Estimation of thermomagnetometry method sensitivity for magnetic phase determination

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Abstract. In this article, the sensitivity of thermomagnetometry method for magnetic phase determination in lithium substituted ferrites was estimated by thermogravimetric analysis in magnetic field of lithium-zinc ferrite and iron dioxide ($Li_{0.4}Fe_{2.4}Zn_{0.2}O_4+\alpha$-$Fe_2O_3$) components mixture with different mass proportions: 2, 4, 6, and 100 mass% $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ phase in total mixture. Thereby, analyzed samples are mixture of magnetic and nonmagnetic phases. Results of thermomagnetometric analysis were supplemented with the X-Ray diffraction analysis data. It was shown that the thermomagnetometry method allows to determine a magnetic phases with mass content not less than 2 mass% in analyzed mixture. In this case, we can clearly estimate the position and intensity of the peak on derivative thermogravimetric curve, which connected with a magnetic phase transition in ferrite at Curie temperature.

Keywords: lithium-zinc ferrite; lithium-substituted ferrospinel; ferrospinel; thermomagnetometry method, X-Ray analysis.

1 Introduction

Ferrites are the mostly usable elements for electronic and radio devices in our days [1-9]. During production of multicomponent ferrite materials, the great attention is paid to maximization of powder homogeneity in the synthesis stages [10, 11]. One of the more simple technological methods for increase of phase powders homogeneity is intermediate grinding and mixing operation, which is additional step in synthesis technology [12-15]. To optimize the time-temperature regimes of the technological model, it is necessary to control the phase composition of the powders after each stage of annealing.

X-Ray diffraction analysis (XRD) is the mostly used method for control phase composition in ferrites. However, for multicomponent ferrites synthesis, it's needed an additional procedure of phase verification due to formation of wide variety of ferrospinel phases with close values of the lattice parameters. Thus, reflections from these phases in the registered X-Ray diffraction patterns merge into a single reflection; and inability to make a correct separation of X-Ray reflections leads to necessarily of development a new estimation method of phase composition, which would be as an addition to XRD analysis. One of those methods is thermomagnetometric analysis, which is thermogravimetric analysis (TG/DTG) with applied magnetic field to the samples [16]. Possibility of TG/DTG method for estimation of both the qualitatively and quantitatively magnetic phase analyzes for lithium substituted ferrites was shown in several works [17-20]. However, for extensive use of this technique in practice, should be carefully considered the conditions of its application.

Thereby, in present work, we tried to define a sensitivity of thermomagnetometric analysis for magnetic phase detection in $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ lithium-zinc ferrites. Results of thermomagnetometric analysis were supplemented with the XRD data.

2 Experimental

Lithium-zinc ferrite was prepared by solid phase synthesis method in accordance with the reaction $Li_2CO_3+6Fe_2O_3+ZnO \rightarrow 5Li_{0.4}Fe_{2.4}Zn_{0.2}O_4+CO_2$ using resistance furnace at temperature of 800°C in air atmosphere during 6 hours with additional intermediate grinding and mixing operations after each 120 minutes. XRD analysis showed 100% presence of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ phase after synthesis. After that, lithium ferrite was mixed with α-Fe_2O_3 (nonmagnetic phase) powder in an agate mortar in different mass proportions, so that the samples had 2, 4, 6 and 100 mass% of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ phase. Thereby, samples were mixture of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4+Fe_2O_3$ magnetic with nonmagnetic phases with different mass content.

X-ray diffraction analysis was performed using an ARL X'TRA diffractometer with a semiconductor Peltier Si(Li) detector and CuK_α radiation. The Powder Cell 2.4 software was used for a full-profile analysis of the X-ray diffraction patterns. The phase composition was identified using PDF-4 powder database of the International Centre for Diffraction Data (ICDD).

Thermomagnetometric analysis was carried out on STA 449C Jupiter (Netzsch, Germany) thermal analyzer. The magnetic assemblage consisting of two permanent magnets creating a field of ~5 Oe was attached on the outer side of measurement cell for control of the magnetic state of samples. The heating of samples was carried out in corundum crucibles in air atmosphere with line speed of heating 50°C/min. The results were analyzed by Proteus Analysis (Netzsch, Germany).

3 Results and discussion

XRD patterns are shown in Figure 1 for different samples. It can be seen that all peaks for $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4+Fe_2O_3$ mixture are peak overlapping from reflections of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ and Fe_2O_3 powders; and just one low intensity peak at $2\theta \approx 30{,}4°$ can be assigned only to $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ phase. Figure 2 shows such peaks for samples with different mass content of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ phase. Here, the peak is more intense with increase the $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ phase in the mixture.

It was shown in [17], the content of ferrite phase can be determined from the mass jump (Δm) on TG curve, when the magnetic phase transition at Curie temperature occurs during heating of ferrite sample in an external magnetic field (Fig. 3, TG solid line). Curie temperature can be determined by position of peak maximum on DTG curve (Fig. 3, DTG dotted line). Mass change was not observed in absence of the magnetic field (Fig. 3, TG dashed line).

Figure 4 shows TG and DTG curves for $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4+Fe_2O_3$ samples with different content of lithium-zinc ferrite phase. The values of mass jump and Curie temperature for all samples are summarized in Table 1. According to TG/DTG analysis for pure lithium-zinc ferrite (Fig. 4 a), magnetic phase transition corresponds to Curie temperature for $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ [17]. The height of mass jump on TG curve is maximum and equal to 0.324%. By reduction of magnetic phase in mixture (Fig. 4 b, c, d), a decrease in Δm are observed up to 0.003 % for mixture with 2 mass% $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$. In this case, we can clearly estimate the position, height and half-width of the peak on DTG curve and it was shown in [18], the values of DTG peak areas can be compared with a quantitative content of the ferrite phase.

Thus, the results showed that the thermomagnetometry method allows to determine a magnetic ferrite phases with mass content not less than 2 mass%. However, this work should be continued in terms of determine the sensitivity of thermomagnetometric method for analysis of ferrites with different magnetization.

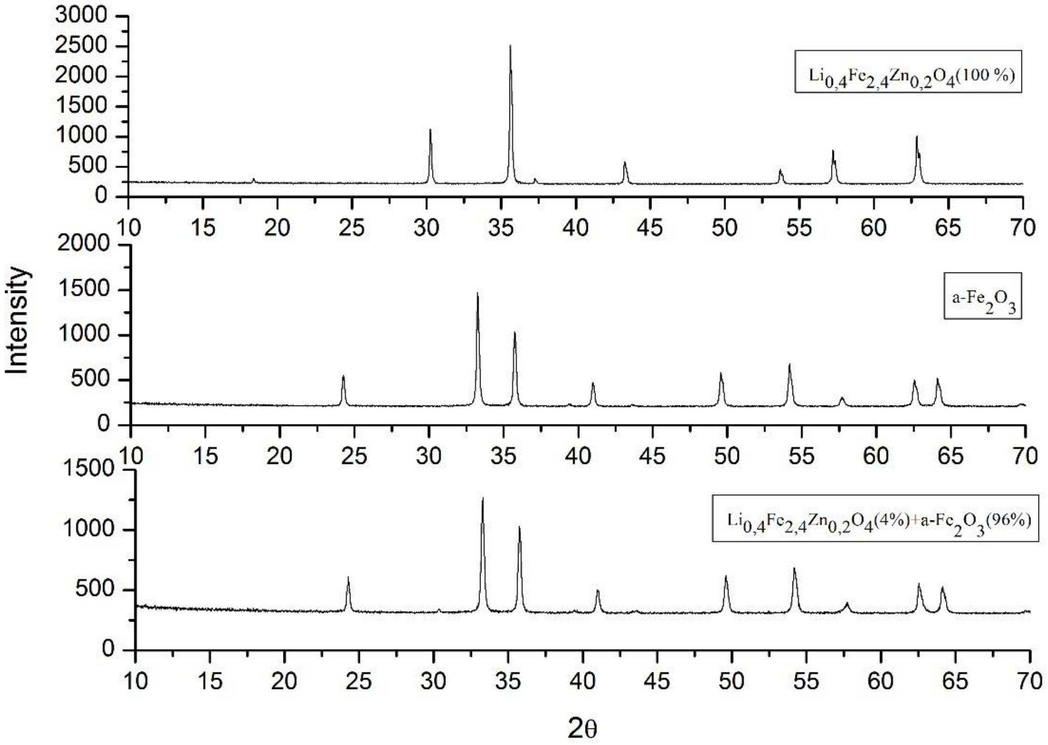

Figure 1. X-Ray diffraction patterns

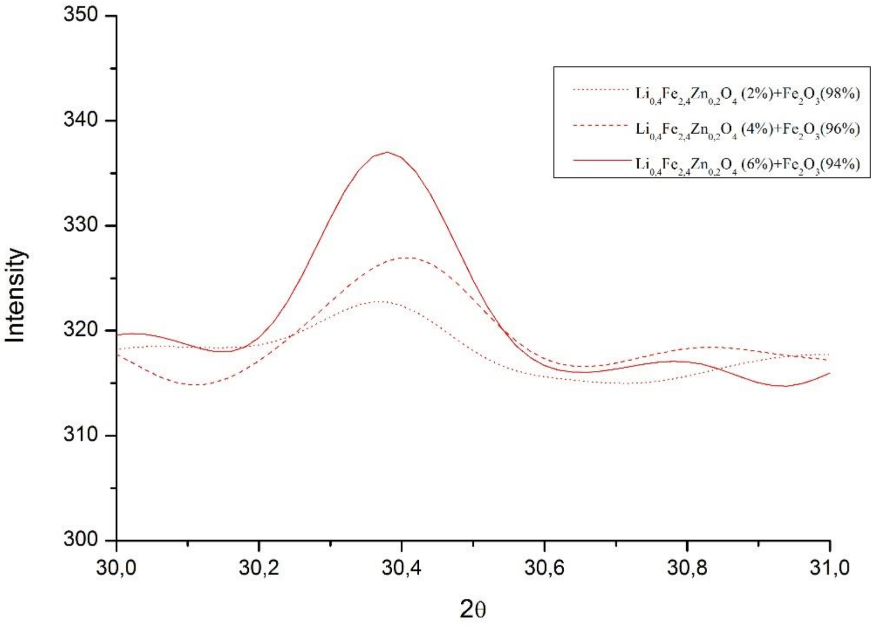

Figure 2. Part of XRD patters for samples with different mass content of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ phase

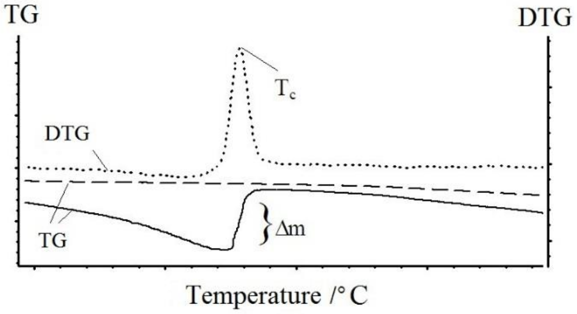

Figure 3. TG/DTG curves for ferrite materials during heating in magnetic field (TG solid line and DTG dotted line) and without magnetic field (TG dashed line)

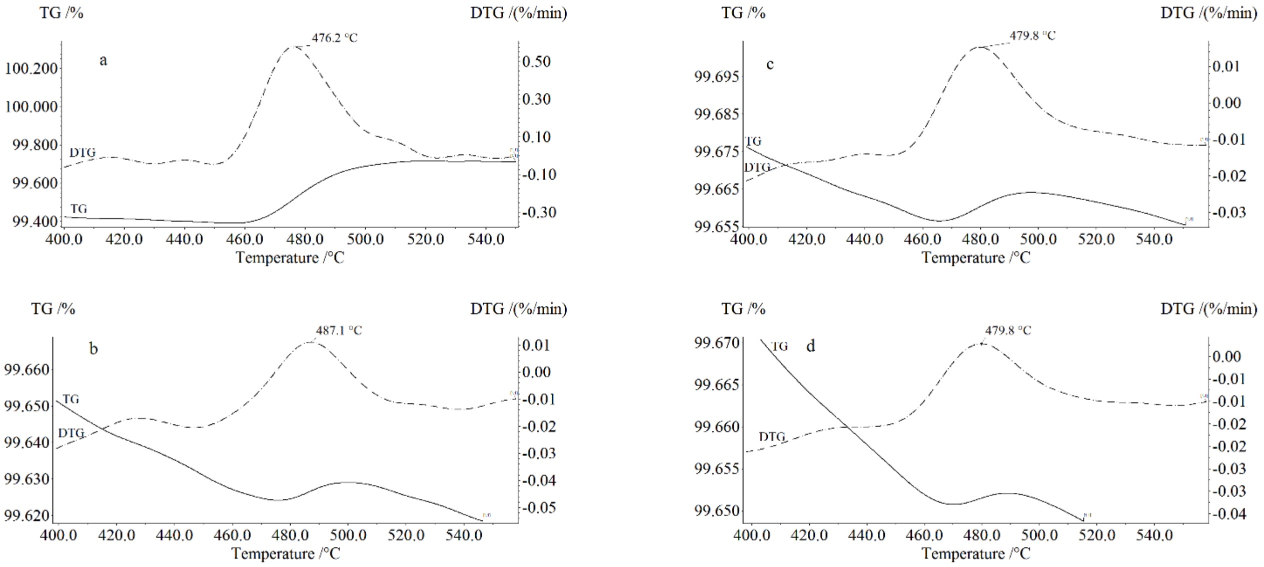

Figure 4. TG/DTG curves for $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4+Fe_2O_3$ samples with different content of lithium-zinc phase in mixture: a – 100 mass %, b - 2 mass %, c- 4 mass %, d - 6 mass %.

Table 1. Parameters of magnetic phase transition for $Fe_2O_3+Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$

Content of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ phase in a mixture (mass %)	Mass jump, Δm (%)	Curie temperature, T_c (°C)
100	0,324	476,2
6	0,01	486,4
4	0,01	478,3
2	0,003	486,4

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