Optical and thermal characteristics of glasses based on TeO₂

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Abstract. Glass samples have been synthesized in quaternary system based on TeO₂–oxide within composition, 85TeO₂–5Nb₂O₅–5ZnO–5Ag₂O, 68TeO₂–5Nb₂O₅–20ZnO–7Na₂O and [(75–*x*)TeO₂–5Nb₂O₅–20ZnO–*x*PbO, *x* = 7, 18 mol%]. Structural characterization of the glasses was studied with respect to their thermal stability, refractive indices, third order nonlinear optical susceptibility, IR spectra and Vickers hardness. For four different prepared glasses, density in the range from 5.3744 to 6.0731 g·cm^{–3}, the glass transition temperature (*T_g*) in the range from 326 to 350 °C and refractive indices, *n*, in the range from 2.1273 to 2.2123 at 435 nm and Vickers hardness, *H_v*, in the range from 2.91 to 3.44 GPa were determined. The value of third order nonlinear optical susceptibilities |*χ*⁽³⁾| ≈ 17.9 · 10^{–13} esu of glass within composition, 68TeO₂–5Nb₂O₅–20ZnO–7PbO, was measured by using degenerate four-wave mixing (DFWM).

Keywords. Oxide glasses; linear and nonlinear refractive index; thermal stability; IR.

1. Introduction

TeO₂–based glasses were frequently studied due to their high potential in optical communication systems. Moreover to having an excellent optical nonlinearity, it had good optical switching optical response, low optical loss, excellent chemical durability and thermal stability (Kim and Yoko 1995; Hoppe *et al* 2002; Narayanan and Zwanziger 2003). These properties due to high polarizability of Te⁴⁺ ions can be even more enhanced by means of incorporation of other heavy metal oxides that can be easily polarized (e.g. Pb²⁺, Bi³⁺) and with empty *d* orbital (Ti⁴⁺, Nb⁵⁺). It was reported that such additions lead to remarkable changes in the physical, especially the optical properties (Hoppe *et al* 2004). Hence, these glasses are regarded as promising optical materials for up conversion lasers and nonlinear optical materials, which exhibit high third order nonlinear optical susceptibilities (Yousef *et al* 2004, 2007). It is well known that the unit structures of TeO₂ crystal is positioned in [TeO_{4/2}]⁰ which has a trigonal bipyramidal (tbp) and [TeO_{3/2}]⁰ which has a trigonal pyramidal (tp) structure. Trigonal pyramidal units form chains while [TeO_{4/2}]⁰ tbp units lead to three dimensional structures. Tellurite glasses in the systems such as TeO₂–Nb₂O₅, TeO₂–ZnO and TeO₂–Nb₂O₅–PbO have demonstrated to have excellent nonlinear optical performance (Komatsu *et al* 1994). The structure and nonlinear optical performance of TeO₂/Nb₂O₅/ZnO glasses have been studied. These glasses had high nonlinear optical response time due to the deformation of electron clouds, such an ultra fast nonlinear optical response

makes these TeO₂/Nb₂O₅/ZnO glasses highly suitable for all optic switching applications (Lin *et al* 2004). The value of third order nonlinear optical susceptibility of TeO₂/Nb₂O₅/ZnO with additive CdS glasses was found up to 7.8 × 10^{–13} esu, which indicates that these glasses can be used for optoelectronic application (Yousef *et al* 2008). Hence, in this work we investigated thermal and nonlinear optical properties of TeO₂–Nb₂O₅–ZnO ternary glasses with added Ag₂O, PbO and Na₂O. This work may be of importance in the design of nonlinear devices of the prepared glasses.

2. Experimental

Glasses with composition (85TeO₂–5Nb₂O₅–5ZnO–5Ag₂O), (68TeO₂–5Nb₂O₅–20ZnO–7Na₂O) and [(75–*x*)TeO₂–5Nb₂O₅–20ZnO–*x*PbO, *x* = 7, 18 mol%] were melted with reagent grade ingredients of TeO₂ and pre-dried oxides. The batches were put into a gold crucible and heated at a temperature of 820–920 °C. The melt was allowed to cool to 750 °C and then cast in a graphite mould. Subsequently, the samples were transferred to an annealing furnace and kept at 300 °C for 2 h. Then the furnace was switched off and allowed to cool. The densities, *ρ*, of the glass samples were measured by a helium pycnometer (AccuPyc 1330 Pycnometer) with an accuracy of +0.03%. The glass sample in powdered form of about 20 mg was heated in a platinum pan at a heating rate of 10 °C/min in the 30–750 °C temperature range to record DTA curves. From the glassy samples, prisms of dimension 30 × 15 × 15 mm³ were cut. The prisms were used to measure the linear refractive indices at wavelengths of 643.8, 589.3, 546.1, 479.98 and 435.8 nm.

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To measure nonlinear refractive indices, flat samples with a thickness of 1 mm were prepared. Degenerated four-wave mixing (DFWM) was applied to measure n_2 . Figure 1 shows experimental set up used. A Ti sapphire laser system delivering 150 fs pulses of a wavelength of 800 nm was used. The pulse energies were in the range from 3–4 μJ with a repetition rate of 10 s^{-1} . Due to the small repetition rates and short duration of the pulses, thermo optical effects are negligible. DFWM set up used tuneable laser splitters; each of them consisting of a rotatory half-wave plate and a glan prism. This enables an easy adjustment of the intensities of the three pump beams. Two of the pump beams were sent through delay stages. The first served to adjust the temporal overlap of two of the pump beams, whereas the second delay stage was tuned to set the third pump beam to a delay Δt in relation to a other two pulses. The three beams were focused onto the sample by a lens with a focal length of 12.5 cm. The angle between the pump beams was 4° . All three beams had approximately the same intensity and were linearly polarized in the same direction. For each time delay, the measured signals were averaged over at least 30 laser pulses. In order to minimize the effect of pulse energy fluctuations, for each pulse, the DFWM signal was divided by a reference signal obtained by a reference detector measuring pulse energy. For a Kerr-like nonlinearity and negligible absorption in the sample at the respective wavelength, the maximum DFWM signal intensity, I_{DFWM} , is given by (Samoc *et al* 1998) (with I = intensity of the pump beams, L = length of the sample):

$$I_{\text{DFWM}} = \text{const} \cdot \frac{|\chi^{(3)}|}{n^4} \cdot L^2 \cdot I^3 = \text{const}' \cdot |n_2|^2 \cdot L^2 \cdot I^3. \quad (1)$$

The signal intensity depends on $|n_2|^2$ and hence no statement on the sign of n_2 is possible. The signal intensity was referenced to fused silica; the $|n_2|$ values were calculated using (2)

$$\frac{|n_2(\text{sample})|}{|n_2(\text{ref.})|} = \sqrt{\frac{I_{\text{DFWM}}(\text{sample})}{I_{\text{DFWM}}(\text{ref.})} \frac{L(\text{ref.})}{L(\text{sample})}} \times \left(\frac{1 - R(\text{ref.})}{1 - R(\text{sample})} \right)^2. \quad (2)$$

Figure 1. Experimental set up for degenerate four-wave mixing (DFWM).

The last term in (8) introduces a correction of the reflection losses at the samples and reference surfaces (which are notably different for tellurite glass and fused silica). The reflectivity, R , was calculated from the linear refractive indices using Fresnel equation. The nonlinear refractive index, n_2 , of fused silica was assumed to be $3 \cdot 10^{-16} \text{ cm}^2/\text{W}$ (Vijaya *et al* 2001). Vickers hardness (H) at room temperature was measured by using Metkon (NH3) in air. The applied load was in the range 0.245 to 9.8 N and the time of loading was 10 s. Measurements for each sample were conducted 5 times under the same measuring conditions. IR spectra were recorded in the range $900\text{--}4000 \text{ cm}^{-1}$ using a Polytec M200 FTIR spectrometer. Abscissa accuracy is better than $\pm 5 \text{ cm}^{-1}$; ordinate accuracy and % T repeatability are better than $\pm 0.2\%$.

3. Results and discussion

3.1 Density and thermal characteristics

Compositions, densities, molar volume, oxygen molar volume, oxygen packing density, glass transition temperature and softening temperature of the prepared glasses are summarized in table 1. Sample A with a composition of $85\text{TeO}_2\text{--}5\text{Nb}_2\text{O}_5\text{--}5\text{ZnO--}5\text{Ag}_2\text{O}$ has lowest value of density ($\rho = 5.3744 \text{ g}\cdot\text{cm}^{-3}$). Otherwise, sample C with composition, $57\text{TeO}_2\text{--}5\text{Nb}_2\text{O}_5\text{--}20\text{ZnO--}18\text{PbO}$, has a highest value of density ($\rho = 6.0731 \text{ g}\cdot\text{cm}^{-3}$). But sample D with a composition of $68\text{TeO}_2\text{--}5\text{Nb}_2\text{O}_5\text{--}20\text{ZnO--}7\text{Na}_2\text{O}$ has lowest value of molar volume ($V = 26.32 \text{ in cm}^3$) and sample A has highest value of molar volume ($V = 30.628 \text{ cm}^3$). The observed change of density of the present glasses may be attributed to atomic mass and change of interatomic spacing inside the prepared glass matrix. When a higher molecular weight is substituted by a lower molecular weight, it will result in increase in strong connectivity in the glass network. Moreover Pb^{2+} ions occupy interstitial positions in the glass network modifiers besides some Nb^{5+} ions existing as NbO_4 tetrahedra which takes part as network formers, forming three-dimensional structural units of sample C leading to increasing density and consequently decreasing molar volume. From the density value and molar volume of the prepared glass, we can calculate the oxygen molar volume, V_O , as follows (Ataf and Ashraf Chaudhry 2010);

$$V_O = \left(\frac{\sum x_i M_i}{\rho} \right) \left(\frac{1}{\sum x_i n_i} \right), \quad (3)$$

where x_i is the molar fraction of each component i ; M_i the molecular weight and n_i the number of oxygen atoms in each oxide. The value of V_O in the prepared samples lies between 14 to $14.951 \text{ cm}^3 \cdot \text{mol}^{-1}$. Oxygen packing density (OPD) was estimated by using the following equation

$$\text{OPD} = \frac{1000 \times \rho \times O_i}{M_i}, \quad (4)$$

Table 1. Density, ρ , molar volume, V_m , oxygen molar volume, V_O , oxygen packing density, glass transition temperature, T_g and softening temperature, ΔT_s of prepared glasses.

Sample name	System composition				ρ (g·cm ⁻³)	V_m (cm ³)	V_O (cm ³ ·mol ⁻¹)	OPD (g·atom l ⁻¹)	T_g (°C)	ΔT_s (°C)
A	85TeO ₂	5Nb ₂ O ₅	5ZnO	5Ag ₂ O	5.3744	30.628	14.94	66.933	350	403
B	68TeO ₂	5Nb ₂ O ₅	20ZnO	7PbO	5.6637	27.141	14.437	69.267	347	390
C	57TeO ₂	5Nb ₂ O ₅	20ZnO	18PbO	6.0731	26.464	14.951	66.884	344	389
D	68TeO ₂	5Nb ₂ O ₅	20ZnO	7Na ₂ O	5.4116	26.32	14	71.429	326	382

Figure 2. DTA curves of prepared glasses (sample A, 85TeO₂–5Nb₂O₅–5ZnO–5Ag₂O, sample B, 68TeO₂–5Nb₂O₅–20ZnO/7PbO, sample C, 57TeO₂–5Nb₂O₅–20ZnO–18PbO and sample D, 68TeO₂–5Nb₂O₅–20ZnO–7Na₂O).

where O_i is number of oxygen atoms in the composition. The OPD value of prepared sample lies between 66.267 and 71.429 g·atom·litre⁻¹. The largest value of oxygen molar volume and smallest value of oxygen packing density have been observed at 18 mol% PbO. This can be explained by the lower field intensity of Pb²⁺ ions (0.26–0.27) compared with higher field intensity of Te⁴⁺ ions (0.71) expanding the glass network and increasing the V_O value.

Thermal stability of the prepared glasses has been examined by measuring the differential thermal analysis (DTA) as has been shown in figure 2. The exothermic peaks of crystallization do not appear in DTA curves of samples A, B and C. This indicated that sample A has very low tendency to crystallization and extremely high thermal stability, similar to samples B and C, however, sample D has thermal stability, $\Delta T = 135$ °C. So, these prepared glasses especially samples

A, B and C may be desirable for candidate optic preparation. Highest value of glass transition temperature ($T_g = 350$ °C) was determined for sample A but sample D has lowest value of $T_g = 326$ °C. It is considered that these glasses of TeO₄ polyhedra added with Ag₂O attributed to the higher binding energy leads to increase in T_g . The number of non-bridging oxygens increase with decreasing Te⁴⁺ former of the glass 68TeO₂–5Nb₂O₅–20ZnO–7Na₂O. This leads to the glass network of sample D open which leads to decreasing glass transition temperature. The ratio of Te⁴⁺ former increases for sample A due to increasing bridging oxygen in the glass matrix. Consequently, the glass transition temperature, T_g , value, for sample A was increased. We can conclude that the behaviour of glass transition temperature is strongly related to the ratio of TeO₂ oxide in the constituent of the prepared glass.

3.2 Refractive indices, nonlinear susceptibility and IR spectra

The substitution of additional cations of Ag₂O, Na₂O or PbO induces a structural variation from (TeO₄)⁴⁻ to (TeO₃)²⁻ entities as an intermediate asymmetric structure. This leads to change in the optical properties of prepared glasses. The Lorentz–Lorenz equation relates molar refraction to refractive indices and molar volume as done (Kordes 1939; Fajans and Kreidl 1948):

$$n_0 = \left(\frac{V_m + 2R_m}{V_m - R_m} \right)^{1/2}, \quad (5)$$

$$\alpha = \left(\frac{3M}{4\pi N\rho} \right) \cdot \left(\frac{n_0^2 - 1}{n_0^2 + 2} \right), \quad (6)$$

where n_0 is the linear refractive index, R_m the molar refraction, V_m the molar volume and N the Avogadro's number. Linear refractive index measured at wavelengths of 435.8, 479.98, 546.1 and 643.8 nm as well as the Abbe numbers calculated, polarizability, α (in Å³) and molar refraction, R_m (in cm³ mol⁻¹) are summarized in table 2. The results show that highest values of refractive index were obtained when Pb²⁺ was incorporated into the tellurite glasses. It is observed that the glass 68TeO₂–5Nb₂O₅–20ZnO–7PbO has highest value of refractive index, n_0 , accompanied by highest value of electronic polarizability, α , ($n_0 = 2.2123$ at 435 nm,

$\alpha = 5.77 \text{ \AA}^3$). But a glass $68\text{TeO}_2\text{--}5\text{Nb}_2\text{O}_5\text{--}20\text{ZnO--}7\text{Na}_2\text{O}$ has smallest $n_0 = 2.1273$ at 435 nm and $\alpha = 5.36 \text{ \AA}^3$. Ions of greater mass, e.g. Pb^{2+} , with double s -orbitals will have a low lying exciting configuration (ns^1) (np^1) due to the electron movement of the s - to the non-occupied p -orbitals. Hence, the polarizability and refractive index increase with founding of PbO_2 in the glasses matrix. According to the proposed theory on metallization of condensed matter (Herzfeld 1970; Burger *et al* 1995; Reddy *et al* 2001), the condition $\rho \cdot R_m/M = 1$ in the Lorentz–Lorenz equation, the refractive index becomes infinite which corresponds to the metallization of covalent solid materials, and two conditions for predicting the non-metallic ($\rho \cdot R_m/M < 1$) and metallic ($\rho \cdot R_m/M > 1$) materials. The metallization criterion, $M(n)$, is the difference from 1 as given below;

$$M(n_0) = 1 - \frac{\rho \cdot R_m}{M}. \quad (7)$$

The glasses reported here possess metallization criterion in the range 0.464 to 0.487. Sample B has the smallest value of $M(n_0) = 0.464$ but sample D has the largest value of $M(n_0) = 0.487$ (column 2 in table 3). The small metallization criterion means that the width of both valence and conduction bands becomes large due to a narrow bandgap and increased tendency for metallization of the glasses (Himan *et al* 1994). The linear refractive index depends on the wavelength and was found as follow (Wamale 1977):

$$\frac{1}{n^2(E) - 1} = \frac{E_s}{E_d} - \frac{E^2}{E_s E_d}, \quad (8)$$

where E_s is the so-called Sellmeier gap energy and E_d the dispersion energy. Figure 3 shows a plot of $1/(n^2(w) - 1)$ vs E^2 for all glasses studied. From the linear regression, values of E_s and E_d are obtained for each studied glass composition. As shown in table 3, sample D has the smallest

value of E_d ($= 19.78 \text{ eV}$) but sample B has the highest value ($E_d = 20.97 \text{ eV}$). The decreasing of E_d values due to decrease of the covalent bond in the prepared glasses on incorporation of Na_2O mol% in glass matrix of sample D is seen and consequently a decrease in dispersion energies.

Figure 4 presents a typical DFWM measurement at a wavelength of 800 nm of a glass with the composition, $68\text{TeO}_2/5\text{Nb}_2\text{O}_5/20\text{ZnO}/7\text{PbO}$ (sample B), with fused silica as a reference. The intensity of the signal of tellurite glass is about 300 times larger than that of fused silica.

The third order nonlinear susceptibility, $\chi^{(3)}$, depends on the nonlinear optical susceptibility as follows

$$\chi^{(3)}(n_0) = \left[\frac{(n_0) \cdot (n_2)}{3\pi} \right] \cdot 10^{-12} \text{ esu}, \quad (9)$$

where n_0 is the linear refractive indices of composition at 800 nm and the nonlinear refractive indices $|n_2|$ values of prepared glasses are in the range from 5.4 to $8.1 \cdot 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$, which increase with increasing refractive indices. The largest values of nonlinear refractive indices ($n_2 = 8.1 \cdot 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$) and measured third order of nonlinear indices $\chi^{(3)} = 17.9 \cdot 10^{-13} \text{ esu}$ were obtained for glass B with the composition, $68\text{TeO}_2\text{--}5\text{Nb}_2\text{O}_5\text{--}20\text{ZnO--}7\text{PbO}$, while the smallest values of $n_2 = 5.4 \cdot 10^{-15} \text{ cm}^2 \cdot \text{W}^{-1}$ and $\chi^{(3)} = 11.5 \cdot 10^{-13} \text{ esu}$ were obtained for glass D with composition, $68\text{TeO}_2\text{--}5\text{Nb}_2\text{O}_5\text{--}20\text{ZnO--}7\text{Na}_2\text{O}$. The increasing of third order can be attributed to bridging oxygens that increase in the glass matrix and it is also due to virtual electron transitions from non-bonding $\text{O}_{2p}\pi$ orbital to the empty non-bonding orbital of TeO_2 . The optical bandgap relation to the nonlinear refractive index was shown by using the relation

$$n_{2\text{cal}} = \beta/(E_g)^4,$$

where $\beta = 1.26 \times 10^{-9} \text{ (esu(eV})^4)$. The calculated value of nonlinear refractive index is reported in table 3. They

Table 2. Refractive indices, Abbe number, molar refraction, R_m , electronic polarizability, α_m , of glasses studied.

Sample name	435 nm	479 nm	546 nm	587 nm	643 nm	Abbe number	Vickers hardness (GPa)	R_m ($\text{cm}^3 \text{mol}^{-1}$)	$\alpha_m (\text{\AA}^3)$
A	2.1684	2.1355	2.1041	2.091	2.077	18.9	3.447	16.08	6.38
B	2.2123	2.1764	2.1425	2.128	2.1132	17.7	3.225	14.55	5.77
C	2.2118	2.175	2.1403	2.1255	2.1105	18.1	3.116	14.161	5.62
D	2.1273	2.0958	2.0657	2.053	2.0398	19	2.91	13.5	5.36

Table 3. Metallization, $M(n_0)$, energy gap, E_g , Sellmeier energy gap, E_s , dispersion energy, E_d , nonlinear refractive indices, n_2 , calculated nonlinear refractive index, $n_{2\text{cal}}$ and third order nonlinear susceptibilities $\chi^{(3)}$ of studied glasses.

Sample name	Metallization criterion	$E_g(\text{eV})$	$E_s(\text{eV})$	$E_d(\text{eV})$	$n_2(10^{-15} \text{ cm}^2/\text{W})$	$n_{2\text{cal}}(10^{-12} \text{ esu})$	$\chi^{(3)}(10^{-13} \text{ esu})$
A	0.475	4.007	6.76	20.6	7.9	4.885	17.1
B	0.464	2.2083	6.61	20.97	8.1	6.126	17.9
C	0.465	3.79	6.54	20.65	7.8	6.11	17.2
D	0.487	4.227	6.8	19.78	5.4	3.946	11.5

are in good agreement with the data corresponding between experimental and calculated n_2 values. The third order non-linear optical susceptibility, $\chi^{(3)}$, is inversely related to mean excitation energy, E_g ,

$$\chi^{(3)} = \frac{C (n_0^2 + 2) (n_0^2 - 1) E_d}{576\pi^2 N_b E_g}, \quad (10)$$

where N_b is the cationic bulk concentration of the glass and C is a constant. Sample B has higher value of the third order nonlinear optical susceptibility with lowest value of optical energy gap. The calculated values of energy gap band for samples A, B, C and D are 4.007, 2.082, 3.79 and 4.227 eV, respectively. It is well known that tellurite glasses follow the pattern of crystalline α -TeO₂ which are formed

by TeO₄ group as trigonal bipyramids (tbp), such structural units can progressively form TeO₃₊₁ and non-bridging oxygens are created due to the incorporation of modifier ions (Sekiya *et al* 1994). It can be concluded that TeO₄ tbp with low E_g will contribute more to optical nonlinearity than TeO₃ tp with high E_g in the glass TeO₂-Nb₂O₅-ZnO. Berthereau *et al* (1996) reported that the energy gap, E_g , between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in TeO₄ tbp is 10.2 eV and that in TeO₃ tp is 12.1 eV. Fargin *et al* (1996) confirmed that the mean polarizability for TeO₄ tbp is about 20% higher than that for the TeO₃ tp. PbO behaves both as a network former and as network modifier in glasses. When PbO acts as a network former, Pb atoms take up four coordinating positions and the lead oxygen polyhedron can be represented as $[\text{PbO}_{4/2}]^{2-}$. Formation of $[\text{PbO}_{4/2}]^{2-}$ requires additional oxygen atoms and carry lone pairs in bounded states with high polarizability. Therefore, in the system of glasses investigated here 68TeO₂-5Nb₂O₅-20ZnO-7PbO will be those showing higher number of value of TeO₄ tbp due to smallest value of energy gap and highest value of nonlinear susceptibility. When increase of PbO content leads to TeO₄ tbp into TeO₃ tp which decreases the refractive index and nonlinear susceptibility.

IR spectra of prepared glasses have been shown in figure 5. This figure reveals broad, strong and weak absorption bands in the investigated range of wave numbers 1200–400 cm⁻¹, the precision of recording band maxima is + 2 cm⁻¹. Tomokatsu *et al* (2010) studied Raman and infrared spectra of TeO₂-Nb₂O₅-ZnO glass. They found that the band at

Figure 3. Dependency of refractive indices as a function of photon energy (illustrated as $1/(n^2 - 1)$ vs $(h\nu)^2$) in prepared glasses.

Figure 4. DFWM signal of sample ($\square$ 68 TeO₂/5Nb₂O₅/20ZnO/7PbO) and compared to signal of fused silica reference sample at 800 nm (Δ , signal of fused silica is multiplied by a factor of 100 for better visibility).

Figure 5. Infrared spectra of prepared glass (sample A, 85TeO₂-5Nb₂O₅-5ZnO-5Ag₂O, sample B, 68TeO₂-5Nb₂O₅-20ZnO/7PbO, sample C, 57TeO₂-5Nb₂O₅-20ZnO-18PbO and sample D, 68TeO₂-5Nb₂O₅-20ZnO-7Na₂O).

190–230 cm^{-1} was attributed to the vibration of Nb–O in NbO_6 octahedra, and that at 440 cm^{-1} was due to the symmetric stretching of the $\text{Te}_{\text{eq}}\text{--O}_{\text{ax}}\text{--Te}$ band. The stretching bond of tellurium and axial oxygen (Te--O_{ax}) in TeO_4 trigonal bipyramids (tbp) at 657–663 cm^{-1} , and the stretching band in TeO_3 trigonal pyramids (tp) occurs at 732 cm^{-1} . So, the band which appeared at 440 cm^{-1} in prepared glasses are due to the symmetric and bending vibration if $\text{Te}_{\text{eq}}\text{--O}_{\text{ax}}\text{--Te}$ linkages are connected with TeO_4 units. The first overtone of these peaks are observed at around 950–1001 cm^{-1} . The shoulder band appears at 748, 732 and 756 cm^{-1} in samples B, C and D, respectively; this is attributed to TeO_3 tp. When the PbO molar increases substituting TeO_2 in sample C the bands shift towards lower frequency. This shift may be attributed to the Pb^{2+} ions incorporation as network modifiers which form bridging oxygen in $\text{Te--Pb}^{2+}\text{--Te}$ linkages. The band at 880 cm^{-1} is attributed to NbO_4 tetrahedra groups which will contribute to restore bridging bonds and will increase the number of $[\text{TeO}_4]$ groups.

3.3 Vickers hardness

From deformation fracture patterns in Vickers indentation tests, the values of Vickers hardness, H_V , for prepared glasses were calculated using (7) (Tadashi *et al* 2001),

$$H_V = \frac{P}{\alpha_0 d^2}, \quad (11)$$

where P is the applied load, d a characteristic indentation diagonal and α_0 the indenter constant ($\alpha_0 = 2.15$) in the present experiment which used a diamond pyramid indenter. The calculated values of Vickers hardness at room temperature are shown in table 2. It is seen that sample B has a highest value ($H_V = 3.447$ GPa) but sample D has a lowest value ($H = 2.91$ GPa). As expected, the Vickers hardness increases with increasing cross link density and strength chemical bonds of the network. By addition, the

bridging oxygen ion produces rigidity of the glass. Since the Vickers hardness increases with increasing PbO content in the prepared glass matrix, we know that Na_2O has a packing density lower than that of TeO_2 and this leads to decreasing of Vickers hardness in prepared glasses, when TeO_2 is replaced by Na_2O . The values of Vickers hardness for the prepared glasses are higher than that of 70 TeO_2 –15 ZnO –15 Na_2O and 70 TeO_2 –20 WO_3 –10 K_2O glasses (Watanabe *et al* 2001). Figure 6 shows the relation between glass transition temperature and Vickers hardness of prepared glasses. This means that, the weakening of the glass structure reduces the hardness hence a decrease in T_g and *vice versa*. The glass transition temperature of an oxide glass increases with cross link density of the network, with increasing strength of the chemical bonds and with the packing density of the oxide network.

4. Conclusions

The molar polarizability, dispersion energy and third order of nonlinear susceptibility have been estimated on the basis of measurement of the linear refractive indices, n_0 . The values of glass transition temperature of prepared glasses increase in the order of modifier as follow: $\text{Ag}_2\text{O} > \text{PbO} > \text{Na}_2\text{O}$. The value of Vickers hardness of the prepared glasses increase in the same way as glass transition temperature in the order of $\text{Ag}_2\text{O} > \text{PbO} > \text{Na}_2\text{O}$. The sample within composition, 68 TeO_2 /5 Nb_2O_5 /20 ZnO /7 PbO , in mole % has largest value of third order of nonlinear indices, extremely high thermal stability, very low tendency to crystallization and smallest value of energy gap ($E_g = 2.2082$ eV). Finally the value of refractive indices changes in the order, $\text{PbO} > \text{Ag}_2\text{O} > \text{Na}_2\text{O}$.

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Figure 6. Vickers hardness vs glass transition of prepared glasses (line is guide to eye).

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