

*Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)*

SPINELIC FERRITES FROM POLYNUCLEAR COMPOUNDS AS PRECURSORS

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Copper ferrite, CuFe_2O_4 , and lithium ferrite, $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$, were synthesized by the thermal decomposition of polynuclear coordination compounds precursors, containing α -alanine as ligand. The precursors were characterized by chemical analysis, IR and UV-VIS spectra, magnetic measurements and thermal analysis. The XRD patterns of the samples obtained by the decomposition were shown the formation of the single-phase CuFe_2O_4 – tetragonal structure and the cubic-phase $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ with α - Fe_2O_3 traces. The crystallite sizes were 21-29 nm for CuFe_2O_4 and 33-39 nm for $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$.

INTRODUCTION

Spinelic ferrites, like lithium ferrite and copper ferrite are soft magnetic materials. They are promising materials for microwaves applications, memory core, as catalysts.¹ It is well known that the synthesis route plays a very important role in determining the chemical, structural and magnetic properties of the nanocrystalline mixed oxides. Traditionally, the mixed oxides have been prepared by solid state methods which involve physical mixing of oxides/carbonates/oxalates, followed by high temperature treatment for a long period. The obtained powders are inhomogeneous, nonuniform size; they have agglomerate structure and very low surface.^{2,3}

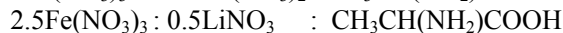
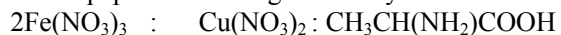
In order to obtain nanoscale mixed oxides at low temperature, various chemical methods belonging to the soft chemistry are proposed: hydro/solvothermal synthesis, microemulsion, sol-gel technique, complexation technique.⁴⁻¹¹ In all these methods, the precursors–polynuclear coordination compounds – are separated from the solution. They are heated to decompose with a view to obtain the mixed oxide phases, particularly, the ferrite phases. Another group of chemical methods relies on the formation of an amorphous phase oxide, directly from the liquid precursor, so-called self-propagating combustion.¹²⁻¹⁶

The combustion reaction depends on the type of the fuel, the fuel to oxidizer ratio, the ignition temperature, etc. This combustion process is rapid and may approach the molecular mixture of the precursor solution to the mixed oxide phase.¹⁵ The combustion synthesis may be: solid state combustion and solution combustion.¹² In 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 nitrates (oxidizer) and fuels like urea/hydrazides (carbohydrazide (CH), oxalyldihydrazide (ODH), malonic acid dihydrazide (MDH), glycine, etc.

In two previous papers^{16,17} we described the obtaining of the lithium ferrite and copper ferrite from polynuclear complex compounds containing glycine as ligands. Moreover, we tried to demonstrate that the polynuclear compounds are the precursors of these ferrites, both in “the complexation method” (the thermal decomposition of the compounds) and in the self-propagating combustion (if the compounds are separated from the precursor solution).

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In this paper we investigated the systems:



in order to obtain copper ferrite and lithium ferrite, respectively, by thermal decomposition of heteropolynuclear coordination compounds containing α -alanine as ligands.

EXPERIMENTAL

1. Preparation of complex compound precursors

All chemicals: $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, LiNO_3 , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and α -alanine ($\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$) were of reagent quality (Merck). Copper and iron nitrates in the 1 : 2 ratio of cations, and, lithium and iron nitrates in the 0.5 : 2.5 ratio of cations, respectively, are dissolved in a minimum amount of water and mixed with an aqueous solution of α -alanine. The metal cations : ligand ratio was 1 : 2 : 8 and 0.5 : 2.5 : 8. To this solution, a solution of $\text{NH}_4\text{OH} : \text{H}_2\text{O}$ (1 : 1) is added until the pH rose to $\sim 6 - 7$ under continuous stirring. A brown-green precipitate is formed for the first system, until for the second a brown-red precipitate is separated. After 24h at 4°C , the complex compounds are filtered and dried on P_4O_{10} .

Elemental chemical analysis was consistent with the formula:

I $[\text{Fe}_2\text{Cu}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COO})_4(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_2](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$: Anal.: Calcd.: Fe%:11.31; Cu%:6.41; C%:21.83; N%:14.15; Found: Fe%:10.78; Cu%:6.27; C%:21.86; N%:14.83

II $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_6](\text{NO}_3)_8 \cdot \text{H}_2\text{O}$: Anal.: Calcd.: Fe%:11.75; C%:18.13; N%:16.45; Li%:0.29; Found: Fe%:12.11; C%:18.55; N%:16.34; Li%:0.32.

2. Physical measurements

In order to obtain information about the coordination of the ligands, the **IR spectra** (KBr pellets) of the compounds and of the α -alanine were recorded on a Bio-Rad FTS-135 spectrophotometer, in the $4000\text{-}400\text{ cm}^{-1}$ 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 $400\text{-}1000\text{ nm}$.

The thermal decomposition curves were obtained with a Q-1500D Paulik-Paulik-derivatograph in a static atmosphere at a heating rate of $5\text{ K}\cdot\text{min}^{-1}$, in the temperature range $20 - 1000^\circ\text{C}$, with Al_2O_3 as the inert reference compound.

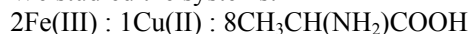
The crystalline phases of the powders were identified by **XRD** powder methods using a Rigaku-Multiflex X-ray diffractometer, with CuK_α . For quantitative analysis a step scanning technique was applied in the 2θ range $20\text{-}80$ with a step of $2^\circ/\text{min}$.

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

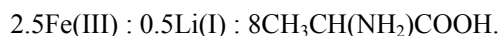
RESULTS AND DISCUSSION

It is well known that the aminoacids are very good complexing agents for transition metals as they contain one or two carboxylic groups and amino-group. The first member of the aminoacid class is the glycine which is not only a very good chelate agent, but, also, a very good fuel.^{13,18} We obtained copper ferrite and lithium ferrite using glycine, both as a ligand and a fuel.^{16,17} The second representative of this class is α -alanine. We tried to see if this aminoacid can be used as chelate agent, in order to obtain precursors for these two ferrites.

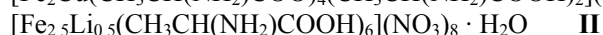
We studied the systems:



and



The formula of the compounds were established correlating elemental chemical analysis with physico-chemical measurements (IR and UV-VIS spectra, thermal analysis):



The IR spectra of the compounds are recorded in the $400\text{-}4000\text{ cm}^{-1}$ range and are compared with the spectrum of α -alanine-zwitterion (Table 1).

The IR spectra of these compounds suggest that α -alanine acts, as a monodentate ligand in the first compound **I** and as a bridge ligand between two metal ions in the second **II**: $\Delta(\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-))$ is $\sim 280\text{ cm}^{-1}$ for the compound **I** bigger than that of the α -alanine zwitterion (185 cm^{-1}), and $\sim 190\text{ cm}^{-1}$ for the

compound **II**. If the ligand acts as a bridge between two metal ions, the symmetry of the ligand doesn't change very much.

Table 1

Infrared frequencies (cm^{-1}) and band assignments of α -alanine and compounds

α -alanine	I	II	Assignment
1597 vs	1636 s	1595 s	$\nu_{\text{as}}(\text{COO}^-)$
1624 m	-	1625 s	$\delta_{\text{d}}(\text{NH}_3^+)$
1527 w	-	-	$\delta_{\text{s}}(\text{NH}_3^+)$
1453 m	1453 vs	1453 vs	$\delta_{\text{d}}(\text{CH}_3)$
1410 s	1364 vs	1397 vs	$\nu_{\text{s}}(\text{COO}^-)$
1354 m	1355 vs	1354 vs	$\nu_{\text{as}}(\text{NO}_3^-)$
1307 m	-	1308 s	$\delta_{\text{s}}(\text{CH}_3)$
1237 w	-	-	$\delta(\text{CH})$
1113 m	-	1113 m	$\rho_{\text{t}}(\text{NH}_3^+)$
1148 w	-	-	$\nu_{\text{a}}(\text{CCN})$
1015 w	1015 w	1014 w	$\rho_{\text{t}}(\text{CH}_3)$
918 w	-	-	-
851 m	851 w	841 w	$\nu_{\text{s}}(\text{CCN})$
770 w	765 w	769 w	$\nu_{\text{s}}(\text{NO}_3^-)$
646w	-	646 w	$\delta(\text{COO}^-)$
544 m	575 m	540 m	$\rho_{\text{w}}(\text{COO}^-)$ $\rho_{\text{t}}(\text{COO}^-)$

vs = very strong, s = strong, m = medium, w = weak

$[\text{Fe}_2\text{Cu}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COO})_4(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_2](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ **I**

$[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_6](\text{NO}_3)_8 \cdot \text{H}_2\text{O}$ **II**

(The value obtained for Δ of the compound **II** sustained this binding mode.)

The reflectance spectra of these compounds reveal the presence of the weak forbidden transition band in an octahedral high spin environment of the $\text{Fe}^{3+}(\text{d}^5)$ ion: ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}(\text{G})$. In the reflectance spectrum of the first compound **I**, the characteristic band of the pseudooctahedral environment of $\text{Cu}^{2+}(\text{d}^9)$ ion, ${}^2\text{E}_{\text{g}} \rightarrow {}^2\text{T}_{2\text{g}}$ is, also, present, (Table 2).

Table 2

The reflectance spectra for compounds **I** and **II**

Compound	Transition (nm)	
	${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}$	${}^2\text{E}_{\text{g}} \rightarrow {}^2\text{T}_{2\text{g}}$
I	~ 480	~ 600
II	~ 470	-

$[\text{Fe}_2\text{Cu}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COO})_4(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_2](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ **I**

$[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_6](\text{NO}_3)_8 \cdot \text{H}_2\text{O}$ **II**

In order to establish the optimal conditions for the conversion into ferrites, the thermal decomposition of the polynuclear compounds was investigated by means of the thermogravimetric analysis (Fig. 1). The complex compounds underwent stepped thermal decompositions in the range 50 – 470 °C. The alaninate iron-copper compound **I** decomposed by a process in four steps (1: 92 – 202 °C, weight loss 25.94 %; 2: 202 – 252 °C, weight loss 26.65 %; 3: 252 – 414 °C, 23.90 %; 4: 414 – 470 °C, 4.15%). The total experimental weight loss is 80.64 % and calculated weight loss is 79.09 %. The alaninate iron-lithium compound **II** decomposed by a similar process in four steps (1: 68 – 210 °C, weight loss 29.24 %; 2: 210 – 312 °C, 24.00 %; 3: 312 – 432 °C, 23.36 %; 4: 432 – 462 °C, 3.44 %). The total experimental weight loss is 80.04 % and calculated weight loss is 80.58 %.

The XRD patterns of the samples resulting from the decomposition of these two polynuclear compounds, treated 1h/800 °C showed the formation of the single-phase- CuFe_2O_4 – with tetragonal structure and the cubic phase $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ with $\alpha\text{-Fe}_2\text{O}_3$ traces, respectively (Fig. 2,a,b). The crystallite sizes of copper ferrite were 21-29 nm; those of lithium ferrite were rather bigger 33-39 nm.

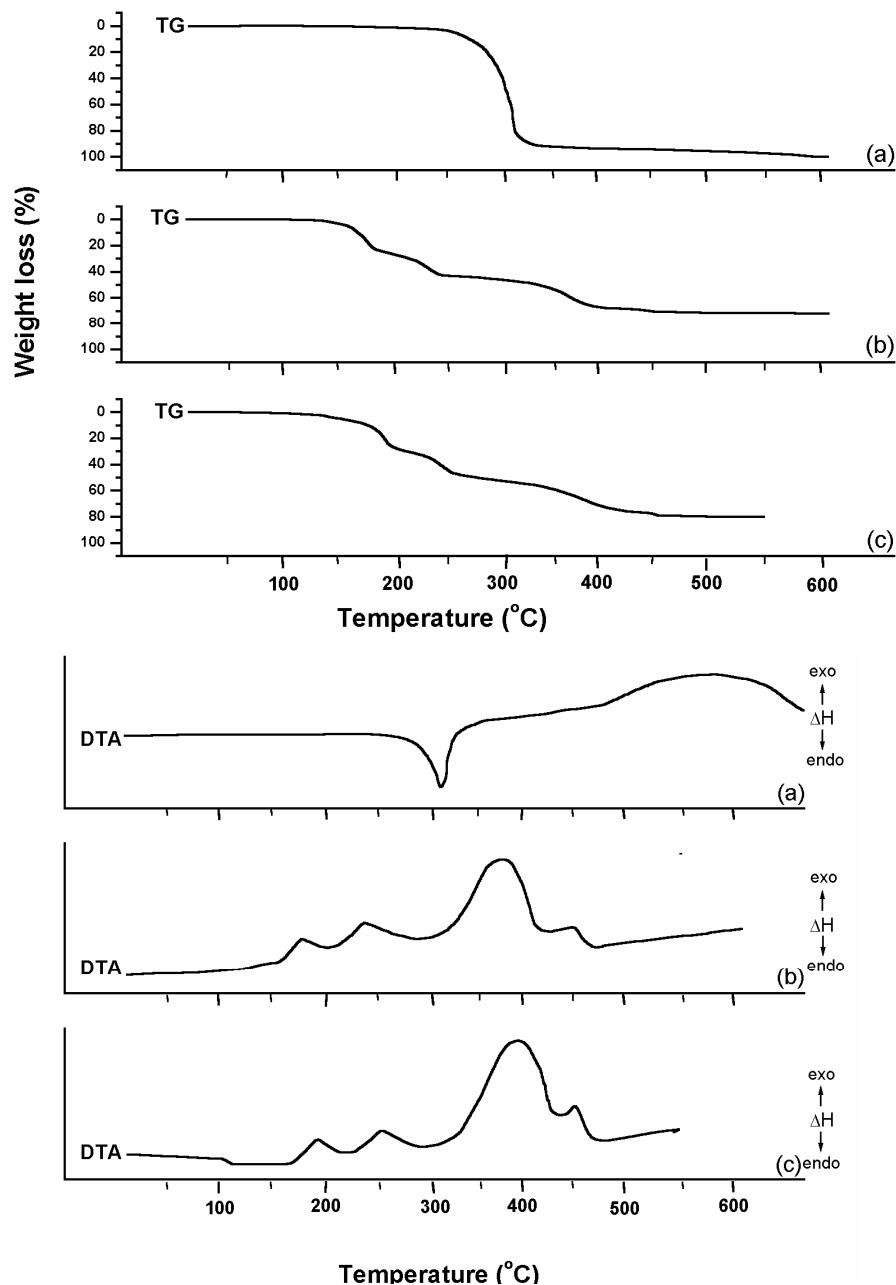


Fig. 1 – Thermal analytical curves (TG and DTA) of the α -alanine (a) and polynuclear complex compounds
 $[\text{Fe}_2\text{Cu}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COO})_4(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_2](\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$ **I** (b);
 $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_6](\text{NO}_3)_8 \cdot \text{H}_2\text{O}$ **II** (c).

The lithium ferrite was characterized with respect to the size and shape of the particles using scanning electron microscopy, at different resolutions (Fig. 3). The morphology of lithium ferrite composed of spherical particles with a large distribution and elongated particles with small dimensions (under 1 μm), due to the selected obtained method. The spherical particles have dimensions between 1 – 5 μm . The difference between the dimensions of particles from XRD and those observed by SEM is probably due to the agglomeration caused by the thermal decomposition of the precursor **II**.

To confirm the formation of the spinel ferrite phase, the IR spectra are recorded in the range 400 – 4000 cm^{-1} (Fig. 4). The spectrum of the CuFe_2O_4 indicated the presence of two intense absorption bands at $\sim 540 \text{ cm}^{-1}$ (ν_1) and at $\sim 465 \text{ cm}^{-1}$ (ν_2). The first band (ν_1) is attributed to the stretching vibration of $\text{Fe}^{3+} - \text{O}^{2-}$ in the

tetrahedral complexes and the second band (ν_2) to that of $\text{Cu}^{2+} - \text{O}^{2-}$ in the octahedral one. The bands appearing in the IR spectrum of the $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ ($\nu_1 \sim 564 \text{ cm}^{-1}$, $\nu_2 \sim 465 \text{ cm}^{-1}$) confirmed the formation of the $\alpha - \text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ phase.

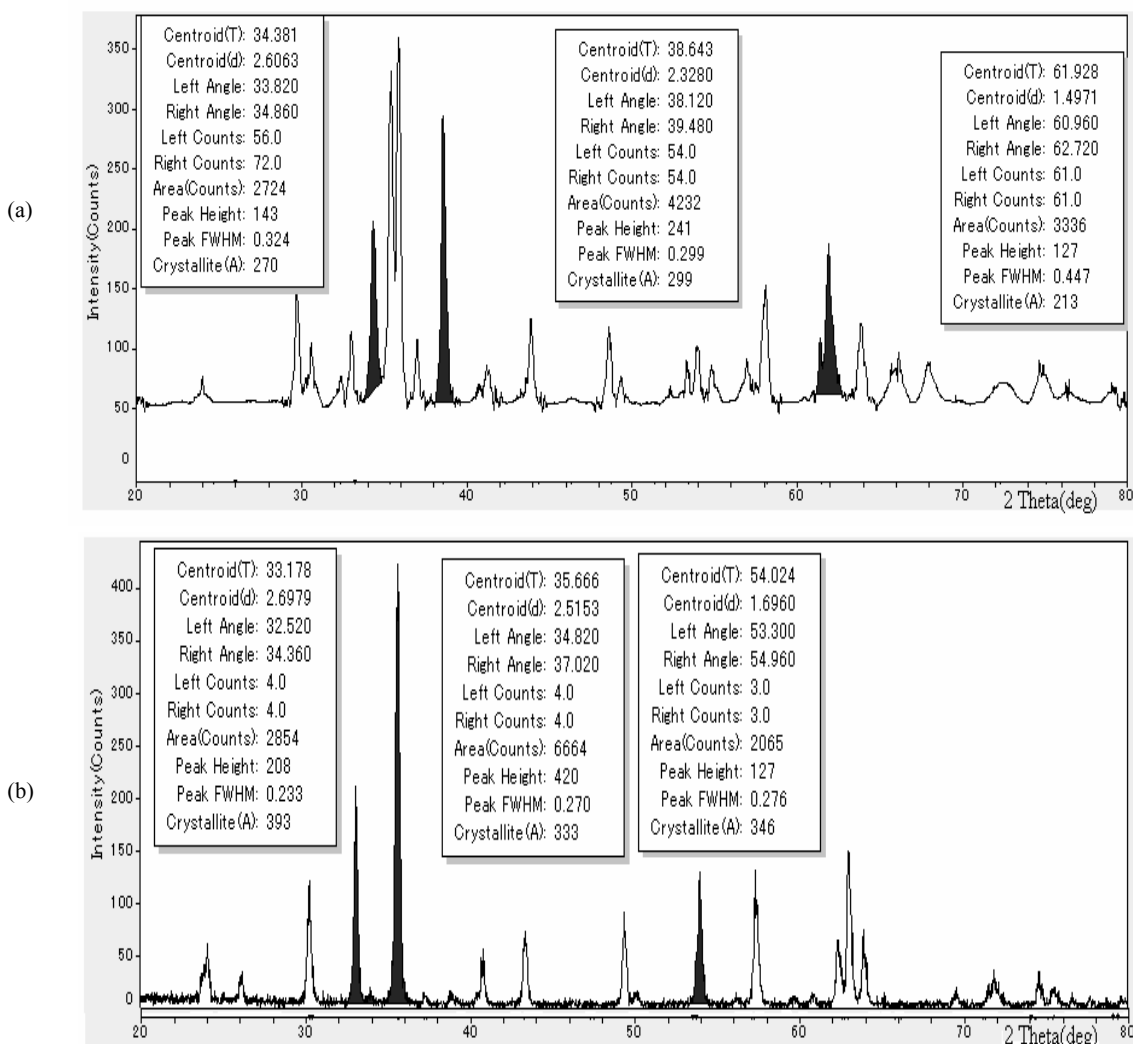


Fig. 2 – XRD patterns of the copper ferrite (a) and lithium ferrite (b) obtained by the thermal decomposition of the polynuclear complex compounds.

CONCLUSIONS

The copper ferrite with tetragonal structure and the cubic lithium ferrite were obtained by the thermal decomposition of polynuclear coordination compound precursors, in the temperature range 50 – 470 °C.

Two polynuclear coordination compounds containing α -alanine as ligand were synthesized. These compounds were characterized by chemical analysis, IR and UV-VIS spectra and magnetic measurements.

Copper and lithium ferrites were obtained between 400 – 470 °C. These ferrites were characterized by XRD, SEM and IR spectra.

The average crystallite diameter of the samples ranged between 21 – 39 nm.

We demonstrate that the thermal decomposition of the coordination compounds containing α -alanine as ligand is a “classical” one. That process is very different in comparison with that corresponding to the decomposition of glycinate complexes which are a self propagating combustion.

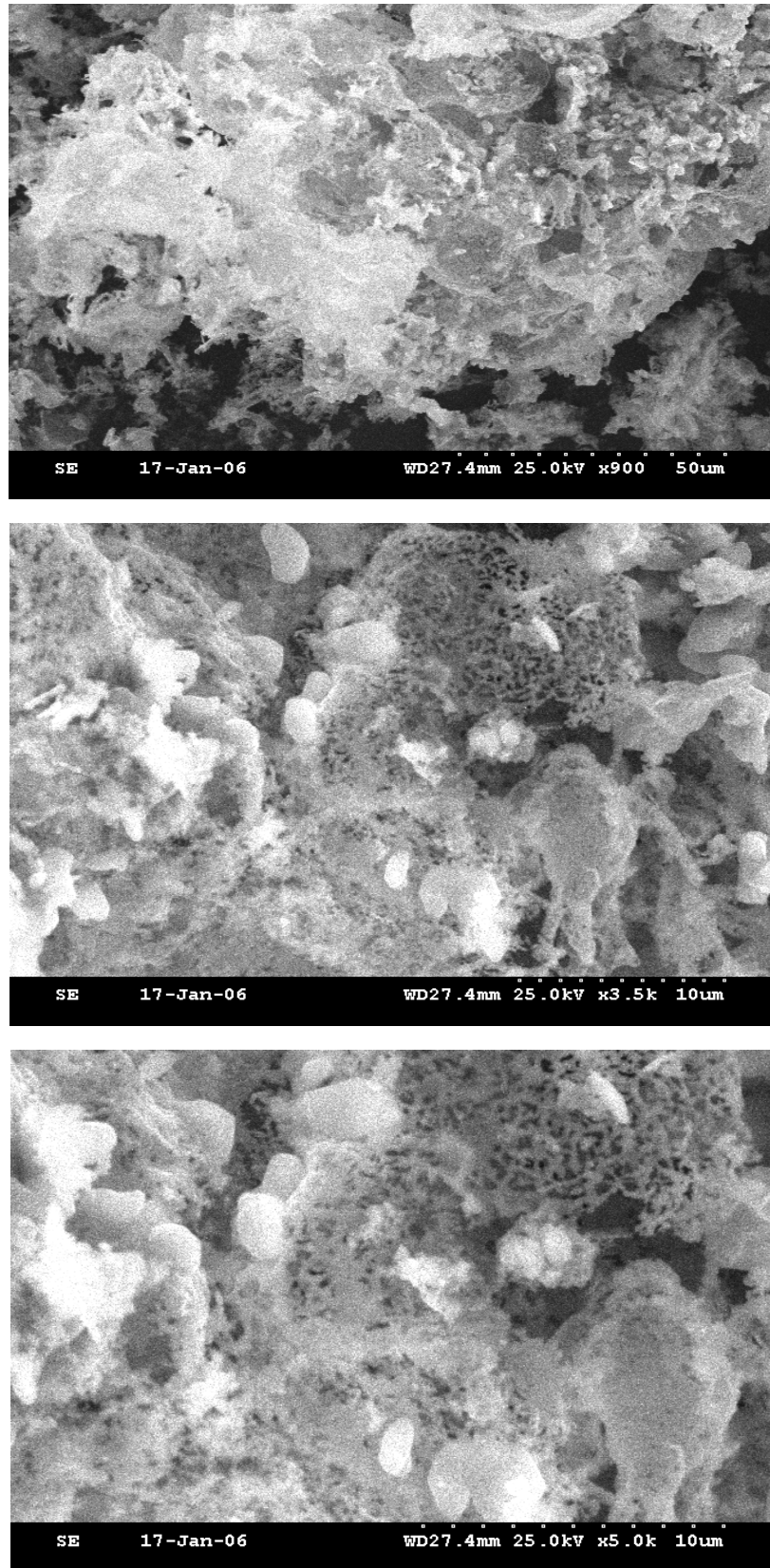


Fig. 3 – SEM of the lithium ferrite obtained by the thermal decomposition of $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH})_6](\text{NO}_3)_8 \cdot \text{H}_2\text{O}$.

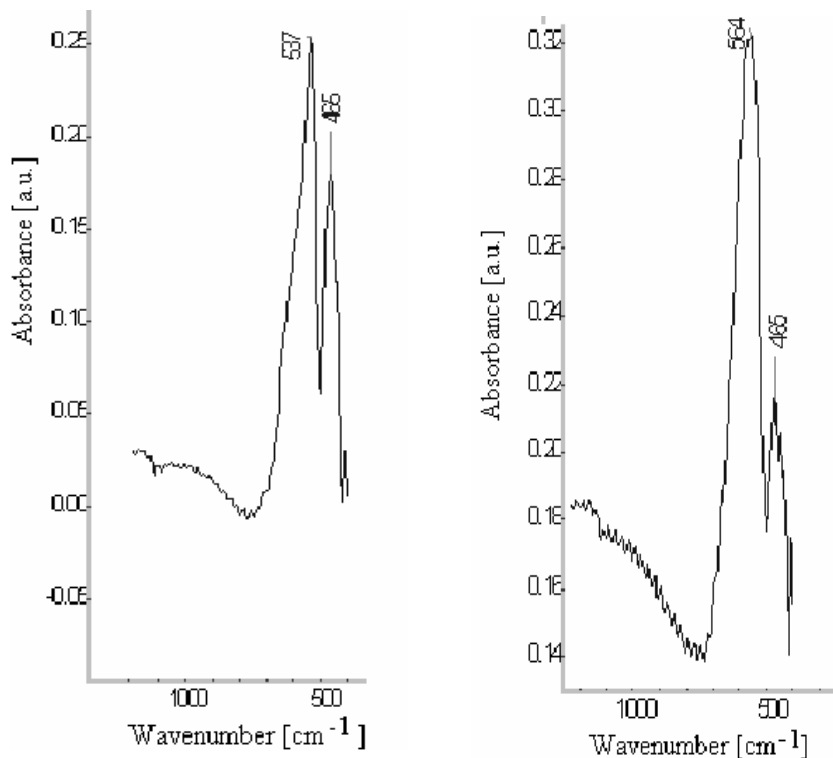


Fig. 4 – IR spectra recorded for the copper (a) and lithium (b) ferrite obtained by the thermal decomposition of the polynuclear complex compounds and annealed at 800 °C/1h.

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