Journal of Non-Crystalline Solids 356 (2010) 607–610

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Dielectric and structural properties of SiO_2-$LiFe_5O_8$ glass–ceramics prepared by sol–gel processing

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ARTICLE INFO

Article history:
Available online 28 January 2010

Keywords:
Crystal growth
Glass ceramics
X-ray diffraction
Conductivity
Dielectric properties, relaxation, electric modulus

ABSTRACT

The lithium ferrite ($LiFe_5O_8$) is a very interesting ferromagnetic material due to its square hysteresis loop and high Curie temperature. It has attracted the attention of scientists and engineers for a long time with regard to their application as a low-cost substitute of garnet ferrites in several devices. In this work we present the first studies of the $(x)SiO_2$-$(1-x)[Li_2O.5Fe_2O_3]$ (% mol) glass and glass–ceramic, with $x = 94$ and $x = 97\%$, prepared by the sol–gel method. The influence of the heat-treatment parameters, in the glass and glass–ceramics structure prepared was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and impedance spectroscopy measurements. The increase of the volume ratio between the $LiFe_5O_8$ particles and the glass matrix leads to an increase of the conductivity. The dielectric measurements show that the crystalline growth orientation of the $LiFe_5O_8$ particles, embedded in the glass matrix, is random.

1. Introduction

The preparation of nanoparticles is of largest interest for the materials sciences because small dimensions reduce diffusion lengths within particles, increases the number of active sites for surface reactions and decrease the local current density. The control of crystallinity, particle size and morphology are important for industrial applications [1].

Lithium ferrite ($LiFe_5O_8$), with a mixed inverse spinel structure $Fe(Li_{0.5}Fe_{1.5})O_4$, is a very promising ferromagnetic compound for the microwave field regime, due to its square hysteresis loop and high Curie temperature. $LiFe_5O_8$ have attracted the attention of scientists and engineers for a long time with regard to its application as a low-cost substitute of garnet ferrites in microwave devices, high-density magnetic recording, magnetic fluids, ferrofluid technology, magnetocaloric refrigeration, magnetic resonance imaging (MRI) enhancement and magnetically guided drug delivery [2–4].

The conventional preparation of $LiFe_5O_8$ through ceramic methods, involve high temperature sintering and often lead to low specific surface areas, loss of metal oxides (Li_2O) and phase transitions [5]. Dey et al. [5] used a citrate precursor gel method to produce single crystallites in the 10–20 nm range, although with several preparation steps [6]. The lithium ferrite is, also, a promising cathode material in rechargeable Li-ion batteries [7,8].

The preparation of $LiFe_5O_8$ nanoparticles embedded in a glass matrix, through the sol–gel method is a topic with a few numbers of published works. The sol–gel method shows considerable advantages relatively to the conventional methods because it allows to prepare new glass and glass–ceramic compositions, at low temperatures and permit, through heat-treatments, control the size and morphology of the crystallized particles [9,10].

The goals of this study are: (i) to prepare, by the sol–gel route, a lithium silicate glass with iron (ii) to grow lithium ferrite particles in the glass matrix through heat-treatment and (iii) to characterize the samples by XRD, SEM microscopy and electrical measurements as a function of the molar composition and heat-treatment temperatures.

2. Experimental details

The glasses of composition $(x)SiO_2$-$(1-x)[Li_2O.5Fe_2O_3]$, with $x = 94$ (94Si samples) and 97 (97Si samples) (% mol), were prepared by the sol–gel route [20,21] using tetraethylorthosilicate (TEOS-Merck), ethanol (C_2H_5OH-Merck), lithium nitrate ($LiNO_3$-Merck), iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$-Merck), deionised water (H_2O) and chloridric acid (HCl) as starting materials. The $Fe(NO_3)_3{\cdot}9H_2O$ and $LiNO_3$ were dissolved in the H_2O and added to the TEOS–Ethanol solution (1:3 M ratio) and was allowed to mix for 1 h at room temperature. HCl was added to the TEOS–Ethanol solution shifting the pH from 6 to 1, approximately. The final solution was poured into Petri dishes and allowed to gel and dried at 40 °C for 5 days. The molar ratio between TEOS and H_2O was 1:8. The dried gel samples

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doi:10.1016/j.jnoncrysol.2009.07.034

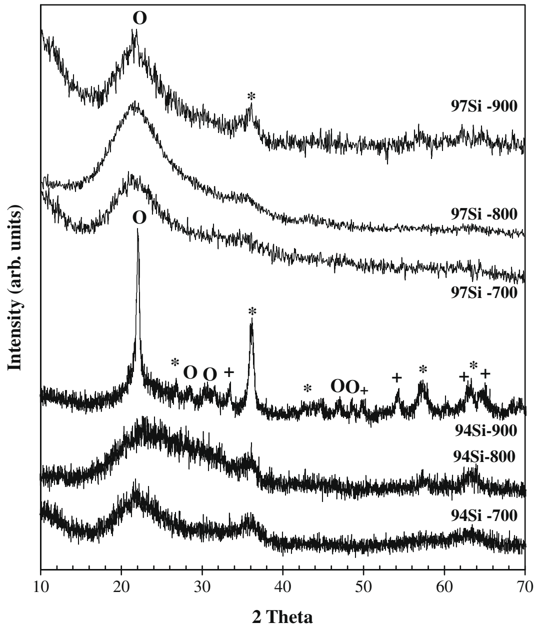

Fig. 1. XRD patterns of the all samples ((O) SiO_2 (82-1410); (∗) $LiFe_5O_8$ (76-1590); (+) Fe_2O_3 (84-0310)).

were heat-treated, in air, first at 120 °C (24 h) and after at 500 °C (4 h). The 500 °C sample was heat-treated in air with a rate of 75 °C/h, at 700, 800 and 900 °C during 4 h.

The X-ray diffraction (XRD) patterns were obtained at room temperature, using powdered samples, in a *Philips X'Pert* system, with a $K\alpha$ radiation ($\lambda = 1.54056$ Å) at 40 kV, and 30 mA, with a step of 0.05° and a time per step of 1 s.

The microstructure of the glass and glass–ceramics was observed by scanning electron microscopy (SEM), performed in a *Hitachi S4100-1* system, on the surface and fracture surface of all samples covered with carbon before microscopic observation.

For the electrical measurements the samples were prepared as disc of approximately 10 mm in diameter and with a thickness of about 1 mm. The opposite sides of the samples were painted with silver paste and electric contact was made through wires bonded to each surface. The dc electrical conductivity (σ_{dc}) was measured with a Keithley electrometer, model 617, as a function of the temperature (200–360 K). The impedance spectroscopy measurements were carried out between 200 K and 350 K, in the frequency range from 1 Hz to 100 kHz using a *SR850 DSP Lock-In Amplifier*, in the typical lock-in configuration [11], measuring the "in-phase" and the "out-of-phase" components of the output signal [12]. During these electrical measurements the samples were in helium gas, to improve the heat transfer and eliminate the moisture.

The analytical background, used in the electrical data analysis, is fully described elsewhere [12].

3. Results

Fig. 1 shows the XRD patterns of all samples. It was detected the presence of the $LiFe_5O_8$ crystal phase in the 94Si samples, treated above 700 °C, and in the 97Si samples, treated above 800 °C. In these samples it was also observed the formation of a SiO_2 crystal phase (Fig. 1). In the sample 94Si treated at 900 °C, the XRD pattern presents also the Fe_2O_3 phase.

The samples microstructure and morphology are shown in Fig. 2. It is observed particles in the free and fracture surface of all the samples. Their size decreases with the rise of the heat-treatment temperature. In the fracture surface micrograph of the 94Si-

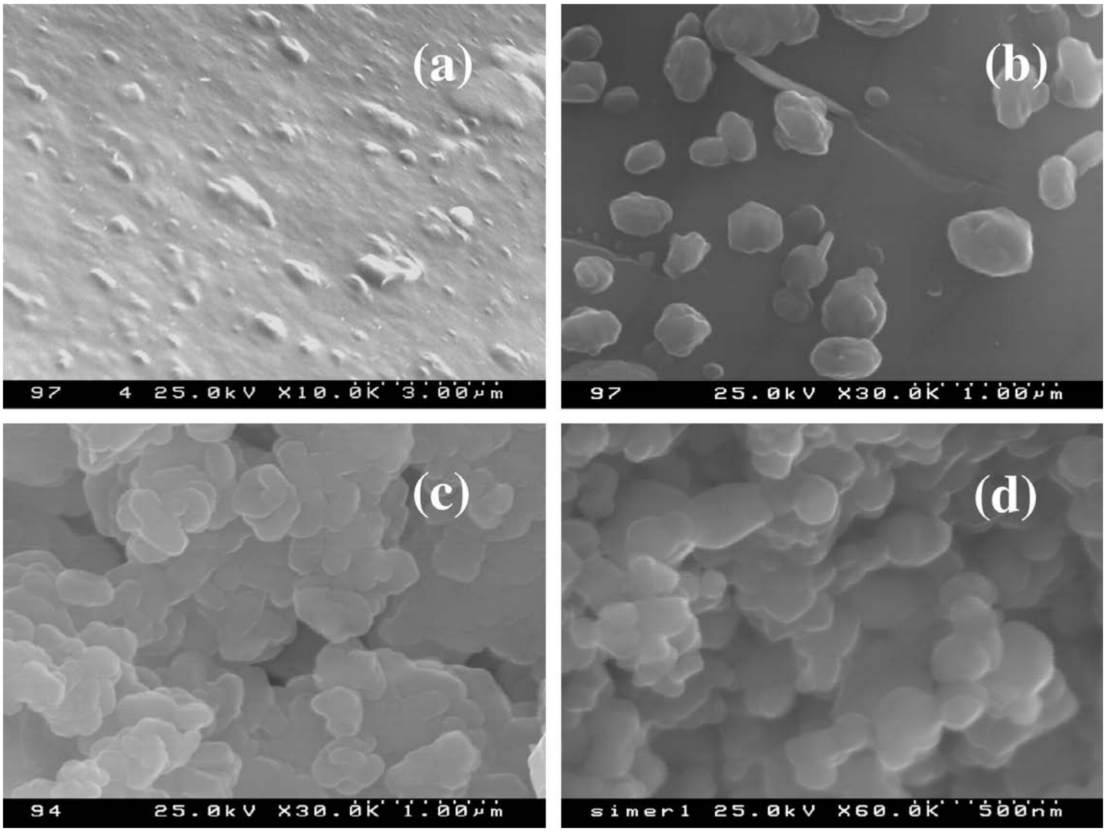

Fig. 2. SEM micrographs of: (a) 97Si-700 (free surface); (b) 97Si-900 (free surface); (c) 94Si-800 (fracture surface); (d) 94Si-900 (fracture surface).