

INFLUENCE OF MECHANICAL ACTIVATION OF INITIAL REAGENTS ON SYNTHESIS OF LITHIUM FERRITE

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The influence of mechanical activation of the $\text{Li}_2\text{CO}_3\text{-Fe}_2\text{O}_3$ initial reagents on ferrite phase formation in lithium ferrite LiFe_5O_8 is investigated. Methods of x-ray powder diffraction (XRD) and thermomagnetometry with differential scanning calorimetry (TG(M)/DSC) are used to compare the efficiency of nonisothermal synthesis at identical temperatures and burning times of the initial and mechanically activated reagent mixtures. It is demonstrated that preliminary mechanical activation of the initial $\text{Li}_2\text{CO}_3\text{-Fe}_2\text{O}_3$ reagent mixture considerably increases the reactivity of the solid phase system, thereby allowing the temperature of the thermal synthesis of lithium ferrite LiFe_5O_8 to be decreased significantly.

Keywords: lithium ferrite, LiFe_5O_8 , solid phase synthesis, mechanical activation, TG(M)/DSC, XRP.

INTRODUCTION

Lithium ferrite LiFe_5O_8 is the simplest representative of the wide class of lithium oxide ferros spinels characterized by a wide variety of compositions and structural modifications. Therefore, it is always considered as a model object for a study of fundamental physical phenomena proceeding in materials based on LiFe_5O_8 . However, lithium ferrite LiFe_5O_8 has attracted considerable recent attention of researchers because of its possible technological applications, for example, as a cathode material in recharged lithium batteries because of its low toxicity and low cost [1], as a substitute for more expensive garnets in microwave technique [2], and as elements of gas sensors because of high temperature and chemical stabilities [3].

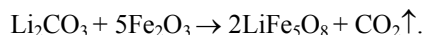
In most practical applications listed above, it is required to produce nanostructured LiFe_5O_8 which, as a rule, excludes the application of conventional high-temperature solid-phase synthesis for which coarsely dispersed powders are typical. In this regard, numerous studies have been devoted to the development of methods of low-temperature synthesis such as coprecipitation, zol-gel-method, hydrothermal method, etc. However, the procedure of implementation of these methods of synthesis often requires precursor annealing at high temperatures and application of high-grade inorganic or metal organic chemical products more expensive than oxides and carbonates.

It is well known that mechanical activation in high-energy ball mills is a method of synthesis of powder materials with disordered structure in finely dispersed states. Powders prepared by this method have high reactivity and allow the end products to be produced at lower temperatures with shorter thermal treatment period. Originally, mechanochemistry was developed for synthesis of intermetallic composites and alloys [4], and later on, it was used to synthesize magnetic and nanocrystal materials [5, 6]. In the scientific literature, data on the synthesis of lithium ferrite with mechanical treatment are few in number. In the present work, results of investigations into the influence of mechanical activation of initial reagents – lithium carbonate Li_2CO_3 and hematite $\alpha\text{-Fe}_2\text{O}_3$ – on the process of solid-phase LiFe_5O_8 synthesis are presented.

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EXPERIMENTAL PROCEDURE

As initial reagents, iron oxide Fe_2O_3 (analytically pure) and lithium carbonate Li_2CO_3 (chemically pure) were used. Before weighing, powders were dried for 3 h at a temperature of $\sim 200^\circ\text{C}$ in a desiccator. The ratio of the initial components in the reaction mixture was calculated by the equation



The reagents were mixed in the ratio 91.5 mass% of iron oxide and 8.5 mass% of lithium carbonate. The initial reagent mixture was mechanically activated in an AGO-2S planetary-type mill [7] with the use of steel grinding bowls and balls at room temperature for 60 and 180 min. Grinding was performed in the dry state. Masses of the material and balls were in the ratio 1:10. For a comparison, a part of the mixture was not mechanically activated.

Samples were compacted by single-ended cold pressing in the form of pellets 15 mm in diameter with thickness of 2 mm in a PGr-10 hydraulic press at a constant pressure of 200 MPa for 3 min. Ferritizing burning of compacts from initial and mechanically activated reaction mixtures was performed in the measuring cell of a thermal analyzer STA 449C Jupiter (Netzsch, Germany) in nonisothermal regime at temperatures in the range 20–900°C. Simultaneously, TG(M)/DSC measurements of samples were performed. The heating rate was 5 deg/min. In some experiments, the heating rate was increased to 50 deg/min. To control over the magnetic sample state during the entire thermal treatment period, permanent magnets were applied that created the magnetic field $H \sim 5$ Oe.

The XPD analysis was carried out using an x-ray diffractometer ARL X'TRA (Switzerland) with a semiconductor Si (Li) Peltie detector and Cu radiation. X-ray diffraction patterns were measured in the range $2\theta = 10\text{--}80^\circ$ with scanning rate of 0.02 deg/s. Phases were identified by the PDF-4 powder database of the International Center for Diffraction Data (ICDD). The x-ray diffraction patterns were processed by the full profile analysis using the *Powder Cell 2.5* software.

Effects of mechanical activation were estimated by a comparison of LiFe_5O_8 phase concentration obtained by synthesis of the initial and mechanically activated reagent mixtures at identical temperatures and burning times. The content of the LiFe_5O_8 phase was estimated by the XPD and TG(M)/DSC methods. The choice of the TG(M)/DSC method was caused by its high efficiency in the study of solid-phase ferrite synthesis [8–10]. The content of the LiFe_5O_8 phase was determined from the DSC peak at $\sim 755^\circ\text{C}$ caused by the order-disorder transition ($\alpha \rightarrow \beta$ phase transition) and from the mass jump in the dependence of x-ray diffraction pattern of the sample when going through the Curie temperature in an external magnetic field. These data were then compared with the results of full profile analysis of x-ray diffraction patterns.

For a comparative analysis of nonisothermal lithium ferrite synthesis, reference samples with high content of the LiFe_5O_8 phase were synthesized by the conventional method from mechanically non-activated reagents in an MPL-6 laboratory furnace “KhimLabo” equipped with a programmable timer Varta TP-403 at a temperature of 900°C for 2 h.

EXPERIMENTAL RESULTS AND DISCUSSION

The x-ray diffraction pattern of the reference LiFe_5O_8 sample is shown in Fig. 1. An analysis of the number of peaks demonstrates the dominating α - LiFe_5O_8 phase. As is well known (for example, see [11–13]), the cation distribution of Fe^{+3} and Li^+ ions between the tetrahedral (A) and octahedral (B) sublattices corresponds to the structure of inverted spinel $\text{Fe}^{+3}[\text{Li}_{0.5}\text{Fe}^{+3}_{1.5}]\text{O}_4$. The presence of superstructural reflections on the x-ray diffraction pattern demonstrates the existence of the process of atomic ordering 1:3 at which three Fe^{+3} ions and one Li^+ ion are naturally localized in octahedral positions along the $\langle 110 \rangle$ crystallographic directions. The presence of atomic ordering is confirmed by the DSC data shown in Fig. 2. The high-temperature peak on the DSC curve at $\sim 760^\circ\text{C}$ is associated with the phase transition of the ordered LiFe_5O_8 structure to the disordered state. The enthalpy of the $\alpha \rightarrow \beta$ transition characterizes the degree of ordering of the lithium spinel structure. The value of this parameter (~ 11 J/g) is in satisfactory agreement with the literature data [14].

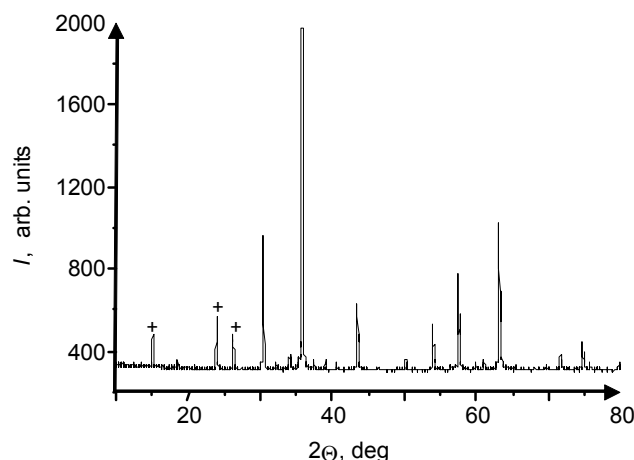


Fig. 1. X-ray diffraction pattern for reference lithium ferrite samples; superstructural LiFe_5O_8 reflections are indicated by (+).

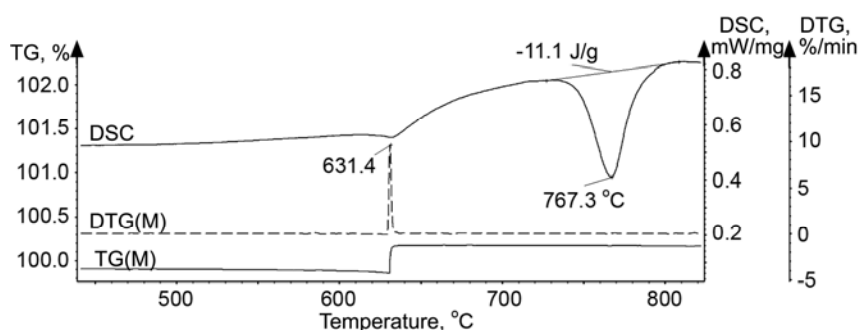


Fig. 2. TG(M)/DSC/DTG(M) curves for reference lithium ferrite samples.

The weak peak on the DSC curve approximately at 630°C corresponds to the magnetic (ferrimagnetic \rightarrow paramagnetic) phase transition and demonstrates the magnetocaloric effect in LiFe_5O_8 [10]. Indeed, during TG(M) measurements, the mass jump caused by the termination of magnetic interaction between lithium ferrite and applied field was observed at this temperature. The differential thermogravimetry (DTG(M)) curve shows the Curie temperature of the examined lithium ferrite sample.

Figure 3 shows x-ray diffraction patterns for the initial (a) and mechanically activated (b) mixtures of reagents. The data of XRD analysis (Fig. 3a) testify to the presence of two phases $\alpha\text{-Fe}_2\text{O}_3$ and Li_2CO_3 . In the x-ray diffraction patterns in Fig. 3b, $\alpha\text{-Fe}_2\text{O}_3$ peak broadening is observed due to decreased crystalline sizes and increased microstrains as a result of mechanical grinding. In addition, the XRD analysis of these samples demonstrated the presence of small amount of $\gamma\text{-Fe}_2\text{O}_3$. The absence of lithium carbonate peaks on the x-ray diffraction pattern of mechanically activated mixture (Fig. 3b) is most likely due to its transition to the ultradisperse state and dominating amorphous Li_2CO_3 phase. Using the *Powder Cell* software, the structural parameters, sizes of coherent scattering regions (CSR), and internal elastic microstresses $\Delta d/d$ of the examined materials were calculated. These data are tabulated in Table 1.

In Fig. 4, the TG(M)/DSC curves are shown for the initial reagent mixture (Fig. 4a) and the reagent mixture mechanically activated for 180 min (Fig. 4b). Irrespective of the method of preparation of the reaction mixture, the TG(M) curves demonstrate smeared mass decrease starting from a temperature of $\sim 500^\circ\text{C}$ for the initial mixture and $\sim 400^\circ\text{C}$ for the mechanically activated mixture. The endothermic peaks on the DSC curves which correlate well with the DTG(M) dependences correspond to the mass decrease. These mass changes were caused by the interaction of iron

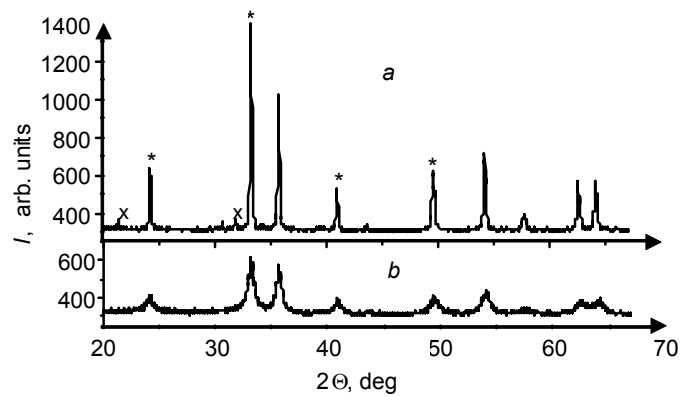


Fig. 3. X-ray diffraction patterns of the $\text{Li}_2\text{CO}_3\text{-Fe}_2\text{O}_3$ mixture before (a) and after (b) mechanical activation for 180 minutes. Reflections of the components Fe_2O_3 (*) and Li_2CO_3 (x).

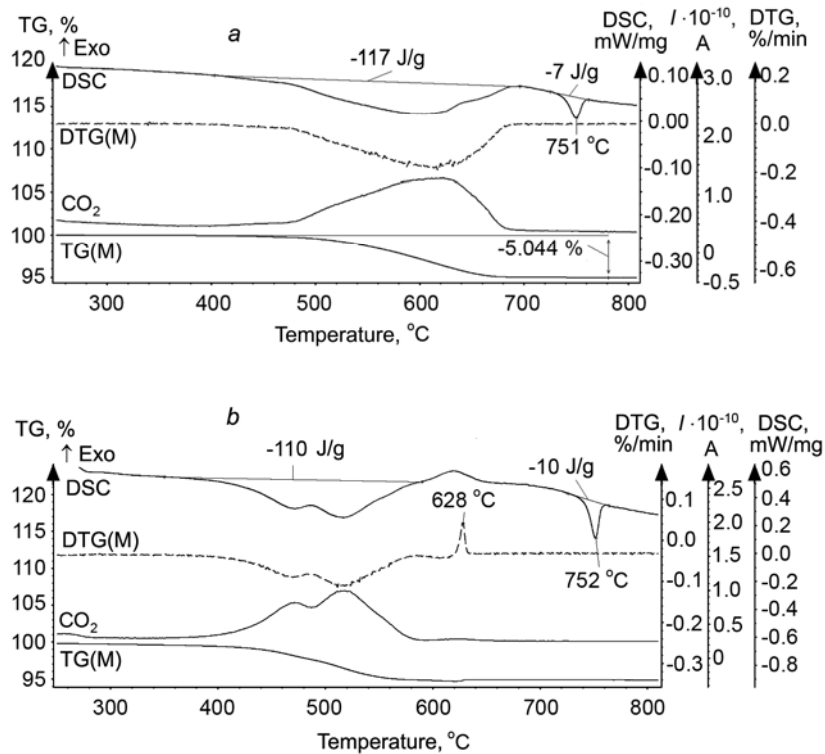


Fig. 4. TG(M)/DSC curves for the compacted initial reaction mixture (a) and the mixture mechanically activated for 180 min (b). The rate of heating was 5 deg/min.

oxide and lithium carbonate and, as demonstrated the data of mass spectrometry, they were accompanied by liberation of carbon dioxide gas with the corresponding mass losses. Since the Li_2CO_3 melting temperature is equal to 730°C [15], this interaction was diffusive in character. The calculated change of the sample mass with allowance for CO_2 liberation was 5.044 mass%, which was in agreement with the TG(M) data.

The difference between the DSC peak areas at $\sim 750^\circ\text{C}$ whose experimental value for single-phase LiFe_3O_8 is shown in Fig. 2 seems to be important. Since the area of this peak is determined by the energy spent for polymorphic

TABLE 1. Structural Parameters of the Reagent Mixture from the Data of XRD Analysis

Mixture	Composition	Lattice parameter, nm	CSR, nm	$\Delta d/d \cdot 10^3$
Initial	Fe ₂ O ₃	$a = 5.036, b = 13.755$	78	0.6
	Li ₂ CO ₃	$a = 8.368, b = 4.979, c = 6.198$	86	0.3
Mechanically activated for 180 min	Fe ₂ O ₃	$a = 5.038, b = 13.765$	17	2.4
	Li ₂ CO ₃	–		
	γ -Fe ₂ O ₃	$a = 8.346$	15	2.8

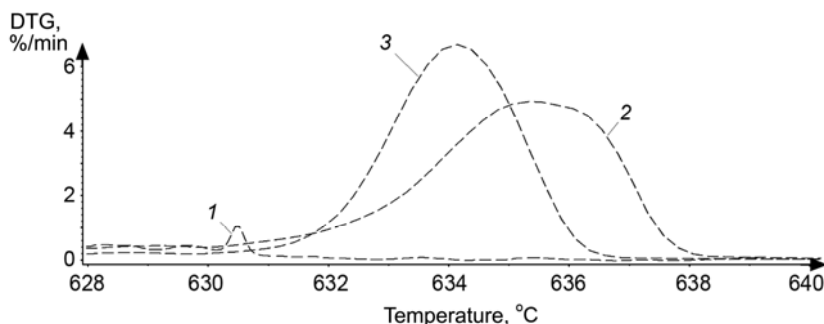


Fig. 5. DTG(M) curves for the initial sample (curve 1) and samples mechanically activated for 60 (curve 2) and 180 min (curve 3). The dependences were measured in the regime of cooling with a rate of 50 deg/min after nonisothermal heating of the samples.

$\alpha \rightarrow \beta$ transition in the LiFe₅O₈ phase, the difference between the peak areas of the $\alpha \rightarrow \beta$ transition observed in Fig. 4 testifies to much higher concentration of α -LiFe₅O₈ formed during nonisothermal burning of mechanically activated samples.

If the enthalpy of the $\alpha \rightarrow \beta$ transition corresponds to the amount of the ordered modification of the lithium ferrite phase, the mass change when going through the Curie temperature characterizes the total content of both LiFe₅O₈ modifications. It is convenient to characterize these changes by the DTG(M) curves that are derivatives of the TG(M) curves. Figure 5 shows the DTG(M) dependences for samples synthesized from the initial reagent mixture (curve 1) and the reagent mixtures mechanically activated for 60 (curve 2) and 180 min (curve 3).

It can be seen that the DTG(M) peak intensities for the initial and mechanically activated samples differ considerably. Hence, mechanical activation of the mixture increases considerably the rate of formation of lithium ferrite. From the ratio of the DTG(M) peak intensities, a 5-fold increase of the ferrite phase formation rate can be estimated for activation period of 60 min and a 7-fold increase for activation time of 180 min. These values exceed the ratio of enthalpies of the $\alpha \rightarrow \beta$ transitions (Fig. 4) equal to ~ 1.4 for activation period of 180 min. This difference can be caused by shorter period of ferritizing burning, because the DSC peaks were registered upon heating to temperature of $\sim 760^\circ\text{C}$, whereas the DTG(M) peaks shown in Fig. 5 were measured after heating of samples to temperature of 900°C (Fig. 4) and burning with subsequent cooling to the Curie temperature. Another reason can be formation of a part of the lithium ferrite phase in disordered β -modification.

CONCLUSIONS

Mechanical activation of the mixture of initial Li₂CO₃-Fe₂O reagents considerably increased the reactivity of the solid phase system, which made it possible to decrease significantly the temperature of thermal synthesis of lithium ferrite LiFe₅O₈.

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