Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Structural, thermal and optical properties of phosphate glasses doped with SiO_2

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ARTICLE INFO

Keywords:
Zinc phosphate-silicate glasses
Depolymerization
Spectroscopic analysis
Optical band gap energy
Polarizability

ABSTRACT

Glasses with a general formula (0.9-x)$NaPO_3$-xSiO_2-0.1ZnO ($0 \leq x \leq 0.1$ mol) have been prepared using the conventional melt-quenching technique. Samples were investigated by means of X-ray diffraction, density evolutions, refractive index measurements (n), differential scanning calorimetry (DSC), Fourier-transformed infrared (FTIR), Raman and UV-Visible spectroscopy.

The variations of density and refractive index of the glass series were attributed to the structural changes of the glass network resulting from the incorporation of SiO_2.

The increase in glass transition temperature (T_g) values reflects an increase of the rigidity of the glass network when SiO_2 is gradually introduced. These results were correlated with FTIR and Raman investigations which revealed the enhancement of the vitreous network when P-O-P bonds were replaced by P-O-Si.

The variation of the optical band gap (E_{opt}) of the amorphous materials indicated an increase in the band gap energy with the glass composition. This behavior can be explained by the increase of number of non-bridging oxygen (NBOs) which is probably due to the depolymerization of phosphate chains.

1. Introduction

During the recent years, phosphate glasses have attracted a considerable technological, scientific and environmental interest due to their low melting and glass transition temperature, ultraviolet transmission, high thermal expansion coefficients and optical characteristics. Phosphate glasses have been the subject of a large number of applications such as: biomaterials, glass to metal seals, optical waveguides, amorphous semi-conductor, nuclear waste immobilization matrices, solid state electrolytes… [1–23].

In fact, phosphate glasses containing transition metal ion (TMI) have attracted much intention due to their interesting electric, magnetic and optical properties. The introduction of alkali metal oxide in phosphate glasses induces the fundamental optical absorption edge falls in the UV region below 400 nm, which makes them applicable in optical systems [1–5,8–10,12–15,17–25]. However, one of the main disadvantages of phosphate glasses is their poor chemical durability which limits their use in such domains [1,3–5,10,12,13,18–21,23,26]. Oxide based phosphate glasses have proven more suitable for practical applications due to their high chemical durability and thermal stability [5,11,13,16,18–23,25,27]. ZnO oxide is widely used to ameliorate the glass quality because it improves the glass production by enhancing the chemical properties and chemical durability [19,23–25]. It acts as an anionic cross linker between different phosphate anions in order to inhibit the hydration reaction [24]. The structural role of ZnO oxide depends essentially on his content. It can act as network former or modifier. As a glass former, ZnO enters the network with ZnO_4 structural units. But, when Zn^{2+} is octahedrally coordinated, it acts as a network modifier [1,12,16–23,25,28–30].

Zinc phosphate based glasses are being largely studied due to their large potential which can implicate them as novel glass-polymer composite [12]. Zinc phosphate glasses have been used as LED light sources and as substrates for optical waveguides. Introducing zinc is a trace element plays an important role in bone formation and mineralization [19,25,26]. ZnO oxide is a very promising material for semiconductor device applications. It has a direct and wide band gap in the near UV spectral region [31].

ZnO is an important component in silicate glasses [29]. It improves the physicochemical properties of glasses by the increase in density, reducing viscosity and affords a better chemical stability [16,25,28]. In phosphate matrix glasses, introducing zinc oxide inhibites the crystallization of silicate phases [26].

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https://doi.org/10.1016/j.jnoncrysol.2017.08.019
Received 23 March 2017; Received in revised form 9 August 2017; Accepted 13 August 2017

Among oxide glasses, silicate glasses are the most popular glass hosts for making optical fibers lasers and amplifiers [27]. They are an excellent host matrix for rare earth oxides due to their glass forming ability compared to phosphate, vanadate and germanate glass families [27]. The pure silicate matrix glass possess relatively a large phonon energy (about 1200 cm^{-1}) and low refractive index (about 1.5) [32]. These interesting properties makes them suitable for various applications such as low-lost optical fibers or an activate medium in Raman amplifiers [32]. On the other hand, silicate glasses with high ZnO content have attacked more intention due to their several technical applications particularly in transparent dielectric layers, varistors and plasma display panels [30].

The present work deals with the structural, thermal and optical properties of zinc phosphate silicate glasses. A glass series with a general formula: (0.9-x)$NaPO_3$-xSiO_2-0.1ZnO ($0 \leq x \leq 0.1$ mol) was investigated using FTIR and Raman spectroscopy in order to elucidate the structural evolution of phosphate groups as a function of composition. Physicochemical properties such as: density, molar volume, refractive index, glass transition and crystallization temperature were also performed with structural changes. Furthermore, the study of optical absorption spectra is a very helpful method which provides information about the band gap energy of amorphous materials.

As usual, the conventional notation used to describe the distribution of phosphate groups adopted in this paper is Q^n ($n = 0$–3) when n is the number of bridging oxygen per PO_4 tetrahedron [8,10,18–22].

2. Experimental

2.1. Glass preparation

Glasses from (0.9-x)$NaPO_3$-xSiO_2-0.1ZnO ($0 \leq x \leq 0.1$ mol) using reagent grade compounds, $NaH_2PO_4{\cdot}H_2O$ (Sigma Aldrich), ZnO (Sigma Aldrich) and silica SiO_2 (Sigma Aldrich) in the suitable proportions. The mixture having desired compositions was heated in platinum crucible at 200 °C for 1 h. The temperature was progressively increased to 1200 °C and held constant for 30 min. Finally, the batch was quenched to room temperature under air in order produce vitreous structure which is confirmed by an X-ray diffraction. Samples were annealed below their glass transition temperature for 2 h for homogenization. The nominal and analyzed glass compositions were reported in Table 1. Samples were stored in a desiccator and taken out only at the time for measurement of their properties.

2.2. XRPD and ICP analysis

The XRPD patterns of the glass series are plotted in Fig.1. This latter indicated the amorphous states for all glass composition with a general formula (0.9-x)$NaPO_3$-xSiO_2-0.1ZnO ($0 \leq x \leq 0.1$ mol).

The XRD study of the glass series confirmed the absence of crystalline phases when x varies between 0 and 10 mol% of SiO_2 in the sample (Fig.1). Since no diffraction maxima were observed and only a broad band between 20° and 35° 2θ was detected for these glass compositions.

For 0.75$NaPO_3$-0.15SiO_2-0.1ZnO glass composition, X ray diffraction shows the presence of crystalline phases which indicates the limit of the vitreous domain for this glass series.

From fig. 1, one can note the dislocation of X ray patterns from 20° to 35°, with the increase of SiO_2 content. This result can be probably correlated to the amorphous state of glasses when x rises also on their content in network former and modifier.

The content of silica, phosphorus, zinc and sodium was analyzed by means of inductively coupled plasma atomic emission spectroscopy (Jobin Yvon Ultra C). The nominal and analyzed glass compositions were reported in Table 1. (0.9-x)$NaPO_3$-xSiO_2-0.1ZnO glass series will be labeled by reference to their molar SiO_2 content x is ranging from 0 to 10 mol%.

2.3. Measurements of density

Density measurements of the glass samples were made using the standard Archimeds method using water as immersion fluid and the relative error of these measurements is ± 0.01 01 gcm^{-3} [28]. The molar volume of glasses has been calculated from the density ($V_m = M/\rho$) and the molar weight.

2.4. Variations of refractive index

The samples were studied by spectroscopic ellipsometry (SE) technique in order to determine the optical properties such as the refractive index (n). The ellipsometer measures the ratio between the complex Fresnel reflection coefficients r_p, r_s, for the p- and s- polarization components as defined by the following equation [33,34]:

$$\rho = \frac{r_P}{r_s} = \tan\psi \exp(i\Delta)$$

where Ψ represent the amplitude ratio of the perpendicularly polarized waves after their reflection from the surface of the studied samples and Δ denotes their phase shift.

The optical functions are usually in the form of a complex refractive index: N = n + ik, where N is determined from the measured of the reflectance ratio ρ using the following equation [33,34]:

$$N = sin\ \Phi_0 \sqrt{1 + \left(\frac{1-\rho}{1+\rho}\right)\tan^2\phi_0}$$

2.5. DSC study

The glass transition and crystallization temperature were determined using a Metler Toldo instrument differential scanning calorimetry (DSC) at a heating rate of 10°Cmin^{-1}.

Table 1
Analyzed and nominal glass compositions for (0.9-x)$NaPO_3$-xSiO_2-0.1ZnO ($0 \leq x \leq 0.1$ mol) glass series.

Na_2O Nominal/analyzed	P_2O_5 Nominal/analyzed	ZnO Nominal/analyzed	SiO_2 Nominal/analyzed
45/45.24 ± 2.30	45/46.41 ± 2.30	10/8.35 ± 0.42	0/0
44/45.3 ± 2.30	44/44.21 ± 2.20	10/8.82 ± 0.41	2/1.67 ± 0.10
43/45.3 ± 2.30	43/43.55 ± 2.20	10/7.78 ± 0.40	4/3.37 ± 0.20
42/43.1 ± 2.20	42/43.83 ± 2.20	10/8.42 ± 0.42	6/4.65 ± 0.23
41/44.38 ± 2.20	41/40.79 ± 2.00	10/8.75 ± 0.44	8/7.08 ± 0.35
40/40.34 ± 2.00	40/42.2 ± 2.10	10/9.02 ± 0.45	10/8.44 ± 0.42