Study of the influence of thermal treatment on the magnetic properties of lithium ferrite prepared by wet ball-milling using nitrates as raw material

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ABSTRACT

Lithium ferrite ($LiFe_5O_8$) is an attractive material for several potential technological applications. Critical to such attractiveness are its physical properties, such as high Curie temperature, square hysteresis loop and high magnetization. Knowing that the properties of these crystals depend on the preparation method and raw materials, in this work $LiFe_5O_8$ crystallites were obtained by controlled heat-treatments, between 200 and 1400 °C, of homogeneous Li_2O-Fe_2O_3 powders prepared by wet ball-milling method and using lithium and iron nitrates as raw materials. $LiFe_5O_8$ crystal phase was formed through heat-treatments at temperatures above 500 °C. At higher temperatures the formation of lithium ferrate and hematite is promoted, leading to a decrease in the magnetic moment. Heat-treated the sample at 1200 °C results in the highest levels of magnetic saturation, presenting a magnetic moment of 73 emu/g at 5 K and 66 emu/g at 300 K, respectively.

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1. Introduction

Ferrites are one of the most studied magnetic ceramic oxides, characterized by containing iron as the main component. Below the Curie temperature and without applying a magnetic field ferrites show spontaneous magnetization, high permeability, low magnetic losses, high electrical resistivity, low eddy current losses and very good thermal and chemical stability [1–6].

Cubic lithium ferrites, such as $LiFe_5O_8$, belong to the class of soft magnetic materials with high Curie temperature (620 °C), square hysteresis loop and high magnetization [7]. Cubic ferrite because of its low cost [8] is a very attractive material for several applications. It is mainly used as a substitute for the expensive yttrium iron garnet (YIG) in mass-scale microwave devices for high-density magnetic recording, magnetic fluids, ferrofluid technology, magnetocaloric refrigeration, magnetic resonance imaging enhancement and magnetically guided drug delivery [9–11]. The lithium ferrite is, also, a promising cathode material in rechargeable Li-ion batteries [12,13].

$LiFe_5O_8$ presents a spinel structure and can be formed in two different crystalline forms: ordered (space group $P4_132/P4_332$) and disordered ($Fd3m$ space group) [9]. In the ordered form, α-$LiFe_5O_8$, the octahedral *12d* and tetrahedral *8c* sites are occupied by iron ions, Fe^{3+}, and in the octahedral *4b* positions are occupied only by lithium ions, Li^+, in the cubic primitive cell. The disordered form, β-$LiFe_5O_8$, has an inverse spinel structure, where in tetrahedral *8a* positions are occupied by Fe^{3+} ions. In this case, Li^+ and Fe^{3+} ions are randomly distributed over the *16d* octahedral positions [10,11]. In general β-$LiFe_5O_8$ is obtained by the rapid quenching of samples from high temperatures, above 800 °C, to room temperature. Upon slow cooling, and below 750 °C, a structural transformation occurs, leading to the formation of the ordered spinel phase, α-$LiFe_5O_8$ [14].

The preparation of $LiFe_5O_8$, through conventional ceramic methods, usually involves high temperatures, which represents a major issue due to the volatility of lithium above 1000 °C. Following this conventional method results in a low quality material because the sintering process normally leads to low specific surface areas [15] that affect its electrical and magnetic properties. Therefore, the study of methods of preparation of this material at lower temperatures is a topic of interest. Several chemical methods have been analyzed, such as the citrate precursor method, which promotes the production of single crystallites in the 10–20 nm range, although with several preparation steps [11,15].

The purpose of this work is to analyze physical characteristics of lithium ferrite ceramics, prepared by solid state reaction by using lithium and iron nitrates as raw materials. Firstly, the use of nitrates

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as raw materials and, secondly, the implementation of the planetary ball-milling method to prepare the base material for further heat-treatments, are not conventional, and represent innovations not quite explored in the literature. The electrical properties of this ferrite prepared by the present method were already published [6]. In this work the determination of the best treatment temperature range, mainly to enhance the magnetic properties, was done by thermal analysis. The dependence of the particle size on the sintering temperature was also studied. The obtained results were analyzed and compared with those presented in the literature, which have followed other methods. Finally, studies of the structural and morphological properties of the samples were related to their magnetic properties.

2. Experimental

In this work, the raw materials used were iron (III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and lithium nitrate ($LiNO_3$). The experimental procedures took into account the stoichiometry of the lithium ferrite, which presents a molar ratio between the lithium and iron ions of 1:5. After weighting the $Fe(NO_3)_3 \cdot 9H_2O$ and the $LiNO_3$, the two powders were homogenized in a planetary ball mill system (Fritsch – Pulverisette 7.0), at 250 rpm during 1 h. An equal volume of powders and balls were used. Both vessels and balls were made of Agata. After this first mixing step, ethanol was added in a mass ratio of 1:2 between ethanol and powder weighted. The wet mixture was placed again in the planetary ball mill system for 3 h, at 500 rpm, for further homogenization, stopping 5 min after every milling hour. After this process, the vessels with the mixture were placed in a furnace, at 80 °C, for 24 h in order to promote the evaporation of the ethanol.

The obtained mixed powder was thermally analyzed by differential thermal analysis (DTA), using a Linseis apparatus. This measure was carried out from room temperature up to 1200 °C, with a heating rate of 20 °C/min and using Al_2O_3 as reference. The obtained spectra allowed us to define the temperatures to be used in the heat-treatments. The chosen temperatures were 200, 400, 600, 1000, 1200 and 1400 °C. In every heat-treatment, which had a heating rate of 5 °C/min, a dwell time of 2 h was defined at the maximum temperature.

The X-ray diffraction (XRD) patterns data were obtained on a Siemens D5000 difractometer (CuKα radiation, λ = 1.54056 Å) at 40 kV, and 30 mA, with a curved graphite monochromator, an automatic divergence slit (irradiated length 20.00 mm), a progressive receiving slit (height 0.05 mm) and a flat plane sample holder in a Bragg–Brentano parafocusing optics configuration. Intensity data were collected by the step counting method (step 0.02° in 1 s) in the 2θ angle range of 10–60°.

The infrared spectroscopy (FTIR) measurements were performed using a Mattson-7000 spectrometer, with a resolution of 2 cm^{-1}, where 64 scans were done in transmittance (%T) mode. The IR pellets were prepared by mixing 200 mg (KBr) with 1.0–1.5 mg (heat-treated samples) in a mortar and later pressed using an uniaxial pressure system.

The morphology of the samples obtained was analyzed by scanning electron microscopy (SEM), using a Hitachi S4100-1 on the free and fracture surfaces. The samples were covered with carbon before microscopic observation.

The applied magnetic field (B) and the temperature (T) dependences of the magnetization were studied using a vibrating sample magnetometer (VSM). The measurements of the dependence of the magnetization versus temperature were done under the field-cooled (FC) and zero-field-cooled (ZFC) modes. The FC measurements mode was done in the range of temperatures of 300–5 K, with an applied magnetic field of 0.1 T for the samples treated at 200 and 400 °C and with an applied magnetic field of 0.01 T for the samples treated at 600, 1000, 1200 and 1400 °C. The ZFC measurements mode was done, also, in the range of temperatures of 5–300 K. The curves of the moment (M) versus magnetic field (B) were measured at several different temperatures, between 5 and 300 K.

3. Results and discussion

Fig. 1 shows the XRD patterns of the heat-treated powders. The XRD spectra of the sample treated at 200 °C reveals the presence of lithium nitrate crystal phase, which disappears with the increase of the heat-treatment temperature. The powders treated at 200 °C and 400 °C are characterized by presenting the α-Fe_2O_3 crystal phase as the major phase. The non-detection of the lithium nitrate phase in the sample treated at 400 °C suggests the existence of an amorphous phase containing mainly lithium ions. This result also revealed that the planetary ball milling process did not promote the formation of new crystal phases. For the powders heat-treated at 600 °C, the XRD pattern shows diffraction peaks related to the lithium ferrite ($LiFe_5O_8$) crystal phase. The sample heat-treated at 1000 °C presents the $LiFe_5O_8$ as the major phase. For the sample treated at 1200 °C it is also detected the presence of lithium ferrate (Li_2FeO_3) phase. In the sample heat-treated at 1400 °C the major phase is the lithium ferrate. However, some characteristic peaks of hematite are also evident. Very broad and weak diffraction peaks associated with lithium ferrite are also visible in this high-temperature treated sample.

The FTIR spectra of the samples heat-treated at 200 °C and 400 °C (Fig. 2) show vibration bands in the ranges of 468–484 cm^{-1} and 574–575 cm^{-1}, confirming the presence of the α-Fe_2O_3 phase [16,17], which is in agreement with the XRD results (Fig. 1). According to the literature, ferrites with spinel structure present four characteristics IR bands: υ_1 (630–560 cm^{-1}), υ_2 (525–390 cm^{-1}), υ_3 (380–335 cm^{-1}) and υ_4 (255–170 cm^{-1}) [18–22]. The υ_1 band can be attributed to the vibrations of the MO_6 octahedral, the υ_2 and υ_3 bands are due to the complex vibrations involving mutually the octahedral and tetrahedral sites and the υ_4 band is assigned to a vibration of the tetrahedral sublattice [23]. Wolska et al. verified that the ordered phase of lithium ferrite presents the IR bands at 328, 374, 396, 439, 469, 548, 582, 673 and 708 cm^{-1}, respectively [18].

The infrared spectroscopy of the samples treated at temperatures above 400 °C, shows vibration bands at 711, 676 and 399 cm^{-1}, which demonstrates that the lithium ferrite has an ordered spinel structure [18]. It is also noticed that the increase of the heat-treatment promotes the formation of the lithium ferrite crystal phase. For the sample heat-treated at 400 °C it is shown a weak vibration band, centred at 442 cm^{-1}, which can be assigned to α-lithium ferrite [16,18]. The XRD peak centred at 2θ ≈ 35°, observed in the sample heat-treated at 400 °C, can be the overlap of diffraction peaks of hematite and lithium ferrite, justifying the initial non-assignment of this phase. Comparing the relative intensity of the XRD peaks of the 200 °C and 400 °C heat-treated samples, it can be assumed that the contribution of the lithium ferrite for the diffraction peak observed at 2θ ≈ 35° is very low. This indicates a low amount of this crystal phase in the 400 °C heat-treated sample.

The morphological analysis of the samples (Fig. 3) shows the increasing of the grain size with the heat treatment temperatures. The magnification scales were chosen in order to improve the quality and analysis of the micrographs. The sample heat-treated at 200 °C presents grains with a quasi spherical shape, whose geometrical definition increases for the sample treated at 400 °C. As it can be seen, for the thermal treatments up to 600 °C, the samples' grain pattern is spherical and their size increases with the