THERMAL STABILITY, LINEAR AND NONLINEAR REFRACTIVE INDICES OF HEAVY TERNARY TELLURITE GLASS

A. E. AL-SALAMI
Physics Department, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia

Heavy glass with composition 90TeO$_2$/5Bi$_2$O$_3$/5Ta$_2$O$_5$ (TBT) in mol% based glasses have been prepared by using melt-quenching method. The optical properties and physical parameter of these glass studied with respect to density, $\rho$, molar volume, $V_m$, optical packing density, $\text{Opd}$, refractive index, $n_0$, oxygen molar volume, $V_o$, electronic polarizability, $\alpha_{\text{m}}$, molar refraction, $R_m$, metallization criterion, $M$ ($n_0$), and third order non-linear optical susceptibility. These glass has highest value of density $\rho=6.2209$ gm/cm$^3$ compared with other glass reported. Moreover this glass has advantage optical properties such as: Opd $=72.4$, $V_m=30.39$ cm$^3$, $V_o=13.81$, $n_0=2.295$ at 435.84 nm, $\alpha_{\text{m}}=7.08$ Å$^3$ and $R_m=17.84$ mol$^{-1}$cm$^3$ at 435.84 nm. Thermal characterization of present glass investigation by using (Shimadzu DTA 50). It is found that the glass transition temperature, $T_g=384$ °C, onset crystallization temperature, $T_c=500$ °C, and melting temperature, $T_m=631$ °C and anticrystallization factor, $S=\frac{\Delta T(T_c-T_g)}{T_g}$. It is found that the addition of heavy oxides Ta$_2$O$_5$ and Bi$_2$O$_3$, incorporation to TeO$_2$ based glasses leads to largest refractive index and third order nonlinear optical susceptibility were reported.

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1. Introduction

Heavy metals like that W, Bi, Nb, Pb, and Ta are added to tellurite glasses is studied extensively because such addition seem that show change in optical properties of these glasses. Moreover the tellurite glasses containing heavy metal oxides were found to display a high optical nonlinearity (NLO), which due to its electronic polarizability nature is further characterized by a rapid delay response time [1-3]. High optical nonlinearity devices are currently studied for use in telecommunication system which required these glasseshad high third order susceptibility tensor, $\chi^{(3)}$, and nonlinear index. Also the heavy glasses were promising for application in up conversion laser optical materials [4,5].

The effects of nonlinear optical material are induced by the polarization, $P$, in a power series expansion of the relation with the applied electric field, $E$, as follows [6-8]:

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \ldots$$

(1)

Where $\chi^{(1)}$ is the first order of linear susceptibility tensor, $\chi^{(2)}$ is the second order susceptibility and $\chi^{(3)}$ is the third order susceptibility. The linear susceptibility is related the linear refractive index, $n_0$, by $\chi^{(1)}=12.56(n_0^2-1)$. We note that the refractive index of bulk material induced to high intense electric field can be computed as follow: $n=n_0+n_2E^2$, where $n_2$ is the nonlinear refractive index. The refractive index $n_2$ is related with many physical mechanisms, it can determine as: $n_2=n_2(\text{nuclear})+n_2(\text{electronic})+n_2(\text{electrostrictive})+n_2(\text{thermal})$ where the $n_2(\text{nuclear})$ is nuclear, $n_2(\text{electronic})$ electronic, $n_2(\text{electrostrictive})$ and $n_2(\text{thermal})$ parts of $n_2$.

*Corresponding author: aeslami@kku.edu.sa
Besides, the total index of refraction, \( n \), is given by: \( n = n_0 + n_2 \langle E^2 \rangle \), where \( \langle E^2 \rangle \) is the time averaged square of the electric field of the incident light beam. The nonlinear refractive index \( n_2 \) is related to the third order nonlinear susceptibility \( \chi^3 \), as follow \([9]\):

\[
n_2(w) = 1.7 \times 10^{-14} (n_0^2 + 2)^3 (n_0^2 - 1) \left( \frac{d}{n_0 E_s} \right)^2 f \left( \frac{\hbar \nu}{E_g} \right)
\]

Where,

\[
\chi^{(3)} = \frac{0.26 \times 10^{-12} f_i^3 (n_w^2 - 1) d^2 E_s^6}{(E_s^2 - E^2)^4}
\]

Where \( f_i \) is the Lorentz field factor \( \left( \frac{n_w^2 + 2}{3} \right) \), \( n_w \), the refractive index at wavelength \( w \), \( E_s \) is the Sellmeier gap, \( E \) the photon energy (\( \hbar \nu \)) and \( d \) is the bond length between the metal \( M \) and oxygen atom \( O \), in \( \text{Å} \), by the combining Equ. (3) and Equ. (4) it can be determine third order of nonlinearity as follow:

\[
\chi^3 = A(n_w^2 + 2)^3 (n_w^2 - 1) \frac{E_d}{E_s^2}
\]

Where \( A \) is a phenomenological constant, we can transform the unit’s nonlinear refractive indices as follow \([7-9]\):

\[
n_2(m^2/W) = \left( \frac{1}{cn \epsilon_0} \right) n_2(m^2/V^2)
\]

\[
n_2(m^2/V^2) = \frac{3}{8n} \chi^{(3)}(m^2/V^2)
\]

\[
\chi^{(3)}(m^2/V^2) = \frac{4\pi}{9 \times 10^8} \chi^{(3)}(\text{esu})
\]

In the present work, studying the effect of heavy oxide \( \text{Ta}_2\text{O}_3 \) and \( \text{Bi}_2\text{O}_3 \) on the thermal and optical properties of \( \text{TeO}_2 \) based glass.

### 2. Experimental work

Batches (50 gm) of the glass with composition 90TeO\(_2\)/5Bi\(_2\)O\(_3\)/5Ta\(_2\)O\(_5\) in mol% glass was melted in an Pt crucible and heated at a temperature of 950 °C. The melt was allowed to cool to 850 °C and then cast in a graphite mould. Subsequently, the samples were transferred to an annealing furnace and kept at 320 °C for 2 h. Then the furnace was switched off and allowed to cool. From the glassy samples, prisms of the dimension 30x15x15 mm\(^3\) were cut. The prisms were ground and polished using water as liquid component. 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. The densities were measured by a helium pycnometer (AccuPyc 1330) with an accuracy of ± 0.03 %. The glass transition temperature \( (T_g) \), softening temperature, \( T_s \), the onset temperature of crystallization \( (T_c) \), the peak temperature of crystallization \( (T_p) \) and the melting temperature \( (T_m) \) were obtained by using differential thermal analysis technique (Shimadzu DTA 50). The prepared glass was
examined by X-ray diffraction, (Siemens D 6000) using CuKα radiation at 40 kV in the 2θ range from 5 to 90°.

3. Results and discussions

X-ray diffraction patterns (XRD) of prepared glass 90TeO₂-5Bi₂O₃-5Ta₂O₅ in mole% and it is found peaks caused by crystalline phases so the sample is in nature of amorphous phase (glass) was shown in Fig. 1. The present glass is transparent with high homogeneity and it has high value of density (ρ= 6.2209 in g.cm⁻³). The change in the density of the glass attributed by addition of heavy modifier like that Ta₂O₅ and Bi₂O₃ as a constituent elements, hence the present glass has higher density comparing with other tellurite glass like that 75 TeO₂-5 WO₃-15 Nb₂O₅-5 CuO (ρ= 5.3107 gm·cm⁻³), 75 TeO₂-5 WO₃-15 Nb₂O₅-5 MnO₂ (ρ=5.2937gm·cm⁻³), 75 TeO₂-5 WO₃-15 Nb₂O₅-5 NiO (ρ=5.3388gm·cm⁻³), 75 TeO₂-5 WO₃-15 Nb₂O₅-5 Ag₂O (ρ=5.444gm·cm⁻³), 75 TeO₂-5 WO₃-15 Nb₂O₅-5 ZnO (5.3235gm·cm⁻³), 75 TeO₂-5 WO₃-15 Nb₂O₅-5 MgO (ρ=5.285 gm·cm⁻³), 75 TeO₂-5 WO₃-15 Nb₂O₅-5 TiO₂ (ρ=5.244gm·cm⁻³), 75 TeO₂-5 WO₃-15 Nb₂O₅-5 Na₂O (ρ=5.2178 gm·cm⁻³) [10]. The molar volume, Vₘ, of the prepared glass related by the density by relation; 

\[ V_m = \frac{M}{\rho}, \]  

where M is the molecular weight and \( \rho \) is the density and it is equal (Vₘ= 30.39in cm³). Also the oxygen molar volume, \( V_o \), related to the molecular weight of sample, it is can be calculated by the relation as follows:

\[ V_o = \left( \frac{\sum x_i M}{\rho} \right) \left( \frac{1}{\sum x_i n_i} \right) \]  

where \( x_i \) is the molar fraction of component in mol%, \( i \), and \( n_i \) is the number of oxygen atoms for each oxide. Besides, the oxygen packing density, Opd, computed from relation as follow;

\[ Opd = \frac{100 \rho O_i}{M_i} \]  

where \( O_i \) is number of oxygen atoms in the constitute of sample. The data of \( V_m, V_o \), are 13.81 cm³·mol⁻¹ and 72.4 gm.atm respectively, hence, \( V_m, V_o \) and Opd data of the present glasses gives a good information on their structure.

Fig. 1. Show X-ray diffraction patterns of the 90TeO₂-5Bi₂O₃-5Ta₂O₅ in mol%.

Fig. 2 shows the DTA traces of the prepared glass 90TeO₂-5Bi₂O₃-5Ta₂O₅ in mol% at heating rate of 10K·min⁻¹. From DTA curve it can be determine different characteristic temperatures like that \( T_g, T_c, T_p \), and \( T_m \) in °C. Thesis data are summarized in Table 1 and the value (\( \Delta T\text{T}_{c} \)) has been denote the glass thermal stability. As obtain in Fig. 2, the present glass has \( T_g= 384 \) °C, \( T_c= 459 \) °C, \( T_p= 521 \) °C, \( T_p= 550 \) °C and \( T_m= 655 \) °C. Thermal parameters are very important of prepared glass, anticrystallization,
\[ S = \frac{\Delta T (T_p - T_c)}{T_g} \]  

(8)

**Table 1.** Thermal and optical properties of glass 90TeO$_2$- 5Bi$_2$O$_3$- 5Ta$_2$O$_5$ in mol% have been studied.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>at different wavelength (in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>435.84</td>
</tr>
<tr>
<td>Density, ( \rho ) (in g·cm$^{-3}$)</td>
<td>6.2209</td>
</tr>
<tr>
<td>Molar volume, ( V_m ) (in cm$^3$)</td>
<td>30.39</td>
</tr>
<tr>
<td>Oxygen molar volume (in cm$^3$/mol)</td>
<td>13.81</td>
</tr>
<tr>
<td>Oxygen packing density (in gm.atm)</td>
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</tr>
<tr>
<td>Glass transition temperature, ( T_g ) (°C)</td>
<td>384</td>
</tr>
<tr>
<td>Onset of crystallization temperature, ( T_s ) (°C)</td>
<td>459</td>
</tr>
<tr>
<td>Peak of crystallization temperature, ( T_p ) (°C)</td>
<td>521</td>
</tr>
<tr>
<td>Melting temperature, ( T_m ) (°C)</td>
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<tr>
<td>Peak of crystallization temperature, ( T_c ) (°C)</td>
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<tr>
<td>Glass transition temperature, ( T_g ) (°C)</td>
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<td>Anticrystallization factor</td>
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<td>Glass stability, ( \Delta T )</td>
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</tr>
<tr>
<td>( H ) factor</td>
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<td>Refractive index, ( n_0 )</td>
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</tr>
<tr>
<td>Abbe number, ( V_d )</td>
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<tr>
<td>Molar refraction, ( R_m ) (in cm$^3$·mol$^{-1}$)</td>
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<tr>
<td>Polarizability, ( \alpha_m ) (in Å$^3$)</td>
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<td>Metallization criterion, ( M(n_0) )</td>
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<tr>
<td>Sellmeier energy gap, ( E_s ) (in eV)</td>
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<tr>
<td>Dispersive energy, ( E_d ) (in eV)</td>
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</tr>
<tr>
<td>( n_2 ) in 10$^{-15}$ cm$^2$/W</td>
<td>9.1</td>
</tr>
<tr>
<td>( \chi^{(3)} ) in 10$^{-13}$ esu/Å$^2$</td>
<td>4.94</td>
</tr>
</tbody>
</table>

**Fig. 2.** DTA traces of prepared glass with composition 90TeO$_2$-5Bi$_2$O$_3$-5Ta$_2$O$_5$ in mol%.

The ratio of \( T_g/T_m \) and Hurby's developed \( H' = AT/T_g \) were calculated. These parameters are \( \Delta T = 137 \) °C, \( S = 10.35 \), \( T_p/T_m = 0.586 \) and \( H = 0.357 \) and hence the present glass has high thermal stability compare with other glass system were reported in Ref [4, 5, 11, 12].

The optical parameter such as linear, non-linear refractive index, \( n_2 \), Molar refraction, molar polarizability and third-order susceptibility \( \chi^{(3)} \) are used in fabrication the optical devices from oxide glasses. Here in the present work the linear refractive index, \( n \), of prepared glass was measured at different wavelength are shown in Table 1. The effect of heavy oxide Bi$_2$O$_3$ and Ta$_2$O$_5$ on the TeO$_2$ based glass leads to high refractive \( n = 2.295 \) at 435.8 nm of prepared sample with composition 90TeO$_2$-5Bi$_2$O$_3$-5Ta$_2$O$_5$ was obtain. It is related to TeO$_4$ trigonal bipyramid (tbp) structural units form in the glass matrix. Hence it can be suggested that the glass has high
density and TeO\textsubscript{4} consequently it has high refractive index. Moreover other factors effects on the value of refractive index of glass such as; (i) polarizability of the first neighbor ions, (ii) electronic polarizability of the oxide ion, and (iii) optical basicity. The relation between refractive index and molar volume can be estimated as follow:

\[
R_m = \frac{v_m(n_0^2-1)}{(n_0^2+2)}
\]

Where, \(R_m\) is the molar refraction also the relation electronic polarizabilities, \(\alpha_m\) (in \(\text{Å}^3\)) has and \(n_0\) can be calculated by using relation [13]:

\[
\alpha_m = \frac{3}{4\pi N} \left( \frac{n_0^2-1}{n_0^2+2} \right) \frac{M}{\rho}
\]

Where \(N\) is the Avagadro’s number. The values of \(R_m\)= 17.84 in cm\(^3\)mol\(^{-1}\) and \(\alpha_m= 7.08\) (in \(\text{Å}^3\)) at 435.8 nm for prepared glass, these data are summarized in Table (1). Fig. 3 show the relation between, \(n_0\), and molar polarizability, \(\alpha_m\), (in \(\text{Å}^3\)), at different wave length, it is obtained that \(n_0\) strongly depend on the, \(\alpha_m\), Also it is found that the refractive index value strongly dependent on the ratio, \(\alpha_m / V_m\), (i.e. the, n, value increase with increasing the ratio \(\alpha_m / V_m\). The present glass 90TeO\textsubscript{2}/5Bi\textsubscript{2}O\textsubscript{3}/5Ta\textsubscript{2}O\textsubscript{3} has (n= 2.295 at 435.8 nm) is highest comparing with other tellurite glass such as: 75 TeO\textsubscript{2}-5WO\textsubscript{3}-15 NbO\textsubscript{3}-5CuO (n= 2.2898 at 435.8 nm), 75 TeO\textsubscript{2}-5WO\textsubscript{3}-15 NbO\textsubscript{3}-5MnO\textsubscript{2} (n= 2.2765 at 435.8 nm), 75 TeO\textsubscript{2}-5WO\textsubscript{3}-15 NbO\textsubscript{3}-5NiO (2.252 at 435.8 nm), 75 TeO\textsubscript{2}-5WO\textsubscript{3}-15 NbO\textsubscript{3}-5Al\textsubscript{2}O\textsubscript{3} (n= 2.2323 at 435.8 nm), 75 TeO\textsubscript{2}-5WO\textsubscript{3}-15 NbO\textsubscript{3}-5ZnO (n= 2.2087 at 435.8 nm), 75 TeO\textsubscript{2}-5WO\textsubscript{3}-15 NbO\textsubscript{3}-5MgO (n= 2.204 at 435.8 nm), 75 TeO\textsubscript{2}-5WO\textsubscript{3}-15 NbO\textsubscript{3}-5TiO\textsubscript{2} (n= 2.1875 at 435.8 nm), 75 TeO\textsubscript{2}-5WO\textsubscript{3}-15 NbO\textsubscript{3}-5Na\textsubscript{2}O (n= 2.1627 at 435.8 nm). These means that, glass has high density is clear to has high value refractive index depend on the kind of the oxide modifier inter the composition of glass matrix, beside, \(n_0\), is proportional to the inverted mole volume unit and the polarizability of ions in. Other important optical parameters like that metallization criterion, \(M(n_0)\), Sellmeier gap, \(E_s\) in eV, and dispersion energy, \(E_d\) in eV, are summarized in Table (1). The metallization criterion, \(M(n_0)\), depend on the basis of linear refractive index and can be calculated from the relation as follow:

\[
M(n_0) = \frac{(n_0^2+2)-(n_0^2-1)}{(n_0^2+2)}
\]

**Fig. 3. Relation between refractive index, \(n_0\), and electronic polarizability in \(\text{Å}^3\) at different wavelength of glass with composition 90TeO\textsubscript{2}-5Bi\textsubscript{2}O\textsubscript{3}-5Ta\textsubscript{2}O\textsubscript{3} in mol%.
**

From previous literature it is found that oxides had large refractive index with small energy gap possesses small value of \(M(n_0)\) hence the nature of metallic and non metallic of bulk glass can classified into condition as; when \(R_m/V_m < 1\) (non-metal) and \(R_m/V_m > 1\) (metal).
Moreover the value of metallization criterion depends on the value of optical energy gap of glasses. This means that when the metalalizationn criterion increase leads to increase in the optical energy gap. The present glass have high refractive index with smallest value of optical gap with small value of $M(n_0)= 0.413$ at 435.8 nm these means that it has broadband of conduction and valence band. Fig.4 show the relation between refractive index, $n_0$, and metallization criterion, $M(n_0)$ at different wave length. The Sellmeier gap energy $E_s$, is the dispersion energy, $E_d$, and linear refractive index depends on wavelength by the relation as follow:

$$n^2(\nu) - 1 = \frac{E_s E_d^2}{E_d - E_s^2}$$  \hspace{1cm} (12)$$

Fig. 4. Relation between refractive index, $n_0$, and metallization criterion, $M(n_0)$ at different wavelength of glass with composition 90TeO$_2$-5Bi$_2$O$_3$-5Ta$_2$O$_5$ in mol%.

Fig.5 shows a plot of $1/(n^2(\nu) - 1)$ versus $E^2(h\nu)$ of prepared glass. From the linear relation it can be determine values of $E_d$ and $E_s$ are obtained (see Table 1). In the present glass obtain that $E_d= 21.71$ eV and $E_s= 6.36$ eV values, if the decrease in dispersion energies with the composition this means that the decrease in the covalent bond in glass matrix. The third order nonlinear susceptibility of empirical Miller’s, depend on the linear refractive indices and linear optical susceptibility $\chi^{(1)}$ determine by the relation as follow:

$$\chi^{(3)}(n_0) = \left[ \frac{(n_0)^2 - 1}{4\pi} \right]^4 \times 10^{-10}$$

$$\chi^{(1)} = \left[ \frac{(n_0)^2 - 1}{4\pi} \right]$$  \hspace{1cm} (14)$$

Fig. 5. show the relation between $1/(n^2 - 1)$ versus $h\nu$ in (eV)$^2$ of glass with composition 90TeO$_2$-5Bi$_2$O$_3$-5Ta$_2$O$_5$ in mol%.
The glass 90TeO$_2$/5Bi$_2$O$_3$/5Ta$_2$O$_5$ have largest value of measured third order of nonlinear indices by method DFWM [4], the present glass has $\chi^{(3)}_{me.} = 4.94 \cdot 10^{-13}$ esu, and also it have largest value of polarizability 7.08Å$^3$. The value of third order nonlinear susceptibility, $\chi^{(3)}$, of present sample are in the order as follows; 90TeO$_2$/5Bi$_2$O$_3$/5Ta$_2$O$_5$> 85TeO$_2$/5Nb$_2$O$_5$/5ZnO/5TiO$_2$> 68TeO$_2$/5Nb$_2$O$_5$/20ZnO/7PbO > 85TeO$_2$/5Nb$_2$O$_5$/5ZnO/5Ag$_2$O > 90TeO$_2$/5ZnO/5Nb$_2$O$_5$/20ZnO/7Na$_2$O [4, 10, 14]. The ions with lone pair of electrons in the valence shell of the Te$^{4+}$, Bi$^{3+}$ and transition element ions has empty d atomic orbital like that Ta$^{5+}$leads to increase in optical nonlinearity. Because the field strength of these transition metals are very small with very high oxide ion polarizability moreover oxides Ta$_2$O$_5$ and Bi$_2$O$_3$ posse high coordination number toward oxide ions with low O 1s binding energy. Hence this explain; the glass 90TeO$_2$/5Bi$_2$O$_3$/5Ta$_2$O$_5$ (sample 4) have the largest value of polarizability, higher nonlinear indices and higher third order nonlinear susceptibility. It is found that relation of the third order nonlinear susceptibility, $\chi^{(3)}$, measured by using THG technique of the binary tellurite glasses with the molar polarizibility, $\alpha_m$, and showed that the $\chi^{(3)}$ increase with increasing, $\alpha_m$. Dimitrov and Sakka [15] estimated that the simple oxides such as PbO, Ta$_2$O$_5$, Nb$_2$O$_5$, CdO have large nonlinear refractive indices which posses a metallization criterion value in the range 0.35–0.45, otherwise Bi$_2$O$_3$ and SiO$_2$ oxides have a small value of nonlinear refractive indices posses large value of metallization criterion are in range from 0.5 to 0.7. As the same case the binary tellurite glass composition containing Nb$_2$O$_5$, TiO$_2$, Ta$_2$O$_5$, WO$_3$, MoO$_3$, and Bi$_2$O$_3$[15, 16] have large value of nonlinear indices where posses a metallization criterion in value the range 0.42-0.5 range. The present glass posses value metallization criterions $M(n_b) = 0.413$ at 435.8 nm which is a good agreement with reported value in binary glasses. Hence, it can be conclude that the refractive index and third order nonlinear susceptibility, $\chi^{(3)}$, decrease with increasing the metallization criterion $M(n_b)$.

Finally, the prepared glass has high refractive indices and evaluated third order nonlinear optical susceptibility values observed in Bi$_2$O$_3$, Ta$_2$O$_5$ inter in TeO$_2$ based glass matrix, indicate that these glasses can be use for optical devices applications.

4. Conclusions

The incorporation of heavy oxide Ta$_2$O$_5$ and Bi$_2$O$_3$ into TeO$_2$ based glass has been synthesized. The thermal properties and optical properties of this glass have been obtained by measuring DTA and the linear refractive indices, $n_b$.

It is found that this glass has high density value $\rho = 6.2209$ in g.cm$^{-3}$ with high thermal stability parameters$\Delta T = 137$ °C and $S = 10.35$. Moreover these glass has large glass transition temperature, $T_g = 384$ with large linear refractive index. Moreove the glass 90TeO$_2$/5Bi$_2$O$_3$/5Ta$_2$O$_5$ has high value of third order of nonlinear indices, $\chi^{(3)}_{me.} = 4.94 \cdot 10^{-13}$ esu, and also it has high value of polarizability 7.08 Å$^3$

References