Research Article

Effect of Neodymium Nanoparticles on Elastic Properties of Zinc-Tellurite Glass System

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Received 14 February 2017; Revised 20 June 2017; Accepted 9 July 2017; Published 29 August 2017

1. Introduction

Tellurite glasses were found to be interesting glasses due to their unique properties and applications [1, 2]. The glass science and technology have found so much interest in tellurite glasses over the years. This may be due to their low melting points, high refractive indices, high dielectric constants, and good infrared transmission [3, 4]. Tellurite glass doped with nanoparticles system has found great interest, mostly in the study of the effect of nanosize particles on optical behavior [2].

Tellurite glasses have also been employed for the synthesis of metallic nanoparticles (NPs) and for the enlargement of metallic NPs. This is especially in the design of simple and sensitive electrochemical and optical sensors through the integration of NPs into biocatalytic reactions. Development of nanobiotechnology has been rapid with the introduction of biocatalysts on metal nanoparticles (MNP) [3].

In recent times, neodymium oxide nanoparticles (Nd\(^{3+}\) NPs) had been in the application of optical and magnetic nanomaterials due to their unique optical properties [5]. Like other lanthanides, Nd has a contracted nature of the 4f orbitals shielded by the 5s and 5p shells that affect their physical properties. Below 10 nm particle size, the quantum properties of neodymium compounds are size dependent and exhibit a secondary morphology that is well defined. Such property of Nd compounds makes them suitable for applications in surface catalytic systems, photonics, and advanced NP-based materials and protective coatings [5, 6].

Neodymium doped tellurite glasses are suitable candidates for the development of optical fibers and optical amplifiers, waveguide lasers, and color display devices [7–9].
The study of the elastic properties of glasses by using the nondestructive ultrasonic technique gives some details about the structure of the studied glasses and can be directly connected to the interatomic potentials of the glasses under probe [10, 11]. The study of the elastic properties is of fundamental importance in studying the nature of interatomic bonding and the mechanical properties of materials [12–14].

However, there is no information on elastic properties of neodymium nanoparticles doped zinc-tellurite glass. Therefore, this research is focused on the determination of the elastic properties of neodymium NPs doped zinc-tellurite glass. This is important as it will help the continued research on both scientific and technological applications of the Nd nanoparticles/compounds.

2. Experimental Section

The glass samples of Nd\textsuperscript{3+} doped zinc-tellurite glass system with chemical formula [(TeO\textsubscript{2})\textsubscript{0.70}(ZnO)\textsubscript{0.30}](1−x)(Nd\textsubscript{2}O\textsubscript{3} NPs)\textsubscript{x}, x = 0.01, 0.02, 0.03, 0.04, and 0.05 mol, were prepared by using a conventional method of melt quenching. High purity raw materials (99.99%, purity grade) of TeO\textsubscript{2} (Puratronic, Alfa Aesar), ZnO (Assay, Alfa Aesar), and Nd\textsubscript{2}O\textsubscript{3} nanoparticles (Assay, Alfa Aesar) were used to prepare the glass samples. The oxide components used in preparing the glasses were weighed by using a high accuracy (±0.0001 g) digital weighing machine and mixed together in an alumina crucible. The mixture was put in a furnace for 1 hour at 400 °C to allow complete drying of the mixture. After heating, the mixture was transferred to a second furnace at 830 °C for 90 minutes for the melting process [2]. Then, the molten sample was immediately poured into a stainless steel mould and annealed at 400 °C in an electrical furnace before cooling down to room temperature [14]. All the prepared samples were cut into the required dimension, and the sample thickness (4–6 mm) was measured using a digital Vernier caliper with an accuracy of 0.0001 mm, and the samples were then polished using sandpaper to obtain parallel surfaces on both sides. The excessive glass samples were crushed into a powder form for structural analysis. Structural analysis of the prepared samples was studied using X-ray diffraction (XRD) and the FTIR analysis. The density, \(\rho\), of the glasses was measured using electronic densimeter MD-300S based on Archimedes' principle and the molar volume, \(V_m\), was calculated. The longitudinal and shear velocities for the samples were measured using the ultrasonic pulse-echo technique by Ritec Ram-5000 Snap System. All ultrasonic measurements were taken at 5 MHz frequency and at room temperature.

2.1. Elastic Modulus. Elastic moduli (longitudinal, shear, bulk, and Young's) of [(TeO\textsubscript{2})\textsubscript{0.70}(ZnO)\textsubscript{0.30}](1−x)(Nd\textsubscript{2}O\textsubscript{3} NPs)\textsubscript{x} glasses were calculated from the measured ultrasonic velocities and density using the following standard relations:

Longitudinal modulus is expressed as

\[
L = v_l^2 \rho. \tag{1}
\]

Shear modulus is expressed as

\[
G = v_s^2 \rho. \tag{2}
\]

Bulk modulus is expressed as

\[
K = L - \left(\frac{4}{3}\right)G. \tag{3}
\]

Young's modulus is expressed as

\[
E = (1 + \sigma)2G. \tag{4}
\]

Poisson's Ratio. Poisson's ratio gives the description of the sample's expansion in a direction that is perpendicular to the applied stress [16]. It is expressed mathematically as

\[
\sigma = \left(\frac{(L - 2G)}{2(L - G)}\right). \tag{5}
\]

Microhardness is expressed as

\[
H = \frac{(1 - 2\sigma)E}{6(1 + \sigma)}, \tag{6}
\]

where \(v_l\) and \(v_s\) are ultrasonic longitudinal and shear velocities, respectively, and \(\rho\) is the sample density [10, 17, 18].

Softening temperature is expressed as

\[
T_s = \left(\frac{Mv_s^2}{Cn}\right), \tag{7}
\]

where \(M\) is the molecular weight of the glass, \(C\) is constantly equal to 5074 m\textsuperscript{s} K\textsuperscript{−1/2}, and \(n\) is the number of atoms in the chemical formula [10, 17].

Debye temperature is expressed as

\[
\theta_D = \frac{h}{k}\left(\frac{3nN_A}{4\pi V_m}\right)^{1/3} U_m. \tag{8}
\]

Mean ultrasonic velocity is expressed as

\[
U_m = \left[\frac{1}{3}\left(\frac{1}{v_l^2} + \frac{2}{v_s^2}\right)\right]^{-1/3}, \tag{9}
\]

where \(h\) is Plank's constant, \(k\) is the Boltzmann constant, \(U_m\) is the mean ultrasonic velocity, \(N_A\) is Avogadro’s number, and \(V_m\) is the molar volume [17, 19].

3. Results and Discussion

The XRD spectra of [(TeO\textsubscript{2})\textsubscript{0.70}(ZnO)\textsubscript{0.30}](1−x)(Nd\textsubscript{2}O\textsubscript{3} NPs)\textsubscript{x} are shown in Figure 1. The XRD pattern of the glass shows a broad hump at 20–35° for 2\(\theta\) values without any distinguishable sharp peaks. Such kind of spectra indicates the characteristics of amorphous structures. There are absent sharp peaks from the XRD spectra which in turn confirms the nonexistence of a crystalline phase. This result is consistent with the previous work of many authors [20, 21].
3.1. Fourier Transform Analysis. The Fourier transform infrared (FTIR) spectrometry is an analysis technique that provides structural studies to explore the basic and functional groups in crystalline and noncrystalline matrices. The result of FTIR shows the characteristics of chemical bonds that exist between elements. Absorption peaks in the spectrum represent the frequencies of vibrations between the bonds of the atom or molecule [8]. Tellurite oxide is characterized by two major structural configuration units: trigonal bipyramid (TeO$_4$) and trigonal pyramid (TeO$_3$). Pure TeO$_2$ is characterized by infrared absorption at around 640 cm$^{-1}$. The absorption band at 600–700 cm$^{-1}$ represents the stretching vibration of Te-O bonds in the trigonal bipyramid (TeO$_3$) and trigonal pyramid (TeO$_3$). The stretching vibration of TeO$_3$ group is between 650 and 700 cm$^{-1}$ while the stretching vibration of TeO$_4$ is between 600 and 650 cm$^{-1}$ [22].

Figure 2 shows the FTIR spectra that had been obtained within the region 250–1300 cm$^{-1}$ of wavenumber. The spectra contain a valley which indicates the type of bonding present. The IR characteristic of the two tellurium oxide structural units is observed in the range of 600–700 cm$^{-1}$. It was reported that, after glass formation, tellurium oxide is formed in two structural units, namely, trigonal pyramid (TeO$_3$) and trigonal pyramid (TeO$_4$). The primary cluster of the band is observed within the range 604.48–614.22 cm$^{-1}$ that correlates to the symmetrical pyramid, TeO$_4$ structural unit. This result is in agreement with the previous work done by Hajer et al. (2016) [15].

The presence of ZnO band does not show in the spectra, indicating that the zinc lattice is completely broken down. The formation of TeO$_4$ in the glass samples leads to the tight binding of oxygen anions in the glass network. Hence, increasing the TeO$_4$ concentration leads to a decrease in the amount of nonbridging oxygen, whereas the decrease in the concentration of TeO$_4$ leads to the increase in the amount of nonbridging oxygen [15, 21].

Using the FTIR spectra, the concentration of TeO$_4$ in each of the glass samples was calculated. In order to calculate the concentration of TeO$_4$, the transmission spectra were changed to absorption spectra. The area under the TeO$_4$ absorption curve then represents the concentration of the TeO$_4$ in the glass. To calculate the concentration, Origin 6.0 software was used to obtain the area under the absorption curve. The absorption value is calculated and plotted against the wavenumber, and the software can be used to calculate the area under each Gaussian absorption curve for each of the functional groups present. The area, therefore, is considered as the concentration of TeO$_4$ in the glass. Table 1 and Figure 3 present the variation of TeO$_4$ concentration against the Nd molar fraction.

In this experiment, it was observed that the concentration of TeO$_4$ decreased as the concentration of Nd$^{3+}$ ions increased from 0.01 to 0.02 mol, indicating an increasing amount of nonbridging oxygen. On the other hand, as the concentration of Nd$^{3+}$ ions increases from 0.02 to 0.05 mol, the TeO$_4$ concentration was seen to increase steadily. The TeO$_4$ concentration increase indicates the closely packed network due to the formation of more bridging oxygen (BO) [23]. This trend is supported by the formation of trigonal pyramidal TeO$_3$ structural units within the glass system and results in a change of structural units from TeO$_3$ to TeO$_4$ with the formation of bridging oxygen [22].
where $\rho$ is the density of glass [25].

$$V_m = \frac{M_w}{\rho}, \quad (10)$$

where $M_w$ is the molecular weight of the glass sample and $\rho$ is the density of glass [25].

The molar volume shows increasing values from 25.464 cm$^3$/mol to 26.922 cm$^3$/mol as the concentration of Nd$_2$O$_3$ NPs increases from 0.01 to 0.05 mol%.

### 3.2. Density and Molar Volume

The values of density and molar volume of [(TeO$_2$)$_{0.70}$(ZnO)$_{0.30}$]$_{1-x}$ (Nd$_2$O$_3$ NPs)$_x$ glasses are tabulated in Table 2. Figure 4 shows the variation of density and molar volume. The density of the prepared glasses increased from 5346 kg/m$^3$ to 5580 kg/m$^3$ as the concentration of Nd$_2$O$_3$ increased from 0.01 to 0.05 mol%.

The increase in density of the prepared glass is due to the substitution of lighter atoms of ZnO with heavier atoms of Nd. The substitution of larger atoms of Nd eventually results in an extension of the glass network [26]. After $x = 0.02$, the increase in the molar volume may be due to the substitution of smaller atoms of Te and Zn in the network with larger atoms of Nd. In the present work, it is shown that the molar volume of the glasses increases with an increase in Nd$_2$O$_3$ NPs concentration. Hence, the increase in molar volume indicates the increasing of free volume in the glass network. This result is consistent with previous work done by Chimalawong et al. (2010) and Zaid et al. (2012) [26, 27].

### 3.3. Elastic Properties

The variations of shear and longitudinal ultrasonic velocities of [(TeO$_2$)$_{0.70}$(ZnO)$_{0.30}$]$_{1-x}$ (Nd$_2$O$_3$ NPs)$_x$ glasses at room temperature are listed in Table 3 and shown in Figure 5. The measured values of the longitudinal and shear ultrasonic velocities ($V_L$ and $V_S$) for the studied (NdNPsZT) glass system with a variation of Nd$_2$O$_3$ content are listed in Table 3. The longitudinal and shear ultrasonic velocities decreased from 3737 to 3045 ms$^{-1}$ and 1959.3 to 1887 ms$^{-1}$, respectively, as the amount of Nd$^{3+}$ NPs ions increased from 0.01 to 0.02 mol. The decrease in the ultrasonic velocities may be due to the decrease in the connectivity in the glass network caused by the increase in non-bridging oxygen (NBOs) [17].

However, as more Nd$^{3+}$ ions are introduced into this glass network from 0.02 to 0.05 mol, the ultrasonic velocities increase. This may be due to an increase in the particle compactness as a result of an increase in the amount of bridging oxygen as TeO$_2$ increases [28].

#### Table 2: Density and molar volume of [(TeO$_2$)$_{0.70}$(ZnO)$_{0.30}$]$_{1-x}$ (Nd$_2$O$_3$ NPs)$_x$ glasses.

<table>
<thead>
<tr>
<th>$X$ (Nd molar fraction)</th>
<th>$\rho$ (±0.05 kg/m$^3$)</th>
<th>$V_m$ (±0.00722 × 10$^{-5}$ m$^3$/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>5590</td>
<td>2.5628</td>
</tr>
<tr>
<td>0.02</td>
<td>5437</td>
<td>2.5772</td>
</tr>
<tr>
<td>0.03</td>
<td>5507</td>
<td>2.5811</td>
</tr>
<tr>
<td>0.04</td>
<td>5570</td>
<td>2.5879</td>
</tr>
<tr>
<td>0.05</td>
<td>5606</td>
<td>2.6070</td>
</tr>
</tbody>
</table>

#### Figure 4: Density and molar volume of [(TeO$_2$)$_{0.70}$(ZnO)$_{0.30}$]$_{1-x}$ (Nd$_2$O$_3$ NPs)$_x$ glasses.

#### Figure 5: Ultrasonic velocities of [(TeO$_2$)$_{0.70}$(ZnO)$_{0.30}$]$_{1-x}$ (Nd$_2$O$_3$ NPs)$_x$ glasses
Table 3: Ultrasonic velocities (longitudinal, shear, Young’s, and bulk modulus) and fractal bond connectivity of \([\text{TeO}_2]_{0.70} [\text{ZnO}]_{0.30} [1-x] [\text{Nd}_2\text{O}_3] \text{NPs}(x)\) glasses.

<table>
<thead>
<tr>
<th>X</th>
<th>(v_x) (m/s)</th>
<th>(v_y) (m/s)</th>
<th>(L) (GPa)</th>
<th>(G) (GPa)</th>
<th>(E) (GPa)</th>
<th>(K) (GPa)</th>
<th>(d = 4 \frac{G}{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>3357.464</td>
<td>1931.559</td>
<td>60.7591</td>
<td>20.1097</td>
<td>50.3805</td>
<td>33.9462</td>
<td>2.3695</td>
</tr>
<tr>
<td>0.02</td>
<td>3190.886</td>
<td>1931.000</td>
<td>55.3582</td>
<td>20.2733</td>
<td>49.1052</td>
<td>28.3272</td>
<td>2.8627</td>
</tr>
<tr>
<td>0.03</td>
<td>3281.337</td>
<td>1933.777</td>
<td>59.295</td>
<td>20.5934</td>
<td>50.8222</td>
<td>31.8369</td>
<td>2.5873</td>
</tr>
<tr>
<td>0.04</td>
<td>3310.329</td>
<td>1936.346</td>
<td>61.0376</td>
<td>20.8844</td>
<td>51.7908</td>
<td>33.1918</td>
<td>2.5168</td>
</tr>
<tr>
<td>0.05</td>
<td>3364.002</td>
<td>1937.360</td>
<td>63.4404</td>
<td>21.0414</td>
<td>52.6819</td>
<td>35.3852</td>
<td>2.3785</td>
</tr>
</tbody>
</table>

Table 4: Poisson’s ratio, microhardness, Debye temperature, and softening temperature of \([\text{TeO}_2]_{0.70} [\text{ZnO}]_{0.30} [1-x] [\text{Nd}_2\text{O}_3] \text{NPs}(x)\) glasses.

<table>
<thead>
<tr>
<th>X</th>
<th>(\nu)</th>
<th>(H) (GPa)</th>
<th>(\theta_D) (k)</th>
<th>(T_s) (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.2526</td>
<td>3.3161</td>
<td>255.4863</td>
<td>735.1503</td>
</tr>
<tr>
<td>0.02</td>
<td>0.2111</td>
<td>3.9048</td>
<td>254.5954</td>
<td>739.1378</td>
</tr>
<tr>
<td>0.03</td>
<td>0.2339</td>
<td>3.6526</td>
<td>256.1572</td>
<td>745.6174</td>
</tr>
<tr>
<td>0.04</td>
<td>0.2399</td>
<td>3.6207</td>
<td>257.1575</td>
<td>751.8914</td>
</tr>
<tr>
<td>0.05</td>
<td>0.2519</td>
<td>3.4807</td>
<td>257.7215</td>
<td>756.9057</td>
</tr>
</tbody>
</table>

Figure 6: Elastic moduli of \([\text{TeO}_2]_{0.70} [\text{ZnO}]_{0.30} [1-x] [\text{Nd}_2\text{O}_3] \text{NPs}(x)\) glasses.

The elastic moduli \((L, G, K, \text{and } E)\) are presented in Table 3 and are shown in Figure 6. It is shown that the elastic moduli decreased with the increase in Nd\(^{3+}\) NPs concentrations from 0.01 to 0.02 mol. The elastic moduli of glass are related to the number of bonds per unit volume of the glass samples. The decrease observed in elastic moduli is related to the increase of nonbridging oxygen (NBO) and consequently increased glass network connectivity [29].

Also, like the ultrasonic velocity, the elastic moduli showed the same trend that is increasing with an increment of Nd\(^{3+}\) NPs 0.02 to 0.05 mol content. The increase in the elastic moduli of the prepared glasses can be attributed to the change in the structural unit due to the formation of more TeO\(_4\) which in turn leads to the formation of more bridging oxygen (BO) atoms [18]. This increased the rigidity of the glass and consequently increased the elastic moduli of the glass samples [18, 30].

Figure 7 shows the variation of fractal bond connectivity \((d)\). This parameter tells about the effective dimensionality of the glass network. From the obtained result, it increased with Nd NPs concentration from 0.01 to 0.02 mol and decreased with Nd NPs concentration from 0.02 to 0.05 mol. The initial increase may be due to the increase in the amount of nonbridging oxygen which in turn decreases glass connectivity. The increase in the value may be associated with the increasing amount of bridging oxygen which causes an increase in the glass network connectivity [31].

Poisson’s ratio is shown in Table 4, and Figure 8 shows a decrease in Poisson’s ratio from 0.01 to 0.02 mol and increase from 0.02 to 0.05 mol as Nd NPs increase. The initial decrease may be associated with a decrease in the rigidity in the glass network. The increase in the Poisson ratio value recorded beyond 0.02 mol may be attributed to increasing rigidity in the glass network due to increasing connectivity [29].

The microhardness is the amount of stress required to remove the free volume of glass [32]. It is associated with the glass rigidity as it increases as the glass gets less rigid and decreases with increasing rigidity. Hence, the trend in Figure 9 shows an initial increase in the value with the increase in Nd ion concentration from 0.01 to 0.02 mol and may be due to decreasing rigidity. The observed decrease in the values of microhardness (H) with Nd ion concentration from 0.02 up to 0.05 can be said to be due to increasing rigidity [29]. The rigidity increase is due to increasing connectivity [33].

The variations of Debye and the softening temperatures with Nd\(_2\)O\(_3\) concentration are presented in Table 4 and Figure 10. Debye temperature represents the temperature at which almost all the vibration modes in the glass are at excited states. The observed decrease in the value may be due to the increase in the rigidity as a result of the amount of nonbridging oxygen increase and Debye temperature also decreases with a decrease in the ultrasonic velocities. The increase observed from 0.02 to 0.05 mol of Nd NPs ions is attributed to the increasing rigidity and connectivity [34].

The observed value of the softening temperature as shown in both Table 4 and Figure 10 may be attributed to the increase...
in the connectivity in the glass and increase in the degree of compactness [29].

4. Conclusion

A series of neodymium nanoparticles doped zinc-tellurite glass systems of composition \([\text{TeO}_2]_{0.70}\text{(ZnO)}_{0.30}(1-x)\text{Nd}_2\text{O}_3\text{NPs})(x)\), for \(x = 0.01, 0.02, 0.03, 0.04, \) and \(0.05 \text{ mol}\), have been successfully prepared. The structural characteristics of neodymium nanoparticles doped zinc-tellurite glasses were studied thoroughly. XRD patterns showed that the present glasses were amorphous in nature. The density of neodymium nanoparticles doped zinc-tellurite glasses increased as Nd\(_2\)O\(_3\) NPs content increased while molar volume showed both decreasing and increasing values. The changes in density and molar volume are due to the high molecular weight of Nd\(_2\)O\(_3\) NPs and structural change in the glass network. It is observed that the ultrasonic velocities and elastic moduli decreased from 0.01 to 0.02 molar concentrations of Nd NPs ions and later increased from 0.02 to 0.05 molar concentrations. This decrease and the later increase are due to the increase in the amount of nonbridging oxygen in the beginning and bridging oxygen after 0.02 molar Nd NPs. The increase in the nonbridging oxygen leads to the decrease in rigidity while the increase in bridging oxygen increases its rigidity. The microhardness was found to decrease after 0.02 which can be attributed to the increase in glass rigidity and compactness. The observed variation of Poisson’s ratio, Debye temperature, and softening temperature was attributed to the change in the rigidity and connectivity in the glass system caused by the introduction of high Nd\(^{3+}\) NPs ions in the glass network.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors would like to appreciate the financial support from the Ministry of Higher Education of Malaysia and Universiti Putra Malaysia through FRGS (5524817).

References


