

IMPROVED CHEMICAL DURABILITY AND THERMAL STABILITY OF ZINC BORO-TELLURITE GLASS

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Glasses with compositions $(60-x) \text{TeO}_2 + 30\text{B}_2\text{O}_3 + 10\text{ZnO} + x\text{Er}_2\text{O}_3$ (where $x=0, 0.5, 1, 1.5$ and 2.0 mol%) were prepared by melt quenching method. The chemical durability of these glasses measured from their weight before and after weathering by water and ammonium hydroxide showed significant improvement with the increase of rare earth contents. X-ray diffraction (XRD) measurements confirmed the amorphous nature of the as-prepared glasses. The glass transition temperature, crystallization temperature and melting point of the samples were determined using differential thermal analyzer. The elemental analyses are performed using EDX and the surface morphology by SEM technique. The enhancement in the thermal stability with the addition of the erbium contents indicates the increased glass forming tendency against crystallization. The fragility factor and Hruby parameter are increased from 1.098-2.897 and 145-160 respectively as the erbium concentration increased from 0-2.0 mol%. The influence of erbium oxide on the surface morphology, chemical durability and water resistivity of the zinc-boro-tellurite glasses are examined. These attractive features on improved chemical durability and thermal stability suggests that these glasses can be nominated as suitable host for the development of solid state lasers with good performance in different temperature and environments.

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1. Introduction

Inorganic oxide glasses have great commercial importance, scientific and technological interest since the past due to their diverse application as glass solders, shielding for nuclear radiation and in optical devices [1]. Among these glasses, some remarkable characteristics of erbium doped boro-tellurite glasses make them attractive for optoelectronic and photonic applications. The high linear and nonlinear refractive indices with a wide transmission window ($\sim 0.4\text{--}6 \mu\text{m}$) [2], good mechanical strength, chemical durability, thermal stability and rare earth (RE) solubility offer them promising materials for photonic applications such as up-conversion lasers, optical fiber amplifiers and nonlinear optical devices. Excellent thermal stability of tellurite glasses make them good solid state material doped with RE ions tolerant to high temperature ranges [3].

The term “chemical durability” has been used conventionally to express the resistance offered by a glass towards the attack by aqueous solutions and atmospheric agents. There is no absolute or explicit measure of the chemical durability and different glasses are usually graded relative to one another after subjecting them to similar experimental conditions [4]. The chemical durability of glass in different media depends on many factors, the more important of which are the chemical composition of the glass and the nature of attacking medium. It is also established that their chemical durability depend on the bond strength, field strength and volume of various cations present in the glass [5, 6].

Strong alkali hydroxides are the most corrosive solutions to the glass followed by hydrofluoric acid. The rate of attack by the alkali ion is generally linear in time and may be influenced in the presence of other ions. Conversely, acids react much more slowly with the glass

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in comparison to the strong alkali hydroxides and the rate of aggression in the ideal case is square root in time [7].

The structural, thermal and optical properties of erbium doped boro-tellurite glass are extensively studied [8-11]. However, to the best of our knowledge no report on the thermal stability and chemical durability of boro-tellurite glasses are exists. Therefore, we aim to investigate the thermal stability, fragility and chemical durability of Er^{3+} -doped boro-tellurite glass in different solutions. It is believed that the remarkable chemical durability of boro-tellurite glass makes them potential for widespread applications.

2. Experimental

Erbium doped boro-tellurite glasses with varying concentration of the erbium oxide were prepared by melt quenching method. Details of the studied glass compositions are given in Table 1. Boron oxide was introduced in the form of boric acid. Each melt was made in a porcelain crucible in the electrically heated furnace (Carbolite ELF 11/6B) at 950 °C for 15 min. The glass melt was poured between two stainless steel moulds and then the glass samples were annealed for about 3h at 300 °C to remove the thermal and mechanical strains before cooling down slowly to room temperature. Finally, the casted samples were cut into 20×20×2.7 mm regular shape of four pieces each for the test of chemical durability.

Table 1. Composition and some properties of the investigated glass samples.

Physical or Chemical Properties	S1	S2	S3	S4	S5
TeO_2	60	59.5	59	58.5	58
ZnO	10	10	10	10	10
B_2O_3	30	30	30	30	30
Er_2O_3	0	0.5	1	1.5	2
Density ρ (g/cm ³)	4.46	4.49	4.73	4.67	4.65
Molar Volume (cm ³ mol ⁻¹)	27.99	27.03	26.823	27.45	27.83
V_m^B	19.99	19.30	19.16	19.61	19.88
$\langle d_{B-B} \rangle$ (nm)	0.321	0.318	0.317	0.319	0.321
OPD	35.73	37.00	37.27	36.423	35.94
Ion concentration N ($\times 10^{20}$ ions/cm ³)	-	1.07	2.24	3.29	4.33
M	4	4.01	4.02	4.03	4.04
Field Strength F ($\times 10^{15}$ cm ²)	-	0.417	0.682	0.880	1.057
Inter nuclear distance r_i (Å)	-	21.034	16.46	14.489	13.22
n_b ($\times 10^{29}$ m ⁻³)	0.8607	0.894	1.263	0.884	0.874

Each pieces of the sample were weighted using analytical digital balance (AND, GR-200) by error in the order of $\pm 10^{-4}$ g. One sample was kept as reference (R), and other three pieces were put in 5 mL of different de-ionized water, hydrofluoric acid (Orec, 49%) and ammonium hydroxide (Mallinckrodt Chemicals, 30% NH_4OH). The immersion temperature was 27 °C for 8 and 14 days. The volume of the leaching solution was large enough relative to the weight of the glass samples to avoid the formation of saturated solution which may prevent further leaching of the glasses [3]. At a fix time (8 day) interval, samples were removed from the solution, washed by running water, dried at 127 °C for 15 min in a furnace before weighed by the same balance, and then placed in the respective solution again. The chemical durability of the glass sample was expressed by weight loss per surface unit in different solutions.

The mass loss (W_L) was then calculated using the relation,

$$W_L = \frac{W_B - W_A}{W_A} \times 100 \quad (1)$$

Where W_A and W_B refer to sample weights after and before corrosions, respectively.

The morphology of the glasses was analyzed using energy dispersive spectrometry (SwiftED3000 EDX) attached to a TM3000 Hitachi tabletop scanning electron microscope (SEM). Furthermore, the XRD measurements were performed using Bruker D8 Advance diffractometer ($K\alpha=1.54 \text{ \AA}$) at 40kV and 100 mA, at room temperature. Thermal characteristics of samples were obtained using a differential thermal analyzer (DTA, Model: Pyris Diamond TG-DTA, Japan) by heating at a rate of $10 \text{ }^\circ\text{C}/\text{min}$ in the temperature range of $200\text{-}1000 \text{ }^\circ\text{C}$ to determine the endothermic and exothermic peaks. The glass transition temperature T_g , crystallization temperature T_c and melting point T_m of the composition were defined by one onset of endothermic peak, one exothermic peaks and one endothermic peak at higher temperature, respectively. The thermal stability of the glass was defined by calculating the difference between crystallization and glass transition temperatures [12].

3. Results and discussion

Fig. 1 shows the XRD patterns of the glasses. Absence of any sharp peak confirms the nonexistence of any crystalline phases and the presence of a broad hump shows the characteristic of the amorphous materials. The morphology of the glass surface is presented in Fig.2 as observed by naked-eye. The glass designations and the measured physical and chemical properties of the as-prepared glasses are listed in Table 1.

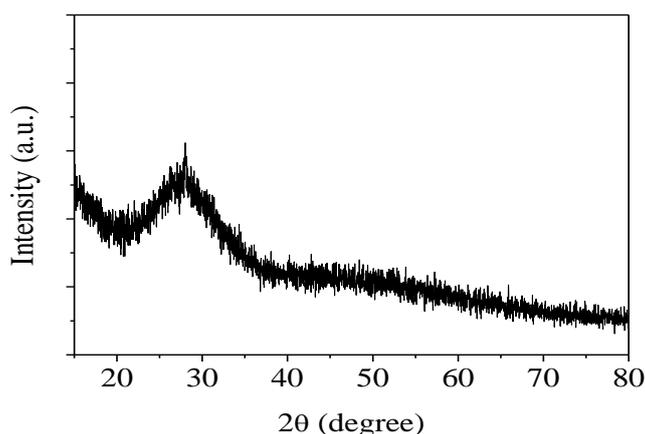


Fig.1. XRD pattern of Er^{3+} -doped zinc boro-tellurite glass.



Fig.2. Increase of transparency of samples kept in water (a) and NH_4OH (b) after 4 days by addition of erbium content in zinc boro-tellurite glass.

The specific volume containing 1 mol of boron is calculated using

$$V_m^B = \frac{V_m}{2(1-X_B)} \quad (2)$$

and the average boron-boron distance is estimated from [16]

$$\langle d_{B-B} \rangle = \left(\frac{V_m^B}{N_A} \right)^{1/3} \quad (3)$$

The oxygen packing density (OPD) [17], the average coordination number (m) and the bond density (n_b) of the samples were calculated using following relations

$$OPD = 1000C \left(\frac{\rho}{M} \right) \quad (4)$$

$$m = [\sum_i n_{ci} x_i] \quad (5)$$

$$n_b = \frac{N_A}{V_M} m. \quad (6)$$

Table 1 clearly indicates that the density and the oxygen packing density of the glasses are maximized for sample containing 1 mol% Er_2O_3 , while they possess the minimum values of molar volume and average boron-boron separations. However, the average coordination number of the glasses is increased by further addition of the erbium oxide.

The weight loss of glass samples in de-ionized water are illustrated in Fig 3a. It is evident that the mass loss decreases with the increase of erbium oxide contents. All the studied samples show a decrease in weight when immersed in distilled water at temperatures 27 °C. The weight loss in water varies linearly with time except for the sample without erbium (S1). The increase in the mass loss with the increase of the immersion time is attributed to the fact that the glass constituents find sufficient time to be released into the immersion solution. The weight loss of samples in NH_4OH solution (Fig.3b) clearly reveals an increase in the mass loss with the increase of the immersion time. The decrease in the mass loss with the gradual increase in the erbium oxide content can be ascribed to the decline in the corrosion rate due to the reduction in the possibility of leaching process. Generally, the corrosion rate depends on the chemical compositions, bond strengths, bond lengths and coordination number of the atoms in the glass matrix. As listed in Table 1, the coordination number of the glasses increases due to the incorporation of the erbium content. Moreover, the average oxygen packing density and the bond density of the samples containing RE ions are higher than the sample S1. Therefore, the enhanced chemical durability of the glasses is in agreement with the expectations through the results of Table 1.

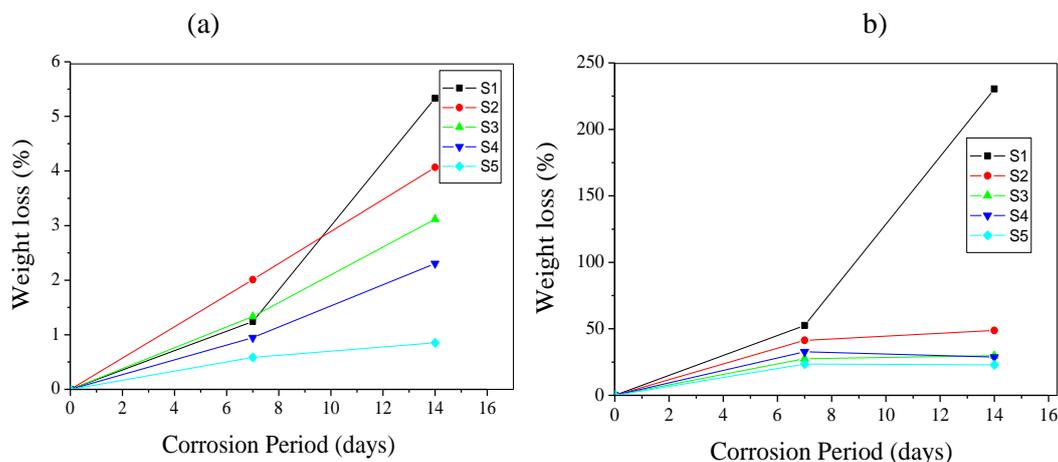


Fig.3. Weight loss of different boro-tellurite glass samples in water (a) and NH_4OH (b).

To realize further insight into the chemical durability, the morphological and chemical compositions of the surface of the specimens before and after immersing in the solutions are examined by SEM and EDX. Fig. 4 (a), (b) and (c) show the surface morphologies for the glass samples after immersion in de-ionized water of the samples S1, S3 and S5, respectively. A morphological analysis of the specimen using SEM shows spherically and irregularly round-shaped powder particles. As can be seen in Fig. 4, with the increase of the concentration of rare earth ions the morphology of the particles transformed to flower-like shaped. Fig. 5(a), (b) and (c) show the surface morphologies for the glass samples S1, S3 and S5 respectively after immersing in ammonium hydroxide for 14 days. Two different microstructures are evidenced, one round-shape and the other acicular (characteristic of the wollastonite). As clearly shown in Figs. 4 and 5, immersing the glass samples in the same solution caused changes in the grain shape, size and the surface state of specimens. Therefore, the dopant concentration plays an important role in the formation of crystal inside the host.

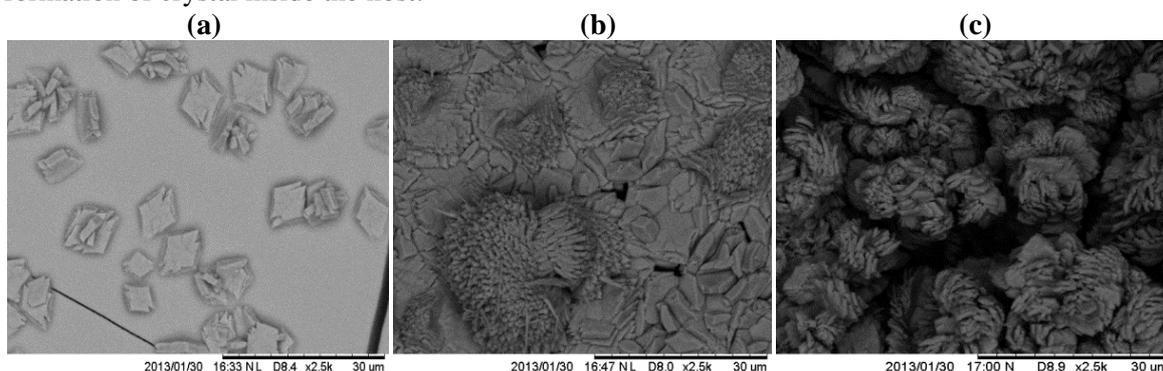


Fig.4. SEM micrographs of glass samples S1 (a) S3 (b) and S5 (c) immersed in the de-ionized water after 21 days.

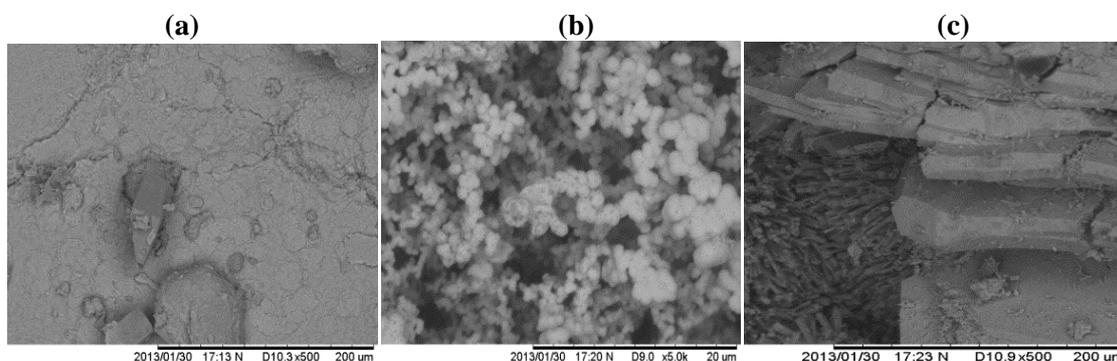


Fig.5. SEM micrographs of glass samples S1 (a) S3 (b) and S5 (c) immersed in the ammonium hydroxide (NH₄OH) after 21 days.

The EDX analysis is performed after the durability test in order to evaluate the amount of each element present on the surface of the glasses. In all the specimens, oxygen, zinc, tellurium and erbium were detected on the surface grains for the samples before and after the immersion as revealed by EDX spectra presented in Fig. 6. Interestingly, the peaks of boron atom cannot be observed in EDX spectra due to the restriction in equipment to analyze boron and lighter atoms. Detailed examination of the EDX spectra for different regions of the sample (not shown here) indicate that in some regions of the weathered samples the existence of tellurium is relatively higher in comparison to the other regions. This is related to the dissolution of tellurium in the solution, clustering and deposition on the surface of the glass. These mechanisms result the

miniature change in the weight loss and widespread distribution of the surface morphological elements.

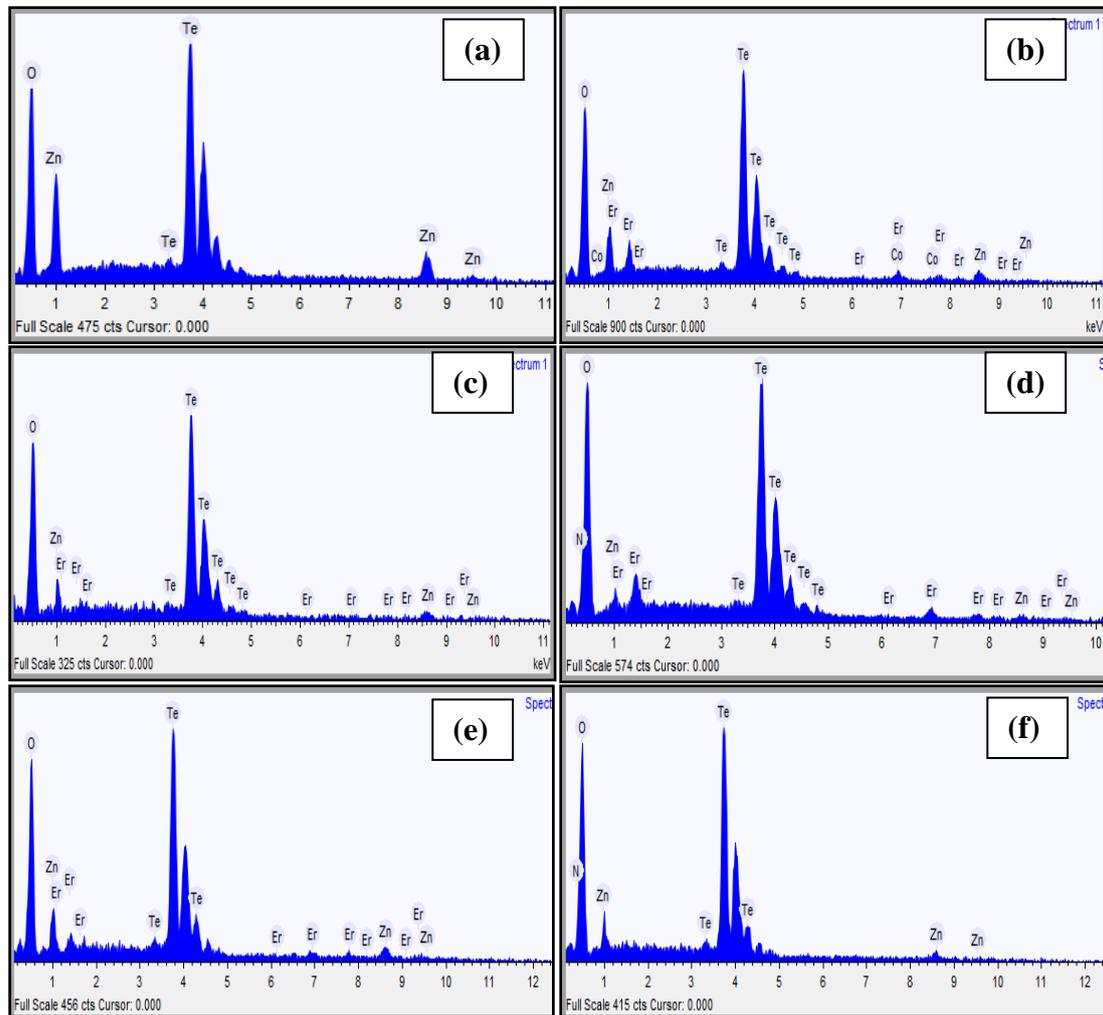
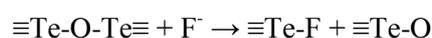


Fig.6.EDX spectra of samples S1, S3 and S5 (a, b and c respectively) immersed in the de-ionized water after 21 days and for the samples S1, S3 and S5 (d, e and f) weathering in NH_4OH solution.

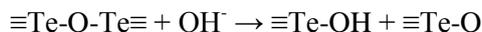
The resistance offered by the glass to the corroding action of different aqueous media is a property of great practical significance and is denoted by the term chemical durability. The interaction between glass and different types of aqueous solutions generally depends on the nature of the glass itself [1, 13]. The leaching mechanism being a characteristic of the acid attack is a diffusion-controlled ion-exchange process, involving exchange of the hydrogen ions for the modifier ions present in the glass network interstices [14, 15]. Conversely, the etching process being a characteristic of the alkaline attack is a first-order reaction that leaves a smooth surface if complete dissolution occurs with no deposition of the reaction products.

The diffusion controlled ions exchange process is expected when the glass of the base composition is immersed. This reaction involves the exchange of the easily detachable from the glass by the hydronium ion from the acid solution. The process is given by



The number of Te-O linkages decreases with the addition of HF which result a decrease in the tellurite bond energy with the formation of more attackable network.

The Te-O-Te network is attacked and broken by OH⁻ ions through a nucleophilic reaction given by,



De-polymerization of the tellurite glass by F⁻ ions is faster and stronger than OH⁻ ions due to larger electro-negativity of F⁻ than O²⁻ ions which is responsible for the decrease in the oxygen packing density in glass samples.

The values of T_g , T_c and T_m of the glass samples are determined using DTA are shown in Fig.7. At higher temperature, an exothermic peak due to the crystallization T_c , followed by another endothermic effect at temperature T_m due to re-melting of the glass is observed. From the measured values of T_g , T_c and T_m the glass stability factor $(T_c - T_g)$ and Hruby's parameter [18] $H = (T_c - T_g)/(T_m - T_c)$ have been evaluated and presented in Table 2.

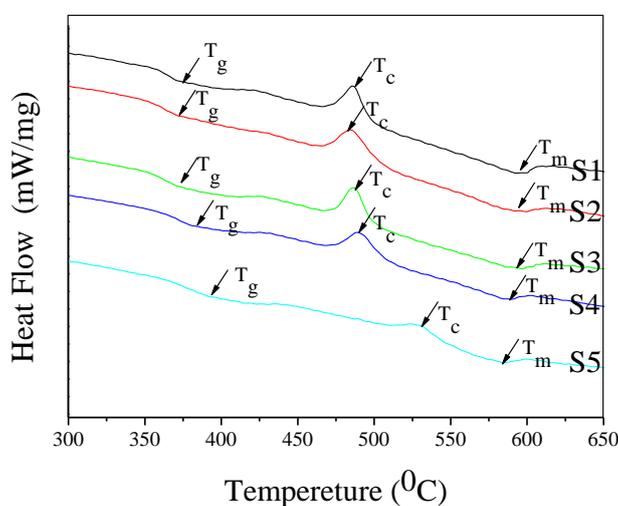


Fig.7. DTA curves of Er³⁺-doped zinc boro-tellurite glass and determination of the glass transition temperature.

Table 2. Thermal properties of Er³⁺-doped zinc boro-tellurite glasses.

Glass Label	T_g	T_{g1}	T_{g2}	T_c	T_m	ΔT	ΔT_g	H
S1	360	280	425	483	595	123	145	1.098
S2	355	275	425	485	600	130	150	1.130
S3	340	275	425	487	593	147	150	1.836
S4	330	275	425	489	585	159	150	1.565
S5	325	275	435	522	590	197	160	2.897

The DTA thermograms for all glass samples reveal one exothermic peak corresponding to a crystallization reaction. The gradual shift in the crystallization temperatures to higher values and the decrease in crystallization tendency with the increase of Er₂O₃ content are ascribed to the increase in number of bonds per unit volume responsible for the increase the cross-linking density. Glasses presenting a high stability factor $(T_c - T_g)$ and low temperature interval $(T_m - T_c)$ are the suitable for fiber fabrication due to the reduced chances of crystallization. Furthermore, ΔT larger than 120 °C suggesting that introduction of Er₂O₃ into boro-tellurite glasses improved their thermal stability. The greater values of the Hruby's parameter indicate higher glass forming tendency. The value of ΔT_g that measures the fragility of the samples is calculated from the

temperature of onset (T_g^1) and the completion (T_g^2) of glass transition. The fragility factors of the glasses are listed in Table 2. The wider the transition region (ΔT_g) is, the harder the glass is against the deformation of amorphous nature and conversion to the crystallized glass-ceramics, ceramics and crystals. Interestingly, the values of ΔT_g in our glasses increased with the addition of the erbium oxide.

5. Conclusion

In conclusion, the chemical durability and thermal stability of the prepared Er^{3+} -doped boro-tellurite glasses were studied via weight loss in different solutions and DTA measurements. The structural and elemental analyses are performed using XRD, SEM and EDX measurements. The SEM images revealed substantial reduction in surface attacks with the increase of the rare earth ions. The incorporation of erbium oxide improved the surface morphology, chemical durability and water resistivity of the zinc-boro-tellurite glasses. The weight loss of the samples increased with the time but decreased with the addition of erbium content. Thermal analysis revealed the increase in thermal stability with the increase of RE ions and improved the fragility of the glasses. Our results on improved chemical and thermal stability of the glasses suggest that these samples are potential candidates for optical applications in solid state optics and optoelectronics.

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References

- [1] F. A. Khelifa, A. A. EL-Kheshen, Fac. Sci. Unvi. Ank. Series B. **43**, 1122 (1997).
- [2] R. Balda, J. Fernandez, M. A. Arriandiaga, J. M. Fernandez-Navarro, J. Phy: Cond Matt. **19**, 036206 (2007).
- [3] V. Pilla, E. F. Chillcce, A. A. R. Neves, E. Munin, T. Catunda, C. L. Cesar, L. C. Barbosa, J. Mater. Sci. **42**, 23042308(2007).
- [4] Z. A. EL-hadi, Department of Chemistry, University College for Girls, (1994).
- [5] R. G. Newton, Glass Technology. **26**, 21(1985).
- [6] A. ELazm, A. L. Hussein, J. Chem. Egypt. **5**, 1 (1962).
- [7] P. B. Adams, Glass Containers for Ultrapure Solutions. **29**, 4327 (1973).
- [8] G. Pavani, K. Sadhana, V. ChandraMouli, Phys B. **406**, 12421247 (2011).
- [9] K. Selvaraju, K. Marimuthu, Phys B. **407**, 10861093 (2012).
- [10] X. Shen, Q. Nie, T. Xu, S. Dai, X. Wang, Spectrochim Acta Part A. **66**, 389393 (2007).
- [11] M. K. Halimah, W. M. Daud, H. A. A Sidek, A. W. Zaidan, A. S. Zainal, Mater Sci-Poland. **28**, 1(2010).
- [12] S. Mahadevan, A. Giridhar, A. K. Singh, J. Non-Cryst. Solids. **88**, 1134 (1986).
- [13] G. Pal Singh, S. Kaur, P. Kaur, D. P. Singh, Phys B. **407**, 1250 (2012).
- [14] M. Abdel-Baki, F. A. Abdel-Wahab, F. El-Diasty, J. Appl. Phys. **111**, 073506 (2012).
- [15] A. Paul, Chemistry of Glasses. Chapman and Hall: London. 926 (1982).
- [16] M. B. Volf, Technical Glasses, Pitman, London, (1961).
- [17] J. R. Hutchins, R. V. Harrington, Encyclop of Chem Tech. 555 (1966).
- [18] H Hruby, Czechoslovak, J. Phy, Sec B. **32**, 1187 (1972).