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Dielectric and structural studies of a SiO_2–Li_2O–Nb_2O_5 glass and glass-ceramic prepared by the sol–gel method

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Abstract

The preparation and properties, of nanocrystals embedded in a glass matrix have recently received a considerable amount of interest. The glass composition $92SiO_2$–$4Li_2O$–$4Nb_2O_5$ (mol%), prepared by the sol–gel route gives origin to a transparent and colorless gel. The dried gel was heat-treated at temperatures between 500 and 750 °C, with and without the presence of an external electrical dc field. X-ray powder diffraction (XRD), scanning electron microscopy (SEM), Raman and dielectric spectroscopy were used to characterize the glass samples. In the samples heat-treated at 650 °C with 1000 kV/m and in the 700 and 750 °C samples series, $LiNbO_3$ crystallites, an important ferroelectric material is present. The behavior of the dc conductivity and the dielectric constant, in the glass and glass-ceramic, reflects the important effect of the temperature and the applied electric field on the sample structure.

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1. Introduction

Lithium niobate ($LiNbO_3$) is a ferroelectric non-linear optical material, widely used in integrated and waveguide optics due to its excellent electrical and optical properties [1–3].

It has scientific and technological interest due to the possibility of producing glass-ceramics with oriented $LiNbO_3$ crystals [4,5]. Their preparation by the sol–gel method presents, relative to the melting method, the advantage of allowing the synthesis of new glass compositions [3,6–8].

In this paper the preparation of a $92SiO_2$–$4Li_2O$–$4Nb_2O_5$ (mol%) glass and glass-ceramic is described by the sol–gel route, with and without the application of an electric field during the heat-treatment (in the text HT denotes heat-treatment and TET the thermoelectric treatment). This composition was chosen for the following reasons: (1) SiO_2 is a glass forming oxide that does not modify the $LiNbO_3$ lattice; (2) due to the $LiNbO_3$ stoichiometric it is suitable to use equal amount of Li_2O and Nb_2O_5. The correlation of the electrical properties of the glasses and glass-ceramics with their microstructure was the main purpose of this work.

2. Experimental

Based on the Alquier et al. method [9], a glass, of molar composition $92SiO_2$–$4Li_2O$–$4Nb_2O_5$, was prepared by the sol–gel route using tetraethylorthosilicate (TEOS-Merck), ethanol (C_2H_5OH-Merck), lithium nitrate ($LiNO_3$-Merck) niobium chloride (Cl_5Nb-Merck), oxygenated water (H_2O_2 (3% V/V)-Merck) and Hydrochloric acid (HCl (0.1 N)-Merck) as starting materials.

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The $NbCl_5$ and $LiNO_3$ were dissolved in oxygenated water and added to the TEOS–ethanol–HCl solution (pH ≅ 1). The final solution was stirred for 1 h at room temperature, poured into Petri dishes and allowed to gel and dried at 40 °C for 5 days. The dried gel samples were heat-treated, in air, first at 120 °C (48 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 650 °C (sample A), 700 °C (sample B) and 750 °C (sample C) during 4 h, with and without the application of an electric field, using a voltage supply (PS325-SRS). The electric field applied was 100, 500, and 1000 kV/m. The samples treated in the presence of the electric field were named according to the field value applied (e.g. A100 – sample heat-treated at 650 °C with a 100 kV/m electric field applied).

X-ray diffraction patterns were obtained at room temperature, using powdered samples, in a Philips X'Pert system, with a K_α 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 Raman spectroscopy, of bulk samples, was carried out in a T64000, Jobin Yvon SPEX spectrometer using an Ar laser ($\lambda = 514.5$ nm). The spectra were obtained, in a back-scattering geometry, between 100 and 2000 cm^{-1}. The scanning electron microscopy (SEM) was performed in a Hitachi S4100-1.

For the electrical measurements the opposite sides of the samples were painted with silver paste. The dc electric conductivity (σ_{dc}) was measured with a Keithley electrometer, model 617, as a function of the temperature (80–370 K). The impedance spectroscopy measurements were carried out at room temperature, in the frequency range of 1 Hz–100 kHz using a SR850 DSP Lock-In Amplifier, in the typical lock-in configuration [10], measuring the 'in-phase' and the 'quadrature' components of the output signal.

3. Results

The XRD spectra (Fig. 1) reveal the presence of $LiNbO_3$ crystalline phase in all the B (700 °C) and C (750 °C) samples series and in the A1000 (650 °C with an electric field of 10^3 kV/m applied).

Fig. 2 presents the Raman spectra of the A, A1000, B, B1000, and C, C1000, surface samples. In the Raman spectra no differences were found between the exterior surface and the fracture surface of all samples. The bands at 630, 590, 435, 375, 335, 330, 325, 280, 265, 240, and 155 cm^{-1} are attributed to NbO_6 octahedron vibrations [11]. The B1000 sample shows also the 465, 415, and 130 cm^{-1} bands, attributed to the Si–O–Si bending [12]. The 330 cm^{-1} broad band, in the C TET samples, seems to be resultant of the overlapping of the 335 and 325 cm^{-1} bands.

On the fracture surfaces, of all samples, the SEM did not detected particles. However, the surface micrographs show particles that increase in size and number, with the increasing of the applied field, in the A sample series. Fig. 3(a) illustrates the A1000 surface morphology. In the B sample aligned particles (Fig. 3(b)) were observed. The number of particles in the surface of the B100 sample, in contact with the anode, is larger than in the opposite side, but with the same size (approximately 100 nm). In the anode side of the B500 sample, the particle distribution is similar to that observed in the B sample, but with a size of 1 μm approximately. In the B1000 sample, the particles suffer aggregation in

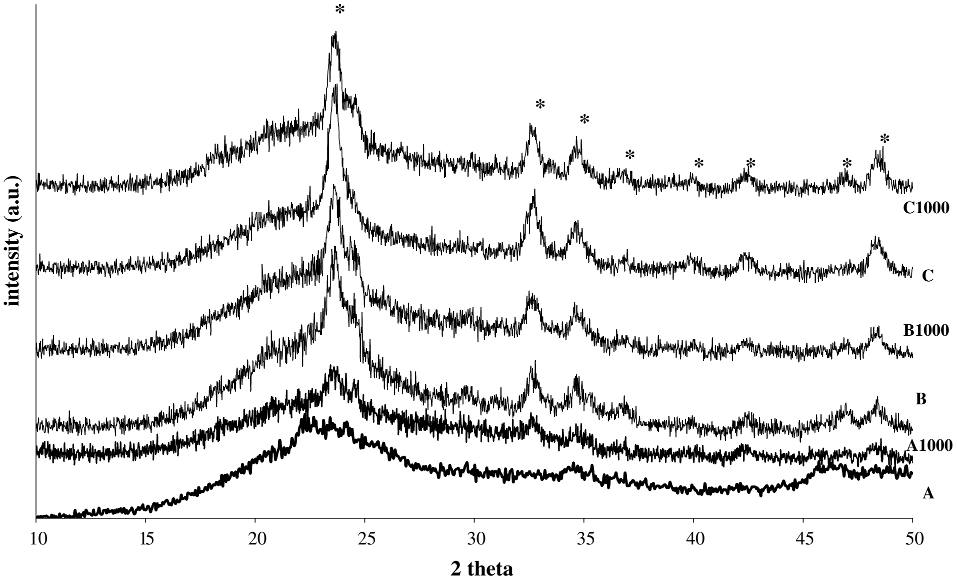

Fig. 1. XRD spectra of the A, A1000, B, B1000, C, and C1000 samples.