Journal of Non-Crystalline Solids 356 (2010) 314–320

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Effect of heat treatment on the hyperfine structure and the dielectric properties of $40P_2O_5$–$40V_2O_5$–$20Fe_2O_3$ oxide glass

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ARTICLE INFO

Article history:
Received 2 May 2009
Received in revised form 24 November 2009
Available online 5 January 2010

Keywords:
Amorphous semiconductors
Conductivity
Glasses
Oxide glasses

ABSTRACT

Oxide glass with a starting composition of $40P_2O_5$–$40V_2O_5$–$20Fe_2O_3$ (mol%) is prepared by the usual melt quenching technique. The prepared sample is heat treated at 500 K for 4, 6 and 8 h. The effect of heat treatment on the hyperfine structure and dielectric properties is studied in more details. The hyperfine structure of these glasses is investigated using Mössbauer spectroscopy. The measured isomer shifts showed that, the ferric ions (Fe^{3+}) are in octahedral and tetrahedral coordinations. The infrared spectra of these glasses is recorded over a continuous spectral range (400–1400 cm^{-1}) as an attempt to study their structure systematically. The structure of these glasses has investigated by means of IR studies which shows the presence of $v(VO_3)$ single chains, VO_4 octahedral and VO_5 trigonal bipyramids. Unmonotonic variation in the ac conductivity, $\sigma_{ac}(\omega)$, the dielectric constant, $\varepsilon_1(\omega)$, and the dielectric loss, $\varepsilon_2(\omega)$, is found with increasing the HT time. The room temperature ac conductivities at a fixed frequency (10 kHz) of the as quenched and the heat treated for 4, 6 and 8 h samples are 1.4×10^{-4}, 4.1×10^{-4}, 1.7×10^{-5} and 4.15×10^{-6} (S cm^{-1}), respectively. The ferroelectric transition temperature is shifted to lower temperature with increasing the HT time.

1. Introduction

Amorphous materials and glasses are of special scientific and technological interest due to their potential application in various industrial fields. The practical applications of phosphate glasses are often limited due to their poor chemical durability. The chemical durability of this kind of glass increases dramatically with the addition of little iron oxide [1], where some P–O–P bonds will be replaced by more chemically durable P–O–Fe^{2+} and/or P–O–Fe^{3+} bonds [2]. However, studies have shown that, the formation of P–O–Fe bonds are responsible for the formation of small polarons and hence the electric conduction in these glasses occurs by thermally activated small polaron hopping from the low valance state Fe^{2+} to the high valance state Fe^{3+} [3]. The same conduction mechanism was found also for vanadium phosphate glasses where electron hopping occurs from V^{4+} sites to the neighboring V^{5+} sites [4,5]. Shapaan et al. [6] studied the hyperfine structure, thermal analysis and the electric–dielectric properties of the ternary vanadium iron phosphate glass system $(60 - X)$ P_2O_5 $(20 + X)$ V_2O_5 $20Fe_2O_3$ (X = 10, 15, 20, 30 and 40 mol%) in more details. It was found that the vanadium ions play the role of glass network modifier (GNM) and the electric conduction in this glass system attributed to small polarons hopping (SPH). The aim of the present work is to determine the effect of the heat treatment (HT) time on the hyperfine structure and the dielectric properties of vanadium iron phosphate glasses with a starting composition of $40P_2O_5$–$40V_2O_5$–$20Fe_2O_3$ (mol%).

2. Experimental procedure

The ternary vanadium iron phosphate glass with the base composition $40P_2O_5$–$40V_2O_5$–$20Fe_2O_3$ (mol%) is synthesized by melting homogeneous mixtures of reagent grade $NH_4H_2PO_4$, V_2O_5 and Fe_2O_3 in porcelain crucibles using an electric furnace at 900 °C for 2 h. The melt is quenched between two pre-cooled copper plates in air to form (2 cm × 2 cm × 2 mm) glass sample. The prepared sample is heat treated for 4, 6 and 8 h at 500 K (about 80 K below the glass transition temperature) in an electric furnace.

X-ray diffraction patterns are recorded to check the non-crystallinity of the as quenched and the heat treated samples using a Philips X-ray diffractometer PW/1710 with Ni filtered, Cu Kα radiation (λ = 1.542 Å) powered at 40 kV and 30 mA. The patterns (not shown) revealed broad humps characteristic of the amorphous materials and did not reveal discrete or any sharp peaks.

The densities of the glass samples have been determined using the suspension weight method based on the Archimedes principle using toluene as an immersion liquid.

For the electrical measurements the glass samples are polished to obtain optically parallel surfaces of 1.5 mm thickness and the

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doi:10.1016/j.jnoncrysol.2009.11.042

glass samples are powdered to suit the IR, ME and DTA measurements. A conventional constant acceleration ME spectrometer with 25 ^{57}Co radioactive source is used to collect the ME spectra at RT. The analysis and fitting of the obtained spectra are carried out relative to a metallic iron spectrum. The infrared (IR) absorption spectra of the glasses in the wave number range (from 400 to 1400 cm^{-1}) with a resolution of 4 cm^{-1} are measured at room temperature by an infrared spectrophotometer type JASCO, FT/IR-430 (Japan). The calorimetric measurements are carried out using Shimadzu (50) differential thermal analysis with an accuracy of ±0.1 K. The calorimeter is calibrated, for each heating rate, (β), using the well-known melting temperatures and melting enthalpies of zinc and indium supplied with the instrument. The values of the glass transition, T_g, the crystallization extrapolated onset, T_c, and the crystallization peak, T_p, temperature are determined with accuracy ±2 K by using the microprocessor of the thermal analyzer. The total conductivity, σ_{tot}, dielectric constant, $\varepsilon_1(\omega)$, and loss factor, tanδ, of the investigated glasses are measured by computerized LCR Bridge MODEL SR 720. Silver paste has been coated on both faces of the pellet in order to achieve the best electrical contact.

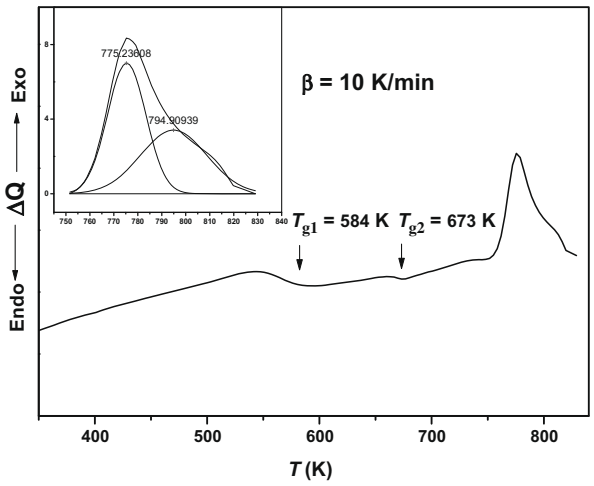

Fig. 2. The DTA trace of the as quenched $40P_2O_5$–$40V_2O_5$–$20Fe_2O_3$ (mol%) glass sample at 10 K/min heating rate. The inset shows the separation of the two overlapped crystallized peaks.

3. Results

3.1. Density and DTA measurements

Density of all samples is measured at room temperature by Archimedes principle using toluene as an immersion liquid which density is known (0.868 g/cm^3). The maximum error is around ±0.01 to ±0.03 g/cm^3. The densities of the investigated glasses are shown in Fig. 1, it is clear from it that, the density increases with increasing heat treatment (HT) time.

Fig. 2 shows the DTA trace of the as quenched sample $40P_2O_5$–$40V_2O_5$–$20Fe_2O_3$ (mol%) at β = 10 K/min heating rate. The investigated glass sample exhibit two glass transition temperatures, T_{g1}, and, T_{g2}, (584 ± 2 K and 673 ± 2 K) followed by two exothermic overlapped crystallized peaks. The inset of this figure shows the separation of the two overlapped crystallized peaks, T_{p1}, and, T_{p2}, (775 ± 2 K and 795 ± 2 K). The thermal stability criteria, $\Delta T = T_c - T_g$ [7] of the investigated glass sample is found 177 ± 2 K. Determination of the activation energy of enthalpy relaxation of the glass transition, or activation energy of glass transition, E_g, of the investigated glass sample can be achieved by using the Kissinger formula [8];

$$\ln(T_g^2/\beta) = E_g/RT_g + \text{const.} \quad (1)$$

Fig. 3(a) shows the relation $\ln(T_g^2/\beta)$ vs. $1000/T_g$ from the slope of the straight line fitting of the experimental data the calculated activation energies for the first and the second glass transition temperatures are E_{ag1} = 151 ± 3 kJ/mol and E_{ag2} = 214 ± 3 kJ/mol, respectively. The activation energy, E_{ag}, is then evaluated by the least squares fitting method of Eq. (1).

For the evaluation of activation energy for crystallization, E_c, by using the variation of T_p with β, Vazquez et al. [9] developed the proposed method by Kissenger [8] for non-isothermal analysis of diversification as follows;

$$\ln(T_p^2/\beta) = E_c/RT_p + ln(E/RK_0) \quad (2)$$

Fig. 3(b) shows the relation $\ln(T_p^2/\beta)$ vs. $1000/T_p$ from the slope of the straight line fitting of the experimental data the calculated acti-

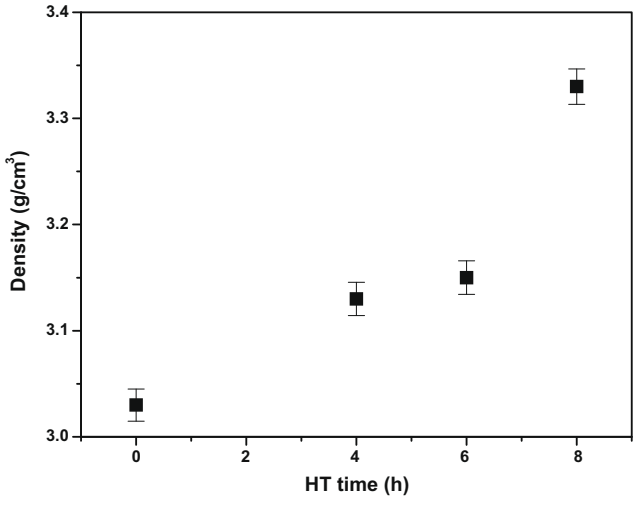

Fig. 1. Densities of the as quenched and the HT for 4, 6 and 8 h at 500 K $40P_2O_5$ –$40V_2O_5$–$20Fe_2O_3$ (mol%) glass samples.

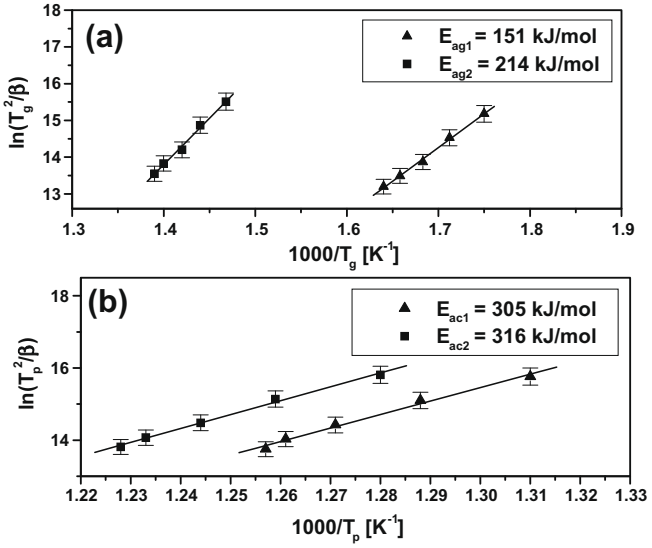

Fig. 3. Plot of (a) $\ln(T_g^2/\beta)$ vs. $1000/T_g$ and (b) $\ln(T_p^2/\beta)$ vs. $1000/T_p$ of the as quenched $40P_2O_5$–$40V_2O_5$–$20Fe_2O_3$ (mol%) glass sample.