubic structure at room temperature. Among the various methods mentioned previously, we studied the synthesis of these ferrites by the complexation method. The complexing agents were the anions of polyhydroxy carboxylic acids (malate, tartarate and gluconate).

## 2. Experimental

### 2.1 Samples preparation

The following systems have been studied:

$2Fe(NO_3)_3{\cdot}9H_2O:0.75Cu(NO_3)_2{\cdot}3H_2O : 0.25Li_2CO_3 : mL$

$2Fe(NO_3)_3{\cdot}9H_2O: 0.50Cu(NO_3)_2{\cdot}3H_2O: 0.50Li_2CO_3 : mL$

$2Fe(NO_3)_3{\cdot}9H_2O: 0.25Cu(NO_3)_2{\cdot}3H_2O: 0.75Li_2CO_3: mL$

where $L=C_4O_5H_4^{2-}$ (malate anion), m=4 ; $L=C_4O_6H_4^{2-}$ (tartarate anion), m=4; $L=C_6O_7H_{11}^{-}$ (gluconate anion), m=6.

All chemicals $Fe(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $Li_2CO_3$, malic acid, tartaric acid and δ-gluconolactone were of reagent quality (Merck).

The iron and copper nitrates were dissolved together in a minimum quantity of water. Lithium carbonate was dissolved in an aqueous solution of polyhydroxy carboxylic acid (malic, tartaric, gluconic acids) under continuous stirring. Methanol was added to the mixture of these two solutions until a precipitate was formed. The pH was raised to 6 by adding $NH_4OH$:methanol (1:1) solution.

The precipitates were filtered and washed with methanol and dried on $P_4O_{10}$. Finally, the dried materials were calcinated at 800 °C for 1h.

### 2.2 Samples characterization

X-ray powder diffraction measurements were obtaining using a Rigaku-Multiflex diffractometer at ambient temperature using $CuK_\alpha$ radiation. For quantitative analysis, a step scanning technique was applied in the 2θ range 20 – 80 with a step of 2°/min.

IR spectra (400-4000 $cm^{-1}$) were recorded with a BIO – RAD FTIR 125 type spectrophotometer, in KBr pellets.

In order to get information about the morphology of the samples, a series of electron-microscopic images was taken by SEM using electron microscope HITACHI S2600N (image analysis with secondary electron detector).

The saturation magnetization of the ferrites, at room temperature, was determined with a Faraday balance using $HgCo(SCN)_4$ as calibrant.

## 3. Results and discussion

In order to have good crystallinity, all samples were calcinated at 800 ºC for 1h.

The samples have been characterized by X-ray diffraction (XRD), IR spectroscopy, scanning electron microscopy (SEM) and magnetic measurements.

Table 1 reports the phase compositions of the samples obtained from $Fe(NO_3)_3$-$Cu(NO_3)_2$-$Li_2CO_3$-malic acid system, calcinated at 800 ºC/1h.

*Table 1. Oxide phases obtained from $Fe(NO_3)_3$-$Cu(NO_3)_2$-$Li_2CO_3$-malic acid system.*

| System | Sample no. | Oxide phase composition |
|---|---|---|
| $2Fe^{3+}$:$0.75Cu^{2+}$:$0.5Li^{+}$:<br>$4C_4O_5H_4^{2-}$ | $S_1$ | $CuFe_2O_4$<br>tetragonal<br>$Li_{0.25}Cu_{0.5}Fe_{2.25}O_4$<br>cubic<br>$\alpha$-$Fe_2O_3$ |
| $2Fe^{3+}$:$0.50Cu^{2+}$:$1Li^{+}$:<br>$4C_4O_5H_4^{2-}$ | $S_2$ | $Li_{0.25}Cu_{0.5}Fe_{2.25}O_4$<br>cubic<br>$\alpha$-$Fe_2O_3$ |
| $2Fe^{3+}$:$0.25Cu^{2+}$:$1.5Li^{+}$:<br>$4C_4O_5H_4^{2-}$ | $S_3$ | $CuFe_2O_4$<br>tetragonal<br>$Li_{0.45}Cu_{0.1}Fe_{2.45}O_4$<br>cubic<br>$\alpha$-$Fe_2O_3$ |

Formation of $(Li_{0.5}Fe_{0.5})_{1-x}Cu_xFe_2O_4$ ferrites was confirmed by powder X-ray diffraction.

XRD patterns of the samples $S_1$-$S_3$ are presented in Fig. 1.

Analyzing the results, the following conclusions may be point out:

- the formation of $Li_{0.25}Cu_{0.5}Fe_{2.25}O_4$ with cubic structure as the main product together with $\alpha$-$Fe_2O_3$ as impurity (when the ratio $Cu^{2+}/Li^{+}=1/2$) ;
- the average size of the crystallite (calculated using Scherrer formula) was found 60 nm.

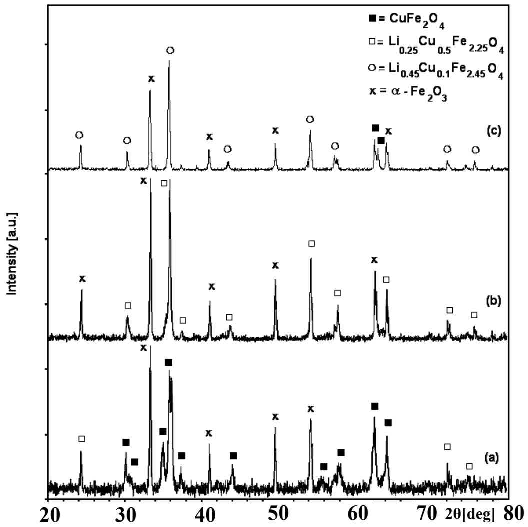


*Fig. 1. XRD patterns of the samples: a) $S_1$; b) $S_2$; c) $S_3$.*

Table 2 describes the phase compositions of the samples obtained from $Fe(NO_3)_3$-$Cu(NO_3)_2$-$Li_2CO_3$-tartaric acid system, treated at 800 ºC/1h .

*Table 2. Oxide phases obtained from $Fe(NO_3)_3$-$Cu(NO_3)_2$-$Li_2CO_3$ - tartaric acid system.*

| System | Sample no. | Oxide phase composition |
|---|---|---|
| $2Fe^{3+}$:$0.75Cu^{2+}$:$0.5Li^{+}$:<br>$4C_4O_6H_4^{2-}$ | $S_4$ | $CuFe_2O_4$<br>tetragonal<br>$\alpha$-$Fe_2O_3$ |
| $2Fe^{3+}$:$0.50Cu^{2+}$:$1Li^{+}$:<br>$4C_4O_6H_4^{2-}$ | $S_5$ | $Li_{0.25}Cu_{0.5}Fe_{2.25}O_4$<br>cubic |
| $2Fe^{3+}$:$0.25Cu^{2+}$:$1.5Li^{+}$:<br>$4C_4O_6H_4^{2-}$ | $S_6$ | $Li_{0.45}Cu_{0.1}Fe_{2.45}O_4$<br>cubic<br>$\alpha$-$Fe_2O_3$ |

The X-ray diffractograms recorded on the samples $S_4$-$S_6$ (Fig. 2) suggested:

- For the ratio $Cu^{2+}/Li^{+}=1/2$, the formation of a single spinel phase with cubic structure ($Li_{0.25}Cu_{0.5}Fe_{2.25}O_4$);
- For the ratio $Cu^{2+}/Li^{+}=1/6$, the formation of a cubic phase ($Li_{0.45}Cu_{0.1}Fe_{2.45}O_4$) as main phase; while in the case of the molar $Cu^{2+}/Li^{+}=3/2$, the formation of a tetragonal phase ($CuFe_2O_4$). For both samples, the X-ray analysis shows the lines characteristic of hematite ($\alpha$-$Fe_2O_3$) as impurities;
- Crystallite sizes of 30 nm ($CuFe_2O_4$), 46 nm ($Li_{0.25}Cu_{0.5}Fe_{2.25}O_4$) and 36 nm ($Li_{0.45}Cu_{0.1}Fe_{2.45}O_4$).

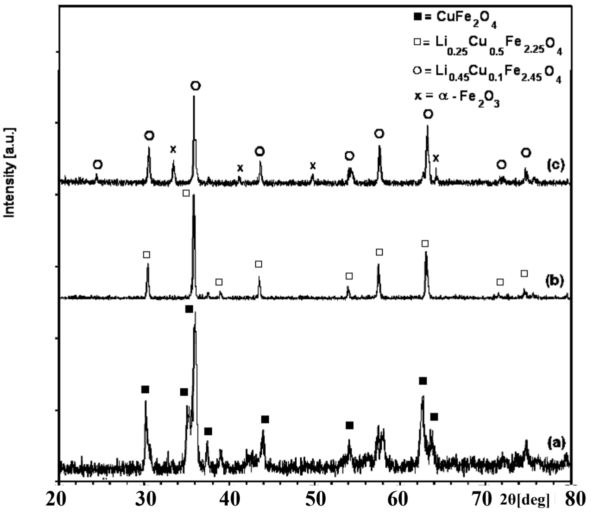


*Fig. 2. XRD patterns of the samples:a) $S_4$; b) $S_5$; c) $S_6$.*

The phase compositions of the samples obtained from $Fe(NO_3)_3$-$Cu(NO_3)_2$-$Li_2CO_3$-gluconic acid system, calcinated at 800 ºC/1h, are listed in Table 3.

*Table 3. Oxide phases obtained from $Fe(NO_3)_3$-$Cu(NO_3)_2$-$Li_2CO_3$ - gluconate acid system.*

| System | Sample no. | Oxide phase composition |
|---|---|---|
| $2Fe^{3+}$:$0.75Cu^{2+}$:$0.5Li^{+}$: $4C_4O_7H_{11}^{2-}$ | $S_7$ | $CuFe_2O_4$ tetragonal<br>$\alpha$-$Fe_2O_3$ |
| $2Fe^{3+}$:$0.50Cu^{2+}$:$1Li^{+}$: $4C_4O_7H_{11}^{2-}$ | $S_8$ | $CuFe_2O_4$ tetragonal<br>$Li_{0.25}Cu_{0.5}Fe_{2.25}O_4$ cubic<br>$\alpha$-$Fe_2O_3$ |
| $2Fe^{3+}$:$0.25Cu^{2+}$:$1.5Li^{+}$: $4C_4O_7H_{11}^{2-}$ | $S_9$ | $Li_{0.45}Cu_{0.1}Fe_{2.45}O_4$ cubic<br>$\alpha$-$Fe_2O_3$ |

As shown in Fig. 3, X-ray diffraction patterns of the samples $S_7$-$S_9$ indicated the formation of the tetragonal copper ferrite for a ratio $Cu^{2+}/Li^{+}=3/2$ and $Li_{0.45}Cu_{0.1}Fe_{2.45}O_4$ cubic mixed ferrite for a ratio $Cu^{2+}/Li^{+}=1/6$. For both ratios, the $\alpha$-$Fe_2O_3$ is present as impurity. The values of the crystallite size are 33 nm for the sample $S_7$ and 48 nm for the sample $S_9$.

One can remark:

- A mixture containing tetragonal copper ferrite and cubic mixed ferrite ($Li_{0.25}Cu_{0.5}Fe_{2.25}O_4$) is formed from $2Fe^{3+}$:$0.75Cu^{2+}$:$0.5Li^{+}$: $4C_4O_5H_4^{2-}$ system ($Cu^{2+}/Li^{+}= 3/2$);
- A mixture containing tetragonal copper ferrite and cubic mixed ferrite ($Li_{0.45}Cu_{0.1}Fe_{2.45}O_4$) is formed from $2Fe^{3+}$:$0.50Cu^{2+}$:$1Li^{+}$: $4C_4O_7H_{11}^{2-}$system ($Cu^{2+}/Li^{+}=1/2$). $\alpha$-$Fe_2O_3$ is present in all these samples as impurity.

Scanning electron microscopy (SEM) was used in order to obtain information about the morphology of the samples. As an example, the morphological characteristics of the samples $S_4$-$S_6$ are shown in Fig. 4.

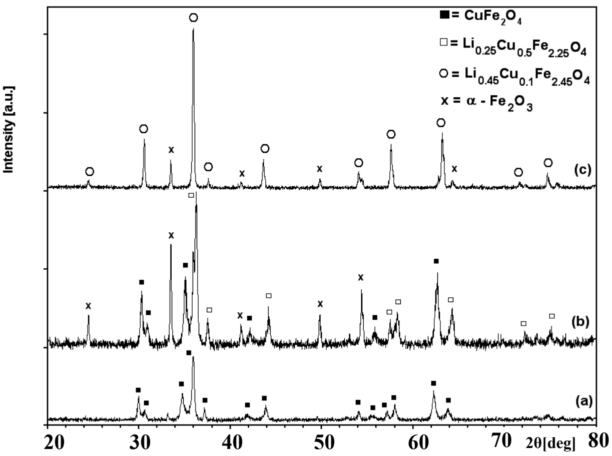
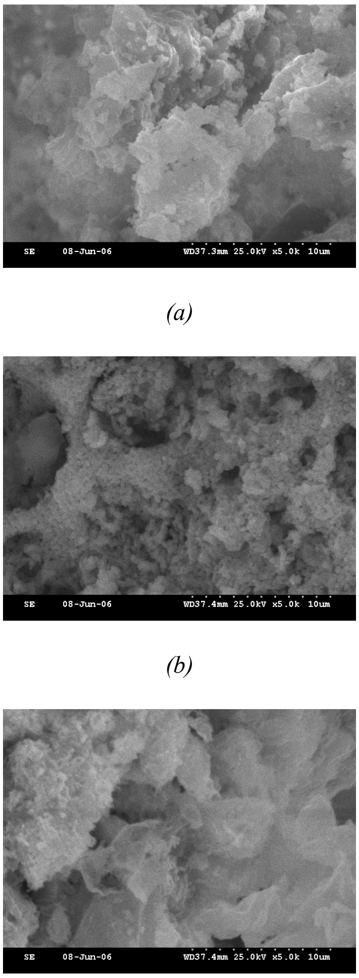


*Fig. 3. XRD patterns of the samples:a) $S_7$; b) $S_8$; c) $S_9$*



*(a)*

*(b)*

*(c)*

*Fig. 4. SEM image of the samples:a) $S_4$; b) $S_5$; c) $S_6$.*

All samples contain spherical particles with a less size of 1 µm and an uniform spectrum. It also seen that these materials tend to agglomerate because the particles are very small.

To confirm the formation of $(Li_{0.5}Fe_{0.5})_{1-x}Cu_xFe_2O_4$ ferrites (where x=1, 0.5 and 0.1), IR spectra of the samples $S_1$-$S_9$ were recorded in the 400-1000 $cm^{-1}$ range. In Fig. 5 is presented the IR spectrum recorded for the sample $S_5$.

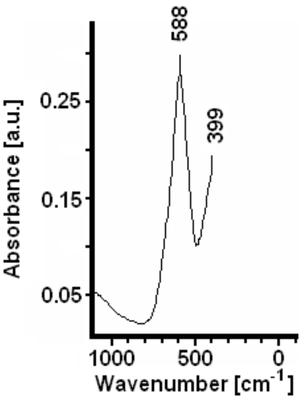


*Fig 5. IR spectrum of the sample $S_5$.*

The relationship between magnetization M and H/T was studied at room temperature. The obtained results are shown in Fig. 6 for the samples $S_4$-$S_6$.

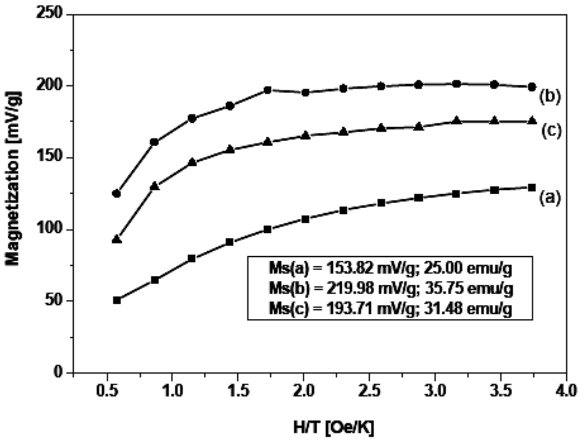


*Fig. 6. Magnetization curves of the samples: a) $S_4$; b) $S_5$; c) $S_6$.*

Sample $S_6$ $(Li_{0.45}Cu_{0.1}Fe_{2.45}O_4)$ has a smaller magnetization value than $S_5$ $(Li_{0.25}Cu_{0.5}Fe_{2.25}O_4)$ due to the presence of impurities (hematite).

## 4. Conclusions

The studied systems gave ferrites with different structural and magnetic properties.

The X-ray diffraction study showed phase tetragonal spinel $(CuFe_2O_4)$ with a little of $\alpha$-$Fe_2O_3$, for ratio $Cu^{2+}/Li^{+}=3/2$ and $L=C_4O_6H_4^{2-}$ (tartarate anion); $C_6O_7H_{11}^{-}$ (gluconate anion).

A molar ratio $Cu^{2+}/Li^{+}=1/2$ leads to a cubic mixed ferrite $(Li_{0.25}Cu_{0.5}Fe_{2.25}O_4)$ when $L=C_4O_5H_4^{2-}$ (malate anion); $C_4O_6H_4^{2-}$ (tartarate anion). This ferrite is obtained like single spinel phase for the tartarate anion.

Another cubic mixed ferrite $(Li_{0.45}Cu_{0.1}Fe_{2.45}O_4)$ is obtained for ratio $Cu^{2+}/Li^{+}=1/6$ and $L=C_4O_6H_4^{2-}$ (tartarate anion); $C_6O_7H_{11}^{-}$ (gluconate anion).

That, for molar ratio $Cu^{2+}/Li^{+}$ = 1/6 to 1/2 it was obtained copper-lithium mixed ferrite with cubic structure at room temperature.

The best results were obtained using the tartarate route. Mixed ferrites obtained by tartarate route have the smallest crystallite sizes (35-45 nm) and the best saturation magnetization ~ 36 emu/g.

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