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Zirconium effect on Sodium Borate Glasses

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ABSTRACT

Zirconium oxide incorporated sodium borate glasses were prepared. Samples were analysed using certain measurements like XRD and UV-Vis. Few parameters like density, molar volume, polarizability and refractive index were calculated and reported. XRD confirms amorphous nature of all samples. UV-Vis spectra evidences that after 1mol% incorporation in sodium borate glass there exist a $^3F_2$- $^3P_1$ transition due to Zr^{2+} ions. Further the Tauc's plots were done for all samples and energy band gap values are tabulated and discussed in detail.

Keywords : Zirconium oxide, sodium borate glasses, XRD and UV-Vis spectra

I. INTRODUCTION

Recently the trend is turned to add two or more glass formers to form the glass materials with modified optical properties for various scientific & technical applications. Boric acid (B_20_3) is one of the good glass formers and can form glass with good transparency, high chemical durability, thermal stability and good rare earth ion solubility. The pure Borate glasses possess low refractive index, high melting point and high phonon energy 1300-1500cm^{-1}. They are highly suitable in designing new optical devices due to their good rare earth ion solubility, easy preparation on large scale shaping & cost effectiveness [1]. The glasses containing the transition ions are being used in the present days to probe the glass structure since their outer d-electron orbital functions have a broad radial distribution and due to their high sensitive response to the changes in the surrounding actions. Among various transition ions, zirconium oxide are opted, which acts as good network former [2,3] Addition of Zirconium to Borate glass represents favourable compromise between the requirements of low phonon energy (300 nm to 800 nm), a relatively high thermal stability, high chemical durability, high viscous and ease of fabrication [4,5]. It is also established that the inclusion of ZrO_2 to silicate glass matrix causes a substantial hike in the refractive index, decreases the cut-off wavelength and reduces the photochromism of the glass [6-8]. Such changes in physical properties make these glasses to offer good environment for hosting the rare earth ions to give luminescence emission with high efficiency. In view of these qualities ZrO_2 containing silicate glasses find variety of applications, such as thermal barrier coating, optical filters, laser mirrors, and alternative gate dielectrics in micro-electronics [9-10]. In addition fluxes like sodium oxide (Na_2O) are added to increase the Homogenization and reduce the melting point of the hosting glass as decreases damages and bubbles [11].

II. EXPERIMENTAL

In the Present discussion, the particular glass system $70B_2O_3$-(x-30) Na_2O-xZrO_2(x ranging from 0 to 7 mol %) was chosen. The Glass Samples are labelled as Zr0, Zr1, Zr3, Zr5 and Zr7 for 0-7mol% Zr^{2+}

respectively. Initially compounds H_3BO_4, Na_2CO_3, ZrO_2 used in the fabrication of glasses were of AR grade quality. Batch calculated compounds with respective gravimetric factor involved were weighed with electrical balance to an accuracy of 0.001g and then mixed thoroughly in an agate mortar. The homogeneous mixture taken in porcelain crucible was kept in furnace at 1030-1040 ^{0}C for 40 min till a bubble free liquid was produced. The resultant melt was then transferred on a brass slab kept at room temperature to obtain solid pellets. The formed glass samples were annealed for 2 hours at 300'C to remove the thermal and mechanical stress. The density of samples is measured using the Archimedes's principle with toluene as buoyant liquid. Xray-diffraction (XRD) measurements were carried out Rigaku Ultima IV using Cu-Ka radiations (λ = 1.54 Å) with copper filters operating at 40 kV and 100 mA. The 2θ range was 20–80^0 with step size of 0.20 and a resolution of 0.010. UV-Vis absorption spectra are recorded using a Perkin Elmer Spectrometer in the range of 250 to 700 nm wavelength. All the measurements were done in room temperature.

III. RESULTS AND DISCUSSION

Physical parameters:

Physical parameters are calculated for Zr series glasses and are reported in Table 1. By applying Archimedes's principle, the weight of the samples was measured in air and in toluene using a microbalance. Then, the density (ρ) is measured using (W_a) weight of the glass sample in air, (W_b) weight of the sample when immersed in toluene of density (ρ_x=0.8669gcm^{-3}),

$$\rho = \frac{W_a}{(W_a - W_b)\rho_x} \quad \text{... (1).}$$

The molar volume (V_m) is calculated using molecular weight (M.W) of the sample,

$$V_m = \frac{M.W}{\rho} \quad \text{.... (2)}$$

Fig 1 represents density and molar volume variation with respect to Zr^{2+} concentration in present glass.

The refractive index (n) can be expressed in terms of optical band gap[12,13]

$$1 - \sqrt{\frac{E_g}{20}} = \frac{n^2-1}{n^2+2} \quad \text{..... (3).}$$

The polarizabilities (α_m) of these glasses can be calculated using the relation [12, 13],

$$\frac{n^2-1}{n^2+2}(V_m) = \frac{3}{4\pi N_A}\alpha_m \quad \text{..... (4).}$$

Where, molar volume (V_m) and Avogadro's number (N_A).

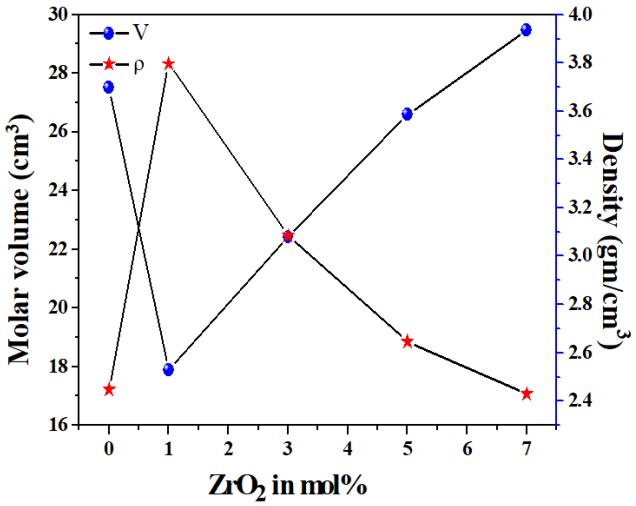


Fig 1. Variation of density and molar volume in Zr: Series.

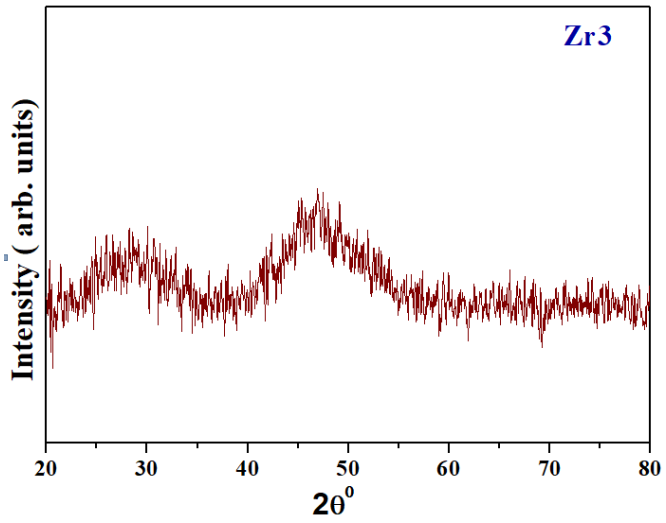


Fig 2. Typical XRD pattern of Zr3 sample

XRD

XRD is an unique technique for amorphous materials as only long range periodic order or disorder can be examined. The XRD measurement was performed for all the samples and was similar to the Zr3 glass shown in Fig. 2. The results reveal the absence of sharp peaks that characterizes amorphous nature of the present glass.

Absorption studies

Spectra in visible region in the range 200nm -700nm range are recorded at room temperature for Zr series glasses. Fig 3 represents absorption spectra. No absorption peaks are determined in the spectrum of pure sample Zr0 as it is radical free till 1mol% substitution of Zr^{2+}. When 3mol%, 5mol% and 7mol% of Zr^{2+} is added to the glass network then the spectra exhibit one intense absorption bands with band positions or peak position at 365, 363 and 360nm respectively. The peak observed in 3mol% above samples is due to Zr^{2+} ions ($^3F_2$- $^3P_1$ transition). The cut off region is 236, 242, 274, 285 and 287nm for 0, 1, 3, 5 and 7mol% of Zr^{2+}. It is the value corresponding to the absorption edge at a certain wavelength in the optical absorption spectrum. The shift in absorption edge to higher energy confirms the creation of non-bridging oxygen's [14].

Further, the optical absorption coefficient □□□□ was calculated for each sample at different photon energies by using the relation□□□□□ = A / d, where A is the absorbance and d is the thickness of the samples. From this absorption coefficient further optical band gap and Urbach energy can be obtained. The mechanism can be explained as the electrons present in the valence band when they interact with the external electromagnetic field. If the energy of the photon is greater than the band gap then the valence electrons absorb energy of photon and get excited to the conduction band. This transition is occurred in two ways, either direct transition or indirect transition. According to Davis and Mott [15] the relation can be written in general form:

$$\alpha(\vartheta) = (B/h\vartheta)(h\vartheta - E_{opt})^n \ldots\ldots (5)$$

Where, B is a constant and hυ the photon energy, E_{opt} the optical energy gap and n is an index which can have any values between 1/2 and three depending on the nature of the inter band electronic transitions[16].The goodness of the fit of the data to the formula for either n = 1/2 (direct band gap) or n = 2 (indirect band gap) is determined. It has been found that for many amorphous materials, a reasonable fit of Eq. (5) with n = 2 are achieved for indirect transitions, where the interactions with lattice vibrations take place [16, 17]. The direct and indirect band gap shown in Fig 4 (a) and (b) which is observed that there exist non linear variation in the values obtained as reported in Table 1. This suggests that the non-bridging oxygen ion content increases with increasing as Zr^{2+} content and there by shifts the band edge and in-turn lead to have a decrease in the E_{opt} values [18,19]. It's also reported that if the molar volume is more the direct and indirect band gaps will be higher as it creates more non bridging oxygen's.

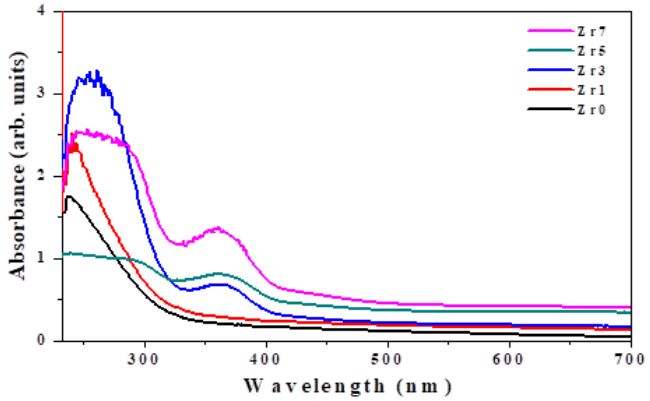
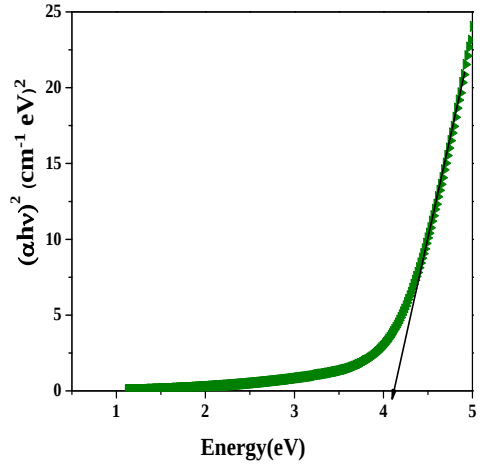
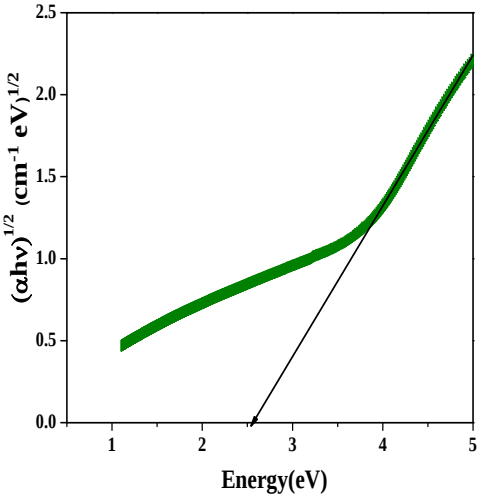


Fig 3. Absorption spectra of Zr: Series.

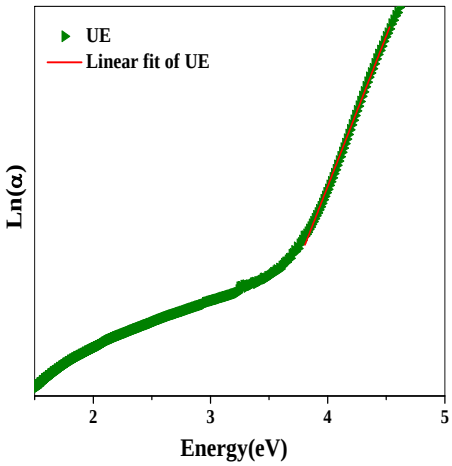
The absorption coefficient at the photon energy below the optical gap (tail absorption) depends exponentially on the photon is called Urbach energy which describes the width of the exponential absorption edge [20]. To calculate the values of Urbach energy, we have plotted logarithm of the absorption coefficient versus photon energy by considering the reciprocals of the slope of linear portion in the lower photon energy region of these curve as shown in Fig 4(c). It was reported that increase of Urbach energy in amorphous solids are due to the creation of large number of defects in glasses [21,22]. Therefore, weak bonds are converted into defects a Zr2+ions concentration is increased in the present glass system. While increasing the Zirconium content in the host matrix, the non-bridging oxygen ion content increases there by shifting the band edge to lower energies, which in-turn decreases the optical band gap energy values and increases the Urbach energy values[22,23].



(a)



(b)



(c)

Fig 4 (a)(b)(c). Typical Tauc's plot of Zr0 sample.

Table 1 Physical parameters and energy band gap values in Zr: Series.

Sample code	Zr0	Zr1	Zr3	Zr5	Zr7
Density *(p)* (gm/cm^3)	2.448	3.865	3.084	2.646	2.435
Molar volume (V_m)(cm^3)	27.505	17.895	22.428	26.598	29.477
Direct band gap (eV)	4.11	4	3.96	3.57	3.72
Indirect band gap (eV)	2.65	2.79	3.18	2.89	2.84
Urbach energy (eV)	1.035	1.044	0.466	1.217	0.714
Polarizability of oxide ions (α_m) x10^{-24} (cm^3)	6.487	9.6845	7.393	6.429	5.844
Refractive index (n)	2.498	2.458	2.353	2.4279	2.445

IV.CONCLUSION

Zirconium oxide incorporated sodium borate glasses were prepared using melt quenching technique. Samples were analysed using certain measurements like XRD and UV-Vis. Few parameters like density, molar volume, polarizability and refractive index were calculated and reported. Density and molar volume variation is expected i.e, both are reciprocal in nature. XRD confirms amorphous nature of all glass samples. UV-Vis spectra evidences that after 1mol% incorporation in sodium borate glass there exist a 3F2- 3P1 transition due to Zr2+ ions and peak intensity is increased as concentration is increased. Blue energy shift observed in absorption edge value of all glass and Tauc's plots calculated energy band gap values evidences that upon incorporating zirconium oxide there exists a formation of non-bridging oxygen's in present matrix.

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