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Effects of Nb_2O_5 Replacement by Er_2O_3 on elastic and structural properties of $75TeO_2–(10-x)Nb_2O_5–15ZnO–(x)Er_2O_3$ glass

N. Baizura, A.K. Yahya *

Faculty of Applied Sciences, Universiti Teknologi Mara, 40450 Shah Alam, Selangor, Malaysia

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ABSTRACT

Tellurite $75TeO_2–(10-x)Nb_2O_5–15ZnO–(x)Er_2O_3$; ($x=0.0$–2.5 mol%) glass system with concurrent reduction of Nb_2O_5 and Er_2O_3 addition have been prepared by melt-quenching method. Elastic properties together with structural properties of the glasses were investigated by measuring both longitudinal and shear velocities using the pulse-echo-overlap technique at 5 MHz and Fourier Transform Infrared (FTIR) spectroscopy, respectively. Shear velocity, shear modulus, Young's modulus and Debye temperature were observed to initially decrease at $x=0.5$ mol% but remained constant between $x=1.0$ mol% to $x=2.0$ mol%, before increasing back with Er_2O_3 addition at $x=2.5$ mol%. The initial drop in shear velocity and related elastic moduli observed at $x=0.5$ mol% were suggested to be due to weakening of glass network rigidity as a result of increase in non-bridging oxygen (NBO) ions as a consequence of Nb_2O_5 reduction. The near constant values of shear velocity, elastic moduli, Debye temperature, hardness and Poisson's ratio between $x=0.5$ mol% to $x=2.0$ mol% were suggested to be due to competition between bridging oxygen (BO) and NBO ions in the glass network as Er_2O_3 gradually compensated for Nb_2O_5. Further addition of Er_2O_3 ($x>2.0$ mol%) seems to further reduce NBO leading to improved rigidity of the glass network causing a large increase of ultrasonic velocity (v_L and v_S) and related elastic moduli at $x=2.5$ mol%. FTIR analysis on NbO_6 octahedral, TeO_4 trigonal bipyramid (tbp) and TeO_3 trigonal pyramid (tp) absorption peaks confirmed the initial formation of NBO ions at $x=0.5$ mol% followed by NBO/BO competition at $x=0.5$–2.0 mol%. Appearance of ZnO_4 tetrahedra and increase in intensity of TeO_4 tbp absorption peaks at $x=2.0$ mol% and $x=2.5$ mol% indicate increase in formation of BO.

1. Introduction

In the last decades, TeO_2-based glasses have been the subject of scientific and technological interest [1] due to their good mechanical strength and chemical durability [2–6], non hygroscopicity [7,8], low melting temperature [6], high refractive indices [5,9–13] and good infrared (IR) [1,8,9] and visible wavelength transmission [7,11,13–15]. These properties make tellurite (TeO_2) glasses good candidates for development of optical devices [2,3,11,16] and photonic applications such as optical window and laser materials [17,18].

Due to their weaker Te–O bonds, the atomic network in tellurite glasses was suggested to be more open than that of silica glasses. This exclusive structure character of tellurite glasses provides the possibility for them to be good hosts of some rare earth and heavy metals while displaying small multi-phonon decay rates [19,20]. Tellurite glasses with heavy metal oxides such as Nb_2O_5, Bi_2O_3 and PbO were found to exhibit remarkable physical and optical properties [21–24]. Present research interest in heavy metal oxide glasses is due to their long infrared (IR) cut-off, optical non-linearity [25], smaller phonon energy [26–29] and larger refraction indices [26–28] compared to borosilicate and phosphate glasses. Previous report on Er^{3+}-doped nonlinear optical glasses involving ZnO and Nb_2O_5 reported improvement in optical nonlinearity, vitrification, and chemical durability of the tellurite glasses [23,30,31].

The study of Er^{3+} doping in glasses has been a subject of research interest over the last few years in view of their potential application in photonics [32,33]. The Er^{3+} ions emit atomic-like luminescence that arises from electronic transitions within its incomplete internal 4f shell [34,35] where the wavelength emitted is of special interest in telecommunication [32,33]. For example, Er^{3+}-doped niobium tellurite glass, $70TeO_2–10Nb_2O_5–20ZnO$, exhibits good thermal stability and also large emission cross-section and broad full width at half maximum (FWHM) [36], which indicate that the niobium tellurite glasses are preferable for broadband amplifiers [36,37]. In addition, rare earth (RE) doped glasses are of particular interest in communication as glass fibers, optical amplifiers, remote chemical sensors, and in medical applications as solid state lasers [38,39]. In these applications RE doping was suggested to enhance elastic moduli due to greater chemical bond strength of the network former ions in oxide glasses [40], compared to fluoride glasses [41]. In the study of elastic

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* Corresponding author.
E-mail addresses: ahmad191@salam.uitm.edu.my, dr_ak_yahya@yahoo.com (A.K. Yahya).

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properties of glasses ultrasonic longitudinal and shear velocity measurements are important tools as sound velocity is related to elastic moduli [42] which can indicate condition of glass network and thus makes it possible to assess strength of amorphous materials [1].

Un-doped ternary TeO_2–Nb_2O_5–ZnO glass has been reported to show interesting structural and elastic properties [43] and was suggested to be a suitable host for Er^{3+}activator ion [36]. Interestingly, spectroscopic study of quaternary tellurite glass of $70TeO_2$–$(15-x)B_2O_3$–$(x)Nb_2O_5$–15ZnO system doped with 1.0 mol% Er_2O_3 [44] showed at low Nb_2O_5 content, most Nb^{5+} ions function as glass former with bridging oxygen (BO) ions but at higher content of Nb_2O_5, the ions transform its role to glass modifier which increases the number of non-bridging oxygen (NBO) ions in the glass network. On the other hand, varying amount of Er_2O_3 added to sodium borosilicate glasses [45] was reported to show that lower amount of Er_2O_3 caused elastic moduli of the glass system to decrease initially, before increasing back at higher content of Er_2O_3. Because the variation of Nb_2O_5 [44] and Er_2O_3 [45] influenced formation of both BO and NBO ions it will be interesting to investigated their influence on elastic properties of TeO_2 glass system. However, to our knowledge, studies on effect of Nb_2O_5 replacement by Er_2O_3 on elastic properties of TeO_2 glass system have not been previously reported.

In this work, we report investigation on structure and elastic properties of $75TeO_2$–$(10-x)Nb_2O_5$–15ZnO–$(x)Er_2O_3$; (x = 0.0–2.5 mol%) glass system using Fourier Transform Infrared (FTIR) spectroscopy and ultrasonic velocity measurements, respectively. In the system, Nb_2O_5 was partially replaced by Er_2O_3 to elucidate their role in glass network formation and elastic properties of the system.

2. Experimental details

2.1. Preparation of glasses

$75TeO_2$–$(10-x)Nb_2O_5$–15ZnO–$(x)Er_2O_3$; (x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 mol%) glass system were prepared using the melt-quenching method by initially mixing appropriate amounts of Tellurium Dioxide (TeO_2, 99.995% purity, Sigma Aldrich), Niobium Pentoxide (Nb_2O_5, 99.99% purity, Sigma Aldrich), Zinc Oxide (ZnO, 99.99% purity, Aldrich) and Erbium (III) Oxide (Er_2O_3, 99.99% purity, Aldrich). Homogeneity of the chemical mixture was achieved by repeated grindings in an agate mortar. The powder mixture was then placed in a ceramic crucible and heated in a melting furnace at 900 °C for 30 min. The melt mixture which had a high viscosity was poured in a stainless steel mold which preheated at 300 °C. Annealing was carried out for a period of 4 h at 300 °C before the samples were then furnace cooled down to room temperature.

2.2. Characterization of glasses

X-ray diffraction (XRD) analysis was performed using X'Pert Pro Panalytical diffractometer to confirm the amorphous nature of the glass samples. Density, ρ, of the samples was determined at room temperature by employing the Archimedes principle using acetone as the immersion liquid using the relation [46]:

$$\rho = \left(\frac{W}{W-W_b}\right)\rho_b \tag{1}$$

where W is the glass sample weight in air, W_b is the glass sample weight in acetone and ρ_b is the density of acetone.

The Infrared (IR) spectra of the glass samples were recorded at room temperature using the KBr pellet technique. The absorption spectra in the wave-number range of 400–1500 cm^{-1} with a resolution of 16 cm^{-1} were measured using Pelkin Elmer model Spectrum One FTIR spectrometer.

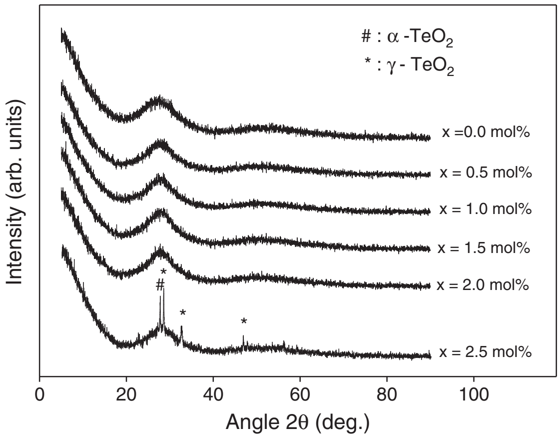

Fig. 1. XRD patterns of the $75TeO_2$–$(10-x)Nb_2O_5$–15ZnO–$(x)Er_2O_3$; (x = 0.0–2.5 mol%) samples.

The glass samples were polished using fine sand paper to produce parallel opposite faces for ultrasonic velocity measurement. Ultrasonic velocity measurements at room temperature were measured in both longitudinal and shear modes at 5 MHz by applying the pulse-echo-overlap technique using Matec model 7700 system. The related elastic moduli were calculated using the equations [7]:

$$\text{Longitudinal modulus, } C_L = v_L^2\rho \tag{2}$$

$$\text{Shear modulus, } \mu = v_S^2\rho \tag{3}$$

$$\text{Bulk modulus, } K = C_L - \left(\frac{4}{3}\right)\mu \tag{4}$$

$$\text{Young's modulus, } Y = \frac{9K\mu}{3K+\mu} \tag{5}$$

$$\text{Debye temperature, } \theta_D = \left(\frac{h}{k_B}\right)\left(\frac{3PN_A}{4\pi V_a}\right)^{\frac{1}{3}} v_m \tag{6}$$

$$\text{Hardness, } H = \frac{(1-2\sigma)Y}{6(1+\sigma)} \tag{7}$$

$$\text{Poisson's ratio, } \sigma = \frac{C_L - 2\mu}{2(C_L-\mu)} \tag{8}$$

where h is the Planck's constant, k_B is the Boltzmann's constant, N_A is the Avogadro number, V_a is the molar atomic volume calculated from the effective molecular mass and the density (i.e. M/ρ), P is the

Table 1
Values of molar volume (V_a), density (ρ), longitudinal velocity (v_L), shear velocity (v_S) and mean wave velocity (v_m) of the $75TeO_2$–$(10-x)Nb_2O_5$–15ZnO–$(x)Er_2O_3$ (x = 0.0–2.5 mol%) glass samples.

x (mol%)	V_a (m^3 mol^{-1})	ρ (kg m^{-3})	v_L (km s^{-1})	v_S (km s^{-1})	v_m (km s^{-1})
	(×10^{-3})	±7	±0.01	±0.01	±0.01
0.0	2.93	5416	3.58	2.13	2.88
0.5	2.92	5456	3.58	2.06	2.80
1.0	2.91	5488	3.56	2.05	2.79
1.5	2.91	5506	3.57	2.05	2.79
2.0	2.90	5542	3.57	2.05	2.79
2.5	2.86	5645	3.67	2.09	2.85