Synthesis and optical properties of Er/Yb/Ag modified bismuth–tellurite based glasses

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Abstract. The Er₂O₃-Yb₂O₃ codoped TeO₂-Bi₂O₃-Na₂O-Glasses along with addition of AgNO₃ in basic compositions glasses have been prepared by traditional melt quench method. Investigation of the synthesized glasses is done by DSC, XRD, and UV-Vis spectroscopy. The glass transition temperature is observed by differential scanning calorimetry. The amorphous nature of the synthesized glasses is confirmed by X-ray diffractogram taken at room temperature. The fluid displacement method on the basis of the Archimedes principle was used to calculated density of prepared samples. The UV-Visible absorption characterizations have been done in the range of 200–1100 nm of synthesized glasses having different percentage of doping of Er₂O₃/Yb₂O₃/AgNO₃. The study of optical properties of the glasses such as the absorption coefficient (α), cut-off wavelength, forbidden energy band gap (E_{opt}), refractive index and Urbach Energy (E_u) have been done. The effect of Er₂O₃/Yb₂O₃/AgNO₃ on optical properties is observed.

1. Introduction

Heavy metal oxide co-doped with rare earth glasses exhibit excellent optical properties and potentially encouraging for opto-electronic devices, especially Bismuth-tellurite glasses are choice among the researchers due to its very good optical properties as high refractive index, wide transmission band in short wavelength UV edge, chemically stable, comparatively low phonon energy[1]. At low temperature Bismuth oxide glasses can provide a high refractive index [2]. Heavy metal oxides (HMO) such as Bi₂O₃ have wide employment in the field of glass-ceramics, optical and optoelectronic devices, sensors, reflecting windows etc. [3-6]. Especially Bismuth oxide doped glasses are well known to have long infrared cut-off and excessive third order nonlinear optical susceptibility due to which they are applicable in ultrafast optical switches, photonic devices and infrared transmission components [7]. The objective of the present work is to study the effect on optical properties of bismuth tellurite glass co-doped with rare earth and silver ions. A systematic study has been performed on the variation of the optical band gap, refractive index and Urbach energy. Other physical properties as density molar mass and molar volume also measured.
2. Experimental Procedure

Bismuth tellurite glasses co-doped with Er$_2$O/Yb$_2$O$_3$/AgNO$_3$ have been prepared by traditional melt quench method. The chemical composition of these glasses are (80-x-y-z)\%TeO$_2$-10\%Bi$_2$O$_3$-10\%Na$_2$O-x\%Er$_2$O-y\%Yb$_2$O$_3$-z\%AgNO$_3$ where the values x are 0, 0.5, 1, 0.5, values of y are 0, 0.5, 0.5, 0.5 and values of z are 0, 0, 0, 0.1 mole percentage, prepared glasses are named TBN, TBNEY1, TBNEY2, TBNEYA. Tellurium oxide (TeO$_2$), bismuth oxide (Bi$_2$O$_3$), sodium oxide (Na$_2$O), erbium oxide (Er$_2$O), ytterbium oxide (Yb$_2$O$_3$) and silver nitrate AgNO$_3$ are taken as raw material having purity of 99%. The batch components are taken in powder form, weighed with sensitive digital weighing machine. Batch component are mixed homogeneously with the help of agate mortar and pestle. The homogeneous batch mixtures are transferred in the alumina crucibles covered with lid, kept inside the muffle furnace and heat up to 960°C then melts were stirred mechanically and put back into the furnace for 10 minutes. The viscose melts were quickly casted into stainless steel mold to get glass pellets at room temperature. For the annealing process glass samples were kept in oven for 10 hours at 340°C. The prepared glasses are yellowish to pinkish in colour. The colour is due Bismuth oxide and erbium oxide. The densities of the synthesized glasses were estimated using Archimedes principle at room temperature. For the study of glass transition temperature DSC is done. For confirmation of amorphous nature of synthesized samples XRD diffractograms is taken, which were obtained by using RigakuMiniflex II. EDS of prepared samples also studied for the confirmations of composition (FEI Nova SEM 430). For the measurement of UV-VIS-NIR optical spectra of synthesized glass samples in 200 to 1100nm rang, spectrometer Research India of model no.RI2SA is used.

3. Result and Discussion

3.1 DSC

Differential scanning calorimery of TBN glass is done in temperature range 25.00°C to 400.00°C by using PerkinElmer (Pyris 6 DSC) figure 1. The glass transition temperature $T_g$ and crystallization temperature $T_c$ were measured. For TBN glass transition temperature to be $T_g =$310°C and $T_c=340°C$.

![DSC curve of TBN glass heat from 25.00°C to 400.00°C at 5.00°C/min](image)

3.2 X-Ray diffraction Analysis

For the confirmation of glassy nature of synthesized TBN and TBNEY glasses, XRD scans were recorded for 20 values from 20° to 90°. The diffractograms of the samples having wide prominence around 30° and no sharp peaks were observed (figure 2). This confirms the glassy nature of the TBN and TBNEY glasses.
3.3 Physical Parameter Measurement

The list of Density is the simplest physical property to calculate. It is estimated according to fluid displacement method which is based on the Archimedes principle. According to the Archimedes buoyancy is equal to the weight of the displaced liquid. The density is calculated by using following relation:

$$\rho = \frac{W_g \rho_w}{W_g - W_b}$$  \hspace{1cm} (1)

Where $W_g$ is the weight of the sample in air, $W_b$ is the weight of the sample in buoyant liquid, $(W_g - W_b)$ is the buoyancy, $\rho_w$ is the density of buoyant. As the immersion liquid distilled water was used.

All the weighing measurements were done using a digital balance.

Molar volumes of TBN glasses were also calculated, the relation for Molar volume ($V_m$), molecular weights (M), and the density ($\rho$) of glass samples can be calculated as:

$$V_m = \frac{M}{\rho}$$  \hspace{1cm} (2)

Calculated densities, molar mass and molar volume of glasses of different batch composition is given in table 1. It is notable that with increase of molar mass density also increases.

| Glass   | Composition                              | Molar mass gm/mol | Density gm/cc | Molar Volume cc/mol |
|---------|-----------------------------------------|-------------------|---------------|---------------------|
| TBN     | 80%TeO$_2$-10%Bi$_2$O$_3$-10%Na$_2$O     | 180.60            | 5.2           | 34.7                |
| TBNEY1  | 79%TeO$_2$-10%Bi$_2$O$_3$-10%Na$_2$O-0.5%Er$_2$O-0.5%Yb$_2$O$_3$ | 183.08            | 5.21          | 35.1                |
| TBNEY2  | 78.5%TeO$_2$-10%Bi$_2$O$_3$-10%Na$_2$O-1%Er$_2$O-0.5%Yb$_2$O$_3$ | 184.20            | 5.24          | 35.1                |
| TBNEYA  | 78.9%TeO$_2$-10%Bi$_2$O$_3$-10%Na$_2$O-0.5%Er$_2$O-0.5%Yb$_2$O$_3$-0.1%AgNO$_3$ | 183.25            | 5.21          | 35.2                |

Table 1. Chemical composition with mole percentage and gram weight of synthesized glass samples

Figure 2. X-Ray diffractograms of TBN and TBNEY glasses
3.4 Optical properties

For the optical studies UV-Visible absorption spectra of the synthesized glasses of composition (80-x-y-z)%TeO$_2$-10%Bi$_2$O$_3$-10%Na$_2$O-x%Er$_2$O$_3$-y%Yb$_2$O$_3$-z%AgNO$_3$ have been taken at room temperature figure 3. Cut-off wavelength is measured (table 2).

The absorption coefficient $\alpha$ of glass of thickness $t$ is given by [8]

$$\alpha = \frac{2.302A}{t} \quad (3)$$

Where $A$ is absorbance of the sample. The absorption coefficient $\alpha$ is related to optical band gap energy ($E_g$) by the relation [9]

$$\alpha h\nu = A(h\nu-E_g)^{r} \quad (4)$$

Where $\alpha$ is the coefficient of absorption, $h\nu$ is the energy of the incident electromagnetic radiation, $A$ is constant, $E_g$ is the optical band gap energy and the exponent $r$ is an index, which establishes the type of electronic transition for absorption. Its values are 1/2 for direct transition band gap, 2 for indirect transition band gap, 1/3 for direct forbidden transition band gap and 3 for indirect forbidden transition. The energy band gap of different glass samples were measured by extrapolation of linear region of the curves to meet to x-axis ($h\nu$) where $(h\nu)^{1/r}=0$ [10]. Change in $(h\nu)^{1/r}$ with $h\nu$ called Tauc’s plot and has been plotted for $1/r=2$ and $1/2$, as shown in figure 4 and figure 5.

![Figure 3. UV-Visible absorption spectra for different compositions of (80-x-y-z)%TeO$_2$-10%Bi$_2$O$_3$-10%Na$_2$O-x%Er$_2$O$_3$-y%Yb$_2$O$_3$-z%AgNO$_3$](image)

![Figure 4. Tauc’s plot for direct forbidden energy gap for different compositions](image)

![Figure 5. Tauc’s plot for indirect forbidden energy gap for different compositions](image)
The refractive index “n” of synthesized glasses can be calculated (table 2) by using following relation [11]

\[
\frac{n^2 - 1}{n^2 + 1} = 1 - \sqrt{\frac{E_g}{20}}
\]  

The band tails in glassy amorphous materials in the forbidden energy band gap is because of variations of imperfection in glass. This imperfection is estimated by using Urbach rule [12]

\[
\alpha = \alpha_0 \exp \left( \frac{h\nu}{E_u} \right)
\]

Where Eu is the Urbach energy and \( \alpha_0 \) is constant. Urbach energy corresponds to the width of the band tail of the electron states. Equation (6) can be written as

\[
\ln \alpha = \frac{h\nu}{E_u} + \text{constant}
\]

For the measurement of Urbach energy Eu a plot of \( \ln \alpha \) has been drawn against the phonon energy \( h\nu \), which are called Urbach’s graph, As shown in the figure 6. The reciprocal of the slope of the linear portion of curve is the value of Urbach energy given in table 2.

**Figure 6**. Urbach’s graphs for different compositions of \((80-x-y-z)\%\text{TeO}_2-10\%\text{Bi}_2\text{O}_3-10\%\text{Na}_2\text{O}-x\%\text{Er}_2\text{O}_3-y\%\text{Yb}_2\text{O}_3-z\%\text{AgNO}_3\).

**Table 2.** Cut-off wavelength, direct energy band gap, indirect energy band gap, refractive index and Urbach energy of \((80-x-y-z)\%\text{TeO}_2-10\%\text{Bi}_2\text{O}_3-10\%\text{Na}_2\text{O}-x\%\text{Er}_2\text{O}_3-y\%\text{Yb}_2\text{O}_3-z\%\text{AgNO}_3\)

| Sample | Cut-off wavelength | Direct energy band gap | Indirect energy band gap | Refractive index | Urbach energy |
|--------|-------------------|------------------------|--------------------------|-----------------|---------------|
| TBN    | 384nm             | 3.02eV                 | 3.00eV                   | 2.036           | 0.625eV       |
| TBNEY1 | 380nm             | 3.18eV                 | 3.05eV                   | 2.004           | 0.476eV       |
| TBNEY2 | 378m              | 3.22eV                 | 3.15eV                   | 2.000           | 0.256eV       |
| TBNEYA | 380nm             | 3.00eV                 | 3.21eV                   | 2.040           | 0.454eV       |

4. Conclusion
The Bismuth-tellurite glasses were prepared by traditional melt quench techniques with composition of \((80-x-y-z) \% \text{TeO}_2-10\% \text{Bi}_2\text{O}_3-10\% \text{Na}_2\text{O}-x\% \text{Er}_2\text{O}_3-y\% \text{Yb}_2\text{O}_3-z\% \text{AgNO}_3\). Synthesized telluride glasses having low transition temperature confirmed by DSC characterization. Study of XRD patterns base glass discloses amorphous nature of the samples. The density and molar volume of the glass sample is high due to the presence of bismuth ions, also the refractive index is more than 2 due to Bi$$^{3+}$$ ion content in tellurite based glasses. The absorption edge of TBN glass without rare earth is 384nm and shifted towards lower wavelength with increasing concentration of Er$$^{3+}$$ ions. The value of forbidden energy gap band gap is increasing along with the concentration of Er$$^{3+}$$ ions in the synthesized glasses. This increase may be due to increase in Er$$^{3+}$$ ions concentration in the synthesized glasses. Urbach tail of \((80-x-y-z) \% \text{TeO}_2-10\% \text{Bi}_2\text{O}_3-10\% \text{Na}_2\text{O}-x\% \text{Er}_2\text{O}_3-y\% \text{Yb}_2\text{O}_3-z\% \text{AgNO}_3\) which is calculate by UV-visible spectra is from 0.256 eV to 0.625 eV which indicate that structural disorder decreases with Er$$^{3+}$$ ions. The studied optical properties justify that synthesized glasses are good for non-linear applications.

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6. References

[1] Lim J M, Jain H, Toulouse J, Marjanovic S, Sanghera J S, Mikklos R and Aggarwal I D 2004 J. Non-Cryst. Solids 34960.
[2] El-Mallawany R A H 2002 Tellurite Glasses Handbook; CRC Press Inc.: Boca Raton, FL, USA
[3] Sailaja S, Raju N C, Reddy C A, Raju B D Pand Jho Y D 2013 J. Mol. Struct. 1038 2934
[4] Farouk M, Samir A, F. Metawe F and Elokr M 2013 J. Non Cryst. Solids 371 14-21.
[5] Vedeanu N, Cozar O, Stanescu R, Cozar I B and Ardelean I 2013 J. Non Cryst. Solids 1044 323-327.
[6] El Batal F H, Marzouk S Y, Nada N and Desouky S M Phys. 2007 B 391 88-97
[7] Majhi K, Varma K. B. R. and Rao K J J. Appl. Phys. 2009 106 084106
[8] Ofelt G S 1962 J. Chem. Phys. 37 511
[9] Ghosh A, Bhattacharya S and Ghosh A 2007 J. Appl. Phys. 101 083511
[10] Tauc J and Menth A 1972 Journal of non-crystalline solids 8 569-585
[11] Fares H, Elhouiuchet H, Gelloz B and Ferid M, 2014 Journal of Applied Physics 116.12 123504
[12] Urbach F 1953 Physical Review 92.5 1324