

# Kinetics of Radiation – Thermal Synthesis of Lithium Pentaferriite from Mechanical Mixture of Ferric Oxide and Lithium Orthoferriite

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**Abstract – The present paper describes the research results of radiation-thermal synthesis of lithium pentaferriite from the mixture of lithium orthoferriite and ferric oxide. By the submitted results it is possible to conclude, that decrease of efficient activation energy under radiation-thermal synthesis can be explained by momentary cation charge decline from  $Fe^{3+}$  to  $Fe^{2+}$ , caused by big concentration of free electrons in the material formed by the accelerating electron beam. Decrease in activation energy for ions  $Fe^{2+}$  can be explained by reducing of electrostatic interaction of the ions with ambient anions, i.e. by reducing of Madelung component of bonding energy of a ferric cation. Bond reduction in crystal environment involves not only decrease in  $E_a$ , but also reducing of local vibration frequency of ion  $Fe^{2+}$ . Thus, decrease in a frequency factor under radiation-thermal synthesis is explained by the above described fact and momentary existence of the recharged state.**

## 1. Introduction

A problem of activation of solid-phase reactions, solving of which would make possible to cut down ceramic synthesis temperature and reduce its duration, is actual for the field of material science of oxide-composite high-temperature compounds. Existing data indicate that one of these methods is an impact of intensive accelerating electron stream on a substance, under which decelerating electrons might heat the substance up to high temperatures (radiation thermal (RT) actions) [1,2]. It was, in particular, shown that under intensive electron beam impact on a equimolar mixture of lithium carbonate and ferric oxide within the temperature range of 600–950°C, synthesis rate of lithium pentaferriite is essentially increasing in comparison with the rate of the ferrite forming under radiation-thermal annealing [2]. Content of impurities of the lithium orthoferriite, an intermediate synthesis product, was also reduced in specimens synthesized by radiation-thermal method.

Since lithium pentaferriite synthesis is a two-stage solid-phase reaction, it is supposed to be necessary to determine efficiency of the electron beam action on each component of ferritization, including a stage of transformation of the orthoferriite into pentaferriite. Thus, the present paper describes the research results of RT synthesis of lithium pentaferriite from the mixture of lithium orthoferriite and ferric oxide.

## 2. Experimental technique.

Initial components of the reaction mixture for lithium pentaferriite synthesis were powders  $\alpha-Fe_2O_3$  and  $LiFeO_2$ . Before weighing the powders were dried up during 7 hours at the temperature of 200°C in a drying box. Then the powders were weighted in proportion corresponding to the reaction:  $LiFeO_2 + 2Fe_2O_3 \rightarrow LiFe_5O_8$ , mixed up by means of quintuple rubbing (cell size is 110  $\mu m$ ) and pressed in the form of pellets with the diameter of 15 mm and thickness of 2 mm.

Radiation-thermal synthesis of specimens was carried out on pulse electron accelerator *ILU-6* (Institute of nuclear Physics, SB RAS, Novosibirsk) at the temperature of 600°C. Electron energy was 2.5 MeV, beam current in the pulse – 400 mA, pulse duration – 500  $\mu s$ , pulse repetition rate – 4÷12 Hz. Heating rate of the mixture and its cooling down were 130 and 90°C/min respectively. The temperature was controlled by a platinum-platinum-rhodium thermopaire, measuring juncture of which was placed in a geometric center of pressed specimens, in the zone of maximum energy-release of the electron beam. To avoid contamination the specimens were placed in a platinum lattice, in the central part of the light chamotte cell. Towards the radiation thickness of the chamotte heat shields does not exceed 0.1 g/cm<sup>2</sup>, which provided for minimum losses of electron energy (~8%).

To define radiation effects experiments on thermal synthesis  $LiFe_5O_8$  were carried out with the use similar initial powders under similar pressing conditions. Thermal annealing was carried out in air in a silit resistance furnace. Rates of heating-up and cooling-down were close to the corresponding rates under RT synthesis.

To determine a phase structure and parameters of the crystal lattice of the tested specimens an automated X-ray diffractometer DRON-4-07 on Fe  $k_{\alpha}$  radiation was used. Shooting geometry with Bragg-Brentano's focusing with pyrolytic graphite monochromator on a primary beam was used. Obtained X-ray pictures were processed by full-profile analysis with the use of software Powder Cell 2.4. Additional control on a synthesis grade was ensured by measuring of specific magnetization of specimens by a magnetometer implementing the method proposed in [3].

## 3. Experimental results.

Analysis of X-ray pictures has shown that they conformed to a superposition of mappings from  $\alpha-Fe_2O_3$ ,

$\alpha$ -LiFeO<sub>2</sub>, and LiFe<sub>5</sub>O<sub>8</sub> during the tested interval of annealing duration. Fig. 1 represents kinetic dependencies of abundances of the phases  $\alpha$  – LiFeO<sub>2</sub> (initial component) and LiFe<sub>5</sub>O<sub>8</sub> (product of synthesis).

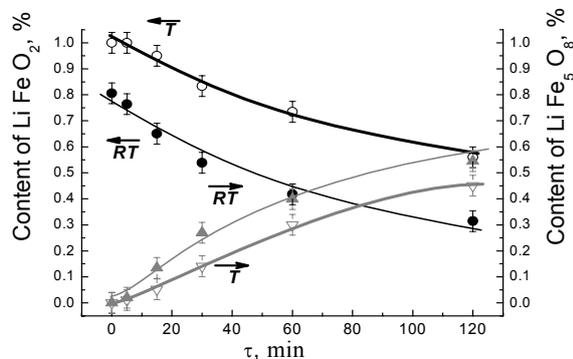


Fig. 1. Dependencies of abundances of phases LiFeO<sub>2</sub> and LiFe<sub>5</sub>O<sub>8</sub> in the mixture on duration of thermal and radiation-thermal annealing under the temperature of 600°C

Kinetic changes in content of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> are similar to dependencies of the orthoferrite phase. Since the lithium pentaferite is a ferromagnetic compound, after annealing the reaction mixture acquires magnetization with the value that correlates with abundance of the pentaferite phase (Fig. 2).

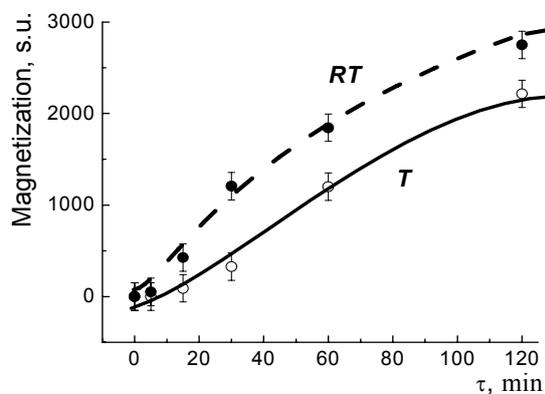


Fig. 2. Dependencies of reaction mixture magnetization on duration of thermal and radiation-thermal annealing under the temperature of 600°C

Data given in Fig. 1 and 2 illustrate increase in grade of ferritization and magnetization of the powder mixture under radiation-thermal annealing. This testifies radiation intensification of the lithium pentaferite synthesis under 600°C. Comparing the magnetization value with lithium pentaferite abundance after both types of annealing we can see that points, corresponding to RT and thermal synthesis, are on a common curve (Fig.3). This fact testifies independence of cation distribution in the ferrite from the type of ferrite annealing.

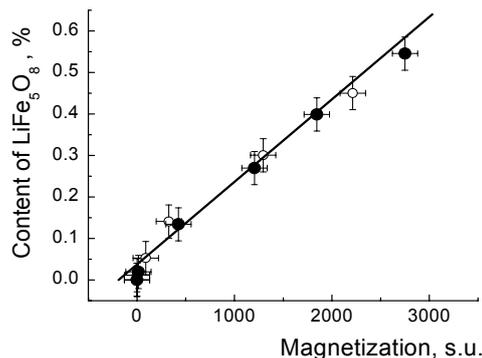


Fig. 3. Dependence of magnetization of the mixture, annealed under 600°C, from the phase abundance LiFe<sub>5</sub>O<sub>8</sub>: ○ – annealing under thermal conditions, ● – annealing under radiation-thermal conditions

With the rise of annealing temperature radiation effect inversion takes place. For example, Fig.4 illustrates kinetic dependencies of abundance of lithium penta-, orthoferrite after thermal and RT annealing of the reaction mixture under 800°C. It is obvious that under 800°C synthesis slows down under the conditions of electron radiation. Behavior of kinetic curves of the mixture magnetization is analogous, while experimental points correlate with the dependence as before Fig.3. Consequently, the radiation effect inversion does not change cation sublattice population of the lithium pentaferite.

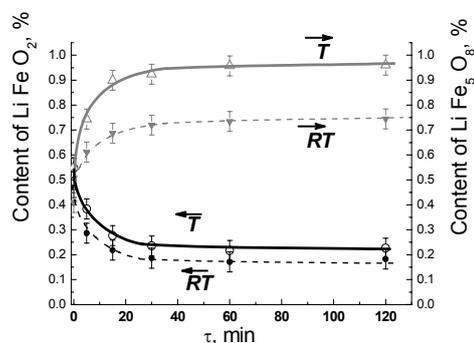


Fig. 4. Dependencies of abundances of phases LiFeO<sub>2</sub> and LiFe<sub>5</sub>O<sub>8</sub> in the mixture on duration of thermal and radiation-thermal annealing under the temperature of 800°C

Thus, electron beam impact under 700°C and over slows down the synthesis reaction of the type  $\text{LiFeO}_2 + 2\text{Fe}_2\text{O}_3 = \text{LiFe}_5\text{O}_8$ . Analysis of kinetic dependencies has shown that they are satisfactorily described within the nucleation model by Avrami-Erofeev equation [3]. Constants of the reaction rate, calculated by this equation, obey the Arrhenius law. Parameters of the reaction rate (preexponential factor  $K_0$  and efficient activation energy  $E_a$ ) for both synthesis modes are given in the table below. It is clear that constants of reaction rates of lithium pentaferite formation and rates of ferric oxide decreasing are practically coincide,

which testifies absence of limiting intermediate stages of ferrite formation. It is also obvious that under radiation-thermal synthesis an activation barrier of the reaction is increasing and a frequency factor is reducing.

Table. Constant parameters of the synthesis rate  $\text{LiFe}_5\text{O}_8$  and decreasing  $\text{Fe}_2\text{O}_3$  in powders after annealing under radiation-thermal and thermal conditions

Parameter	$\text{LiFe}_5\text{O}_8$		$\text{Fe}_2\text{O}_3$	
	T	RT	T	RT
$K_0, \text{s}^{-1}$	$1.4 \cdot 10^4$	$2.2 \cdot 10^2$	$1.4 \cdot 10^4$	$6 \cdot 10^2$
$E_a, \text{eV}$	1.42	1.24	1.42	1.24

Decrease of efficient activation energy under radiation-thermal synthesis can be explained by momentary cation charge decline from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , caused by big concentration of free electrons in the material formed by the accelerating electron beam. Since ions of  $\text{Fe}^{3+}$  in comparison with ions of  $\text{Li}^+$  and  $\text{Fe}^{2+}$  have higher bigger charge, movement of cation  $\text{Fe}^{3+}$  over the spinel lattice is more difficult than movement of the mentioned ions. Therefore a momentary cation recharge with the reducing of their charge value under radiation-thermal conditions causes increase in mobility of

ferric ions and accelerating of the reaction. Decrease in activation energy for ions  $\text{Fe}^{2+}$  can be explained by reducing of electrostatic interaction of the ions with ambient anions, i.e. by reducing of Madelung component of bonding energy of a ferric cation. Bond reduction in crystal environment involves not only decrease in  $E_a$ , but also reducing of local vibration frequency of ion  $\text{Fe}^{2+}$ . Thus, decrease in a frequency factor under radiation-thermal synthesis is explained by the above described fact and momentary existence of the recharged state.

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