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Optical and electrical properties of SeO_2 modified $PbO-Bi_2O_3-B_2O_3$ glasses

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ABSTRACT

SeO_2 doped high polarizable heavy metal oxides $10B_2O_3$-40PbO-$50Bi_2O_3$ glasses have been prepared by normal melt-quenching technique. The SeO_2 modified glass structure, optical and electrical properties were studied using X-ray diffraction (XRD), ultraviolet-visible (UV–VIS), Fourier Transform Infrared Spectroscopy (FT-IR) and electrical measurement. Good vitrification was achieved for SeO_2 up to 15%, exceed this value, Bi_6SeO_{11} crystallines with size ranging from 20 nm to 50 nm would form in glass which was confirmed by XRD, scanning electron microscope (SEM), and energy dispersive X-ray spectrometry (EDS).

Compared with $10B_2O_3$-40PbO-$50Bi_2O_3$ glass, the SeO_2 modification decreased the band energy and accordingly red-shifted the cutoff edge greatly along with an increase of absorption in UV-VIS range. FT-IR spectra ascertained the co-existence of characteristic vibration bands of $SeO_4{}^{2-}$, $SeO_3{}^{2-}$, BiO_6 and BiO_6 frame units changed with SeO_2 concentration. Such change in structure and optical property predominantly influenced the electrical conductivity, showing a progressive increase from 10^{-6} to 10^{-4} at 1–10^5 Hz and 473 K–573 K, due to the low gap energy, high polarizability, and non-bridging oxygen numbers induced by $SeO_3{}^{2-}$ ions in glass.

1. Introduction

The ion conducting optical glasses are technologically important materials and have engrossed a major research thrust due to their potential application in solid state electrochemical devices and sensors etc. [1–3]. Two strategies are used for obtaining highly conductive glasses [4]. The conventional strategy is to dissolve a monovalent ion (Li^+, Ag^+, Na^+) in traditional SiO_2, P_2O_5, B_2O_3 glass [5]. Their high conductivity comes from the increase in mobile monovalence ion concentration, volume increasing effect and structural modification by dissolved transition metal salts which have more than one valences (V, Mo, Ti, Nb), the mobility and conductivity can be improved through hopping of small polarons or electrons between different valence states. The second strategy is so-called “mixed former effect” by combining several glass network formers to enhance the conductivity [6]. Generally, the mixed former glasses show promising characteristics such as high ionic conductivity coupled with good thermal stability. However, the understanding of electrical and optical properties in multiple non-conventional glass network formers (i.e. Bi_2O_3, PbO and SeO_2) system elicits an important scientific challenge.

Heavy metal oxide (such as Bi_2O_3 and PbO) based glasses have been extensively investigated due to their manifold applications in optical and optoelectronic devices such as ultrafast switches and optical isolators [7–9]. The non-conventional glass forming oxides Bi_2O_3 participates in glass structure with presence of B_2O_3 having two possible coordinations: pyramidal [BiO_3] and [BiO_6] octahedral units [10]. PbO, in contrast with the conventional modifiers, forms stable glass due to its dual role—one as modifier (with [PbO_6] structural units) and the other as glass network former in both covalent and ionic bonds with [PbO_4/2] pyramidal units connected in puckered layers. The Bi^{3+} and Pb^{2+} are both highly polarizable ions, the asymmetry of their polyhedra not only inhibits the crystallization processes in melts, but also is beneficial to a high conductivity and good optical performances. In addition, these glasses also possess electronic behavior-notable semiconductivity and electronic switching effects [11] identifying them as important materials for high performance optics, laser technology and optical communication networks.

Even though SeO_2 containing glass show higher ion conductivity of 10^{-3}–10^{-4} S/cm at room temperature due to high polarizability of Se ions [12–15], SeO_2 as a new and exotic class of non-traditional glass former have not been extensively studied up to now. The addition of SeO_2 in glasses forms mostly mixed Se—O— type bonds during the amorphous network formation. It is reported that, due to the conversion of oxygen rich selenate phase to oxygen deficit selenite phase with increase of SeO_2, the selenium coordination changes from 4 to 3, consequently affecting the network structure, electrical and optical properties [12]. It was found that incorporation of SeO_2 into binary Li_2O–B_2O_3 glassy matrix has led to significant enhancement in electrical conductivity due to its high polarizability [13].

Based on previous studies [16–21], in the present work, highly

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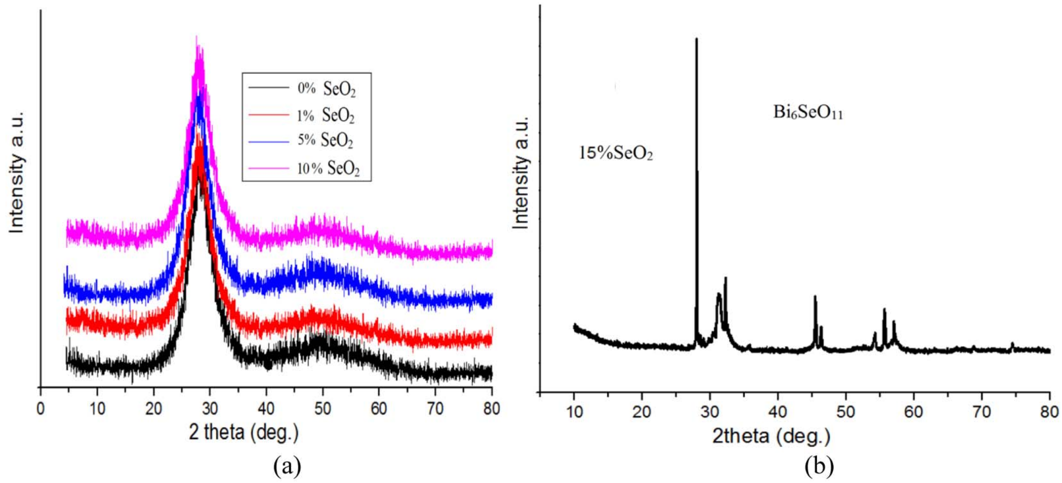

Fig. 1. XRD spectra of glass with 0%, 1%, 5% and 10% (a) and 15% (b) SeO_2 contents.

polarizable SeO_2 was added into $PbO–Bi_2O_3–B_2O_3$ glass as a modifier to enhance the electrical and optical performance. The interest of this glass is the coexistence of traditional network former B_2O_3 and conditional network forming oxide PbO, Bi_2O_3 and SeO_2. Importantly, the high optical basicity and low melting temperature of PbO and Bi_2O_3 based glass can maintain a fairly high content of SeO_2 and is good to the formation of high polarizable lone-pair Se^{4+} ions [22–25]. The ion conductivity of $SeO_2–PbO–Bi_2O_3–B_2O_3$ glasses was characterized by dc impedance technique. UV–VIS and FT-IR spectroscopy were employed to investigate the origin of the conductivity enhancement.

2. Experiments

2.1. SeO_2 containing glass fabrication

The glasses were obtained by melting a chemically pure PbO, Bi_2O_3, B_2O_3 and SeO_2 with the molar composition of $40PbO–50Bi_2O_3–(10–x)$ B_2O_3: $xSeO_2$ (where x = 0, 1, 5, and 10%) and $40PbO–45Bi_2O_3$ $–15SeO_2$ in amounts 30 g batches in a pure Al_2O_3 sealed crucible at 850 °C for 40 min. Good vitrification was achieved by rapid cooling of the melt on a brass plate. The glasses were subjected to cutting, optical polishing (λ-Logitech PM) and grounded into powder for characterization studies.

2.2. Glass characterization

X-ray studies were carried out on a X'Pert-PRO diffractrometer using CuKα radiation at 1.5418 Å and diffractrometer settings in the 2θ range from 10 °C–80 °C by changing the 2θ with a step size of 0.020. The density of glass sample was determined by the Archimedes principle, using anhydrous ethanol as immersion liquid. The crystallines size in 15%SeO_2 doped ceramic was analyzed using SEM, the composition and chemical element was observed using EDS.

Optical measurements such as refractive index, absorption coefficient, optical basicity and FT-IR transmittance were performed on obtained glasses. The refractive index was measured at 633 nm by using a refractometer (Metricon 2010) based on the prism coupler technique. Samples of 1 mm thick with optically polished surfaces were faced on a prism and mounted on a high-resolution rotary table with step size of 0.3 min and nominal resolution of refractive index 5×10^{-5}. The optical absorption spectra were recorded in 200 nm–800 nm range by means of UV–VIS spectrophotometer (Varian Cary 500). The absorption coefficient was calculated by Eq. (1):

$$\alpha = \frac{\log\left({}^{I_0}/_{I}\right)}{z} = A/z \tag{1}$$

where α, A and z are the absorption coefficient, absorbance and sample thickness, respectively. Fourier transforms infrared spectra (FT-IR) of 400–4000 cm^{-1} were recorded using a Varian Cary 500 spectrophotometer.

The electrical conductivity was measured using two methods: one is the standard two-terminal method using colloidal silver paint as an electrode [11]. Another is using a Solartron impedance analyzer mod. 1260A. The 1 mm- thick glass with parallel and well polished surfaces was used for this test. In method 1, samples were heated over a temperature range of 473–573 K, first by increasing and then by decreasing the temperature. A constant voltage of 50 V was applied across the sample and the circulating current was measured by using a Keithley 617 programmable electrometer. In method 2, complex impedance of each sample was measured in $1–10^5$ Hz frequency range at different temperatures. The impedance obtained is a characteristic of a single phase ionic conductor with blocking electrode configuration. The dc conductivity was calculated from the sample resistance R_b (which is the real part of impedance Z' value at selected frequency in which Z'' goes through a local minimum) using the relation in Eq. (2):

$$\sigma = L/(A \times R_b) \tag{2}$$

where L is the thickness and A is the surface area of contact of samples [27]. The R_b (resistance of the sample) can be directly read from the high-frequency intercept of the fitted impedance spectrum on the Z' axis.

3. Results and discussion

3.1. XRD spectra

Fig. 1 shows the X-ray powder diffraction pattern obtained from as-quenched glasses. Bubble-free transparent glasses with high homogeneity and light yellowish color were obtained for SeO_2 amounts of 0%, 1%, 5% and 10%. It is clear that their XRD spectra show typical glassy morphology nature without any crystalline phases. The simultaneous presence of multiple network formers B_2O_5, Bi_2O_3 and PbO in compositions gives rise to two large bands observed in the XRD pattern: a dominant one centered at 2θ = 28.06° followed by a second one at 2θ = 49.92°. This is a common observed feature in glasses containing multiple network former cations [15]. The small amount of larger ionic radius Se^{4+} (0.53 Å than 0.27 Å of B^{3+}) in glass network, as glass modifier, participated as tetrahedron SeO_4 and SeO_3 units by forming mixed Se–O–M (M = Pb, Bi and B) with PbO_4, BiO_3 and BO_3