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Microstructure and reactivity of Fe_2O_3-Li_2CO_3-ZnO ferrite system ball-milled in a planetary mill

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ABSTRACT

In this work, the microstructure of mechanically activated Fe_2O_3-Li_2CO_3-ZnO mixture for the lithium-zinc ferrites production was studied using the Brüner, Emmett, Teller and laser diffraction methods as well as X-ray diffraction and scanning electron microscopy analyses. The reactivity of reagent mixture was investigated by thermogravimetric and calorimetric analyses. The ball milling was performed in a AGO-2S high energy planetary ball mill with a vial rotation speed of 2220 rpm using steel grinding balls. The milling times were 0, 5, 15, 30 or 60 min. It was shown that the composition of mixture changes during the ball milling, which consists in decreasing the α-Fe_2O_3 concentration and increasing the Fe_3O_4 spinel phase, while the Li_2CO_3 and ZnO concentrations remain unchanged. It was found that the milling leads to decrease in the average particle size of the reagents and simultaneously formation of large size agglomerates with denser structure and well-interlinked particles. It was established that observed changes in microstructure and phase composition lead to an increase in the reactivity of the Fe_2O_3-Li_2CO_3-ZnO system and the acceleration of the chemical reaction between reagents.

1. Introduction

The Li_2O-Fe_2O_3 system is of considerable interest for production of a variety of materials such as ferrites with different objective functions, catalysts, solid-oxide electrodes [1–3]. According to the equilibrium phase diagram, the Li_2O-Fe_2O_3 system may form the $LiFeO_2$ lithium orthoferrite (γ – low-temperature high-ordered form and α – high-temperature disordered form; the temperature of γ↔α transition is ca. 670 °C) and the $Li_{0.5}Fe_{2.5}O_4$ lithium ferrite with spinel structure [4,5]. The latter has the structure of an inverse spinel $Fe^{3+}[Li_{0.5}{}^{+}Fe_{1.5}{}^{3+}]O_4$, and at $T < 750$ °C, lithium and iron ions are ordered in the Fd-3m (α-phase) type in the octahedral sublattice. However, disordered form of lithium ferrite has a random statistical distribution of lithium and iron over all the octahedral positions.

The properties of lithium ferrites can be tailor made by substituting them with different metal ions such as Zn^{2+}, Cu^{2+}, Ti^{4+}, Mg^{2+}, Co^{2+}, Ni^{2+}, etc. Zinc is known to play a decisive role in determining the ferrite properties [6–8]. The redistribution of metal ions over the tetrahedral and octahedral sites in the spinel lattice on incorporation of zinc is responsible for the modification of ferrite properties. Thus, substituted lithium ferrites with chemical composition of $Li_{0.5(1-x)}Zn_xFe_{2.5-0.5x}O_4$, in which the ions Fe^{3+} are substituted by ions of zinc, are characterized by high saturation magnetization and this promotes their wide application in microwave technology [9,10].

The conventional way to synthesize lithium ferrites involves the use of high-temperature solid-state reaction including the mixing of oxide/carbonate and then mixtures annealing at high temperatures [11,12]. Such synthesis method has some disadvantages which include chemical inhomogeneity, coarser particle size and volatility of Li_2O from ferrites during synthesis [13].

In order to overcome these drawbacks, a number of chemical methods were developed to prepare ferrites at low temperatures. They include the hydrothermal method, the citrate precursor and sol gel methods and etc. [14–19]. However, many of these methods have major drawback which consists in applying the repeated high temperature to form the monophase of lithium ferrite.

One of the methods that allow to reduce the synthesis temperature is preliminary mechanical activation of ferrite reagents in high energy ball mills [20–23]. Such powders are highly reactive, which makes it possible to obtain reaction products at lower temperatures and shorter thermal treatment period. According to earlier investigation, mechanical activation can be used to produce lithium [24–26] and substituted lithium [27,28] ferrites at lower temperature than in conventional ceramic processing. In our previous work [29], the influence of mechanical activation of Li_2CO_3-Fe_2O_3-ZnO and Li_2CO_3-TiO_2-Fe_2O_3 initial reagent mixtures on the solid-phase synthesis of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ and $Li_{0.6}Fe_{2.2}Ti_{0.2}O_4$ substituted lithium ferrites was studied. It was established that the ferrites can be obtained from mechanically activated

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mixtures at temperatures at least 200 °C lower than in the case of using un-milled mixtures.

Although a substantial literature has accumulated on the use of mechanical milling for ferrite formation, there is only limited information on the microstructure of ferrite powders. In this work, using the Brüner, Emmett, Teller (BET) and laser diffraction methods, as well as XRD and SEM analysis, the microstructure of un-milled and ball-milled initial reagents for the lithium-zinc ferrites production was studied. The reactivity of reagent mixtures was investigated by thermogravimetric and calorimetric analyses.

2. Experimental

The initial reagents were commercially Fe_2O_3, Li_2CO_3 and ZnO (99%, Reahim Co., Russia) powders which were pre-dried and mixed in molar ratios of 86.05 mass%, 6.64 mass% and 7.31 mass%, respectively, according to the reaction

$$Li_2CO_3 + 6Fe_2O_3 + ZnO \rightarrow 5\,Li_{0.4}Fe_{2.4}Zn_{0.2}O_4 + CO_2\uparrow \qquad (1)$$

The mixture was divided into few batches; the samples of first batch were simply mixed in an agate mortar and are considered to be simple un-milled mixture. The rest of the powder was subjected to mechanical activation using a AGO-2S (Novic, Russia) high energy planetary ball mill for 5, 15, 30, and 60 min. The steel vial and grinding balls were used, and the weights of the material and balls were in the ratio 1:10. The milling was performed at 2220 rpm rotation speed for vial in the dry state at room temperature.

The X-ray diffraction analysis was carried out using ARL X'TRA (Switzerland) diffractometer with a semiconductor Si (Li) Peltier detector and CuK_α radiation. XRD patterns were measured in the range $2\theta = (10–70)°$ with scanning rate of $0.02°\,s^{-1}$ and were processed by the full profile analysis using the Powder Cell 2.5 software, where the pseudo-Voigt profile function was used. Phases were identified by the PDF-4+ powder database of the International Center for Diffraction Data (ICDD).

The particle size distribution was analysed by laser diffraction using a Fritsch Analysette 22 MicroTec Plus analyzer. From the Brunauer-Emmett-Teller (BET), the specific surface area (SSA) for powders was estimated. The microstructure of un-milled and milled samples was examined by Hitachi TM-3000 scanning electron microscope.

Simultaneous thermogravimetric (TG) and calorimetric (DSC) analyses were performed using a STA 449C Jupiter (Netzsch-Gerätebau GmbH, Germany) thermal analyzer. Sample with a mass of ca. 10 mg was placed in the alumina crucible and was heated up to 800 °C in air with a heating rate of $5\,°C\,min^{-1}$. A part of the equipment including a heating furnace, a sample holder, and thermocouple is schematically shown in Fig. 1. In addition, the samples were analysed by thermomagnetometry method, which is thermogravimetric analysis in magnetic field. For this, the two permanent magnets (Netzsch-Gerätebau GmbH) were attached on the outer side of the measurement cell so that the sample is located in a magnetic field of ca. 5 Oe. The Netzsch Proteus software packages were used for data analysis.

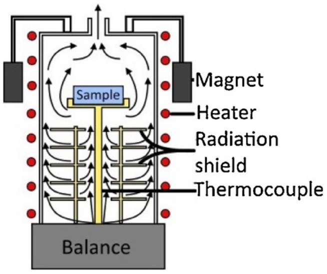

Fig. 1. A schematic of TG/DSC block of thermal analyzer.

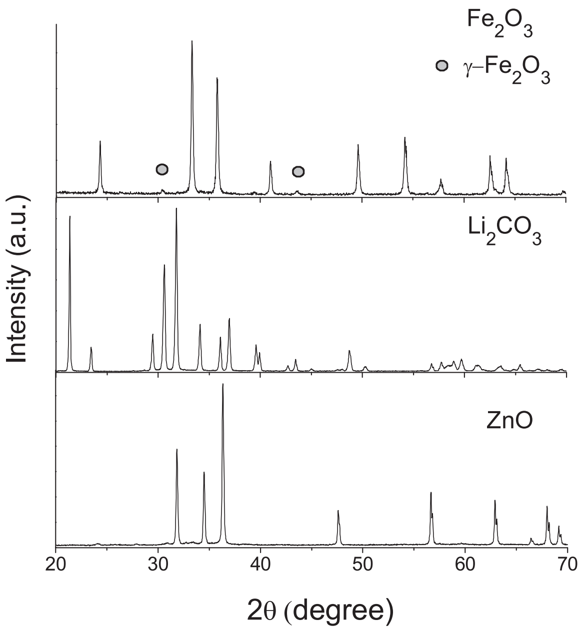

Fig. 2. XRD patterns for initial reagents.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 2 shows XRD patterns for α-Fe_2O_3 (PDF No. 40-142), Li_2CO_3 (PDF No. 66-941) and ZnO (PDF No. 26-170) initial reagents. The Fe_2O_3 peaks at $2\theta \approx 30.3°, 43°$ correspond to γ-Fe_2O_3 spinel phase (PDF No. 79-196), which is added in a small amount (ca. 2 mass%) to the iron oxide powders in the case of ferrites production. Fig. 3a presents the XRD patterns for Li_2CO_3-Fe_2O_3-ZnO mixture mechanically activated for various milling times. The values of the lattice parameters obtained by the Powder Cell 2.5 software and crystallite sizes calculated using the Williamson-Hall method, are summarized in Table 1. Measurement

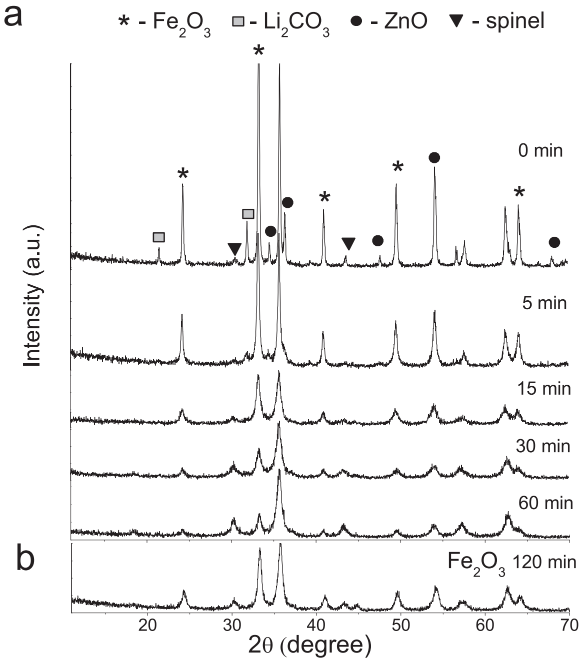

Fig. 3. XRD patterns of Fe_2O_3–Li_2CO_3–ZnO (a) mixture and Fe_2O_3 (b) powder milled for various milling times.