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Effect of Alkaline-earth Metals on Physical and Optical Absorption Studies of Alkali Fluoroborate Glasses

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Abstract

Alkali fluoroborate glasses were prepared using melt quench technique. The prepared glass samples have been characterized using XRD, MDSC, density and molar volume measurements. Density and glass transition temperature increase with atomic mass of alkaline earth metals. The thermal stability values decrease with the increasing mass of alkaline-earth metal. The values of cut off wave length, optical energy band gap are determined from the optical absorption spectra. The cut-off wavelength decreases while the band gap energies increase with increasing the mass of the alkaline-earth metal. Urbach energy, electron polarizability of oxide ion and optical basicity values decreased with increasing mass of alkaline earth metal.

Keywords: Fluoroborate glass, alkaline earth metal, XRD, MDSC, thermal stability, optical absorption.

Introduction

In recent years alkali fluoroborate glasses have attracted great attention because of their interesting optical properties[1]. Addition of alkali fluorides make the glasses more moisture resistant when compared to alkali oxides. The borate glasses containing alkali fluorides are suitable for radiation dosimetry applications. Addition of fluorine lowers the dielectric constant and polarizability of the glass [2]. The addition of alkali earth ions increases the chemical stability of the glass[3].

Material and Methods

Analar grade chemicals were used to prepare the glass samples according to the molecular formula $30NaF\text{-}10AF_2\text{-}60B_2O_3$ (A=Ca, Sr and Ba). The batch compositions in mol% of glasses prepared in the present work are given in table-1.

Table-1
Chemical composition of prepared glasses

S.No.	Glass composition	Glass code
1	$30NaF\text{-}10CaF_2\text{-}60B_2O_3$	NCB
2	$30NaF\text{-}10SrF_2\text{-}60B_2O_3$	NSB
3	$30NaF\text{-}10BaF_2\text{-}60B_2O_3$	NBB

Analar grade reagents NaF, CaF_2, SrF_2, BaF_2 and H_3BO_3 were taken in appropriate proportions and ground together to constitute a 15 g batch. The ground mixture was melted in a porcelain crucible at temperature of 1050°C for 2 hours until bubble free liquid is formed. The melt was then poured into pre-heated steel mould and annealed at temperature 320^0C for 5 hours to remove residual internal strains. For an easy reference, these glasses have been labeled as NCB, NSB and NBB as presented in Table-1.

The glass formation was confirmed by X-ray diffraction measurements. The XRD profiles were recorded on a Philips X-ray diffractometer PW/1710 with Cu-K_α radiation in the Bragg's angle region $20° \leq 2\theta \leq 80°$ and are shown in Figure-1.

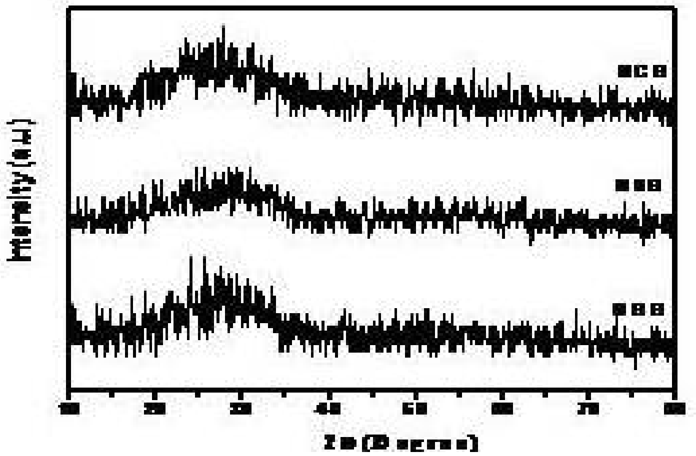

Figure-1
XRD patterns of prepared glasses

The glass transition temperature (T_g) was measured in all the glass samples using Modulated Differential Scanning Calorimeter (TA Instruments, DSC 2910). All the samples were heated at the rate of 10°C/min in the temperature range 350 -550 ^0C. The MDSC thermograms are shown in Figure-2.

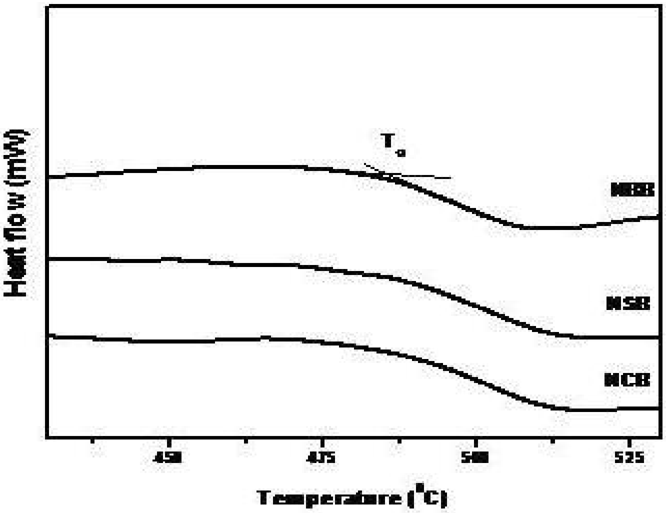

Figure-2
MDSC thermograms of prepared glasses

The optical absorption spectra of the glass samples were recorded at room temperature in the UV-Vis region by using a UV-Vis Elmer Lambda 950 spectrophotometer.

Results and Discussion

The XRD profiles of the prepared glass samples show no discrete sharp peaks but exhibit broad hollow band in the Bragg angle region $20 \leq 2\Theta \leq 30^0$ indicating their amorphous nature. The increase in glass transition temperature is attributed to increase in molecular mass of alkaline earth metals. Glass transition temperature can be used to indicate the glass network rigidity. Yiannopoulos[4] et al also observed similar increase in glass transition temperature (T_g) in binary glass systems xMO-(1-x) B_2O_3 (MO= MgO, CaO, SrO and BaO) and hence the observed increase in T_g from CaF_2 to BaF_2 can be attributed to increase in boron-oxygen connectivity from CaF_2 to BaF_2.

Thermal stability: The temperature difference between the crystallization temperature (T_c) and glass transition temperature (T_g), i.e. $\Delta T = T_c - T_g$ is a measure of the thermal stability of prepared glasses. The values of thermal stability of glasses NCB, NSB and NBB are 43^0C, 38^0C and 30^0C. Table- 2 shows that the thermal stability (ΔT) decreases with the increasing mass of alkaline earth metals from calcium to barium.

Density and molar volume: The density (D) of the glasses was determined by the standard Archimedes's principle using xylene (99.99% pure with density 0.86 gm cm^{-3} at 25^0C) as the buoyant liquid. Micro balance with ± 0.1 mg of variation is used for weighing of the glass samples. The glass sample was suspended on a very thin copper stand that was set in the xylene container. The weights of the sample were determined in the presence of both the liquid and air. The density of all glass samples was estimated from the formula

$$D = \left[\frac{w_1}{(w_1 - w_2)} * 0.86 \right] \quad (1)$$

where w_1 and w_2 are the weights of the glass sample in air and xylene respectively. The density of xylene is 0.86 gm/cm^3. Density values are precise to $\pm 0.02 g/cm^3$. The molar volume of a given glass composition is calculated using the formula,

$$V_m = \frac{\sum_i M_i}{D} \quad (2)$$

where M_i denotes the molar mass of the glass. The molar volume relates directly to the spatial distribution of the oxygen in the glass network. The density and molar volume values are given in Table-2.

Table-2
Physical and thermal parameters of prepared glasses

Glass code	Density (g/cc)	Molar volume (cc/mole)	T_g (^{0}C)	T_c (^{0}C)	ΔT (^{0}C)
NCB	2.39	39.57	470	513	43
NSB	2.58	38.50	474	512	38
NBB	2.71	38.49	476	506	30

Table-3

Glass code	λ_c (nm)	Optical band gap energy (eV)		ΔE (eV)	α_{o2-} (Å^3)	Λ (E_{opt})
		indirect	direct			
NCB	323	2.86	3.26	0.67	4.46	1.29
NSB	317	3.12	3.48	0.43	3.81	1.23
NBB	300	3.36	3.80	0.35	2.75	1.06

The density of present glasses increased with the increase in atomic mass of alkaline earth metals. A reverse trend is observed in the case of molar volume. The increasing values of density reflect the tightness of the glass structure and increase of network rigidity[5,6]. Decrease in the molar volume is easily explained by the difference between the atomic masses of Ca, Sr and Ba, as well as by the decrease in the total number of atoms in the volume of the glass[7]. The increase in density with decrease of molar volume is another indication of more compactness of the glass structure. This result is in support of the DSC findings in the present study. Figure-3 shows the variation of density and glass transition temperature with atomic mass of alkaline-earth metals.

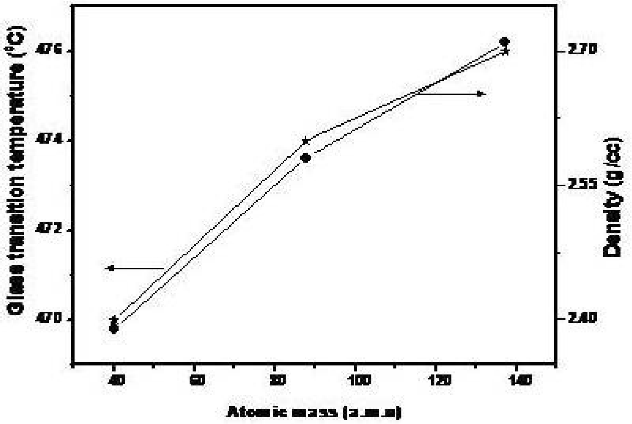

Figure-3

Variation of density and glass transition temperature with atomic mass of alkaline-earth metals

Optical absorption studies: The optical absorption spectra of all glass samples are shown in Figure-4. A distinct cut off wave length (λ_c) was observed for each glass sample and the corresponding λ_c values are presented in Table-3.

Table-3

From the table, it is found that the observed values of cut-off wave length shifts towards lower wavelength with the increasing atomic mass of alkaline earth metals.

The study of optical absorption is useful for the investigation of the band structure and energy gap in both crystalline and non-crystalline materials. The absorption coefficient $\alpha(\upsilon)$ can be determined near the edge using the relation[8].

$$\alpha(\upsilon)=(1/d)\ \ln(I_0/I) = 2.303(A/d) \qquad (3)$$

where the factor $\ln(I_0/I)$ is the absorbance 'A' at a frequency υ and d is the thickness of the sample. For amorphous materials the optical absorption at higher value of $\alpha(\upsilon)$ ($\geq 10^4$ cm^{-1}) above the exponential tail follows the power law given by Davis and Mott [8],

$$\alpha(\upsilon) = B(h\upsilon - E_{opt})^n / h\upsilon \qquad (4)$$

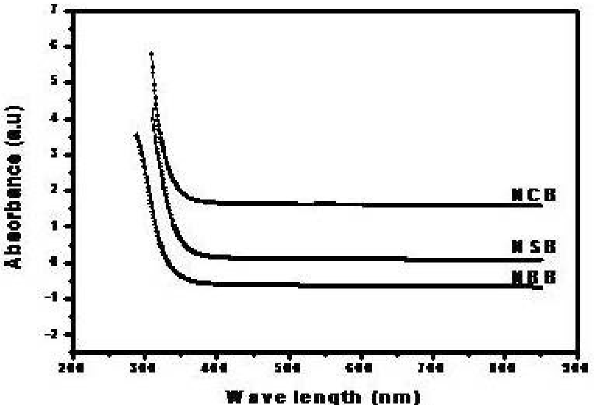

Figure-4

Optical absorption spectra of prepared glasses

where B is an energy independent constant and n takes values of 1/2, 2, 1/3, 3 for direct allowed, indirect allowed direct forbidden and indirect forbidden transitions respectively. By plotting $(\alpha h\upsilon)^{1/2}$ and $(\alpha h\upsilon)^2$ as a function of photon energy ($h\upsilon$) (figure-5 and figure-6), the respective values of $E_{(opt)}$ are obtained by extrapolating to $(\alpha h\upsilon)^{1/2} = 0$ for indirect transitions and $(\alpha h\upsilon)^2 = 0$ for direct transitions. The corresponding values are given in table-3.

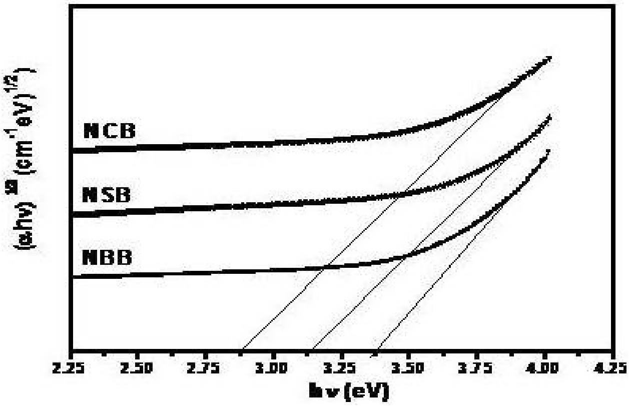

Figure-5

$(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$)

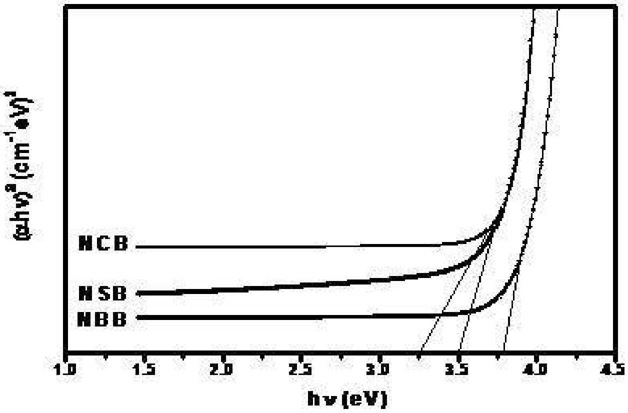

Figure-6

$(\alpha h\nu)^2$ versus photon energy ($h\nu$)

The non-linear variation of ln(α) with photon energy is found near UV absorption edge. This exponential behavior of absorption coefficient near the edge can be represented by

$$\alpha(\upsilon) = B \exp (h\upsilon/\Delta E) \qquad (5)$$

where ΔE is the Urbach energy and is found as the inverse slope of ln (α) vs. hυ plot[9] as shown in the figure-7.

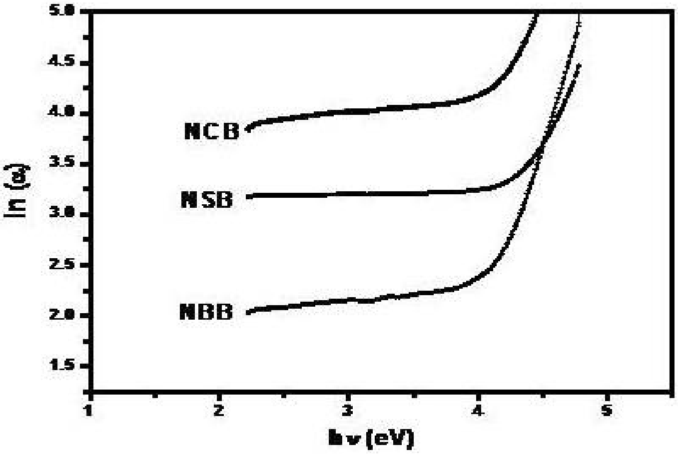

Figure-7
Urbach energy plot

Urbach energy, which corresponds to the width of localized states, is used to characterize the degree of disorder in amorphous and crystalline systems. The ΔE values of the present glass systems are in the range 0.67-0.35 eV (table-3). It can be observed that the Urbach energy deceases with the increasing atomic mass of alkaline-earth metals.

Electronicpolarizability and optical basicity: Polarizability is related to several physical and chemical properties such as optical basicity, chemical stability and optical non linearity[10]. The electronic polarizability is useful in finding the non-linear optical (NLO) response of a material. According to Dimitrov and Sakka[11], the electronic oxide ion polarizability (α_{o2-}) of a simple oxide is given by

$$\alpha_{O^{2-}}(E_{opt}) = \left[\left(\frac{V_m}{2.52}\right)\left(1 - \sqrt{\frac{E_{opt}}{20}}\right) - \sum \alpha_i\right]\left(N_{O^{2-}}\right)^{-1} \qquad (6)$$

$\sum\alpha_i$= molar cation polarizability, N_O^{2-}= number of oxide ions in formula
V_m = Molar volume, $E_{(opt)}$ = Optical band gap energy

The calculated values of oxide ion polarizability (α_{o2-}) for the studied glasses vary between 4.46 to 2.75 Å^3 (table 3). These values are comparable with those reported for other fluoroborate glasses. According to Duffy[12,13] the optical basicity (Λ), an ability to donate negative charges to the probe ion, is given by

$$\Lambda(E_{opt}) = 1.67\left(1 - \frac{1}{\alpha_{O^{2-}}}\right) \qquad (7)$$

Duffy and Ingram reported that the optical basicity, an ability to donate negative charges to the probe ion, can be predicted from the composition of the glass and the basicity moderating parameters of the various cations present in the glass. The values of optical basicity for the studied glasses are found to vary in the range 1.29 to 1.06 (table 3).

Conclusion

The absence of sharp peaks in the X-ray diffraction pattern indicates the amorphous nature of prepared glasses. Density and glass transition temperature values are increased with the mass of alkaline earth metals while the molar volume decreases. This indicates the increase of network rigidity with increasing the mass of the alkaline-earth metal. The direct band gap energy and indirect band gap energies are increased while the cut off wave length and Urbach energies decreased with the mass of the substituted alkaline earth metals. Alkali fluoro borate glasses are highly polarizable due to their large ionic radii and high electro negativity.

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