LITHIUM FERRITES OBTAINED BY THERMAL DECOMPOSITION OF URATE 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-Li0.5Fe2.5O4 with saturation magnetization of \( \sim 56 \text{ Am}^2/\text{kg} \) were achieved from ureate precursor with ratio 2.5Fe\(^{3+}\) : 0.5Li\(^+\) : 7urea after a thermal treatment at 800° C/1h.

INTRODUCTION

Lithium ferrite (Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\)) 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\(_4\). Lithium ferrites have been extensively studied owing their electrical and magnetic properties. They 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.

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.

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

EXPERIMENTAL

All chemicals: Fe(NO\(_3\))\(_3\)·9H\(_2\)O, LiNO\(_3\) and urea (CO(NH\(_2\))) were of reagent grade quality (Merck). Iron and lithium nitrates in the 2.5:0.5 ratio of cations were mixed with urea, in two different proportions: 2.5 Fe(NO\(_3\))\(_3\)·9H\(_2\)O : 0.5 LiNO\(_3\) : 7CO(NH\(_2\)) and 2.5 Fe(NO\(_3\))\(_3\)·9H\(_2\)O : 0.5 LiNO\(_3\) : 16CO(NH\(_2\)) in the agate mortar. The nitrates and urea were solved in the hydration water of the salts that mean a very concentrated solution. The mixing is kept on till homogenous red-brown ureate compounds were obtained. These compounds were dried on P\(_4\)O\(_10\). 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 \( \sim 1000° \) 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\(_\alpha\) radiation.

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

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(HgCo(SCN)₄, χₐ=16.44×10⁻⁶ cgs units and metallic Ni as calibrants) and a magnetometer based on the extraction method with a resolution of 10⁻⁶ 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):

2.5 Fe(NO₃)₃·9H₂O : 0.5 LiNO₃ : nCO(NH₂)₂

where n=7,16

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

I: [Fe₂.₅Li₀.₅(CO(NH₂)₂)₇] (NO₃)₈·6H₂O
II: [Fe₂.₅Li₀.₅(CO(NH₂)₂)₁₆] (NO₃)₈·4H₂O

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.

Both compounds are paramagnetic. The experimental values of magnetic moments at room temperature are μ=6.93 BM for the first compound and 9.47 BM for the second. The value of the

<table>
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<tr>
<th>Urea</th>
<th>I</th>
<th>II</th>
<th>Assignment</th>
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<tr>
<td>3448 vs</td>
<td>3432 s</td>
<td>3455 s</td>
<td>νNH</td>
</tr>
<tr>
<td>3343 s</td>
<td>3346 s</td>
<td>3358 s</td>
<td>ν₁₁NH₂</td>
</tr>
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<td>3256 sh</td>
<td>3241 m</td>
<td>3197 m</td>
<td>νCO + δNH</td>
</tr>
<tr>
<td>1678 vs</td>
<td>1655 vs</td>
<td>1630 vs</td>
<td>νCO + δNH</td>
</tr>
<tr>
<td>1609 vs</td>
<td>1569 s</td>
<td>1567 s</td>
<td>νC-N + δNH</td>
</tr>
<tr>
<td>1466 vs</td>
<td>1497 s</td>
<td>1478 vs</td>
<td>νNO₃</td>
</tr>
<tr>
<td>1153 m</td>
<td>1153 m</td>
<td>1162 m</td>
<td>ρNH₂ (in plane)</td>
</tr>
<tr>
<td>1055 w</td>
<td>1034 w</td>
<td>1030 m</td>
<td>ρNH₂ (in plane)</td>
</tr>
<tr>
<td>902 w</td>
<td>832 w</td>
<td>764 w</td>
<td>ρNO₃</td>
</tr>
<tr>
<td>819 w</td>
<td>613 m</td>
<td>613 m</td>
<td>ρNH₂ (out of plane) + ΦCN</td>
</tr>
<tr>
<td>551 s</td>
<td>550 m</td>
<td>540 w</td>
<td>νM-O</td>
</tr>
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</table>

I: [Fe₂.₅Li₀.₅(CO(NH₂)₂)₇] (NO₃)₈·6H₂O; II: [Fe₂.₅Li₀.₅(CO(NH₂)₂)₁₆] (NO₃)₈·4H₂O

vs = very strong; s = strong; m = medium; w = weak; sh = shoulder
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 $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO(NH}_2)_2)_7](\text{NO}_3)_8\cdot 6\text{H}_2\text{O}$ 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 $\text{Fe}^{3+}$ ions in an octahedral coordination, strong distortion.

![Mössbauer spectra](image)

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

**Table 2**

<table>
<thead>
<tr>
<th>Compound</th>
<th>$H_{dd}$ (T)</th>
<th>IS* (mm/s)</th>
<th>QS** (mm/s)</th>
<th>Relative area (%)</th>
<th>Site/phase assignment</th>
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<tr>
<td>$<a href="%5Ctext%7BNO%7D_3">\text{Fe}<em>{2.5}\text{Li}</em>{0.5}(\text{CO(NH}_2)_2)_7</a>_8\cdot 6\text{H}_2\text{O}$ (I)</td>
<td>-</td>
<td>0.43</td>
<td>0.65</td>
<td>100</td>
<td>$\text{Fe}^{3+}$, strong distorted (octahedral)</td>
</tr>
<tr>
<td>$\text{LiFe}_5\text{O}_8$</td>
<td>49.1</td>
<td>0.28</td>
<td>-0.11</td>
<td>36.8</td>
<td>A(tetra) $\alpha$- $\text{LiFe}_5\text{O}_8$</td>
</tr>
<tr>
<td></td>
<td>51.6</td>
<td>0.35</td>
<td>-0.17</td>
<td>63.2</td>
<td>B(oct) $\alpha$- $\text{LiFe}_5\text{O}_8$</td>
</tr>
</tbody>
</table>

* IS is given relative to $\alpha$-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 $[\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO(NH}_2)_2)_7](\text{NO}_3)_8\cdot 6\text{H}_2\text{O}$ (I) shows the
formation of the single-phase \(\alpha\)-Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\) (Fig. 3a), while in the case of the sample obtained from precursor \([\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO(NH}_2)_2)_{16}]\)(\text{NO}_3)\(_8\)·4\text{H}_2\text{O}\) (II) it can be observed the formation of \(\alpha\)-Li\(_{0.5}\)Fe\(_{2.5}\)O\(_4\) as a main product together with \(\alpha\)-Fe\(_2\)O\(_3\) as impurity (Fig. 3b).

Fig. 2 – Lithium ferrite obtained by the thermal decomposition of the compound \([\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO(NH}_2)_2)_{7}]\)(\text{NO}_3)\(_8\)·6\text{H}_2\text{O}\) (I) calcinated at 800 °C/1h.

Fig. 3 – XRD patterns of the lithium ferrite obtained by the thermal decomposition of the compounds:
(a) \([\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO(NH}_2)_2)_{7}]\)(\text{NO}_3)\(_8\)·6\text{H}_2\text{O}\) (I) and (b) \([\text{Fe}_{2.5}\text{Li}_{0.5}(\text{CO(NH}_2)_2)_{16}]\)(\text{NO}_3)\(_8\)·4\text{H}_2\text{O}\) (II), calcinated at 800 °C/1h.
To confirm the formation of the spinellic 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-Li₀.₅Fe₂.₅O₄ phase.¹⁶

The Mössbauer parameters for the lithium ferrite obtained by the combustion reaction of the ureate compound I confirmed the formation of the spinellic phase α-Li₀.₅Fe₂.₅O₄. The Mössbauer spectrum could be fitted with two discrete sextets (Fig. 1b). The sextet with IS 0.28 mm/s has been attributed to Fe³⁺ ions in the tetrahedral (A) sites of spinel structure. The sextet with IS 0.35 mm/s is assigned to Fe³⁺ 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 Am²/kg for lithium ferrite obtained by thermal decomposition of compound I and 53.8 Am²/kg for lithium ferrite obtained by thermal decomposition of compound II, in agreement with literature data.¹⁷

![Fig. 4](image-url)  
**Fig. 4** – The magnetization versus applied magnetic field of the lithium ferrite obtained by the thermal decomposition of the compounds: (a) [Fe₂.₅Li₀.₅(CO(NH₂))₇](NO₃)₈·6H₂O (I) and (b) [Fe₂.₅Li₀.₅(CO(NH₂))₁₆](NO₃)₈·4H₂O (II), calcinated at 800 °C/1h.

![Fig. 5](image-url)  
**Fig. 5** – Hysteresis loop, at 4.5 K and 295 K, of the lithium ferrite obtained by the thermal decomposition of the compound [Fe₂.₅Li₀.₅(CO(NH₂))₇](NO₃)₈·6H₂O (I), calcinated at 800 °C/1h.

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.
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 $\alpha$-Li$_{0.5}$Fe$_{2.5}$O$_4$ from precursor I. The $\alpha$-Li$_{0.5}$Fe$_{2.5}$O$_3$ phase obtained from coordination compound II was impure and contained $\alpha$-Fe$_2$O$_3$.

The saturation magnetizations measured at 4.5 K were 56.6 and 53.8 Am$^2$/kg, respectively. The formation of the $\alpha$-Li$_{0.5}$Fe$_{2.5}$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.

REFERENCES