

LITHIUM FERRITES OBTAINED BY THERMAL DECOMPOSITION OF UREATE COMPLEX COMPOUNDS

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Lithium ferrites have been obtained by combustion reaction of ureate precursors. Various physico-chemical techniques: IR spectra, XRD, magnetic determinations, Mössbauer spectra have been employed to characterize the precursors and end products. The single spinel phase α -Li_{0.5}Fe_{2.5}O₄ with saturation magnetization of ~ 56 Am²/kg were achieved from ureate precursor with ratio 2.5Fe³⁺ : 0.5Li⁺ : 7urea after a thermal treatment at 800° C/1h.

INTRODUCTION

Lithium ferrite (Li_{0.5}Fe_{2.5}O₄) is an inverse spinel which exists in two crystalline forms: ordered, α -Li_{0.5}Fe_{2.5}O₄, and disordered, β -Li_{0.5}Fe_{2.5}O₄.¹

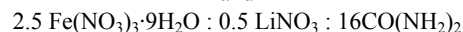
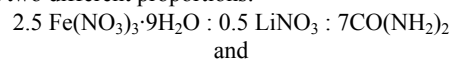
Lithium ferrites have been extensively studied owing their electrical and magnetic properties.² Therefore, lithium ferrites have great potential for technological applications such as: microwave devices, memory core, power transformation in electronics, antennas, high-speed digital tapes, gas sensing and ferrofluids.^{3,4}

It is well known that the synthesis route plays a very important role in determining the chemical, structural and magnetic properties of the ferrites. Thus, the synthesis and characterization of ferrites have received considerable attention in order to improve their properties. Numerous nonconventional routes have been employed to synthesize ferrites. Among these methods a special place is occupied by the complexation method and the self-propagating combustion.⁴⁻¹²

In a previous work we reported the synthesis of lithium ferrites by self-propagating combustion method using glycine as fuel.⁹ In this study, we explored the possibility of obtaining lithium ferrite, by combustion reaction from ureate complex compounds as precursors.

EXPERIMENTAL

All chemicals: Fe(NO₃)₃·9H₂O, LiNO₃ and urea (CO(NH₂)₂) were of reagent grade quality (Merck). Iron and lithium nitrates in the 2.5:0.5 ratio of cations are mixed with urea, in two different proportions:



in the agate mortar. The nitrates and urea were solved in the hydration water of the salts that means a very concentrated solution. The mixing is kept on till homogenous red-brown ureate compounds were obtained. These compounds were dried on P₄O₁₀. In order to obtain lithium ferrites by combustion reaction of these compounds, they are placed on a heater and they are maintained at 250-300 °C. Initially, they underwent dehydration, followed by the decomposition with evolution of a high amount of gases and heat. They burned with flames. *In situ*, the temperature can be attained ~1000° C, in a few minutes. The end product is a foam powder which requires a calcination step at 800° C/1h to improve the crystallinity.

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

IR spectra (KBr pellets) of the ureate compounds and the lithium ferrites were recorded on a Bio – Rad FTS-135 spectrophotometer in the 4000-400 cm⁻¹ region.

The XRD patterns were recorded by a Rigaku-Multiflex X-ray diffractometer using CuK α radiation.

The magnetic measurements of complex compounds and lithium ferrite samples were performed with a Faraday balance

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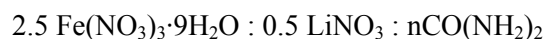
(HgCo(SCN)₄, $\chi_g=16.44 \times 10^{-6}$ cgs units and metallic Ni as calibrants) and a magnetometer based on the extraction method with a resolution of 10^{-4} emu, accessible 1.5 – 300 K, magnetic field max 11 T, increment 10 Oe.

The Mössbauer spectra were obtained at room temperature with a constant acceleration spectrometer (PROMEDA type equipment) with a 10 mCi ⁵⁷Co (Rh) source. The α -Fe foil (Amersham, England) was used to calibrate the Mössbauer spectrometer in a velocity range of ± 10 mm/s. The Mössbauer spectra obtained were least square fitted to the hypothesis of Lorentzian line shape.

RESULTS AND DISCUSSION

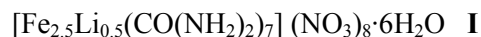
The property of urea to form ureates with inorganic salts has been known for over 50 years. It is, also, known, that urea is a very good fuel, used in the solution-combustion synthesis. The system nitrates-urea usually is used in this synthesis method.¹³⁻¹⁵

We have investigated the following system(s):

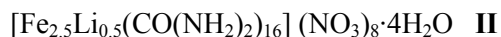


where $n=7;16$

Elemental analyses of the ureate complex compounds were consistent with the formula:



Anal. Calcd/Found: C%:7.19/7.28; H%:3.43/3.50; Fe%:11.99/12.00; Li%:2.99/3.00; N%:26.38/26.45.



Anal. Calcd./Found: C%:11.49/11.61; H%:4.31/4.56; Fe%:8.38/8.41; Li%:2.09/2.10; N%:33.50/33.65.

The IR spectra of these compounds (400 – 4000 cm^{-1}) suggested that urea acts as monodentate ligand by the oxygen atom (Table 1). The band assigned to νCO vibration present in the spectrum of urea at $\sim 1678 \text{ cm}^{-1}$ is shifted at lower frequencies in these spectra ($\sim 1655 \text{ cm}^{-1}$ for **I**, $\sim 1630 \text{ cm}^{-1}$ for **II**), unlike the bands assigned to the vibration of the $-\text{NH}_2$ groups which remained almost unmodified. The spectra of both compounds revealed the presence of the bands due to the vibration modes of NO_3^- ions ($\nu\text{NO}_3^- \sim 1383 \text{ cm}^{-1}$ and $\rho\text{NO}_3^- \sim 819 \text{ cm}^{-1}$ for **I**, $\nu\text{NO}_3^- \sim 1378 \text{ cm}^{-1}$ and $\rho\text{NO}_3^- \sim 832 \text{ cm}^{-1}$ for **II**).

Table 1

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

Urea	I	II	Assignment
	3483 m		
3448 vs	3432 s	3455 s	νNH
3343 s	3346 s	3358 s	$\nu_{\text{sym}}\text{NH}_2$
3256 sh	3241 m		
		3197 m	
	1709 m		
1678 vs	1655 vs	1630 vs	$\nu\text{CO} + \delta\text{NH}$
1609 vs	1569 s	1567 s	
	1509 m		
1466 vs			$\nu\text{C-N} + \delta\text{NH}$
		1497 s	
	1383 vs	1378 vs	νNO_3^-
	1359 vs		
	1317 s		
1153 m	1153 w	1162 m	ρNH_2 (in plane)
1055 w	1034 w	1030 m	
	1018 w		
	902 w		
	819 w	832 w	ρNO_3^-
		764 w	ρNH_2 (out of plane) + ΦCN
		613 m	
551 s	550 m	540 w	
486 s			
	447 w		$\nu\text{M-O}$

I: $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$; **II**: $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_{16}](\text{NO}_3)_8 \cdot 4\text{H}_2\text{O}$
vs = very strong; s = strong; m = medium; w = weak; sh = shoulder

Both compounds are paramagnetic. The experimental values of magnetic moments at room

temperature are $\mu=6.93$ BM for the first compound and 9.47 BM for the second. The value of the

magnetic moment of the first compound lower than the theoretical one ($\mu=9.93$ BM) suggests the presence of the antiferromagnetic interactions between metal ions.

The paramagnetic behavior of the compound $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ is confirmed

by the presence in Mössbauer spectrum, at room temperature, of a single quadrupole doublet (Fig. 1a). The Mössbauer parameters (Table 2) reveal, for the complex compound **I**, the presence of Fe^{3+} ions in an octahedral coordination, strong distortion.

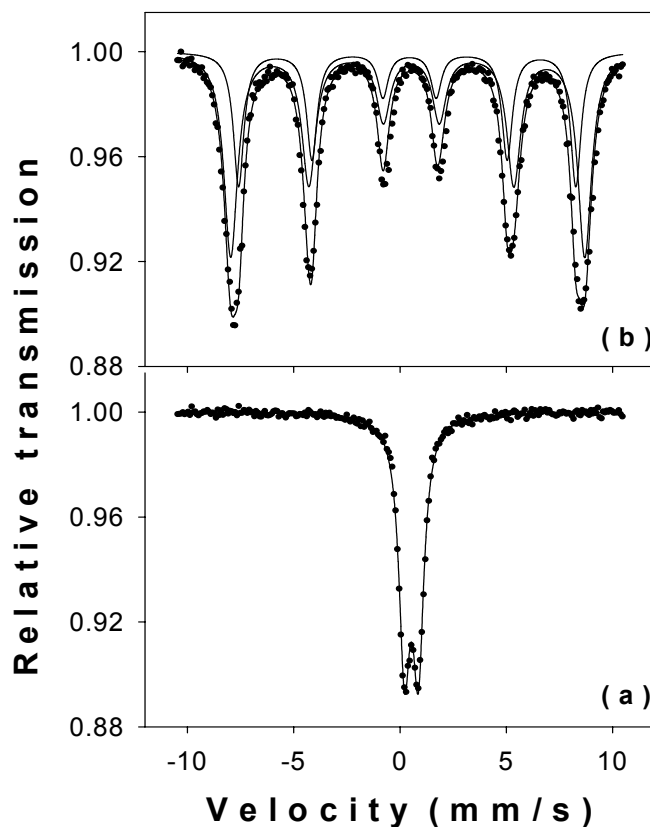


Fig. 1 – Mössbauer spectra of: (a) compound $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ (**I**) and (b) lithium ferrite obtained by the thermal decomposition of the compound $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ (**I**), calcinated at $800\text{ }^\circ\text{C}/1\text{h}$.

Table 2

Mössbauer fit parameters for the compound **I** and lithium ferrite

Compound	H_{hf} (T)	IS* (mm/s)	QS** (mm/s)	Relative area (%)	Site/phase assignment
$[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ (I)	-	0.43	0.65	100	Fe^{III} , strong distorted (octahedral)
LiFe_5O_8	49.1	0.28	-0.11	36.8	A(tetra) α - LiFe_5O_8
	51.6	0.35	-0.17	63.2	B(octa) α - LiFe_5O_8

* IS is given relative to α -Fe

** QS is the quadrupole shift

In order to obtain lithium ferrites, the ureate complex precursors were submitted to a combustion process (see Experimental) (Fig. 2).

The XRD patterns recorded on the sample obtained by thermal decomposition of compound $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ (**I**) shows the

formation of the single-phase α - $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ (Fig. 3a), while in the case of the sample obtained from precursor $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_{16}](\text{NO}_3)_8 \cdot 4\text{H}_2\text{O}$

(II) it can be observed the formation of α - $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ as a main product together with α - Fe_2O_3 as impurity (Fig. 3b).



Fig. 2 – Lithium ferrite obtained by the thermal decomposition of the compound $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ (I) calcinated at $800^\circ\text{C}/1\text{h}$.

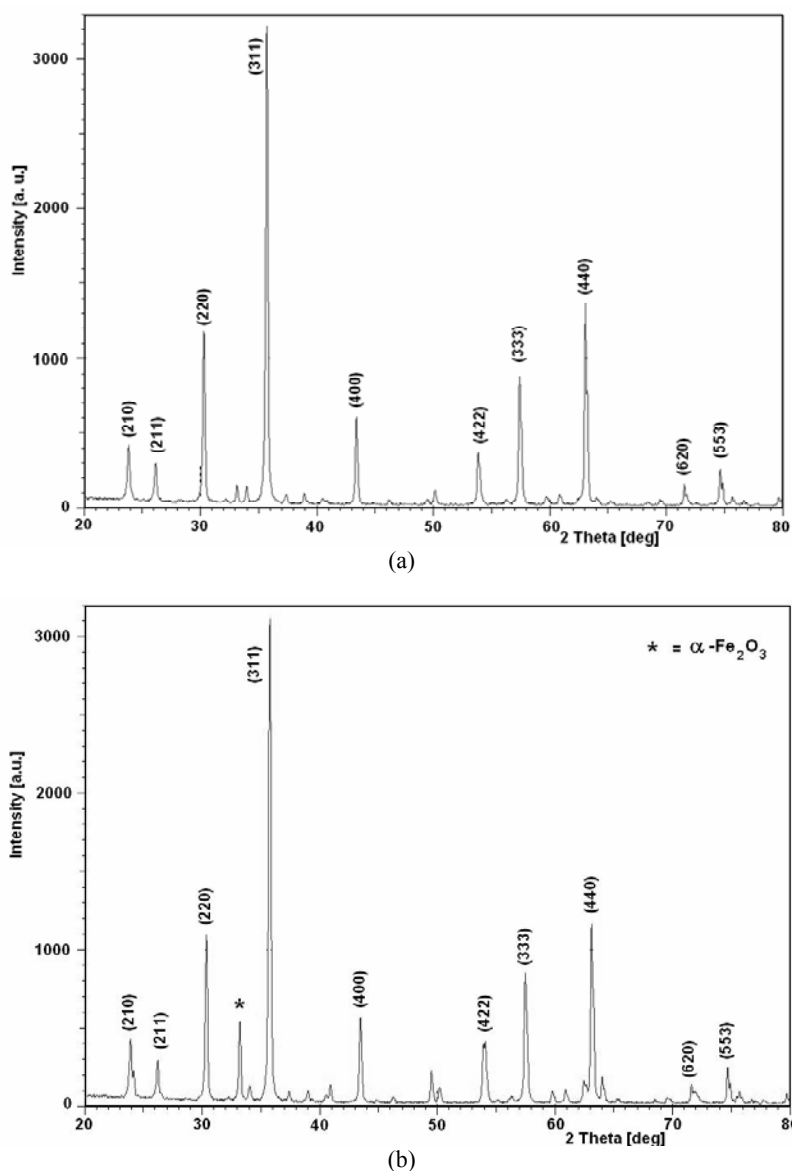


Fig. 3 – XRD patterns of the lithium ferrite obtained by the thermal decomposition of the compounds: (a) $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ (I) and (b) $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_{16}](\text{NO}_3)_8 \cdot 4\text{H}_2\text{O}$ (II), calcinated at $800^\circ\text{C}/1\text{h}$.

To confirm the formation of the spinel phase, the infrared spectra were recorded in the range 400 – 4000 cm^{-1} . The presence in the IR spectra of bands at 590, 549, 471 cm^{-1} with shoulder at ~ 700 and ~ 680 cm^{-1} sustain the formation of the α - $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ phase.¹⁶

The Mössbauer parameters for the lithium ferrite obtained by the combustion reaction of the ureate compound **I** confirmed the formation of the spinel phase α - $\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$. The Mössbauer spectrum could be fitted with two discrete sextets (Fig. 1b). The sextet with IS 0.28 mm/s has been attributed to Fe^{3+} ions in the tetrahedral (A) sites of spinel structure. The

sextet with IS 0.35 mm/s is assigned to Fe^{3+} ions in octahedral (B) sites. The quadrupole shift (QS) computed for A and B sites are -0.11 and -0.17 mm/s, respectively (Table 2). Variations of magnetization with applied magnetic field for the lithium ferrites at temperatures 4.5 K, 150 K, 225 K and 295 K are presented in Fig. 4. The saturation magnetizations at 4.5 K are 56.6 Am^2/kg for lithium ferrite obtained by thermal decomposition of compound **I** and 53.8 Am^2/kg for lithium ferrite obtained by thermal decomposition of compound **II**, in agreement with literature data.¹⁷

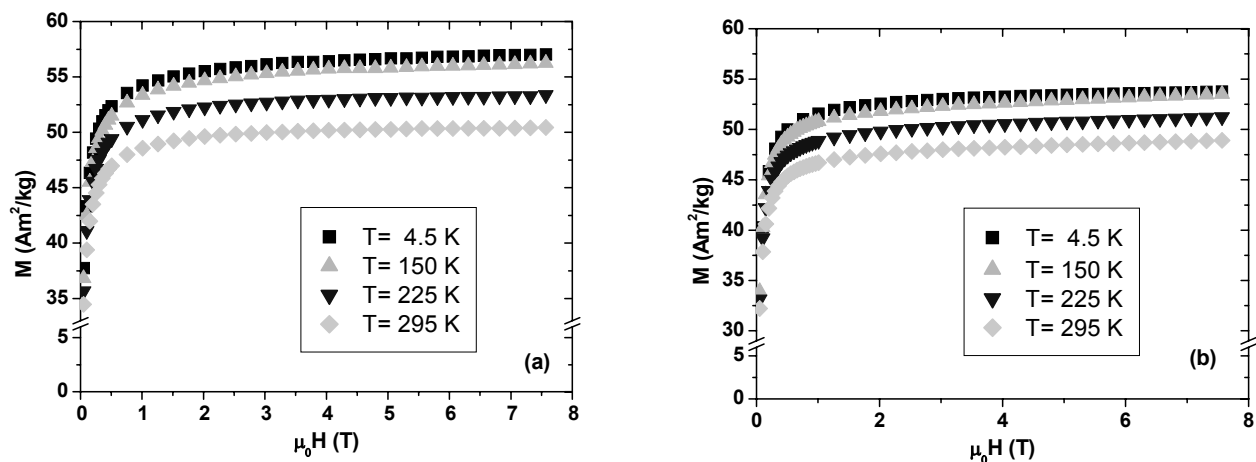


Fig. 4 – The magnetization versus applied magnetic field of the lithium ferrite obtained by the thermal decomposition of the compounds : (a) $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ (**I**) and (b) $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_{16}](\text{NO}_3)_8 \cdot 4\text{H}_2\text{O}$ (**II**), calcinated at 800 $^\circ\text{C}/1\text{h}$.

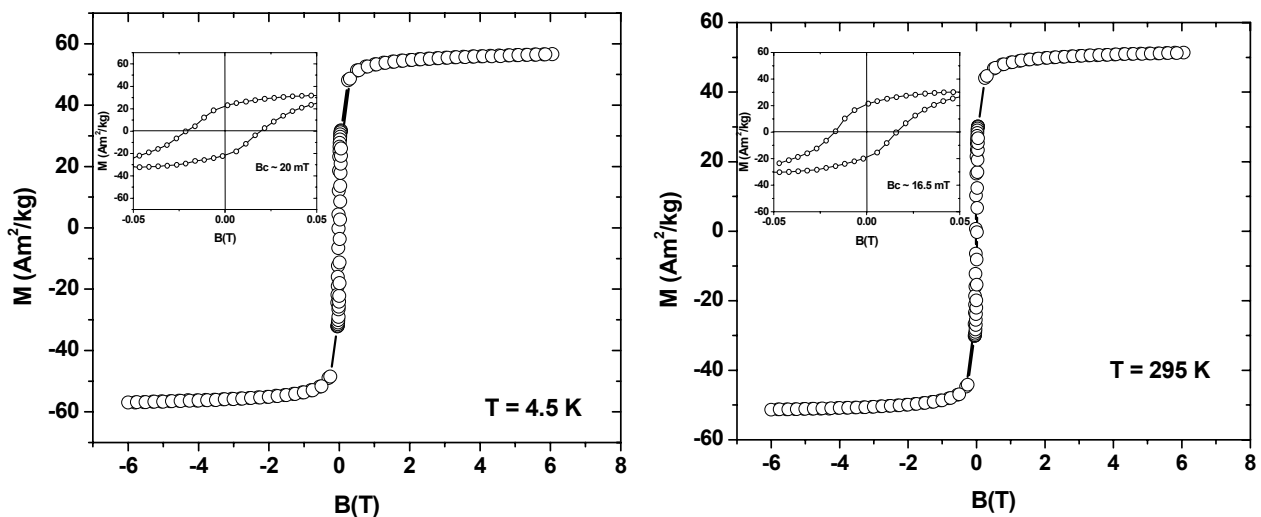


Fig. 5 – Hysteresis loop, at 4.5 K and 295 K, of the lithium ferrite obtained by the thermal decomposition of the compound $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_7](\text{NO}_3)_8 \cdot 6\text{H}_2\text{O}$ (**I**), calcinated at 800 $^\circ\text{C}/1\text{h}$.

Figs. 5 and 6 illustrate the hysteresis loops for the lithium ferrites measured at 4.5 K and 295 K. These indicate that the lithium ferrite is a soft

magnetic material, revealing minimal hysteresis.¹⁸ The value of coercive field is very small and approximately constant with temperature.

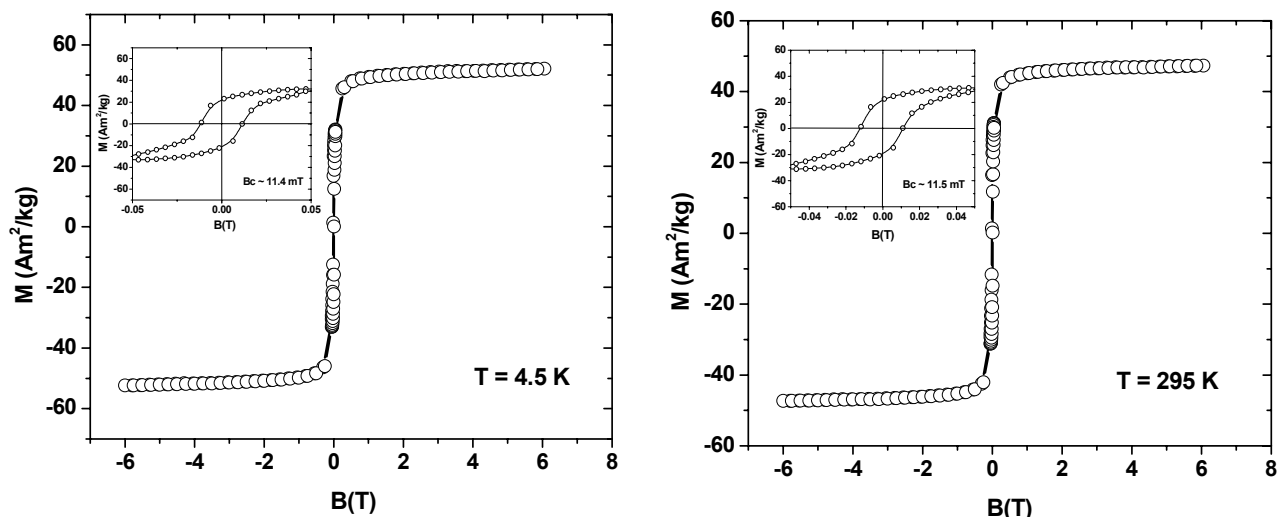


Fig. 6 – Hysteresis loop, at 4.5 K and 295 K, of the lithium ferrite of the lithium ferrite obtained by the thermal decomposition of the compound $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO}(\text{NH}_2)_2)_{16}](\text{NO}_3)_8 \cdot 4\text{H}_2\text{O}$ (II), calcinated at 800 °C/1h.

CONCLUSION

Lithium ferrites have been obtained by the combustion reaction from ureate precursors at low temperature. The structural and magnetic properties of these ferrites have been studied.

The XRD patterns revealed the formation of single-phase $\alpha\text{-Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ from precursor I. The $\alpha\text{-Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ phase obtained from coordination compound II was impure and contained $\alpha\text{-Fe}_2\text{O}_3$.

The saturation magnetizations measured at 4.5 K were 56.6 and 53.8 Am^2/kg , respectively. The formation of the $\alpha\text{-Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$ was confirmed by the IR and Mössbauer spectra.

In agreement with these results, we can conclude that the combustion reaction of the ureate precursors is a very promising route for the obtaining of lithium ferrite with spinellic structure.

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