Composition Dependent Structural and Thermal Properties of Sm$_2$O$_3$ Doped Zinc Fluoroborate Glasses

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ABSTRACT

Glasses based on Sm$^{3+}$ doped zinc fluoroborate have been synthesized and characterized. Formation of glass has been investigated in the 30 ZnF$_2$-20 TeO$_2$-(50-x) B$_2$O$_3$-x Sm$_2$O$_3$ matrix. Fast quenching is required to prevent melt crystallization and adequate heat treatment to diminish thermal stress, which results in an efficient amorphous material. The Differential Scanning Calorimeter (DSC), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDAX), stability, density and refractive index have been recorded, calculated, measured and analyzed for the glass samples with different concentrations of Sm$^{3+}$ ranging between 0 to 3 mol%. Density increases as dopant concentration increases and glass transition temperature $T_g$ ranges between 395 and 420ºC. The increase of molar volume with Sm$_2$O$_3$ content indicates that the extension of glass network is due to the increase of the number of NBOs. The results found in this investigation showed that the refractive index of glass does not only depend on the density but also depends on the electronic polarizability of the glass. The increasing stability of the glass samples shows that they are thermally resistant. The presence of NBOs in the glass network is also approved by the decrease in glass transition temperature ($T_g$). The variation of the properties with different composition of dopant plays a dominant role in determining a good host material in the field of optics and photonics.

Keywords: Hruby’s Parameter, DSC, Zinc Fluoroborate, Samarium Doped

1.INTRODUCTION

Glasses containing rare earth ions have attracted considerable attention because of their wide applications in laser, up-conversion fluorescence, high density optical storage, solar concentrators, wave-guide lasers and in other photo-electronic fields (Polishchuk et al., 2011; Lin et al., 2005). The fluoride glasses possess high elasticity and its best attribute is that these glasses have a low optical attenuation. These rare earth doped fluoroborate glasses with various visible emissions will be useful in developing new light sources, display devices, UV sensors and tunable visible lasers (Polishchuk et al., 2011). Oxfluoride glasses are of interest from the fundamental point of view: The replacement of fluorine by oxygen affects the glass formation and the structure of glass networks, namely, their connectivity. The oxfluoride glass matrix can provide a unique environment for rare earth ions, which will differ from both the oxide and fluoride matrices. It is expected that oxfluoride glasses with high content of rare earth elements can appear to be new functional materials (Polishchuk et al., 2011). Transparent oxfluoroborate rare earth doped glasses are interesting class of materials, which combine the optical advantages of fluoride host with the mechanical advantageous of oxide glass plus highest glass formation tendency of borate atoms.
The investigations of absorption properties of the Sm$^{3+}$ ions have indicated that the optical properties of these rare earth ions can be affected by varying the glass composition, thus opening up the possibility of engineering application-friendly compositions (Lin et al., 2005). With the increasing demand of various visible lasers and light sources, further investigations in other rare earth ions such as Sm$^{3+}$ ions, are becoming more significant. Oxide glasses are attracting hosts for obtaining efficient luminescence in rare earth ions.

In them, borate glasses have been widely investigated due to their technological applications. Boron can be considered as having the highest glass forming tendency because it in the form of B$_2$O$_3$ does not crystallize by itself even when cooled at the slowest rate (Lin et al., 2005). It is a suitable optical material with high transparency, low melting point, high thermal stability and good rare earth solubility. However, interest in borate glass is small due to its high phonon energy and it is difficult to obtain high efficient infrared and up-conversion visible emissions. On the other hand, the high phonon energy in borate glass is not detrimental to Sm$^{3+}$ normal 4f transition emissions and sometimes it can accelerate the relaxation processes, which is necessary and beneficial for visible emissions. In this study, borate glass as a suitable host for Sm$^{3+}$ is demonstrated (Lin et al., 2005).

Lanthanides themselves cannot form glasses, they can be incorporated into the structure by associating with the glass composition by introducing as dopants and act as active luminescence centers. It is noted that, when rare earth ions are involved in the matrices, their state determined by the 4f electronic configuration depends weakly on the surrounding ions. The glasses containing oxides and fluorides are appropriate objects for this purpose. Their properties are determined by the relatively low energy of phonons, which is explained by the presence of oxides and the chemical and mechanical stabilities associated with the fluorides (Polischchuk et al., 2011).

Tellurite glasses are very promising materials for linear and non-linear application in optics, due to some of their important characteristic features such as high refractive index, low phonon maxima and low melting temperature. TeO$_2$ is known as a conditional glass former, as it needs a modifier in order to form the glassy state easily. Tellurite glasses continue to intrigue both academic and industry researchers not only because of their technical applications, but also owing to a fundamental interest in understanding their microscopic mechanisms. In general, application and utilities of glassy materials are enormous and are governed by the factors like composition, refractive index and dopants present in the glass. Moreover, rare earth in glassy matrix is strongly dependent on crystal field effects, local environment, phonon energies extended into the band gap. It has been found that glasses with a high density along with a low dispersion usually have high non-linear refractive index (Eraiah, 2010).

B$_2$O$_3$ is a glass forming oxide, TeO$_2$ is a conditional glass former, however, the structural role of zinc in such glasses is the subject of some controversy with evidence for behavior as a network former or a network modifier. Both Zachariasen and Warren’s theory of glass structure and Dietzel’s crystal field theory classify zinc as a network intermediate, i.e., able to adopt both network former and modifier roles depending upon glass matrix (Cassingham et al., 2010). Sm$_2$O$_3$ is a modifier in the network, with these chemicals in the glass matrix, a low rate of crystallization, moisture resistant, stable and transparent glasses could be achieved.

The aim of the present paper is to describe detailed thermal behavior of oxyfluoroborate glasses, containing different concentration of Sm$^{3+}$ and to find correlations between rare-earth content, phase composition and thermal properties of these glasses. To the best of our knowledge, there is a lack of information in the literature about thermal properties of Sm$^{3+}$ doped oxyfluoroborate glasses. The presented data from the research done indicates that the glass systems with rare earth element that serve as dopants leads to the design of a new material with wide scope in optics and photonics.

### 2. EXPERIMENTAL PROCEDURE

Within the glass forming region of ZnF$_2$-TeO$_2$-B$_2$O$_3$-Sm$_2$O$_3$ glass system, the following compositions with successive increase in the concentration of Sm$_2$O$_3$ are chosen for the present study:

- $S_{m0} = 30$ ZnF$_2$-20 TeO$_2$-50 B$_2$O$_3$
- $S_{m1} = 30$ ZnF$_2$-20 TeO$_2$-49.5 B$_2$O$_3$-0.5 Sm$_2$O$_3$
- $S_{m2} = 30$ ZnF$_2$-20 TeO$_2$-49 B$_2$O$_3$-1.0 Sm$_2$O$_3$
- $S_{m3} = 30$ ZnF$_2$-20 TeO$_2$-48.5 B$_2$O$_3$-1.5 Sm$_2$O$_3$
- $S_{m4} = 30$ ZnF$_2$-20 TeO$_2$-48 B$_2$O$_3$-2.0 Sm$_2$O$_3$
- $S_{m5} = 30$ ZnF$_2$-20 TeO$_2$-47.5 B$_2$O$_3$-2.5 Sm$_2$O$_3$

Appropriate amounts (all in mol%) of reagent grades of ZnF$_2$, TeO$_2$, B$_2$O$_3$ and Sm$_2$O$_3$ powders were thoroughly mixed in an agate mortar-pestle and homogeneously mixed materials were heated in the temperature range 950-1000°C in a PID temperature controlled electric furnace for about 1 h 30 min until a bubble free transparent liquid was formed. The resultant melt was then squeezed on a preheated stainless steel mould and subsequently annealed at 250°C for 2 h. The samples were then ground and optically polished using polisher from Chennai Metco.
Bainpol. The final dimensions of the samples used for structural and thermal analysis were about 0.8×0.8×0.2 cm. The density \( \rho \) of these finely polished glass samples was found through the standard principle of Archimedes in Contech Analytical Balance (with accuracy of 0.0001 g) using xylene (99.99% pure) as the buoyant liquid. The refractive index of these glasses was measured using Abbe refractometer using sodium-D line-589 nm as source of radiation in Medimeas Instrument. The characteristic temperatures of the glasses are measured by a Differential Scanning Calorimeter (DSC) Shimadzu DSC60 at a heating rate 10 K/min under controlled atmosphere (N\(_2\)). The samples (weight≈10-15 mg) are introduced into aluminum pans, which are sealed to prevent the possible contamination of the furnace cell. The estimated values of temperatures are given with an estimated accuracy of about±2°C. Chemical analysis was estimated accuracy of about±2°C. Chemical analysis was implemented in a Scanning Electron Microscope (SEM) using an Energy Dispersive X-ray Spectrometer (EDAX) from Zeiss EVO 18 Special.

3. RESULTS

3.1. Structural Analysis

The measurement of density (\( \rho \)) and refractive index (\( n \)) are the effective tools to explore the degree of structural compactness modification of the geometrical configurations of the glass network (Eraiah, 2006). The density and refractive index of the glass samples determined in the present study are given in the Table 1 with probable errors ±0.001. The molar volume (\( V_m \)) of the glass samples, was calculated using the average Molecular weight (M) and density (\( \rho \)) with the following relation:

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

The number density of rare-earth ions (\( N \)) of Sm\(^{3+} \) was determined using the formula given in equation (Saritha et al., 2008):

\[
N = \left[ 6.023 \times 10^{23} \times \text{mol}\% \text{ of cation}\times\text{valency of cation} \right]/V_m
\]

The dielectric constant (\( e \)) was calculated using refractive index (\( n \)) of the glass:

\[
E = n^2
\]

The Molar Refraction, (\( R_m \)) of the glass samples were calculated using the formula given (Prajnashree et al., 2013, Chimalawong et al., 2010, Sideket et al.,2009) which is well-known as Volf and Lorentz-Lorenz formula:

\[
R_m = \left[ \frac{(n^2 - 1)}{(n^2 + 2)} \right] V_m
\]

where, \( n \) is the refractive index of the glass sample. \( \rho \) is the density and M is the average molecular weight of the glass samples. \( V_m \) is molar Volume (\( V_m \)) and \((n^2-1)/(n^2+2)\) is the reflection loss.

A condition for predicting metallic or insulating behavior in the condensed state matter is metallization criterion, \( M = 1-\frac{R_m}{V_m} \). If \( R_m/V_m>1 \), then the materials show metallic nature and if \( R_m/V_m<1 \) they exhibit insulating behavior (Dimitrov et al., 2010). The so-called metallization parameter values of the present glasses are found to be less than one and are given in Table 1. Hence, the present glass systems with their metallization parameter values should exhibit insulating nature.

The molar refraction is related to the structure of the glass and it is proportion to the molar electronic polarizability of the material (\( \alpha_m \)). According to the Clausius-Mosotti relation, molar polarizability of the materials (\( \alpha_m \times 10^{24} \text{ cm}^3 \)) is given by the relation(Prajnashreet al., 2013, Chimalawonget al., 2010, Sideket et al., 2009):

\[
\alpha_m = [\frac{3}{4} \pi A_{i}^{*}] R_m
\]

where, \( A_i \) is the Avogadro’s number.

The electronic polarizability of oxide ions (\( \alpha_{O}^{2-} \)) can be calculated on the basis of refractive indices using the following equation:

\[
\alpha_{O}^{2-} = [(R_m/2.52) - \sum \alpha_i] \times (N_{O}^{2-})^{-1}
\]

where, \( \sum \alpha_i \) in the above equation is molar cation polarizability and \( N_{O}^{2-} \) is the number of oxide ions in the chemical formula. For the studied glasses the values of \( N_{O}^{2-} \) is equal to 1.9. The value of \( \alpha_{Zn}^{2+} = 0.286 \text{ Å}^3 \) for Zn\(^{2+} \) ions, \( \alpha_{Te}^{5+} = 1.595 \text{ Å}^3 \) for Te ions, \( \alpha_{B} = 0.003 \text{ Å}^3 \) for B\(^{3+} \) and \( \alpha_{Sm} = 0.92 \text{ Å}^3 \) for Sm\(^{3+} \) ions (Dimitrov et al., 2010).

The obtained values of N are used to calculate the polaron radius (\( r_p \)), ionic radius (\( r_i \)) (Moustafa et al., 2008; Rao et al., 2011) and Field strength (F) using the relations:

\[
r_p = \frac{1}{2} \left( \frac{\pi}{6N} \right)^{1/3} \quad r_i = \left( \frac{1}{N} \right)^{1/3} \quad \text{and} \quad F = \frac{z}{r_p^2}
\]

The variation of density, molar volume, electronic polarizability, number density with different composition of \( \text{Sm}_2\text{O}_3 \) is shown in Fig. 1a and b.
Fig. 1. Variation of (a) density and molar volume (b) number density and electronic polarizability with different composition of Sm$_2$O$_3$

Table 1. Physical parameters of the glass system 30 ZnF$_2$-20 TeO$_2$-(50-x) B$_2$O$_3$-x Sm$_2$O$_3$

| Glass code | Sm$_0$ | Sm$_1$ | Sm$_2$ | Sm$_3$ | Sm$_4$ | Sm$_5$ |
|------------|-------|-------|-------|-------|-------|-------|
| Average Molecular Weight (g/mole) | 97.7000 | 99.1000 | 100.5000 | 101.9000 | 103.3000 | 104.7000 |
| Density ($\rho$) (g/cm$^3$) (±0.0001) | 3.7240 | 3.7494 | 3.7860 | 3.8466 | 3.8903 | 3.9328 |
| Refractive index (n) (±0.0001) | 1.4510 | 1.4575 | 1.4610 | 1.4615 | 1.4620 | 1.4630 |
| Optical dielectric constant (e) | 2.1054 | 2.1243 | 2.1345 | 2.1359 | 2.1374 | 2.1403 |
| Molar volume ($V_m$) (cm$^3$/mol) (±0.01) | 26.2300 | 26.3300 | 26.4300 | 26.4900 | 26.5500 | 26.6200 |
| Molar refractivity ($R_m$) (cm$^3$/mol) | 7.0600 | 7.1700 | 7.2600 | 7.2700 | 7.3000 | 7.3300 |
| Metallization criterion ($M$) (1-$R_m/V_m$) | 0.7300 | 0.7270 | 0.7250 | 0.7250 | 0.7250 | 0.7240 |
| Number density ($N$) ($\times 10^{20}$/cm$^3$) | --- | 3.4300 | 6.8300 | 10.2300 | 10.3600 | 16.9700 |
| Inter ionic distance ($r_i$) (Å) | --- | 14.2900 | 11.3400 | 9.5700 | 9.8800 | 8.3800 |
| Polaron radius ($r_p$) (Å) | --- | 5.7500 | 4.5700 | 4.0000 | 3.9800 | 3.3700 |
| Field strength ($F$) ($\times 10^{15}$ cm$^{-2}$) | --- | 3.0400 | 4.8200 | 6.3000 | 6.3500 | 8.8200 |
| Electronic Polarizability ($\alpha_o^2$ (n)) (Å$^3$) | 1.4740 | 1.4970 | 1.5160 | 1.5180 | 1.5250 | 1.5310 |
| Molar Electronic polarizability ($\alpha_m$) ($\times 10^{-24}$ ions/cm$^3$) | 2.7980 | 2.8480 | 2.8780 | 2.8820 | 2.8930 | 2.9050 |

4. DISCUSSION

It is evident from Fig. 1a and 1b and also Table 1 that the density, molar volume, number density of the samarium ions, the electronic oxide ion polarizability of the present glass system increases with increase in the content of Sm$_2$O$_3$. The dielectric constant is directly correlated with the polarizability of the glass. The dielectric constant gradually increases with increase in the Sm$_2$O$_3$ content in the glasses. The chemical compositions of the constituent elements for the thermally evaporated glass sample (where x = 2.5 mol%) have been investigated by means of an Energy Dispersive X-ray Analysis (EDAX) unit interfaced with Scanning Electron Microscope(SEM). Our visual observation, the scanning electron microscope picture of the 2.5% Sm$_2$O$_3$ doped glass shown if Fig. 2a, indicates the amorphous nature of the glass. Figure 2b shows the EDAX spectrum for 2.5 mol% representative sample. The obtained data showed the glass chemicals like Sm, Te, Zn, O and B showing deficiency in Fluorine (F). The deficiency of F may be due to its low melting temperature and there by evaporating after 250°C which is clearly visible in the EDAX spectrum in Fig. 2b and weight loss region in the TGA plot (Fig. 3a).

3.2. Thermal Analysis

Differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) no simple way presently exists to formulate the correlation between the ideal composition and the stability of these types of glasses. Different simple quantitative methods have been suggested in order to evaluate the level of stability of the glass alloys.
Most of them as Dietzel and Hruby, are based on the characteristic temperatures such as the glass transition Temperature ($T_g$), the temperature at which crystallization begins ($T_c$), the temperature corresponding to the maximum crystallization rate ($T_p$), or the melting temperature ($T_m$). Some of the suggested methods are based on the crystallization activation energy. The characteristic Temperatures ($T_c$, $T_g$, $T_p$ and $T_m$) are easily and accurately obtained by the Differential Scanning Calorimetry (DSC) during the heating process of the glass sample. Dietzel introduced the first glass criterion, $\Delta T = T_c-T_g$, which is often an important parameter to evaluate the glass forming ability of the glasses (Sailaja et al., 2001; Aly et al., 2009). In the present work, the results are focused over 2.5 mol% doped glass sample which showed good results compared to other samples. The above mentioned criteria have been applied to the 2.5 mol% Sm$^{3+}$ doped glass with temperature range of 100-600°C. Weight loss was observed in the temperature range between 350-580°C which is clearly indicating the DSC plot under almost the same temperature range. The DSC curve includes temperature of glass Transition ($T_g$), the onset of crystallization ($T_c$) and the exothermal maximum ($T_p$). In most cases the melting Temperature ($T_m$) does not appear in DSC traces, as it is higher than 600°C. An appropriate value may be found by applying the classical two-third rule expressed as $T_p/T_m = 2/3$ (Bouchaour et al., 2005).

The curve exhibits an endothermic effect due to glass transition temperature $T_g$, the value of $T_g$ is evaluated from the point of inflection of this change. At still higher temperature, an exothermic peak $T_p$ due to crystal growth followed by an endothermic effect due to the melting effect denoted by $T_m$ is also observed (Sailaja et al., 2011).

Glass stability may be evaluated using semi-empirical relations based on characteristic temperatures. The thermal stability range ($T_c-T_g$) provides a good estimate of the tendency of the glass to crystallization state. It should usually be larger than 100°C to obtain thick samples (Sailaja et al., 2011; Aly et al., 2009; Bouchaour et al., 2005). A popular stability scale is based on the Hruby’s criterion (Bouchaour et al., 2005; Pablick, 2009) defined as $H_r = [(T_c-T_g)/(T_m-T_g)]$. $H_r$ gives information about the nucleation rate of the sample in ($T_c-T_g$) and growth rate between $T_m$ and $T_g$ embedded in ($T_m-T_c$). Another stability scale introduced by (Bouchaour et al., 2005) takes into account the difference between $T_p$ and $T_c$, which depends on the width of the crystallization peak. When the $(T_p-T_g)$ factor is high the growth rate decreases. This criterion is defined as follows: $S = [(T_p-T_g)/(T_g-T_c)]/T_g$ (Bouchaour et al., 2005).

The values of $T_p$, $T_c$, $T_g$ and $T_m$ of all glass samples obtained are furnished in Table 2. For 2.5 mol% doped Sm$_2$O$_3$ glass the quantity ($T_c-T_g$), which is proportional to glass forming ability, is found to be the largest whereas the quantity ($T_m-T_g$) which is inversely proportional to glass forming ability is the smallest (Table 2). The variation of the parameter ($T_c-T_g$)/($T_m-T_g$) with the concentration of Sm$_2$O$_3$ shows the maximum value for glass Sm$_3$ (Table 2 and Fig. 4a) indicating its highest glass forming ability among all the glasses under investigation. All the quantities of the glass samples ($\Delta T$, $H_r$, $H_g$ and $S$) follow the same trend which indicated the good homogeneity of the glasses prepared. The content of Sm$_2$O$_3$ increases into the glass systems which results in splitting of glass network former bonds and hence the Bridging Oxygens (BOs) are converted into Non Bridging Oxygen’s (NBOs). This results in weakening of the glass structure. Hence, the glass transition temperature decreases with the increase in Sm$_2$O$_3$ content.

![Fig. 2. (a) SEM image and (b) EDAX spectrum obtained from 2.5 mol% Sm$_2$O$_3$ content in the glass matrix](image-url)
Fig. 3. (a) Thermal Gravimetric Analysis (TGA) (b) Differential Scanning Calorimeter (DSC) thermogram of 2.5 mol% Sm$_2$O$_3$ doped sample

Fig. 4. (a) Stability criteria (b) Evolution of characteristic temperatures versus Sm$_2$O$_3$ content in 30 ZnF$_2$-20 TeO$_2$-(50-x) B$_2$O$_3$-x Sm$_2$O$_3$ (x = 0, 0.5, 1.0, 1.5, 2.0, 2.5)

Table 2. Thermal stability parameters of the fluoroborate glasses for the samarium series at a heating rate of 10 K/min. Note that $T_g$, $T_c$, $T_p$, $T_m$ are annotated in degree Celsius [°C] for the calculation of the thermal stability parameters

| Sm sample | Sm (mol%) | $T_g$(mol%) | $T_c$(°C) | $T_p$(°C) | $T_m$(°C) | $\Delta T=T_g-T_p$ | $\Delta T=T_m-T_c$ | $H_g$ | $H_r$ | $S$ |
|-----------|-----------|-------------|----------|----------|----------|------------------|------------------|------|------|-----|
| Sm$_0$    | 0.0       | 420         | 480      | 568      | 630      | 60               | 150              | 0.142| 0.400| 12.6|
| Sm$_1$    | 0.5       | 410         | 495      | 560      | 615      | 85               | 120              | 0.207| 0.708| 13.5|
| Sm$_2$    | 1.0       | 408         | 480      | 555      | 612      | 72               | 132              | 0.176| 0.545| 13.2|
| Sm$_3$    | 1.5       | 405         | 480      | 548      | 608      | 75               | 128              | 0.185| 0.585| 12.6|
| Sm$_4$    | 2.0       | 395         | 464      | 545      | 593      | 69               | 129              | 0.174| 0.534| 14.1|
| Sm$_5$    | 2.5       | 401         | 486      | 589      | 602      | 85               | 116              | 0.211| 0.732| 21.8|

5. CONCLUSION

The structural and thermal properties for the ZnF$_2$-TeO$_2$-B$_2$O$_3$-Sm$_2$O$_3$ glasses has been evaluated by using various criteria. The $H_r$ criterion has been considered in the present work for the evaluation of glass stability by using DSC data. The obtained results of $\Delta T$, $H_g$, $H_r$ and $S$ criteria agree satisfactorily with the DSC and TGA data. Sm$_5$ glass sample showed the good stability factor. This nonmetallic glass with good density exhibits fine structural properties where density reflecting the refractive indices increases with increase in concentration on Sm$^{3+}$ ion in the matrix. This again reproduced in the molar volume, number density, electronic polarizability and different other physical parameters also. SEM reveals the amorphous nature of the glass sample [2.5 mol% glass
sample] and the weight loss in the sample during the DSC is demonstrated in TGA as well in EDAX plot. These findings indicate the structure of Sm$_5$(30 ZnF$_2$-20 TeO$_2$-47.5 B$_2$O$_3$-2.5 Sm$_2$O$_3$) is more stable when the concentration of Sm$_2$O$_3$ present in the glass network is 2.5 mol%. The rise of electronic polarizability in the present glasses indicates the higher ability of oxide ions to transfer electrons to the surrounding cations. The stability of the glasses also increased with increase in Sm$_2$O$_3$ concentration. Since our glass samples show good electronic polarizability and stability factor (S), they are suitable material for the optoelectronic devices. Our study was limited upto 2.5 mol% of Sm$_2$O$_3$, further improvement/ degradation in the properties can be investigated beyond this Sm$_2$O$_3$ concentration.

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