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Synthesis of substituted lithium ferrites under the pulsed and continuous electron beam heating

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ABSTRACT

Synthesis of substituted lithium ferrites with chemical formulas $Li_{0.6}Fe_{2.2}Ti_{0.2}O_4$ and $Li_{0.649}Fe_{1.598}Ti_{0.5}Zn_{0.2}Mn_{0.051}O_4$ under the pulsed and continuous electron beam heating was investigated by X-ray diffraction and thermomagnetometric analysis. The electron beams heating of Li_2CO_3-Fe_2O_3-TiO_2 or Li_2CO_3-ZnO-Fe_2O_3-TiO_2-MnO mixtures was carried out at a temperature of 750 °C during 60 min using two types of electron accelerators: ELV accelerator generating continuous electron beam or ILU-6 accelerator generating pulse electron beam. It was established that a high energy electron beam heating of initial reagents mixtures allows obtaining the substituted lithium ferrites with final composition at significantly lower temperatures (at least 200 °C lower than in the case of using traditional thermal synthesis) and times of synthesis. That statement is in agreement with results obtained by XRD analysis, showing single phase formation; by magnetic measurements, showing high values of specific magnetization; by DTG measurements showing the certain Curie temperatures of the synthesized samples.

1. Introduction

Lithium and substituted lithium ferrites are magnificent materials for use in microwave applications due to their low cost and good magnetic and electrical properties that depend on composition of ferrites and processing techniques [1,2]. Lithium ferrite, $Li_{0.5}Fe_{2.5}O_4$, adopts an inverse spinel structure of the general formula AB_2O_4 in which the Li^+ ions and 3/5 of the Fe^{3+} ions occupy the octahedral B-sites whilst the remaining Fe^{3+} ions occupy tetrahedral A-sites. The magnetic properties of $Li_{0.5}Fe_{2.5}O_4$ can be modified by substituting magnetic and/or diamagnetic cations for Fe^{3+} ions on either sublattice.

Substituted Li ferrites, in which Fe^{3+} ions are substituted by ions of titanium and/or zinc, are characterized by low values of dielectric losses and high temperature stability. The introduction of Ti^{4+} ions into the lithium spinel reduces the probability of Fe^{2+} formation, and leads to a high electrical resistance [3–5]. To increase the saturation magnetization, a partial substitution of Zn^{2+} ions is produced [6,7]. Thus, substituted lithium ferrites with the chemical composition of $Li_{0.5+0.5t-0.5x}Fe_{2.5-1.5t-0.5x}Ti_tZn_xO_4$ are characterized by a high resistivity, squareness of hysteresis loop, low dielectric and magnetic losses over a wide frequency range and high Curie temperature [8,9].

As a soft magnetic material, lithium ferrites are very sensitive to structural and phase imperfections. The solid-state synthesis, where both the high temperatures (above 1000 °C) and long times are used, is the main method to manufacture substituted lithium ferrites powders with homogeneous composition, which are then used for a high-density ferrite ceramics production as microwave elements with specific electro-magnetic properties. However, the high synthesis temperature leads to lithium and oxygen volatility at temperatures above 1000 °C, as a result, low magnetic properties and high dielectric loss occur [10].

In particular, the efficiency of solid-phase synthesis can be increased by application of specific methods that allow the reagents to be activated directly in the process of synthesis. In [11–13], it was demonstrated that a heating of precursors by an intensive electron beam is an efficient method for solid-state reactions intensification. This method is called radiation-thermal (RT) because it combines simultaneous influence of thermal and radiation factors. The ILU- and ELV-type electron accelerators, devel-

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oped at the Institute of Nuclear Physics SB RAS (Novosibirsk, Russia), are appeared to be very convenient for such studies [14,15]. Such accelerators and other modifications with the electron energy range from 1 to 5 MeV allow heating the objects being studied to any given temperature without any additional heat sources [16,17]. Recently, RT method was successfully used in the synthesis of some ferrite systems, such as Ni–Zn ferrites [18], hexaferrites [19], and strontium ferrites [20]. It was established that the substituted lithium ferrites with a homogeneous composition can be obtained at significantly lower temperatures and times of synthesis compared with a standard thermal heating [21], furthermore, the synthesized samples are characterized by the high values of saturation magnetization [22].

It is also known [23,24] that a mechanical activation in a high energy ball mill is a popular technique to prepare the powders with disordered structure and fine fraction. In case of ball milling of ferrites, the mechano-composites with high contact area of reagents are occurs [25]. Such powders are highly reactive, which makes it possible to obtain reaction products at lower temperatures and shorter thermal treatment period [26,27]. In [28] we presented the results of lithium-zinc ferrite synthesis under the high-energy actions including a mechanical activation of the initial reagents mixture in a planetary mill and subsequent heating of the reaction mixtures upon exposure to accelerated high-energy electron beams. It was established that the both the mechanical activation and radiation-thermal heating of Li_2CO_3–ZnO–Fe_2O_3 mixture increases more significantly (compared with the thermal heating of the milled mixture) the reactivity of solid phase systems thereby decreasing strongly the temperature of synthesis and improving the homogeneity of the end product.

For zinc substituted lithium ferrites prepared by the radiation-thermal heating, microstructures as well as electromagnetic and dielectric properties were extensively studied [29,30]. However, all studies in this area were carried out using the ILU accelerator based on the pulsed electron beam.

In this study, the results of substituted lithium ferrites synthesis with various compositions under heating by the pulse and continuous intensive electron beams were obtained.

2. Experimental

The substituted lithium ferrites with chemical formulas $Li_{0.6}Fe_{2.2}Ti_{0.2}O_4$ (Li-Ti ferrite) and $Li_{0.649}Fe_{1.598}Ti_{0.5}Zn_{0.2}Mn_{0.051}O_4$ (Li-Ti-Zn ferrite) prepared from, respectively, Li_2CO_3-Fe_2O_3-TiO_2 and Li_2CO_3-ZnO-Fe_2O_3-TiO_2-MnO mechanical mixtures, were investigated. The initial powders were dried for 3 h at 200 °C and mixed in proportions corresponding to the chemical formulas.

Before RT synthesis, the mixtures were mechanically activated using a high energy planetary ball mill AGO-2S (Novic, Russia) for 60 min at 2220 rpm rotation speed for vial. The steel vial (135 ml) and grinding balls (6 mm) were used, and the weights of the material and balls were in the ratio 1:10. The samples of milled mixtures were compacted by a single-ended cold pressing in the form of pellets in a PGr-10 hydraulic press at a constant pressure of 200 MPa for 3 min.

RT synthesis of samples was carried out at a temperature of 750 °C during 60 min using two types of electron accelerators: ELV accelerator generating continuous electron beam (ELV samples) or ILU-6 accelerator generating pulse electron beam (ILU samples), which were developed in Institute of Nuclear Physics of the SB RAS (Novosibirsk, Russia).

The electron energy of ILU-6 machine was 2.4 MeV; the pulse beam current, the pulse duration, and the pulse repetition rate were 400 mA, 500 μs, 12.5 Hz respectively. The electron energy of ELV machine was 1.4 MeV; the beam current was 6.3 mA. The samples were heated by the electron beam in air using the special cell (Fig. 1) with thermally insulating walls and lid (transparent to the electron beam) from lightweight fireclay. The temperature was controlled by thermocouple (type S), which was located in control sample that placed in the immediate vicinity of the investigated samples. The thermal processing mode is regulated by the pulse repetition frequency of the electron beam in ILU-6 accelerator and the beam current in ELV accelerator that allows providing any changes in a temperature regime.

The sample thicknesses were 0.4 cm and 0.21 cm for the ILU and ELV samples, respectively, and were equal to the maximum range of electron beam, which is given by the formula put forward by Katz and Penfolds for energy region $0.01 < E < 2.5$ MeV [32]:

$$R_{max} = \frac{0.412E^{(1.265-0.0954lnE)}}{\rho}$$

where R_{max} is the maximum range of electron beam in cm, E is the electron energy in MeV, $\rho = 3$ g cm^{-3} is the density of samples.

A necessary condition for radiation-thermal experiments is the uniform distribution of beam current density at the surface of the irradiated material to ensure the uniform temperature field in materials [31]. For this, the samples were placed into the thermostatic cell (Fig. 1) in the central part of the electrons beam areas where the current density non-uniformity is minimal. The unevenness of the current density on the target was assumed as a value of ±(2–3)%, which corresponds to (10–15) °C temperature fluctuations at a temperature of about 750 °C.

The synthesis temperature of ferrite samples depends on an average beam current density. For separate control the ELV and ILU samples, the experimental results for temperature variation in an initial time of heating at the different beam current densities are shown in Fig. 2. The heating rate in the initial part of the each curve is maximal. Under the constant beam current density, the heating rate of the samples is gradually reduced with increase in irradiation time. Fig. 3 shows the registered maximum temperature as function of beam current density for the control samples. For both electron beams heating, the average beam current density was 9 μA cm^{-2} to achieve a temperature of 750 °C. It was established (see Fig. 2) that an almost complete temperature alignment on a depth of samples is observed in condition of irradiation time more than 3 min; i.e. the equilibrium temperature is set in the material, which corresponds to the synthesis temperature in isothermal mode.

The phase composition of the samples was controlled using an ARL X'TRA X-ray diffractometer (Switzerland) with a Peltier Si (Li) semiconductor detector and Cu K_α radiation. XRD patterns were measured for $2\theta = (10–140)°$ with a scan rate of 0.02°/s. The phase

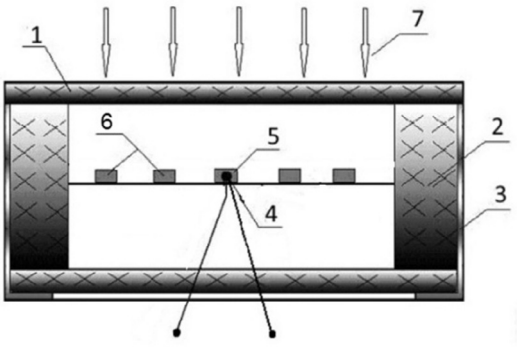

Fig. 1. The experimental cell for ferrite synthesis by accelerated electron beam: 1 – fireclay upper cover; 2 – fireclay insulator; 3 – stainless steel cell; 4 – thermocouple; 5 – control sample; 6 – the ferrite samples; 7 – the electron beam.