Influence of reagents mixture density on the radiation-thermal synthesis of lithium-zinc ferrites

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Abstract. Influence of Li_2CO_3-ZnO-Fe_2O_3 powder reagents mixture density on the synthesis efficiency of lithium-zinc ferrites in the conditions of thermal heating or pulsed electron beam heating was studied by X-Ray diffraction and magnetization analysis. The results showed that the including a compaction of powder reagents mixture in ferrite synthesis leads to an increase in concentration of the spinel phase and decrease in initial components content in lithium-substituted ferrites synthesized by thermal or radiation-thermal heating.

1. Introduction

Zinc doped lithium ferrospinels are the basic ferrite materials that widely used in microwave engineering [1-6]. The introduction of Zn^{2+} ions in $Li_{0.5}Fe_{2.5}O_4$ lithium spinel increases the saturation magnetization (M_s) of ferrites, however, a decrease in M_s is observed with increasing Zn^{2+} content at $x \geq 0.4$.

There are several methods that increase the efficiency of ferrite synthesis and change their properties. One such method, named radiation-thermal (RT), is becoming increasingly important and widespread in the present time. The RT method is successfully tested in the synthesis of some oxide systems, including the synthesis of lithium-titanium [7], and lithium-zinc [8-10] ferrites under high-energy electron heating.

Compaction of reacting mixture is among the most important operations determining the efficiency of RT synthesis, since a compaction degree affects the initial conditions for the diffusion mass transfer. In [11], it was found that an increase in degree of reaction mixture compaction improve the efficiency of $Li_{0.5}Fe_{2.5}O_4$ lithium ferrite thermal (T) synthesis. In the present work, the influence of powder mixture reagents density on an efficiency of lithium-zinc ferrite synthesis under T and RT heating was investigated by XRD and specific magnetization analysis.

2. Experimental techniques

The object of the study was $Li_{0.5(1-x)}Zn_xFe_{2.5-0.5x}O_4$ lithium-zinc ferrite (x=0.2) synthesized from Li_2CO_3-ZnO-Fe_2O_3 mixture. Reagents mixture was obtained by weighing the required amounts of pre-dried components and then dry mixed in agate mortar with 10 fold mixed through a mesh with a cell of 80 μm. We investigated two types of samples: not compacted powder with 0.95 g/cm^3 density

(further, powder samples) and powder with 2.6 g/cm^3 density (further, compacted samples) that compacted by unilateral cold compaction under 200 MPa pressure into tablets with a 15 mm diameter and a 2 mm thickness.

Thermal heating of samples was carried out in a resistance furnace. Radiation-thermal heating of samples was performed on the pulse electron accelerator ILU-6 at Institute of Nuclear Physics SB RAS (Novosibirsk) [12]. The electron energy was 2.4 MeV, beam current pulse – 400 mA, pulse duration –500 μs, pulse repetition frequency – 7-15 Hz. Average radiation dose for isothermal heating mode was ca. 3 kGy/s. In limits of one pulse, a dose was 800 kGy/s. Samples heating and the preset temperature were carried out by decelerated electrons energy, without recourse to heat external sources. Duration of nonisothermal stages (heating and cooling) did not exceed 3 min. Both T and RT synthesis were realized in air. The modes with temperatures of 600 °C and 750 °C and times of 10 min and 120 min were used for both heating.

Analysis of sample phase composition was conducted by X-ray diffractometer ARL X'TRA with Peltier semiconductor Si (Li) detector with Cuk$_\alpha$ radiation. To analyse phase composition and materials structure, we used a symmetric Bragg diffraction geometry [13-14]. Measurements of diffraction patterns were spent in the range 2θ = (20-70)° at 0.02 °/s scanning speed. Phase identification was carried out using the PDF-4+ International Centre for Diffraction Data (ICDD) powder database. Received XRD patterns were processed by full-profile analysis method using Powder Cell 2.4 software.

Moreover, an additional control of synthesized samples was performed by saturation specific magnetization measurements using the automatic complex for study of magnetic properties in pulsed magnetic fields [15].

3. Result and discussion

Figure 1 shows X-ray diffraction patterns for Li_2CO_3-ZnO-Fe_2O_3 samples after T and RT synthesis. The marked reflections correspond to oxides or carbonate phases. Unmarked reflections belong to both α-Fe_2O_3 and spinel phases, from which the reflections merge into single-peak reflections. XRD analysis data, showing the content of $Li_{0.5(1-x)}$ $Zn_xFe_{2.5-0.5x}O_4$ spinel phases in synthesized samples, are summarized in Table 1.

XRD patterns for thermal synthesized samples indicate the presence of initial components phases, lithium orthoferrite, lithium pentaferrite, as well as $Li_{0.5(1-x)}$ $Zn_xFe_{2.5-0.5x}O_4$ lithium-zinc ferrites phases including the $Li_{0.4}Zn_{0.2}Fe_{2.4}O_4$ final composition. $Li_{0.4}Zn_{0.2}Fe_{2.4}O_4$ phase is formed in all modes except 600 °C – 10 min, in which there is only initial components phases and lithium orthoferrite.

According to the XRD data for RT synthesized samples, the reflections from the initial components phases and lithium ferrites spinel phases are observed. $Li_{0.4}Zn_{0.2}Fe_{2.4}O_4$ phase is formed in all modes including 600 °C – 10 min mode in which 9.7 wt.% this ferrite out of 13.7 wt.% spinel phases is observed for powder samples. Lithium-zinc ferrite formation is increased by increasing temperature and time of synthesis and reaches 88.9 wt.% out of 100 wt.% spinel phases in compacted samples at 750 °C – 120 min RT mode.

Overall, the results confirmed previous findings that the rate of ferrites formation is higher in conditions of heating reagents mixture by high-energy electron beam. In additional, the results show that the rate of lithium-zinc ferrite formation is higher in compacted samples, and so, the compaction of reacting mixture is a necessary process in ferrite production.

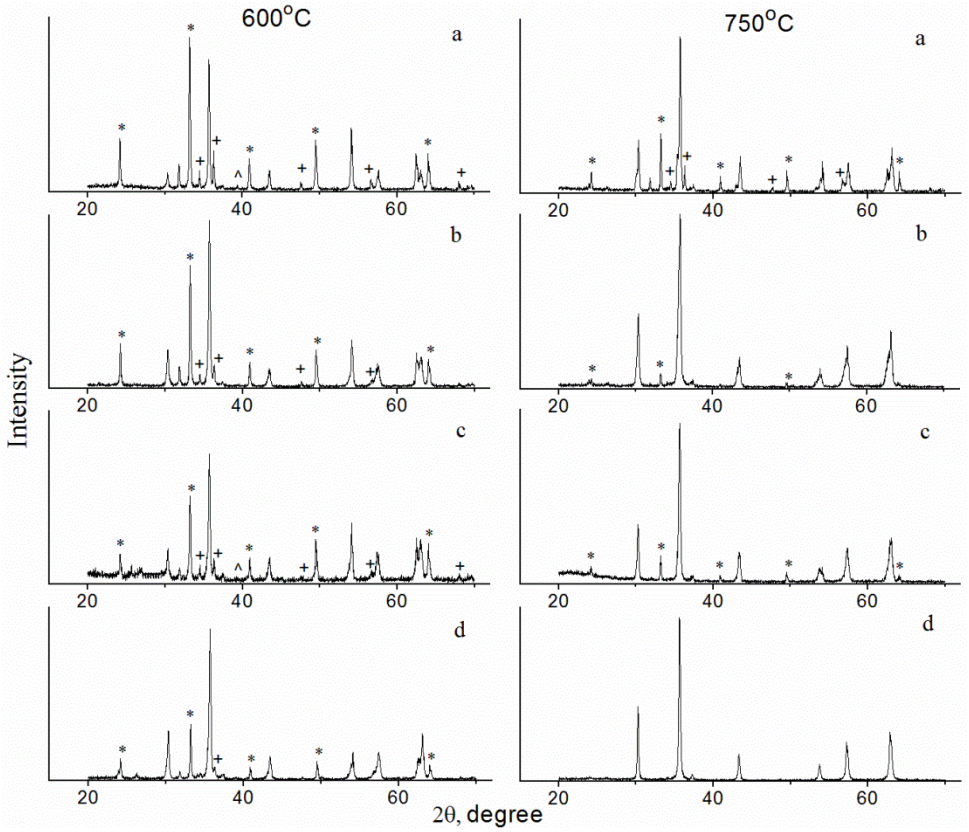

Figure 1. XRD pattern of Li_2CO_3-ZnO-Fe_2O_3 powder samples (a, c) and compacted samples (b, d) after T (a, b) and RT (c, d) heating at 600 and 750 °C for 120 min. Reflections of initial components: (*) - Fe_2O_3; (+) – ZnO; (^) - Li_2CO_3

Table 1. Content of spinel phases in $Li_{0.5(1-x)}Zn_xFe_{2.5-0.5x}O_4$ (weight %)

Synthesis mode	Type of heating	Powder samples	Compacted samples
600 °C –10 min	T	0	0.7
	RT	13.7	67.4
600 °C – 120 min	T	16	45.9
	RT	45.1	75.2
750 °C – 10 min	T	25.4	58.5
	RT	58.1	91.1
750 °C – 120 min	T	65.4	93.9
	RT	88.9	100

Magnetization data of Li_2CO_3-ZnO-Fe_2O_3 mixtures are given in table 2. The results showed an increase in magnetization of compacted samples compared to the powder samples, which also indicates a higher content of magnetic spinel phases in the synthesized compacts.

Table 2. Saturation magnetization of Li_2CO_3-ZnO-Fe_2O_3 mixture (emu/g)

Synthesis mode	Type of heating	Powder samples	Compacted samples
600 °C –10 min	T	1.2	-
	RT	8.9	43.5
600 °C – 120 min	T	10.9	31.5
	RT	20	48.7
750 °C – 10 min	T	13.4	34.2
	RT	40.4	66
750 °C – 120 min	T	36.5	55.9
	RT	59	68.7

4. Conclusions

• Use of uncompacted powder of initial reagents decreases the efficiency of solid-state synthesis of $Li_{0.5(1-x)}Zn_xFe_{2.5-0.5x}O_4$ ferrites.

• The application of compaction operation of powder reagents mixture leads to an increase in spinel phase concentration and decrease initial components content in lithium-substituted ferrites synthesized in thermal and radiation-thermal heating at the same temperature-time modes of synthesis.

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References

[1] Levin B E, Tret’yakov Yu D and Letyuk L M 1979 Physical and Chemical Principles of Synthesis, Properties, and Application of Ferrites [in Russian]. (Moscow: Metallurgiya)
[2] Jiang X N, Lan Z W, Yu Z, Liu P Y, Chen D Z and Liu C Y 2009 *J. Magn. Mater.* **321** 52–55
[3] Mazen S A and Abu-Elsaad N I 2012 *J. of Magnetism and Magnetic Materials* **324** 20 3366-3373
[4] Smit J and Wijn H P J 1959 *Ferrites. Physical properties of ferrimagnetic oxides in relation to their technical applications* (Eindhoven: Philips Technical Library) p 299
[5] Baba P D, Argentina G M, Courtney W E, Dionne G F and Temme D H 1972 *IEEE Trans. Magn.* **8** 83–94
[6] White G O and Patton C E 1978 *J. Magn. Magn. Mater.* **9** 4 299–317
[7] Surzhikov A P, Lysenko E N, Vlasov V A, Malyshev A V and Vasendina E A 2016 *Materials Chemistry and Physics* **176** 110-114
[8] Malyshev A V, Lysenko E N and Vlasov V A 2015 *Ceramics International* **41** 10 13671-13675
[9] Surzhikov A P, Lysenko E N, Malyshev A V, Vlasov V A, Suslyaev V I, Zhuravlev V A, Korovin E Y and Dotsenko O A 2014 *Russian Physics Journal* **57** 5 621-626
[10] Malyshev A V, Lysenko E N, Vlasov V A and Nikolaeva S A 2016 *Ceramics International* **42** 16180-16183
[11] Pritulov A M, Usmanov R U, Galtseva O V, Kondratyuk A A, Bezuglov V V and Serbin V I 2007 *Russian Physics Journal* **50** 2 187-192
[12] Auslender V L 1994 *Nuclear Instruments and Methods in Physical research* **B 89** 46–48
[13] Mittemeijer E J and Welzel U 2013 Modern Diffraction Methods. (Weinheim: Wiley VCH)
[14] Meisner L L, Lotkov A I, Ostapenko M G, Gudimova E Y and Arysheva G V 2012 *Inorganic Materials: Applied Research* **3** 5 401-407
[15] Kreslin V Yu and Naiden E P 2002 *Instruments and Experimental Techniques* **45** 1 55–57