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Synthesis of lithium ferrites from polymetallic carboxylates

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Abstract: Lithium ferrite was prepared by the thermal decomposition of three polynuclear complex compounds containing as ligands the anions of malic, tartaric and gluconic acid: $(NH_4)_2[Fe_{2.5}Li_{0.5}(C_4H_4O_5)_3(OH)_4(H_2O)_2]\cdot 4H_2O$ (**I**), $(NH_4)_6[Fe_{2.5}Li_{0.5}(C_4H_4O_6)_3(OH)_8]\cdot 2H_2O$ (**II**) and $(NH_4)_2[Fe_{2.5}Li_{0.5}(C_6H_{11}O_7)_3(OH)_7]$ (**III**). The polynuclear complex precursors were characterized by chemical analysis, IR and UV–Vis spectra, magnetic measurements and thermal analysis. The obtained lithium ferrites were characterized by XRD, scanning electron microscopy, IR spectra and magnetic measurements. The single α-$Li_{0.5}Fe_{2.5}O_4$ phase was obtained by thermal decomposition of the tartarate complex annealed at 700 °C for 1 h. The magnetization value $\approx$ 50 emu g^{-1} is lower than that obtained for the bulk lithium ferrite due to the nanostructural character of the ferrite. The particle size was smaller than 100 nm.

Keywords: lithium ferrite; chemical synthesis; thermogravimetric analysis (TGA); X-ray diffraction; magnetic properties.

INTRODUCTION

Nanocrystalline lithium ferrite has been investigated in the last years due to its potential use in the microwave field as a replacement for garnets or as a memory core.[1,2] Lithium ferrite has important magnetic properties, *i.e.*, a high Néel temperature, a rectangular hysteresis loop and a high dielectric constant.[3,4]

Lithium ferrite is an inverse spinel which exists in two crystalline forms: ordered, α-$Li_{0.5}Fe_{2.5}O_4$, and disordered, β-$Li_{0.5}Fe_{2.5}O_4$.[5–10]

The method of preparation plays a very important role in determining the chemical, structural and magnetic properties of spinelic ferrites. The conventional ceramic method, which involves high-temperatures sintering, often result in a low quality material; the volatility of lithium above 1000 °C affects the magnetic properties and the resistivity.[6] In order to overcome such difficulties, a

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number of wet chemical methods have been developed to prepare $LiFe_5O_8$ at low temperatures. They include the sol–gel method,[11,12] the microemulsion method,[13] hydrothermal transformations of hydroxide precursors,[14] freeze-drying of Li, Fe-formates,[15] the citrate precursors method,[10,16] and autocombustion.[17]

The nature of the precursors is very important in the synthesis of spinelic ferrites. Polynuclear coordination compounds are preferred as precursors because they can lead directly to mixed oxides by thermal decomposition.[18] A new synthesis route based on the thermal decomposition of compounds with acetylacetone-(2,4-pentadione) ligands was applied to obtain nano-sized Li-ferrites.[19]

The synthesis of nanoferrites by thermal decomposition of polynuclear complex compounds is a non-conventional method which belongs to "chimie douce" (soft chemistry). This method is sometimes referred to as the complexation method for the synthesis of ferrites. The polynuclear coordination compounds, which may be used as precursors for ferrites, should generate only volatile products on decomposition. Ligands that largely satisfy this requirement are the anions of carboxylic and hydroxycarboxylic acids, *i.e.*, acetate, oxalate, citrate, *etc*.

The goals of the present study were to synthesize polynuclear coordination compounds, precursors of lithium ferrite, containing as ligands the anions of malic, tartaric and gluconic acid; to characterize these complex compounds by IR and UV–Vis spectroscopy and magnetic measurements; to decompose them at low temperatures in order to obtain lithium ferrite; and to characterize the samples of lithium ferrite by IR spectroscopy, XRD analysis, SEM and magnetic measurements.

EXPERIMENTAL

All chemicals: $Fe(NO_3)_3\cdot 9H_2O$, $LiNO_3$, malic acid, tartaric acid and δ-gluconolactone were of reagent quality (Merck). The precursors – polynuclear coordination compounds were prepared as follows.

Iron and lithium nitrates were dissolved in the minimum amount of water and mixed with an aqueous solution of carboxylic acid in a 2.5:0.5:4 ratio Fe^{3+}:Li^{+}:malic (tartaric) acid and 2.5:0.5:8 ratio Fe^{3+}:Li^{+}:δ-gluconolactone.

Ethanol was added to the final solution until a yellow precipitate formed. The pH was raised to 5.5–6.0 by adding NH_3:H_2O (25 %):ethanol solution (1:1). The yellow polynuclear compounds were filtered, washed with ethanol and dried over P_4O_{10}.

The metal content of the polynuclear compounds was determined by atomic absorption spectroscopy with an SAA1 instrument and by gravimetric techniques; the C, H, and N values were obtained using a Carbo Erba Model 1108 CHNS-O elemental analyzer.

The IR spectra (KBr pellets) of the polynuclear coordination compounds and the lithium ferrites were recorded on a Bio-Rad FTS-135 spectrophotometer in the 4000–400 cm^{-1} region.

The thermogravimetric, TG, differential TG, DTG, and differential thermal analysis, DTA, curves were simultaneously recorded under an air atmosphere using a Shimadzu DTG-TA--51H instrument. The reference material was Al_2O_3. The heating rate was 10 °C min^{-1} in the temperature range 20–800 °C.

The XRD patterns were recorded on a Rigaku-Multiflex X-ray diffractometer using CuK_α radiation. For quantitative analysis, the step scanning technique was applied in the 2θ

range 20–80° with a scan speed of 2° min^{-1}. The particles size was determined using the Scherrer Equation.

The morphological analysis of the samples was performed by scanning electron microscopy (SEM) using a Hitachi S2600N electron microscope (image analysis with a secondary electron detector (SE)).

The magnetic measurements on the complex compounds and lithium ferrite samples are performed with a Faraday balance ($HgCo(SCN)_4$, $\chi_g = 16.44\times10^{-6}$ cgs units and metallic Ni as calibrants) and a magnetometer based on the extraction method with a resolution of 10^{-4} emu, accessible 1.5–300 K, magnetic field maximum 11 T, increment 10 Oe.

RESULTS AND DISCUSSION

Characterization of the polynuclear complex compounds

Elemental analyses of the polynuclear coordination compounds containing as ligands: malate, tartarate and gluconate anions (**I**, **II**, and **III**, respectively), were consistent with the formula:

$(NH_4)_2[Fe_{2.5}Li_{0.5}(C_4H_4O_5)_3(OH)_4(H_2O)_2]\cdot4H_2O$ ***(I)***. Anal. Calcd.: Fe, 18.63; Li, 0.465; C, 19.16; H, 4.79; N, 3.73 %. Found: Fe, 18.76; Li, 0.46; C, 19.28; H, 4.88; N, 3.84 %.

$(NH_4)_6[Fe_{2.5}Li_{0.5}(C_4H_4O_6)_3(OH)_8]\cdot2H_2O$ ***(II)***. Anal. Calcd.: Fe, 16.13; Li, 0.403; C, 16.60; H, 5.53; N, 9.68 %. Found: Fe, 15.92; Li, 0.395; C, 16.64; H, 5.60; N, 9.85 %.

$(NH_4)_2[Fe_{2.5}Li_{0.5}(C_6H_{11}O_7)_3(OH)_7]$ ***(III)***. Anal Calcd.: Fe, 15.84; Li, 0.396; C, 24.44; H, 5.43; N, 3.17 %.Found: Fe, 16.03; Li, 0.40; C, 24.46; H, 5.26; N, 3.26 %.

The IR spectra of these polynuclear complex compounds suggest that the hydroxycarboxylate anions are coordinated to the metal ions through the COO^- and C–OH groups.

The band at 1700–1730 cm^{-1} of the free carboxylic acid, assigned to $\nu_{C=O}$, is replaced in the spectra of the compounds by two intense bands, $\nu_{as}(OCO) \approx$ 1620–1630 cm^{-1} and $\nu_s(OCO) \approx 1384$ cm^{-1}. On the basis of spectroscopic criteria,[20] the magnitude of the separation $\Delta\nu = \nu_{as} - \nu_s$ may be indicative for establishing the mode of coordination of carboxylate ions. Thus, $\Delta\nu$ values in the range 140–160 cm^{-1}, *i.e.*, higher than those observed for ionic compounds ($\Delta\nu(Na_2L) = 120$ cm^{-1}) suggest a bridging bidentate bonding. On the other hand, values of $\Delta\nu > 180$ cm^{-1} are characteristic for monodentate coordination.

The splitting of the $\nu_{as}(OCO)$ vibration detected in the IR spectrum of the malate complex, compound **I**, suggests two different coordination modes for the $C_4H_4O_5^{2-}$: monodentate bonding ($\nu_{as}(OCO) \approx 1620$ cm^{-1}; $\nu_s(OCO) \approx 1380$ cm^{-1}) and bridging bidentate bonding ($\nu_{as}(OCO) \approx 1560$ cm^{-1}; $\nu_s(OCO) \approx 1380$ cm^{-1}).[20]

For compounds **II** ($\nu_{as}(OCO) \approx 1621$ cm^{-1}; $\nu_s(OCO) \approx 1385$ cm^{-1}) and **III** ($\nu_{as}(OCO) \approx 1630$ cm^{-1}; $\nu_s(OCO) \approx 1384$ cm^{-1}), only the monodentate coordination mode was detected.

An analysis of these spectra within the 1000–1100 cm^{-1} range reveals a considerable difference between the spectra of the free acids and the spectra of the compounds. The peak assigned to the C–O stretching vibration of the secondary OH groups, which appears at ≈ 1100–1097 cm^{-1} in the spectra of the free acids, is splitted and shifted towards lower frequencies (1080–1040 cm^{-1}) in the IR spectra of the coordination compounds. The splitting can be explained by a different bonding of the secondary OH groups present in the molecule of the hydroxycarboxylate anions. One can advance the hypothesis that the secondary OH groups coordinate to two different metal ions.

The reflectance spectra of the polynuclear complex compounds revealed the presence of weak forbidden transition bands with the Fe^{3+} (d^5) in an octahedral high spin configuration ($^6A_{1g} \rightarrow {}^4T_{2g}(G)$ at ≈ 540 nm and $^6A_{1g} \rightarrow {}^4A_{1g},{}^4E_g(G)$ at ≈ 450 nm).[21]

All the compounds were paramagnetic. The magnetic moments were calculated: $\boldsymbol{\mu} = 6.30\ \mu_B$ for **I**, $\boldsymbol{\mu} = 5.93\ \mu_B$ for **II** and $\boldsymbol{\mu} = 6.80\ \mu_B$ for **III**. The experimental values of the magnetic moments were lower than the theoretical ones ($\boldsymbol{\mu} = 8.53\ \mu_B$). The difference can be explained by antiferromagnetic interactions between the metal ions.

In order to establish the optimal conditions for the conversion of polynuclear complex compounds into spinelic lithium ferrites, their thermal decompositions were investigated by of thermogravimetry. The thermal behaviors of the complex compounds **I**, **II** and **III** are presented in Fig. 1.

Based on thermogravimetric analysis and complementary measurements (IR spectra), the following decomposition pathways may be assumed for these compounds:

$$(NH_4)_2[Li_{0.5}Fe_{2.5}(C_4H_4O_5)_3(OH)_4(H_2O)_2]\cdot 4H_2O\ (\mathbf{I}) \xrightarrow{40-160\ ^\circ C}$$

$$(NH_4)_2[Li_{0.5}Fe_{2.5}(C_4H_4O_5)_3(OH)_4(H_2O)_2] \xrightarrow{160-245\ ^\circ C}$$

$$[Li_{0.5}Fe_{2.5}(CO_3)_{2.5}O_{1.5}] \xrightarrow{245-570\ ^\circ C} Li_{0.5}Fe_{2.5}O_4$$

$$(NH_4)_6[Li_{0.5}Fe_{2.5}(C_4H_4O_6)_3(OH)_8]\cdot 2H_2O\ (\mathbf{II}) \xrightarrow{40-140\ ^\circ C}$$

$$(NH_4)_6[Li_{0.5}Fe_{2.5}(C_4H_4O_6)_3(OH)_8] \xrightarrow{140-237\ ^\circ C}$$

$$[Li_{0.5}Fe_{2.5}(C_2O_4)_4] \xrightarrow{237-285\ ^\circ C} [Li_{0.5}Fe_{2.5}O_3(CO_3)] \xrightarrow{285-370\ ^\circ C} Li_{0.5}Fe_{2.5}O_4$$

$$(NH_4)_2[Li_{0.5}Fe_{2.5}(C_6H_{11}O_7)_3(OH)_7]\ (\mathbf{III}) \xrightarrow{400\ ^\circ C} Li_{0.5}Fe_{2.5}O_4$$

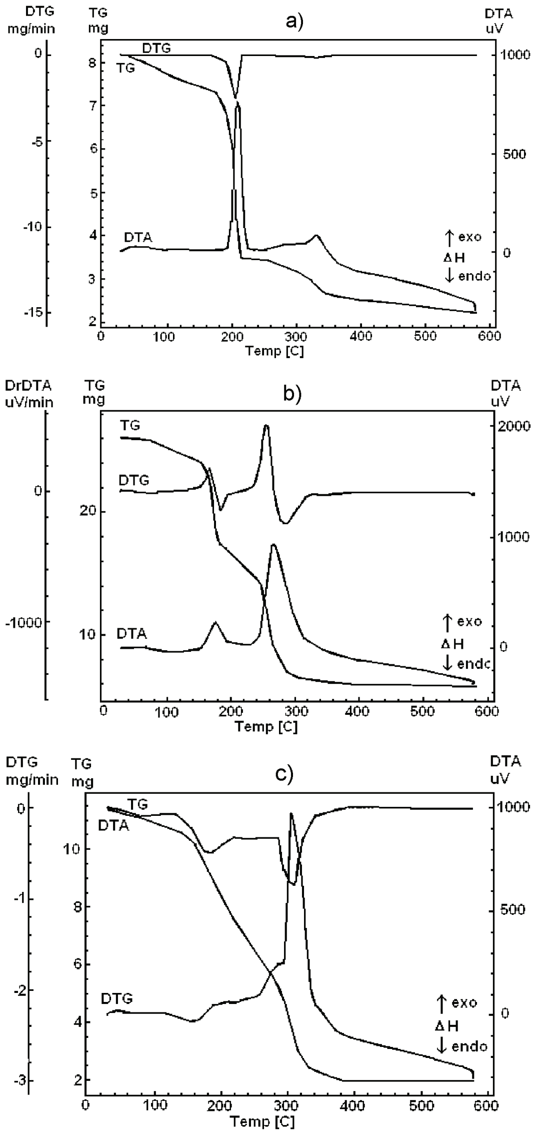


Fig. 1. Thermal analytical curves (TG, DTG and DTA) of the polynuclear complex compounds: $(NH_4)_2[Fe_{2.5}Li_{0.5}(C_4H_4O_5)_3(OH)_4(H_2O)_2]\cdot 4H_2O$ (a), $(NH_4)_6[Fe_{2.5}Li_{0.5}(C_4H_4O_6)_3(OH)_8]\cdot 2H_2O$ (b) and $(NH_4)_2[Fe_{2.5}Li_{0.5}(C_6H_{11}O_7)_3(OH)_7]$ (c).

Characterization of the lithium ferrites

The XRD patterns of the mixed oxides obtained by thermal decomposition of the precursors, at ≈ 570 °C for **I** and ≈ 400 °C for **II** and **III**, indicated very poor crystallinity. In order to increase the crystallinity of the samples, two values of annealing temperature were chosen: 700 °C and 800 °C. After annealing at a temperature of 700 °C for 1 h and slow cooling, α-$Li_{0.5}Fe_{2.5}O_4$ was formed; all the required peaks were present in the diffraction pattern. No secondary phases were detected in the pattern of the sample obtained by the thermal decomposition of compound **II** (Fig. 2a). For the other two samples obtained by decomposition of **I** and **III**, the spinel phase $Li_{0.5}Fe_{2.5}O_4$ was impure and contained also α-Fe_2O_3. Further increasing of the annealing temperature to 800 °C resulted in an augmentation of α-Fe_2O_3 in these two samples and the appearance of α-Fe_2O_3 in the sample obtained by decomposition of compound **II** (Fig. 2b).

According to previously published results,[8–10,14] the single lithium ferrite phase obtained by decomposition of compound **II** annealed at 700 °C for 1 h, followed by slow cooling to room temperature showed the “ordered” ($P4_132$) spinel structure, *i.e.*, α-$Li_{0.5}Fe_{2.5}O_4$. The average crystallite size was between 30–40 nm.

Scanning electron micrographs of the lithium ferrite obtained by thermal decomposition of compound **II**, at different resolutions, indicate that this material tended to agglomerate because the particles were very small (Fig. 3).

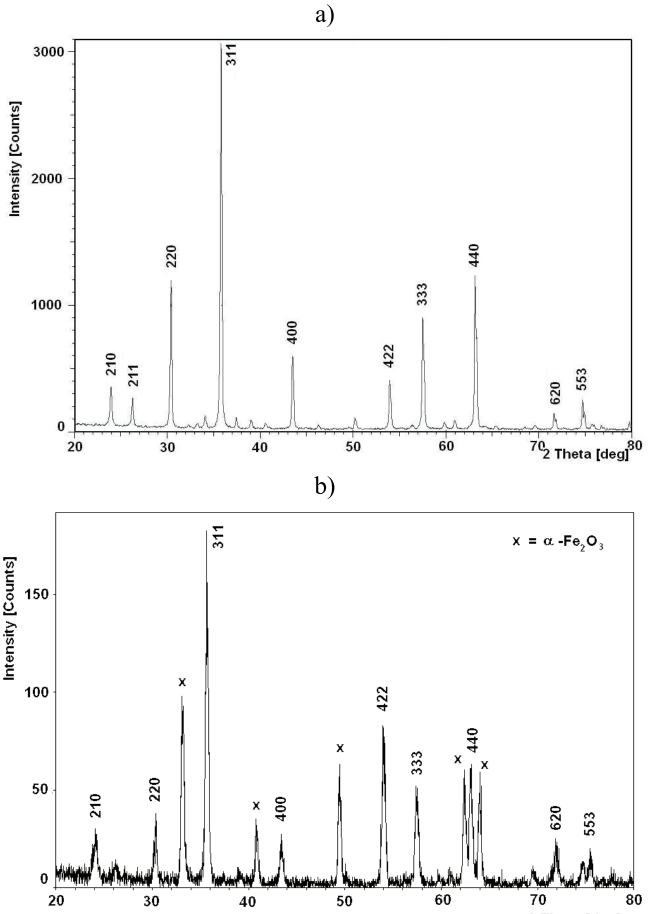


Fig. 2. X-Ray diffraction patterns of $Li_{0.5}Fe_{2.5}O_4$, obtained by thermal decomposition of $(NH_4)_6[Fe_{2.5}Li_{0.5}(C_4H_4O_6)_3(OH)_8]\cdot 2H_2O$ at: a) 700 °C and b) 800 °C.

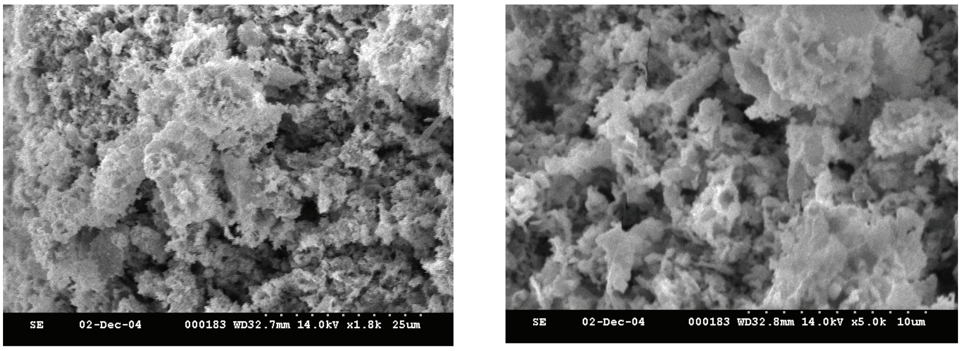


Fig. 3. SEM of the lithium ferrite obtained by thermal decomposition of $(NH_4)_6[Fe_{2.5}Li_{0.5}(C_4H_4O_6)_3(OH)_8]\cdot 2H_2O$.

To confirm the formation of the spinelic phase, the IR spectra of these samples were recorded. All the spectra exhibit four bands corresponding to the four IR active fundamentals inferred by group theory considerations. These bands belong to the same representation, T_{1u}, and appear in the following regions of the spectra: ν_1 (630–560 cm^{-1}), ν_2 (525–390 cm^{-1}), ν_3 (380–335 cm^{-1}) and ν_4 (255–170 cm^{-1}).[5,16,22–24]

The ν_1 band may be attributed to vibrations of the MO_6 octahedral, the ν_2 and ν_3 are assigned to complex vibrations involving both octahedral and tetrahedral sites, and the ν_4 band is assigned to a vibration of the tetrahedral sublattice. The infrared-active modes belong to the same symmetry T_{1u}.[6]

The presence in the IR spectra of bands at ≈ 590, 550, 470 cm^{-1} with shoulders at ≈ 700 and ≈ 680 cm^{-1} substantiate the formation of the "ordered" spinelic phase.[6,25]

The magnetization *versus* *H*/*T* for lithium ferrite obtained by thermal decomposition of compound **II** annealed at 700 °C for 1 h is presented in Fig. 4.

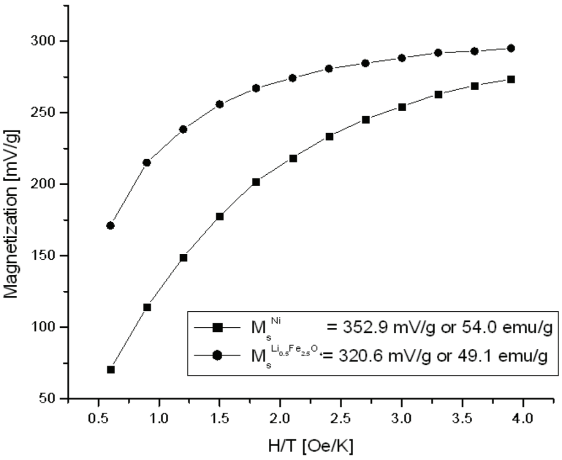
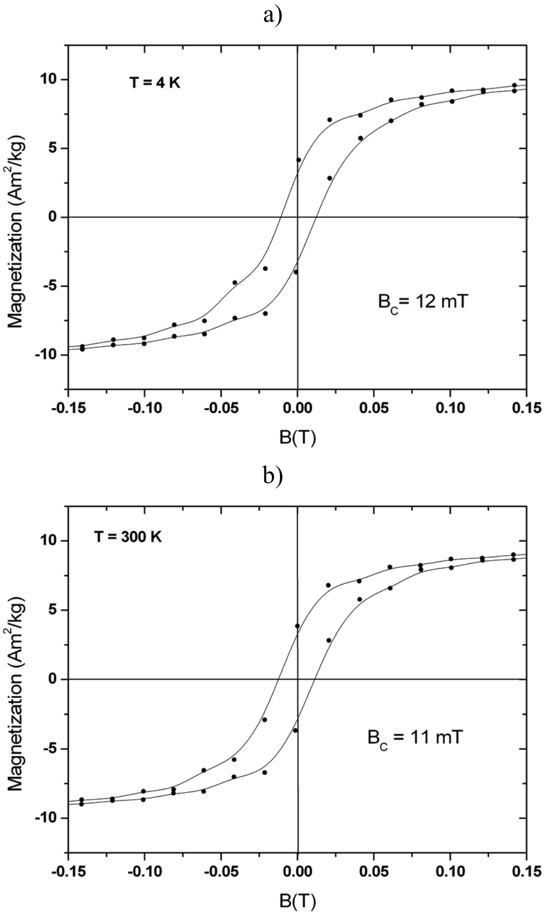


Fig. 4. The saturation magnetization for the lithium ferrite obtained by thermal decomposition of $(NH_4)_6[Fe_{2.5}Li_{0.5}(C_4H_4O_6)_3(OH)_8]\cdot 2H_2O$.

The value of the saturation magnetization (≈ 50 emu g^{-1}) is higher than that of the same sample annealed at 800 °C for 1 h. The presence of α-Fe_2O_3 impurities lowered the magnetization of the sample. The magnetization value ≈ 50 emu g^{-1} is still lower than that obtained for bulk lithium ferrite, in accordance with literature data,[26] due to the nanostructural character of the ferrite.

The hysteresis loops for the lithium ferrite obtained by thermal decomposition of compound **II** and annealed at 800 °C for 1 h are given in Fig. 5. These indicate that the lithium ferrite is a soft magnetic material, revealing minimal hysteresis.[26] It can also been observed from Fig. 5 that the loops deviate from rectangularity. The shape and width of the loop depend not only on the chemical composition and the thermal treatment but also on the particle size.[27] The width of the loop decreases with decreasing particle size. The value of coercive field is very small and approximately constant with temperature.


a)

b)

Fig. 5. The hysteresis loop for the lithium ferrite obtained by thermal decomposition of $(NH_4)_6[Fe_{2.5}Li_{0.5}(C_4H_4O_6)_3(OH)_8]\cdot 2H_2O$ at: a) 4.0 K and b) 300 K.

CONCLUSIONS

Thermal decomposition of polynuclear iron–lithium complex compounds containing as ligands carboxylate anions was found to be a promising method for obtaining nanoferrite α-$Li_{0.5}Fe_{2.5}O_4$.

The formation temperature of α-$Li_{0.5}Fe_{2.5}O_4$.from the malate complex is 570 °C, while for the tartarate and gluconate compounds it is 400 °C.

Single phase α-$Li_{0.5}Fe_{2.5}O_4$.was obtained by thermal decomposition of compound **II** at 700 °C for 1 h, followed by slow cooling. The α-$Li_{0.5}Fe_{2.5}O_4$.phases obtained by thermal decomposition of compound **I** and **III** were impure and contained α-Fe_2O_3.

All the obtained α-$Li_{0.5}Fe_{2.5}O_4$ phases were nanostructured with a size smaller than 100 nm. Due to this nanostructural character, the value of the magnetization was lower than that obtained for bulk lithium ferrite.

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ИЗВОД

СИНТЕЗА ЛИТИЈУМ-ФЕРИТА ИЗ ПОЛИМЕТАЛНИХ КАРБОКСИЛАТА

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Литијум-ферит је добијен термичком разградњом три полинуклеарна комплексна једињења која као лиганде садрже анјоне малеинске, винске и глуконске киселине: $(NH_4)_2[Fe_{2.5}Li_{0.5}(C_4H_4O_5)_3(OH)_4(H_2O)_2]\cdot 4H_2O$ (**I**), $(NH_4)_6[Fe_{2.5}Li_{0.5}(C_4H_4O_6)_3(OH)_8]\cdot 2H_2O$ (**II**) и $(NH_4)_2[Fe_{2.5}Li_{0.5}(C_6H_{11}O_7)_3(OH)_7]$ (**III**). Полинуклерна комплексна полазна једињења окарактерисана су хемијском анализом, IR и UV–Vis спектрима, магнетним мерењима и термогравиметријском анализом. Добијени литијум-ферит окарактерисан је методама дифракције x-зрака и скенирајуће електронске микроскопије, као и IR спектрима и магнетним мерењима. Регистровано је да је добијена једино α-$Li_{0.5}Fe_{2.5}O_4$ фаза термичком разградњом тартаратног комплекса на температури 700 °C током 1 h. Вредност магнетизације од око 50 emu g^{-1} мања је од оне добијене за компактни литијум-ферит због наноструктурних карактеристика синтетисаног ферита. Величина честица мања је од 100 nm.

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