Effect of powder compaction on radiation-thermal synthesis of lithium-titanium ferrites

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Abstract. Effect of powder compaction on the efficiency of thermal and radiation-thermal synthesis of lithium-substituted ferrites was investigated by X-Ray diffraction and specific magnetization analysis. It was shown that the radiation-thermal heating of compacted powder reagents mixture leads to an increase in efficiency of lithium-titanium ferrites synthesis.

1. Introduction

It is known that the titanium doped lithium ferrites are widely used in microwave engineering [1-5]. The ions substitutions significantly improve the properties of ferrites, since the Ti^{4+} introduction in the lithium spinel reduces the probability of Fe^{2+} formation increasing the electrical resistivity of ferrite [6]. These ferrites are characterized by low values of dielectric losses and high temperature stability.

Radiation-thermal (RT) synthesis is one method that allows to synthesize the materials and modify their properties effectively. In [7-12] RT method was successfully used for synthesis of lithium-substituted ferrites under conditions of high-energy electron beams heating. It was found that RT heating of the initial reagents mixture significantly increases the reactivity of the solid-phase system that leads to a decrease in a synthesis temperature and increase in homogeneity of the end product.

Among the most important factors in ferrites preparation, determined the efficiency of solid-phase synthesis, is an operation of compacting the reaction mixtures. This operation forms the initial conditions for the diffusion mass transfer and therefore the study of the compaction effect is necessary in the development of RT methods for ferrites production.

Previously, it was found that the compaction of reaction mixture increases the efficiency of the thermal synthesis of $Li_{0.5}Fe_{2.5}O_4$ lithium ferrites [13]. In the present work we studied the effect of compaction of reagents powder mixture in lithium-substituted ferrites synthesis by thermal heating and RT heating via pulsed electron beam.

2. Experimental techniques

Lithium-titanium ferrite with the general formula of $Li_{0.5(1+x)}Fe_{2.5-1.5x}Ti_xO_4$ (x = 0.2) was synthesized from Li_2CO_3-TiO_2-Fe_2O_3 mixture. Reagents mixture was obtained by weighing the required amounts of pre-dried components and then dry mixed in an agate mortar with 10 fold mixing through a mesh with a cell of 80 μm. Two types of samples were investigated: powder with a density of 0.95 g/cm^3 (powder samples) and powder compacted by the single-action compacting under a pressure of 200 MPa into tablets with diameter of 15 mm and thickness of 2 mm (compacted samples). Average density of compacted samples was 2.6 g/cm^3.

Thermal (T) synthesis of samples was carried out in a laboratory resistance furnace. Radiation-thermal (RT) synthesis of the samples was performed on the pulsed electron accelerator ILU-6 at the Institute of Nuclear Physics SB RAS (Novosibirsk) [14]. The electron energy was 2.4 MeV, beam current in the pulse was 400 mA, pulse duration is 500 μs, and pulse frequency is 7-15 Hz. The dose within the range of one pulse was 800 kGy/s. Average radiation dose was ca. 5 kGy/s and in the mode of isothermal synthesis was ca. 3 kGy/s. Heating of the samples was carried out by electrons energy, without external sources of heat. The desired temperature was kept using certain values of pulse frequency. The duration of heating and cooling stages does not exceed 3 min. The both T and RT synthesis was carried out in air. We used two temperatures (600°C and 750 °C) and times (10 min and 120 min) for each type of heating.

Analysis of the phase composition for investigated samples was conducted by X-ray diffractometer ARL X'TRA with semiconductor Si (Li) Peltier detector with Cuk_α radiation. A diffractogram was measured in the angle range 2θ = (20–70)° at a scanning speed of 0.02 °/s. Phase identification was performed using PDF-4+ powder database of International Centre for Diffraction Data (ICDD). X-ray diffraction patterns were processed by the method of full-profile Rietveld analysis using complex software Powder Cell 2.4.

In addition, the control of synthesis degree by measurements of specific magnetization in synthesized samples was carried out using the automated complex for magnetic properties study in pulsed magnetic fields [15].

3. Result and discussion

Figure 1 presents X-ray diffraction patterns for powder samples (figure 1a, c) and compacted samples (figure 1b, d) after T (figure 1a, b) and RT (figure 1c, d) synthesis of Li_2CO_3-TiO_2-Fe_2O_3 mixture. These reflections are a superposition from the phases of the initial components and phases of $LiFeO_2$, $LiFe_5O_8$ and spinel phases of lithium-titanium ferrites of $Li_{0.5(1+x)}Fe_{2.5-1.5x}Ti_xO_4$ composition, including the $Li_{0.6}Fe_{2.2}Ti_{0.2}O_4$ final composition. The data of XRD analysis for registered spinel phases in synthesized samples are summarized in table 1.

Table 1. Content of spinel phases in $Li_{0.5(1+x)}Fe_{2.5-1.5x}Ti_xO_4$ (weight %).

Synthesis mode	Type of synthesis	Powder samples	Compacted samples
600 °C –10 min	T	0	0
	RT	9.3	29.6
600 °C – 120 min	T	11.5	2.6
	RT	22.4	49.8
750 °C – 10 min	T	28.3	45.6
	RT	43.6	93.6
750 °C – 120 min	T	59	91.9
	RT	77	100

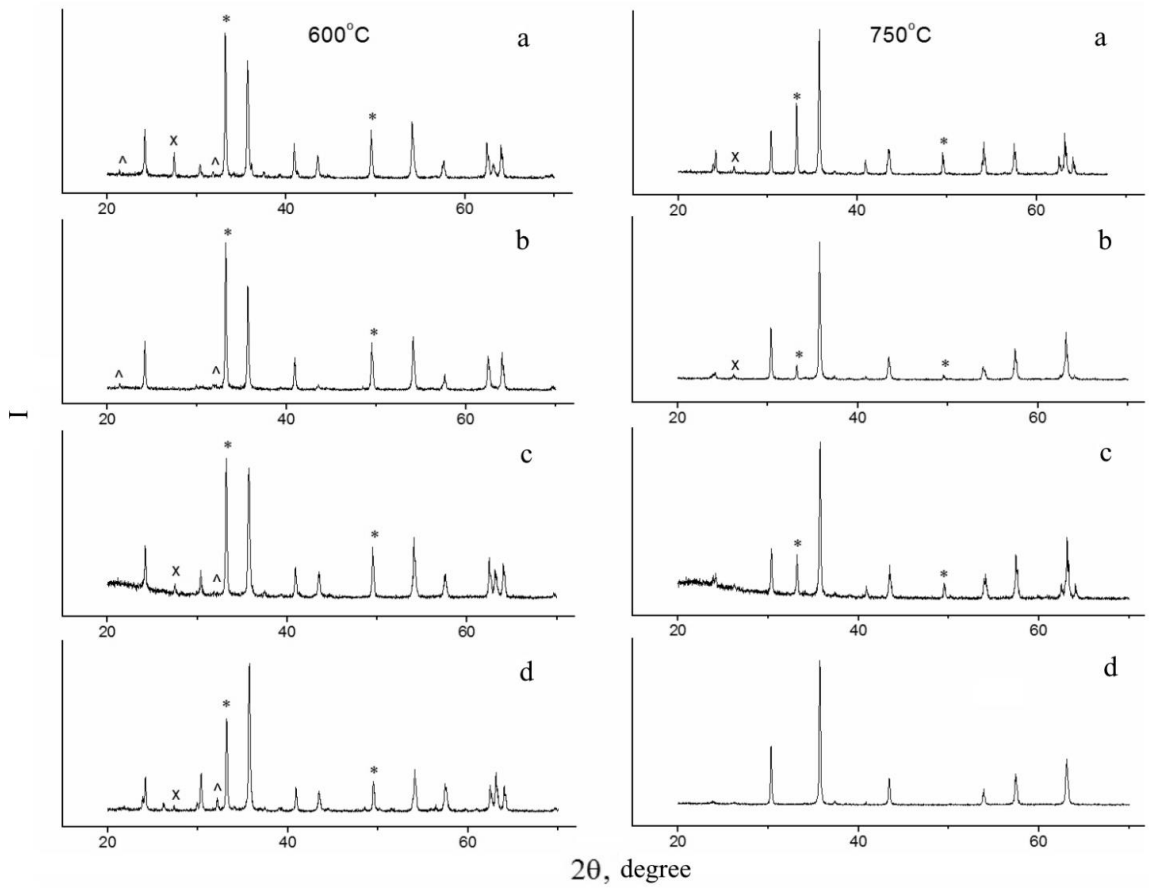

Figure 1. X-ray diffraction pattern of Li_2CO_3-TiO_2-Fe_2O_3 powder mixture (a, d) and compacted mixture (b, d) after T (a, b) и PT (c, d) synthesis at temperatures of 600 °C and 750 °C during 120 min. Reflections of initial components: (*) - Fe_2O_3; (×) – TiO_2; (∧) - Li_2CO_3.

For thermal synthesized samples, $Li_{0.6}Fe_{2.2}Ti_{0.2}O_4$ lithium-titanium ferrite is formed by all modes except heating at 600 ° C for 10 min, in which only the initial components phases are observed. The effect of the electron beam heating even more accelerates this process. For RT synthesized samples, there is a formation of the spinel phases under all conditions of synthesis. It should be noted that 51.8 wt. % of $Li_{0.6}Fe_{2.2}Ti_{0.2}O_4$ out of 77 wt. % spinel phases is observed for powder samples in condition of RT synthesis at 750 °C for 120 min, while 100 wt. % content of spinel phase is formed in compacted samples at the same condition (table 1). The results showed that the synthesis reaction rate of lithium-titanium ferrite is higher in the compacted samples. This is expressed in faster transformation of the initial reagents in the spinel phases.

The data of specific magnetization of Li_2CO_3-TiO_2-Fe_2O_3 mixture are shown in table 2. The results showed an increase in the specific magnetization in compacted samples compared to powder samples. It also indicates a higher content of magnetic spinel phases in the synthesized compacts.

4. Conclusion

Use of non-compacted powder mixture of the initial reagents decreases the efficiency of solid-phase synthesis of $Li_{0.5(1+x)}Fe_{2.5-1.5x}Ti_xO_4$ ferrites. The including a compaction operation of powder reagents mixture in ferrites preparation leads to an increase in concentration of the spinel phases and decrease in content of initial components in a lithium-titanium ferrites, synthesized by thermal and radiation-thermal heating. In the latter case, a radiation-thermal heating is the most effective method to synthesize lithium-titanium ferrites.

Table 2. Specific magnetization of Li_2CO_3-TiO_2-Fe_2O_3 mixture (emu/g).

Synthesis mode	Type of synthesis	Powder samples	Compacted samples
600 °C –10 min	T	1.1	0.3
	RT	5.9	10
600 °C – 120 min	T	1.3	6.6
	RT	14.9	34
750 °C – 10 min	T	11.9	29.4
	RT	22.9	47.8
750 °C – 120 min	T	27.9	53.1
	RT	37.6	53.5

5. Acknowledgements
The research was supported by the Ministry of Education and Science of the Russian Federation in part of the "Science" program.

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