Development of control method for ferrite phase composition using thermomagnetometric analysis

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Abstract. In this paper we evaluated the phase composition of products in synthesis of \(\text{Li}_{0.4}\text{Fe}_{2.4}\text{Zn}_{0.2}\text{O}_4\) and \(\text{Li}_{0.3}\text{Fe}_{2.3}\text{Zn}_{0.4}\text{O}_4\) lithium-substituted ferrites using thermomagnetometric method. Results of thermomagnetometric analysis were compared with X-ray diffraction (XRD) data. It was found that thermomagnetometric analysis in comparison with XRD method better reflects the temperature of phase magnetic transitions and therefore provides a more precise estimate the phase composition of the samples. However, a complex analysis using of both X-ray and thermomagnetometry methods will be the most optimal in case of the formation of non-magnetic or weakly magnetic phases. By the thermomagnetometric analysis it was shown that the homogeneity of synthesized under the same temperature-time regimes ferrites decreases with increasing the concentration of zinc in the initial mixture. Using of intermediate grinding and mixing leads to homogeneity increasing of synthesized ferrite with higher content of the final phase.

Keywords: Ferrite; Thermomagnetometry method; X-ray diffraction; Lithium-substituted ferrospinels.

1 Introduction

During production multicomponent magnetic materials, including ferrites, the great attention is paid to maximization of powder homogeneity at the synthesis stage [1]. Of the existing methods for improving the homogeneity of powders, operations of intermediate grinding and mixing are the most simple and technological which included in the synthesis procedure [2]. The use of such technological operations requires careful phase control at all stages of the annealing.

X-ray diffraction analysis (XRD) is one of the traditional methods for the phase homogeneity control. However, with application to lithium-substituted ferrospinels, the XRD quantitative data and its reliability require additional verification, since it is difficult to separate different spinel phases that can be formed in multicomponent system [3, 4].

In [5, 6] the possibility of application thermomagnetometry method TG(M)/DTG(M) for analysis of phase homogeneity of lithium-substituted ferrites was investigated. This method is thermogravimetric analysis TG/DTG of the samples in magnetic field [7]. Results of investigations allow controlling phase analysis only qualitatively. These results allow us to study the phase composition analysis only on a qualitative level.
In this paper the phase composition of products in synthesis of Li$_{0.4}$Fe$_{2.4}$Zn$_{0.2}$O$_4$ and Li$_{0.3}$Fe$_{2.3}$Zn$_{0.4}$O$_4$ lithium-substituted ferrites widely applied in microwave technology was estimated using TG(M)/DTG(M) analysis. However, since the concentration of the introduced impurity of zinc into microwave lithium ferrites usually do not exceed the value of x = 0.4 (due to the reduction of the saturation magnetization of lithium-zinc ferrites) [8], it is not necessary to investigate the lithium-zinc ferrite synthesis with a higher content of zinc.

2 Experimental
The lithium-substituted ferrospinels were prepared by the solid phase synthesis in accordance to the reaction:

\[ \text{Li}_2\text{CO}_3 + \text{Fe}_2\text{O}_3 + \text{ZnO} \rightarrow \text{Li}_{0.5(1-x)}\text{Fe}_{2.5-0.5x}\text{Zn}_x\text{O}_4 + \text{CO}_2, \text{ where } x_{\text{Zn}} = 0.2, 0.4. \]

The initial reagents are commercial powders of Fe$_2$O$_3$, Li$_2$CO$_3$ and ZnO. The samples were compacted by single-ended cold pressing under a pressure of 200 MPa in the form of tablets with a diameter of 15 mm and thickness of 2 mm.

Then all samples were divided into two groups (samples A and samples B). A solid phase synthesis of the samples was carried out in the air atmosphere using a resistance furnace at the temperature of 800 °C during 360 minutes. Samples A were annealed with inclusion of intermediate grinding and mixing operations every 120 minutes during isothermal annealing. Samples B were annealed without any operations at the same time-temperature parameters.

The samples were investigated by XRD and TG(M)/DTG(M) analyses. XRD analysis was performed using an ARL X'TRA diffractometer with a semiconductor Peltier Si(Li) detector and CuK$_\alpha$ 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 performed in air atmosphere using thermal analyzer STA 449C Jupiter (Netzsch). The magnetic assemblage 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. Determination of the phase composition was carried out using mathematical modeling and the software Peak Separation developed by Netzsch.

3. Result and discussion
X-Ray diffraction patterns for samples A and samples B were shown in Figure 1 and 2 for lithium-substituted ferrospinel with zinc concentration $X_{\text{Zn}}=0.2$ (Figure 1) and $X_{\text{Zn}}=0.4$ (Figure 2).

To analysis of the sample phase composition, a discrete set of lithium-zinc ferrite phases with $X_{\text{Zn}}=0; 0.2; 0.4; 0.6; 0.8$ was included in the full-profile analysis by means of Powder Cell 2.5 software. If necessary, a discrete set was expanded to include phase particles of the starting components. Phase concentration and lattice parameters were determined after fitting of calculated and experimental XRD patterns. Then, the values of $X_{\text{Zn}}$ in spinel phases were refined using the dependence of lithium-zinc ferrite lattice parameters on the content of zinc.

The results of XRD analysis presented in Table 1 show that all observed reflections belong to the spinel phases. Phase identification detected the presence of transition lithium-zinc phases with different concentration of zinc for all samples, except for samples A of Li$_{0.4}$Fe$_{2.4}$Zn$_{0.2}$O$_4$, where there is a 100% yield of the final phase. Thus, the samples synthesized under different conditions, have demonstrated varying degrees of homogeneity of the phase composition. For samples A, which were synthesized using intermediate grinding and mixing operations, there is a large phase content with a concentration of zinc that is close to the final product. In contrast, samples B are characterized by a high content of transitional phases of lithium-zinc ferrite and the presence of pure lithium ferrite of Li$_{0.3}$Fe$_{2.5}$O$_4$. 

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Figure 1. X-Ray diffraction patterns for Li$_{0.4}$Fe$_{2.4}$Zn$_{0.2}$O$_4$ after synthesis at different regimes.

Figure 2. X-Ray diffraction patterns for Li$_{0.3}$Fe$_{2.3}$Zn$_{0.4}$O$_4$ after synthesis at different regimes.

Table 1. Results of X-Ray analysis

| Concentration of zinc (X$_{Zn}$) | Sample type | Phases | Phase concentration, % |
|---------------------------------|-------------|--------|------------------------|
| 0.2                             | A           | Li$_{0.4}$Fe$_{2.4}$Zn$_{0.2}$O$_4$ | 100 |
|                                 | B           | Li$_{0.4}$Fe$_{2.4}$Zn$_{0.2}$O$_4$, Li$_{0.3}$Fe$_{2.3}$O$_4$ | 88, 12 |
| 0.4                             | A           | Li$_{0.375}$Fe$_{2.375}$Zn$_{0.25}$O$_4$, Li$_{0.315}$Fe$_{2.315}$Zn$_{0.25}$O$_4$, Li$_{0.295}$Fe$_{2.295}$Zn$_{0.25}$O$_4$ | 33, 64, 3 |
|                                 | B           | Li$_{0.385}$Fe$_{2.385}$Zn$_{0.25}$O$_4$, Li$_{0.295}$Fe$_{2.295}$Zn$_{0.45}$O$_4$, Li$_{0.215}$Fe$_{2.215}$Zn$_{0.57}$O$_4$ | 48, 20, 18 |

The presence of mass jumps on TG curves at the Curie temperatures was observed for each of the magnetic phases in the sample (not shown in this paper). Thus, number of peaks on DTG(M) curves derived from TG(M) curves indicates a number of dominant magnetic phases in the samples. Figure 3 and 4 show DTG(M) curves for Li$_{0.4}$Fe$_{2.4}$Zn$_{0.2}$O$_4$ (Figure 3) and Li$_{0.3}$Fe$_{2.3}$Zn$_{0.4}$O$_4$ (Figure 4). It was shown that experimental dependence of DTG(M) are complex peaks for all types of samples (symbols in Figure 3 and 4), which were separated to the simpler peaks by the mathematical modeling (dotted lines in Figure 3 and 4). Mathematical modeling results of separation DTG(M) curves are shown in solid lines in figures and are in good agreement between the experimental and calculated curves.
Figure 3. Experimental and calculated DTG(M) curves for lithium-substituted ferrospinel with zinc content $X_{Zn}=0.2$; symbols – experimental points, lines – calculated curves

Figure 4. Experimental and calculated DTG(M) curves for lithium-substituted ferrospinel with zinc content $X_{Zn}=0.4$; symbols – experimental points, lines – calculated curves

Table 2 presents numeric values of peak parameters, which were determined via the modeling. Temperature position of each peak corresponds to Curie temperature of the magnetic phase with a zinc content determined from the concentration dependence of Curie temperatures for reference samples with zinc content $X_{Zn}=0 \div 4$ [5]. It can be seen that TG(M)/DTG(M) analysis allows to define the temperature of the magnetic phase transition more precisely, thereby it can more fully characterize the phase composition of sample. On the contrary, the result of XRD analysis is largely determined by the availability of complete catalogs of XRD patterns for reference samples. In the absence of non-magnetic or weakly magnetic phases in the samples, as confirmed by XRD analysis, a values of the peak areas obtained from DTG(M) analysis (see Table. 2) can be compared with quantitative content of ferrite phase.
4. Conclusions
It was shown that thermomagnetometric analysis allows to define the temperature of the magnetic phase transition more precisely, thereby it can more fully characterize the phase composition of sample as compared to X-Ray diffraction analysis. However, the complex analysis using of both X-ray and thermomagnetometric methods will be the most optimal in case of the formation of non-magnetic or weakly magnetic phases in the samples.

The phase composition of products in synthesis of Li_{0.4}Fe_{2.4}Zn_{0.2}O_4 and Li_{0.3}Fe_{2.3}Zn_{0.4}O_4 lithium-substituted ferrites under different conditions including the operations of intermediate grindings and mixings was evaluated using thermomagnetometry and XRD methods. It was shown that the synthesis process of lithium-zinc ferrites passes through the formation of intermediate Li_{0.5(1-x)}Zn_xFe_{2.5-0.5x}O_4 phases, where 0 ≤ x ≤ 0.6. Moreover, the degree of homogeneity of the synthesized ferrite at the same time-temperature parameters decreased with increasing concentration of zinc in initial mixture. Using the operations of grinding and mixing leads to increasing the homogeneity degree of ferrite with large zinc concentration.

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| Table 2. Results of DTG(M) analysis |
|--------------------------------------|
| Content X_{Zn} | Samples type | Number of peak | Peak position, ˚C | Peak area, % | X_{Zn} |
|----------------|--------------|----------------|------------------|-------------|--------|
| 0.2            | A            | 1              | 479.0823         | 60.9        | 0.28   |
|                |              | 2              | 502.066          | 17.5        | 0.18   |
|                |              | 3              | 522.6296         | 2.938       | 0.15   |
|                |              | 4              | 550.7789         | 8.307       | 0.11   |
|                |              | 5              | 573.8409         | 2.042       | 0.09   |
|                |              | 6              | 595.3677         | 3.282       | 0.05   |
|                |              | 7              | 616.894          | 1.602       | 0      |
|                | B            | 1              | 472.1778         | 39.171      | 0.21   |
|                |              | 2              | 507.5629         | 30.701      | 0.17   |
|                |              | 3              | 552.4597         | 17.340      | 0.07   |
|                |              | 4              | 622.5932         | 12.788      | 0      |
| 0.4            | A            | 1              | 327.31           | 49.9        | 0.41   |
|                |              | 2              | 346.84           | 36.2        | 0.38   |
|                |              | 3              | 377.3            | 13.89       | 0.34   |
|                | B            | 1              | 274.69           | 28.83       | 0.48   |
|                |              | 2              | 365.5            | 23.55       | 0.36   |
|                |              | 3              | 462.51           | 35.54       | 0.22   |
|                |              | 4              | 621.93           | 12.06       | 0      |
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