

Thermal and Optical Studies of Rare Earth Doped Tungston–Tellurite Glasses

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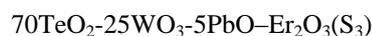
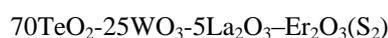
Abstract—The goal of this work is to prepare and characterize rare earth doped Tungston- Tellurite glasses. Tellurite glasses are well known for their use in optical fibre communication system, device technology etc. These glasses are stable at room temperature, and have good thermal, mechanical and optical properties. Er_2O_3 and Gd_2O_3 doped $\text{TeO}_2\text{-WO}_3\text{-La}_2\text{O}_3$ and $\text{TeO}_2\text{-WO}_3\text{-PbO}$ glasses are prepared from high purity oxides mixtures, melting in an alumina crucible in air atmosphere. Differential Scanning Calorimetry is used to study the thermal stability of the glass systems and UV/Vis/NIR spectroscopy is used to study the optical properties of the glasses. The glass transition temperature, Crystallization temperature, melting temperature and the variation in the optical band gap, and refractive index of these samples are calculated with the addition of Er_2O_3 and Gd_2O_3 .

Index Terms—Tellurite glasses, thermal stability, optical band gap, non bridging oxygen.

I. INTRODUCTION

Among various oxide glasses heavy metal oxide glasses doped with rare earth elements have wide area of application such as developing photonic and signal processing devices for communication and computing applications [1]. Tellurite glasses are technologically important since they are chemically stable, have high homogeneity and are resistant to divetrification at low temperature [2]. Tellurite oxide (TeO_2) used as a host material has several advantages over other oxide glass hosts and the most important one is being its low phonon frequency. TeO_2 glasses are known to be low melting and high refractive index materials, therefore considered to be potential nonlinear materials [3]. Their highest refractive indices among oxide glass in the visible and near IR region cause that the TeO_2 based glass systems are the most promising materials in optoelectronic devices [4]. The relatively high refractive index is a consequence of high polarizability of Tellurium ions. Due to the same reasons, they also possess large third order non-linear optic susceptibilities, which are about 100 times higher than in case of traditional silicate glasses [5]. They are used in infrared optics, optical electronics, and magneto- optics as well as in optical wave guide technology [6]. Erbium doped fiber amplifiers composed of Tellurite glasses provide a wider band width than Erbium doped silica based amplifiers [7]. Their unusually large infrared transparency, high linear and

non linear refractive indices, good thermal stability and corrosion resistance and suitability as a matrix for active element doping, represent the main justification for their continuous technological interest [8], which could be a good candidate for fibre drawing [9]. The effects of rare earth ions on the thermal stability and optical properties of Tellurite glasses have been discussed. From the differential Scanning Calorimetry (DSC) Studies the glass transition temperature (T_g), Crystallization temperature (T_c), and melting temperature (T_m) are estimated. Crystallization of glasses plays an important role in determining their transport mechanism, thermal stability and practical applications. The thermal stability factor defined as $\Delta T = T_c - T_g$ is higher than 100°C . There for Tellurite glasses exhibit good thermal stability and is a suitable candidate for fibre drawing. When the rare earth atoms are incorporated into the glasses they do as network modifiers with ionic bonding. Rare earth- doped Tellurite glasses are chosen because of their narrow emission bands, high quantum efficiencies, non interference with common fluorescent labels, and inertness to most organic and aqueous solvents. Optical absorption in solids occurs by various mechanisms, in all of which the photon energy will be absorbed by either the lattice or by electrons where the transferred energy is covered. It is a useful method for optical investigation of induced transitions and for getting information about the band structure and energy gap of the non- crystalline materials. My aim in this paper is to discuss the thermal stability, variations in optical band gap, and refractive index of



and $70\text{TeO}_2\text{-}25\text{WO}_3\text{-}5\text{PbO}\text{-}\text{Gd}_2\text{O}_3(\text{S}_5)$ glasses.

II. EXPERIMENTAL

The glass samples were prepared from powders of TeO_2 (99.995% purity, Alfa acer), WO_3 (99.99% purity, Alfa acer), PbO (99.999% purity, Alfa acer), La_2O_3 (99.99% purity, Alfa acer) Er_2O_3 (99.99% purity, Alfa acer), and Gd_2O_3 (99.99% purity, Alfa acer). Tellurite glasses were obtained by melting 15g batches in alumina crucibles. In order to introduce the rare-earth ions such as Er_2O_3 and Gd_2O_3 into the tellurite glass matrix, the respective oxides of an amount of .06 g have been added to the batch. Appropriate amount of materials were weighed and taken into the mortar and grounded thoroughly for homogeneous mixing. After

Manuscript received November 2, 2013; revised January 23, 2014.

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thorough mixing these materials were melted in an alumina crucible at 850 °C for 30 minutes in an electrical furnace in air atmosphere. The melt was poured on to a steel plate at room temperature. Bulk samples were obtained. The amorphous natures of the samples were confirmed using X-ray diffraction technique. Differential Scanning Calorimetry (DSC) is used to study the thermal stability of the prepared samples using Mettler Toledo DSC 822°. The scanning temperature was in the range of 0-600°C with a heating rate of 10°C/min. UV/Vis/ NIR absorption spectra for all samples were measured at room temperature using an Avantes Ava Space 2048 spectrometer in the range 200-1000 nm. From the absorption spectra optical band gap and refractive index of the material were calculated.

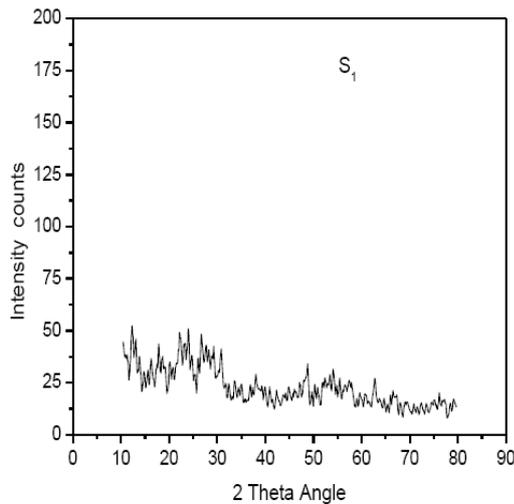


Fig. 1. XRD of a typical sample.

III. RESULT AND DISCUSSION

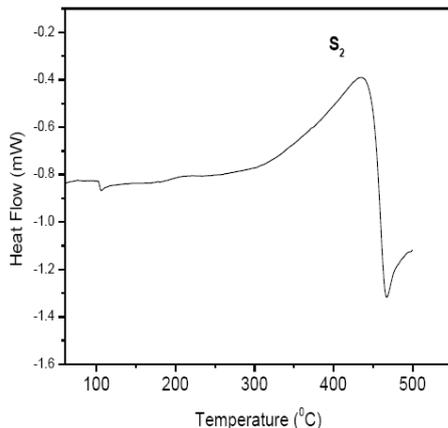


Fig. 2. DSC scans of a typical sample.

The XRD of a typical Tellurite glass (S_1) is reported in Fig. 1 and it shows no sharp peaks resulting from the crystalline phase of the material and this confirms the amorphous nature of the material. All other samples show the same pattern of the diffraction spectra which confirms the amorphous nature of the samples. From the DSC curves Fig. 2, characteristic temperature such as glass transition temperature (T_g), Crystallization temperature (T_c), and melting temperature (T_m) are obtained. Thermal stability factor defined as $\Delta T = T_c - T_g$

is calculated. The thermal stability parameter is the most important parameter in fibre drawing. Since the fibre drawing is a reheating process, to achieve a large working range of temperature during the sample fibre drawing it is desirable for a glass host to have ΔT as large as possible [10]. The values of ΔT for all samples are given in Table I. From the literature [11] it is found that, if the value of ΔT is higher than 100°C, the glass can be considered as thermally stable. From the value of ΔT it is found that for all samples the value of ΔT is higher than 300°C. Therefore these samples are suitable for fibre drawing. Among these samples, sample 4 (S_4) has higher thermal stability. From the data it is found that Tellurite glasses containing La_2O_3 are thermally more stable than the Tellurite glasses containing PbO .

The variation in optical band gap and refractive index of glasses with composition are studied from the UV/Vis/ NIR absorption spectra. The number of electrons excited into the conduction band is a function of both the temperature and the magnitude of the energy band gap E_g , which is defined as the separation between the maximum energy in the valence band and the minimum energy in the conduction band. If E_g is small (0-3eV or 4eV) a material is considered to be semiconductor if E_g is large (4-12eV) a material is considered to be an insulator. As the electrical and optical properties are depending on the energy gap these data are very important in semiconductor device design. The study of the optical absorption edge in UV-region has proved to be a very useful method for elucidation of optical transitions and electronic band structure of materials. The optical band gap of the samples are calculated from absorption spectra, using the formula [12]

$$ahv = [A(hv - E_{opt})^n] / hv \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the incident photon energy, A is a constant and E_{opt} is the optical band gap. The value of $n = 2$ corresponds to indirect allowed transitions and $n = 1/2$ corresponds to direct allowed transition Fig. 8 represents the variation of $(ahv)^2$ versus $h\nu$ for indirect transitions and Fig. 9 represents the variation of $(ahv)^{1/2}$ versus $h\nu$ for direct transitions. The E_{opt} values with an accuracy of ± 0.01 eV obtained by extrapolation to $(ahv)^2 = 0$ for indirect allowed transitions and $(ahv)^{1/2} = 0$ for direct allowed transitions. The values of E_{opt} for indirect and direct allowed transitions are given in Table (1). Its value shows that these glasses have direct band gap since the value of E_{opt} for indirect band gap exceeds the value of E_{opt} for direct band gap [13].

The optical band gap of the five samples are found to be lower than the pure TeO_2 glass of value 3.79 eV reported in reference [14]. The optical band gap of the Tungston-Tellurite glass sample (S_1) is found to be higher than that containing rare earth ions. This reflects the influence of rare earth ions in the optical properties of rare earth ion doped Tellurite glasses. The optical band gap decreases with the addition of Er_2O_3 and Gd_2O_3 . This is due to the presence of modifiers. The reduction of band gap after rare earth doping is attributed to the structural changes that are taking place in the glass with the incorporation of rare earth elements which act as the modifiers. The study of variation of optical band

gap with Er_2O_3 and Gd_2O_3 composition gives information regarding the structure and the nature of bonds [13]. All values are given in Table I, Fig. 3, Fig. 4, Fig. 5, Fig. 6 and Fig. 7 shows absorption spectrum of S_1, S_2, S_3, S_4 and S_5 .

TABLE I: VALUES OF OPTICAL BAND GAP, ΔT AND REFRACTIVE INDEX OF THE SAMPLES

Sample Name	Optical Band gap (indirect)	Optical Band gap (direct)	$\Delta T = (T_c - T_g)^{\circ}\text{C}$	Refractive index
S_1	3.08	2.3	333	2.377
S_2	2.91	1.96	330	2.421
S_3	2.94	1.965	318	2.413
S_4	3	2	338	2.3971
S_5	3.03	2.07	313	2.389

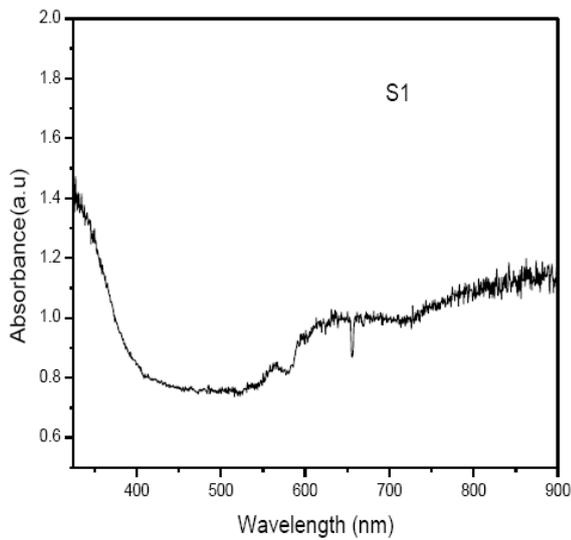


Fig. 3. Absorption spectra of sample (S1).

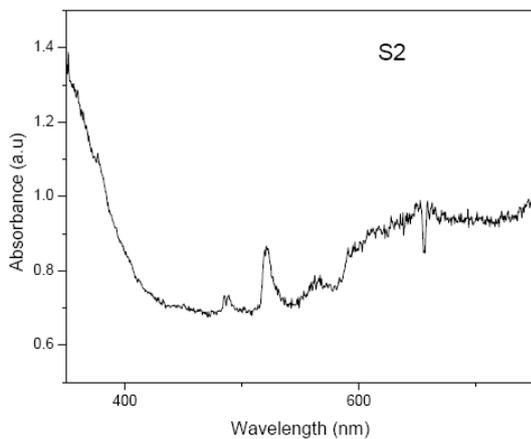


Fig. 4. Absorption spectra of sample (S2).

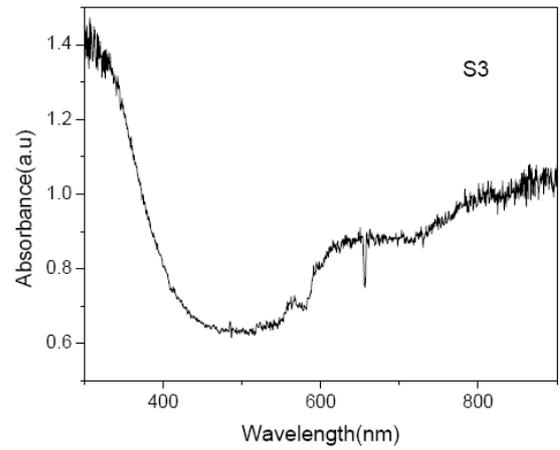


Fig. 5. Absorption spectra of sample (S3).

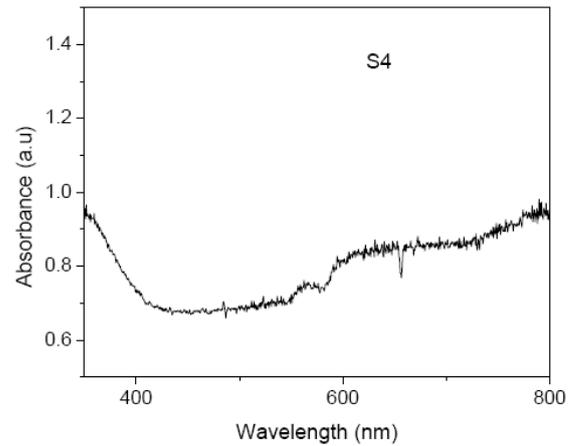


Fig. 6. Absorption spectra of sample (S4).

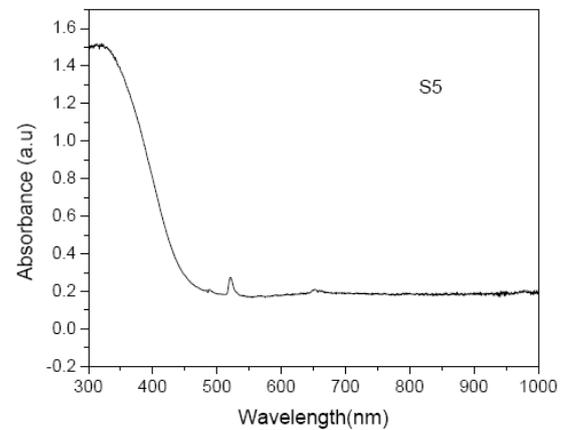


Fig. 7. Absorption spectra of sample (S5).

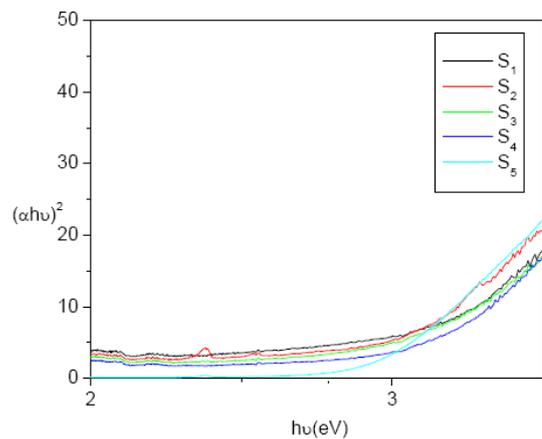
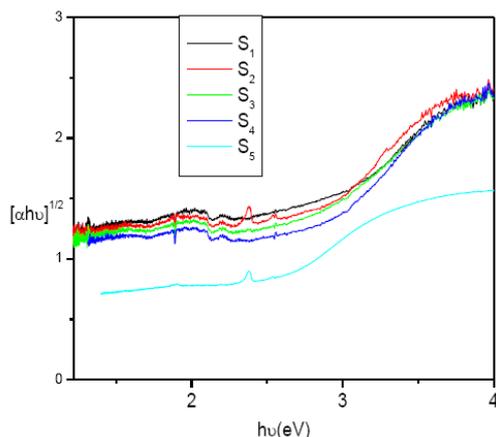


Fig. 8. Plot of $(\alpha hu)^2$ versus hu .

Fig. 9. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$.

The introduction of RE ions changes the oxygen bonding in glass forming network and any change of oxygen bonding in glass forming network such as formation of Non Bridging Oxygen changes the absorption characteristics which accordingly decreases the optical band gap. When rare earth is introduced into the Tellurite matrix, its coordination number changes. The optical band gap is influenced not only by a chemical composition but also by a structural arrangement of the sample matrix [13]. When Er_2O_3 is replaced by Gd_2O_3 the increase in optical band gap is due to the replacement of Er-O bond by Gd-O bond. The increase in optical band gap with Gd_2O_3 content can be explained with the movement of electron density [15]. When Gd_2O_3 is added instead of Er_2O_3 in the samples the number of Non-Bridging Oxygen decreases which accordingly increases the optical band gap [13]. The reduction in the number of Non-Bridging Oxygen is due to the value of molar mass of the materials. The molar mass of Gd_2O_3 is less compared to the molar mass of Er_2O_3 . Again from the study of optical band gap, the value of optical band gap containing PbO is higher than that containing La_2O_3 . This is because the molar mass of PbO is less than that of La_2O_3 . There for there is a reduction in the number of Non Bridging Oxygen atoms and this in turn increase the value of optical band gap for the samples containing PbO.

The refractive index is calculated for all the samples and it is found to be higher than 2.39 within the 400- 475 nm spectral range which are considerably higher than those obtained for standard optical glasses [16]. Doping of rare earth atoms increases the refractive index. High values of refractive index of Tellurite glasses allow using such material in optical wave guides, where a self focusing effect is observed. [6], [17]. The relationship between refractive index 'n' and the optical energy gap is examined by the equation [18]

$$\frac{(n^2 - 1)}{(n^2 + 2)} = 1 - \sqrt{E_g / 20} \quad (2)$$

The addition of rare earth ions to the network leads to the formation of dense packing of rare earth modifiers into the host materials [19]. These have a direct effect on increasing the refractive index, because of the direct proportional relationship between dense packing and the refractive index.

High refractive index of these glass samples are attributed to the high polarization of host material TeO_2 [18]. Doping of Gd_2O_3 instead of Er_2O_3 to a Tellurium matrix results in the reduction of refractive index of the glass. Non bridging Oxygen also has an effect on the refractive index, because the polarity of Non Bridging Oxygen is higher than that of Bridging Oxygen [20].

IV. CONCLUSION

Rare earth doped Tungston–Tellurite glasses are prepared by melting and quenching techniques. Since the value of ΔT is higher than 100°C , the glass can be considered as thermally stable. The optical band gap of the Tungston–Tellurite glass sample (S_1) is found to decrease with the addition of rare earth ions. The optical band gap depends on the number of Non-Bridging Oxygen produced. The refractive indexes of all samples are considerably higher than those obtained for standard optical glasses.

ACKNOWLEDGMENT

The authors acknowledge University Grants commission for supporting this work financially under the research awardees scheme.

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