

Effect of Pb²⁺ Ions on the Mechanical, Structural and Thermal Behaviour of B₂O₃-CaO Glasses

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B₂O₃-CaO-PbO glasses with different concentrations of PbO (5-20 mol % in four steps) were prepared by melt quench technique. The amorphous nature and homogeneities of the prepared glasses were confirmed by XRD and SEM analyses. Ultrasonic velocities and density were measured at 303 K using pulse-echo technique and Archimedes' principle respectively. Various parameters, viz., molar volume, longitudinal modulus, shear modulus, bulk modulus, Young's modulus, Poisson's ratio, micro-hardness and Debye temperature have been evaluated from the measured data. The results of ultrasonic properties indicate that the incorporation of lead ions expand the calcium borate network structure. FTIR spectra revealed that boron exists in both trigonal and tetrahedral structural units and no boroxial ring formation takes place in the glass structure. The transition temperature, melting temperature and crystallization temperature have been identified using DTA measurements.

Keywords: Borate glasses, Ultrasonic velocity, Lead oxide.

INTRODUCTION

Over the past few decades, a great deal of interest has been focused towards the development of glassy material for various applications [1-4]. Amongst a wide variety of glasses, particularly, borate based glasses has become popular and having transparency, several other physical and chemical properties can be modified by composition and preparation techniques for technological applications. The structures of pure vitreous borate glass consist of a random network of B₃O₆ and BO₃ triangular units connected by B-O-B linkages. It is well known that the addition of alkaline earth oxides improving the glass forming nature of borate glass network. Particularly calcium containing glasses have received much attention for the potential as bioactive materials [5,6]. Manupriya *et al.* [7], studied the acoustical properties of calcium borate glasses and reported that the gradual incorporation of CaO upto 0.5 mol fraction into the pure borate glass leads to the conversion of BO₃ to BO₄ structural units and further increase of CaO content leads to the formation of non-bridging oxygen.

A borate rich glasses containing alkaline earth oxide along with TeO₂, ZnO, PbO, Bi₂O₃, etc., as glass modifier and have their applications in the area of optical fibers, photonic device, X and γ -ray absorbers, laser host, *etc.* [8]. Lead oxide doped glasses have high refractive indices with low crystallization tendency as well as lower melting point and glass transition temperature [9-11]. It is also have a good radiation shielding properties. PbO is considered as intermediate oxides and cannot build their own glassy network *i.e.* they play a dual role and enter the glass structure, as the glass modifier/former or both network modifier and network former at the same time. The role depends on the type of bond between lead and oxide. According to EI-Batal [12], ions of lead exist as glass modifier with ionic bond at lower content (< 50 mol %) and network former existing PbO₄ structural units with covalent bond at higher content (\geq 50 mol %). Such differences in the dual role of Pb²⁺ ions would imply significant modifications of its local environment and of its coordination. The aim of the present work is to investigate the effect of PbO as a replacement for CaO in B₂O₃-CaO-PbO (BCP) glass system on its mechanical,

structural and thermal properties by ultrasonics, infrared and differential thermal analyses, respectively. These techniques were incorporated in order to correlate the changes in the properties as a result of gradual addition of PbO.

EXPERIMENTAL

The chemicals used in the present research work were of Analytical Reagent (AR) grade with minimum assay 99.9 % and obtained from Sd. Fine Chemicals, India. The compositions in mol % of glass specimen are listed in Table-1.

Sample preparation: The required amounts (approx. 15 g) in mol % of different chemicals in powder form were weighed using digital balance (Model SHIMADZU AX 200) having an accuracy of 0.1 mg. The homo-genization of appropriate mixture of the component of chemicals was effected by repeated grinding using a pestle and mortar. The temperature controlled muffle furnace was gradually raised to a higher temperature and a glass structure was noticed for B₂O₃-CaO-PbO glasses system at 900 °C. The melt was immediately poured into a brass to form samples of dimensions 10 mm diameters and 6 mm thickness. Glass samples were annealed at 375 °C for 2 h to avoid the mechanical strain developed during the quench process. Then the furnace was switched off and glass was allowed to cool gradually to room temperature. All glasses are cleaned with acetone to remove the presence of any foreign particles. The prepared samples are chemically stable and non-hygroscopic.

XRD and SEM analyses: The amorphous nature of the samples is confirmed by X-ray diffraction. XRD technique using diffractometers de rayons X-Inel-Equinox 1000 at a range of 2θ = (10-100) degrees utilizing copper radiation with operating voltage of 40 kV 30 mA anode current. The morphology of the samples was examined using Scanning Electron Microscope with an acceleration voltage of 20 kV and working distance of 20-26 mm at high vacuum mode. The glass samples for investigation is kept in hot air oven dried for about 1 h at 110 °C, then coated with the help of gold coater using JEOL auto fine coater model JES-1600, coating time is 120 s, 10 mA and deposited with a thin layer of gold on the sample and later taken for morphology observation.

Density: The density of the glass samples was measured using Archimedes' principle and water was used as a buoyant liquid. The glass samples were weighed both in air and water at 303 K. The density was calculated using the formula.

$$\rho = \rho_w \left(\frac{w_1}{w_1 - w_2} \right) \quad (1)$$

where w_1 and w_2 are the weights of the glass samples in air and water, respectively and ρ_w is the density of water.

Ultrasonic velocities: The ultrasonic longitudinal and shear velocities of the glass specimens were determined by using the Pulse-Echo overlapping method at room temperature by making use of 5 MHz X-cut and Y-cut transducers. These transducers act as both receivers and transmitters of the ultrasonic pulse. The transducers were brought into contact with each of the sample by means of couplant. In order to ensure that there was no air void between the transducer and the specimen. By applying constant pressure on the probe, the echo waveforms were obtained on the display unit and stored in the memory. The velocity of sound can be calculated as:

$$v = \frac{2d}{t} \quad (2)$$

where d and t are the thickness of the specimen (mm) and transit time, respectively in microsecond.

FTIR analysis: The FTIR transmitter spectra of the glasses in 4000-400 cm⁻¹ spectral range were obtained with a resolution of 4 cm⁻¹ by FTIR spectrometer using KBr pellet technique. The glass transition temperature, crystallization temperature and melting temperature of these glasses were determined by differential thermal analyzer NETZSCH-STA449FS JUPITER instrument at a heating rate of 20 °C/min in nitrogen atmosphere.

Thermal studies: The DTA is very useful for determination of melting points of crystals and glass transformation and crystallization temperatures of glasses. In all glasses, the DTA curve exhibits a small endothermic hump at lower temperature in the glass samples, which is characteristic of the transition temperature. Single exothermic peak at high temperature region is characteristic of crystallization temperature and other endothermic events corresponding to the melting temperature.

RESULTS AND DISCUSSION

XRD analysis: The prepared glasses were transparent, homogeneous and bubble free. The spectra of glasses (Fig. 1) confirmed the absence of Bragg peaks, indicating the amorphous nature of the glasses. The broad hump around 2θ ≈ 30° also suggests the presence of short range order.

SEM analysis: The morphology of BCP10 and BCP20 glasses (Fig. 2) showed that different sized grain particles are distributed and the size of the particles varies in the micrograph. Some sphere like agglomerates were found spreading in the glass surface, due to the deposition of amorphous apatite. The image clearly indicates that there is no crystalline phase existing in the overall surface of the samples. This further confirms the amorphous nature of the glass samples.

Density and molar volume: The variations of density and molar volume as a function of PbO content are shown in

TABLE-1
VALUES OF DENSITY (ρ), MOLAR VOLUME (V_m), LONGITUDINAL VELOCITY (U_l) AND SHEAR VELOCITY (U_s),
POISSON'S RATIO (σ), MICROHARDNESS (H) AND DEBYE TEMPERATURE (θ_D) OF B₂O₃-CaO-PbO GLASS SYSTEM

Composition (mol %)			ρ (10 ³ kg m ⁻³)	V_m (10 ⁻⁶ m ³ /mol)	U_l (m s ⁻¹)	U_s (m s ⁻¹)	σ	H (GPa)	θ_D (K)
B ₂ O ₃	CaO	PbO							
60	40	0	2.6733	24.02	6602.1	3575.4	0.2923	4.7337	497.77
60	35	5	2.7190	26.39	6330.9	3375.2	0.3015	4.1000	455.78
60	30	10	2.7816	28.51	6102.5	3199.0	0.3105	3.5955	421.50
60	25	15	2.8401	30.59	5898.8	3019.1	0.3225	3.0628	389.22
60	20	20	2.9002	32.56	5719.7	2842.1	0.3361	2.5602	359.52

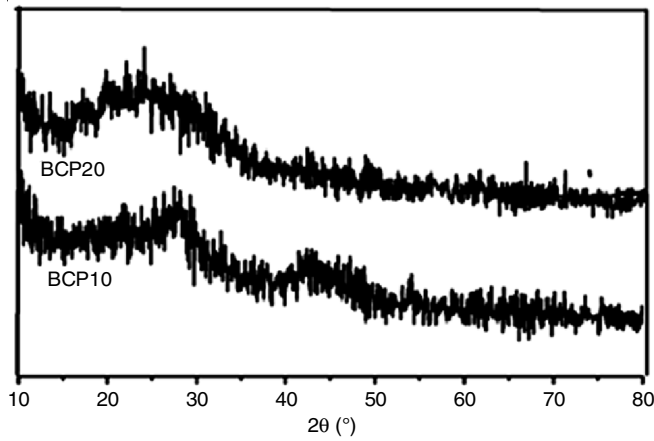


Fig. 1. X-Ray diffractogram for BCP10 and BCP20 glasses

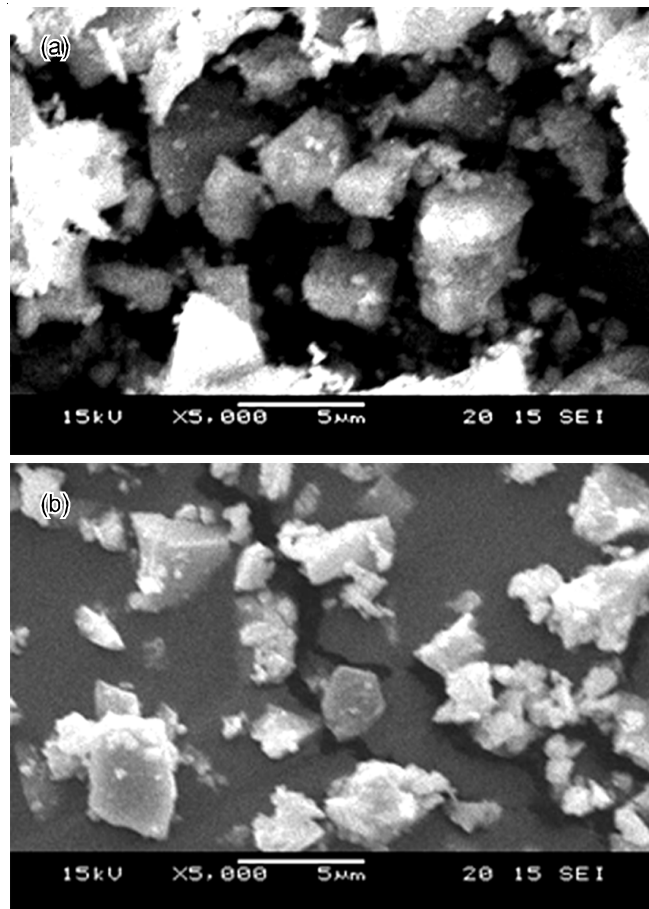


Fig. 2. SEM photographs of (a) BCP10 and (b) BCP20 glasses

Fig. 3. It is observed that the density increases gradually from 2.7190 to 2.9002 kg m⁻³ with increasing lead oxide content. The molar volume (V_m) of the glasses was calculated using eqn 3.

$$V_m = \frac{M}{\rho} \quad (3)$$

where M and ρ are the molecular weight and density of the glasses, respectively. Molar volume increased from 24.02 to 32.56 cm³ with increasing lead ions in calcium borate glasses. These results might be attributed to the change of molar mass and interatomic spacing between atoms in the glass matrix.

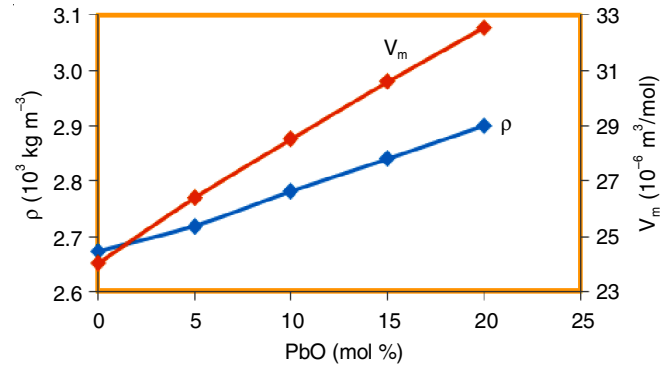


Fig. 3. Variation of density and molar volume

Generally, the density of glass is discussed in terms of a competition between the mass and size of different structural units takes place in the non-crystalline materials. In other words, density explains how the tightly the ions and ionic groups are placed together in the network structure [13]. Monotonic increase of density in the present system is expected due to the replacement of lighter molar mass by heavier molar mass. The molar mass of calcium atom is 40.07 g and lead atom, which has molar mass 207.2 g and the density depends on molar mass of lead ions. Similar trend of variation is also observed in the molar volume. As the ionic radius of PbO (1.19 Å) is higher than CaO (0.99 Å) that results in the expansion of network structure which increases the overall molar volume of these glasses. Usually, the density of glass changes inversely with the molar volume, but in this study, both the density and molar volume increase linearly with the PbO content [14,15].

Ultrasonic velocity and elastic properties: Table-1 shows both longitudinal and shear ultrasonic velocities in calcium borate glasses modified with lead oxide. It is clear from the table that both longitudinal and shear ultrasonic velocities decrease from 6602.1 to 5719.7 m s⁻¹ and 3575.4 to 2842.1 m s⁻¹ with increase of PbO content, respectively. It is well known that lead oxide has unique features on the structure of glasses. At lower concentration, lead ions is in network modifying position with PbO₆ structural units whereas at higher concentration, it is in network forming position with PbO₄ structural units [16]. In the prepared glasses, the successive replacement of Ca²⁺ ions by Pb²⁺ ions into the calcium borate network breaks down, some of bridging bonds by ionic bonds between lead ions and NBO's of the network. The glass structures get relax as a result of gradual substitution of PbO which implies that lead oxide acts as modifier and does not contribute to network formation but cleaves the glass matrix and causes to enhance the molar volume of glasses. This means that boron changes from BO₄ units to BO₃ units. The elastic moduli such as longitudinal, shear, bulk and Young's moduli as well as Poisson's ratio, micro-hardness and Debye temperature were calculated from the standard relations.

$$L = \rho U_l^2 \quad (4)$$

$$G = \rho U_s^2 \quad (5)$$

$$K = L - \frac{4}{3}G \quad (6)$$

$$E = (1 + \sigma)2G \quad (7)$$

$$\sigma = \frac{L-2G}{2(L+G)} \quad (8)$$

$$H = (1-2\sigma) \frac{E}{6(1+\sigma)} \quad (9)$$

$$\theta_D = \frac{h}{K} \left(\frac{9N}{4\pi V_m} \right) \quad (10)$$

Glass is considered as an elastic substance and can be characterized through the modulus of elasticity. From Fig. 4, the elastic moduli show a gradual fall over the entire range of composition of lead ions in the glass matrix. This is due to the creation of NBOs and form more reactive depolymerization boron structural units. Also, the decrease in crosslink density is affected strong B-O-B and B-O-C bonds to weak B-O-P bonds transformation in association with increase in concentration of PbO.

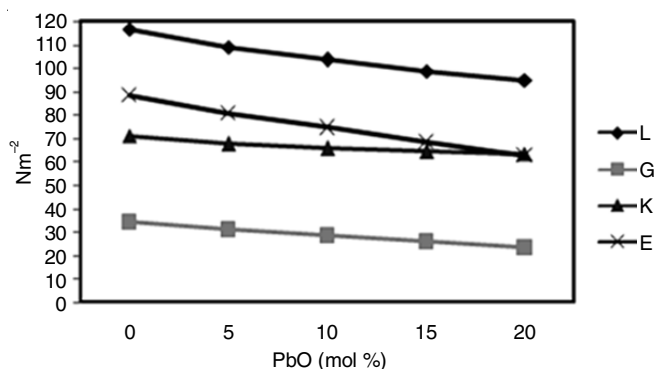


Fig. 4. Variation of elastic moduli with PbO mol %

According to Rao *et al.* [17], Poisson's ratio depends on the network structure and crosslink density. A three dimensional network structure has a lower σ value probably between 0.1 and 0.2 than that of two dimensional network structure with σ value between 0.3 and 0.5 since the number of bonds resisting a transverse deformation decrease in that order. The ultrasonic velocities and elastic moduli show similar variations. The Poisson's ratio is nearly opposite to the variations observed for the elastic moduli. From Table-1, the observed increase in Poisson's ratio from 0.2923 to 0.3361 with the addition of PbO indicates the two dimensional network structures. Gradual addition of lead ions in calcium borate network increases the concentration of NBOs and also octahedral coordination of lead oxide. This leads to decrease in crosslink density between the chains and concludes that it acts as modifier.

The micro hardness and Debye temperature decrease due to the modifier effects of lead ions. That is a gradual incorporations of lead ions decrease the hardness and makes the glass matrix more open. Besides, the back conversion ($BO_4 \rightarrow BO_3$) effect of borate structural units is exists. The variation of all parameters revealed that the replacement of CaO with PbO reduces the crosslink between the chains of borate network.

FTIR analysis: The infrared spectra of the glasses were measured at room temperature in the wavenumber range 4000-400 cm^{-1} as shown in Fig. 5. Borate glasses generally consist of several structural groups like $[BO_3]$, $[BO_4]$, boroxial rings,

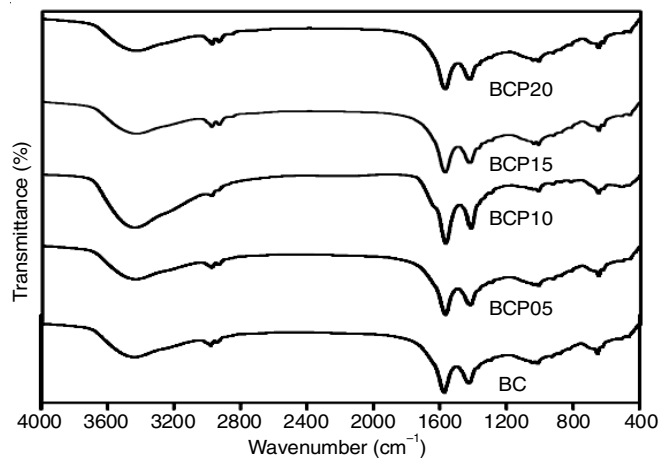


Fig. 5. FTIR spectra with different concentrations of PbO

diborate units, *etc.* Thus, vibrational modes of vitreous modified borate network are mainly active in three infrared spectral regions. The first group of band in the range 1500-1200 cm^{-1} is due to the asymmetric stretching vibration of B-O bond of trigonal BO_3 units containing non-bridging oxygen ions. Second group lies between 800 and 1200 cm^{-1} is due to B-O bond stretching of the tetrahedral BO_4 units. The third group is observed around 700 cm^{-1} and is due to bending of B-O-B linkages in the borate network [18].

The absence of peak at 806 cm^{-1} in B_2O_3 -CaO spectrum is due to the addition of CaO into the borate network, it breaks the boroxial rings and hence consists of BO_3 and BO_4 groups. The bands observed around ~ 1383 cm^{-1} is assigned to symmetric stretching vibration of B-O bonds in BO_3 structural units and the band observed around ~ 1029 cm^{-1} is due to the stretching vibration of BO_4 units. The weak band around ~ 692 cm^{-1} is assigned to B-O-B bending vibrations of BO_3 groups. The observed infrared transmission peak around at ~ 454 cm^{-1} is attributed to stretching vibrations of PbO [19,20].

Differential thermal analysis: DTA technique has been employed to determine the glass transition temperature, glass melting temperature and to test the possibility of formation of crystallization and phase separation in borate glasses [21]. DTA curves and the corresponding thermal data are shown in Fig. 6 and Table-2, respectively. It is found that first endothermic hump corresponding to the glass transition temperature appears at 274 $^{\circ}C$ followed by the exothermic peak of crystallization temperature at 543 $^{\circ}C$ and endothermic peak of melting temperature at 904 $^{\circ}C$. All the thermal transition parameters decrease with the increasing PbO concentration. This is expected because the bond strength of Ca-O (402.1 KJ/mol^{-1}) is higher than that of Pb-O (382.0 KJ/mol^{-1}). The gradual replacement of Ca-O

TABLE-2
SUMMARY OF DTA DATA OF B_2O_3 -CaO-PbO GLASS SYSTEM

Name of samples	T_g ($^{\circ}C$)	T_c ($^{\circ}C$)	T_m ($^{\circ}C$)	Thermal stability (S)	Hruby's parameter (K_{gl})
BC40	274	543	904	269	0.7451
BCP05	225	450	807	225	0.6302
BCP10	209	379	775	170	0.4292
BCP15	199	337	768	138	0.3201
BCP20	181	302	716	121	0.2922

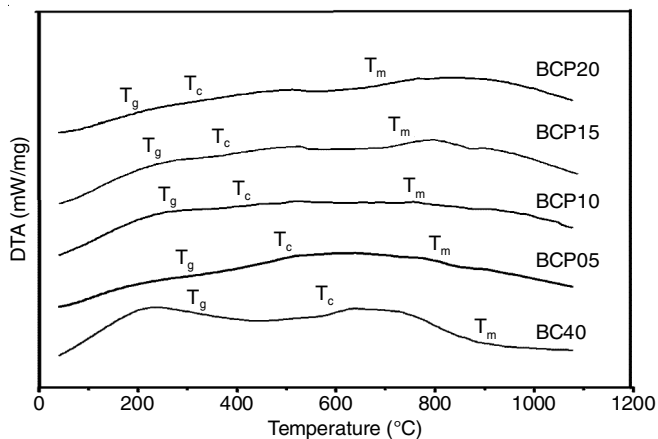


Fig. 6. DTA curves for BCP glasses

linkages by the weaker Pb-O linkages decreases the T_g , T_c , T_m , S and K_{gl} values as well as the stability of glasses.

Conclusion

In summary, it is concluded that the glass samples of composition $60B_2O_3-(40-x)CaO-xPbO$ (where $x = 0, 5, 10, 15$ and 20) has been successfully developed which is transparent and moisture resistant XRD and SEM analyses support the amorphous and homogeneity of the glasses. The density as well as the molar volume increase, which is due to the molar mass of cations. Ultrasonic velocities, elastic moduli and other parameters decrease where Poisson's ratio increases with the increasing concentration of lead oxide and thereby enhance the BO_3 structural units and decrease the crosslink density and strength of the glass network. FTIR spectra revealed the presence of BO_3 and BO_4 structural units. A decrease in the thermal data is due to the replacement of higher bond strength by lower bond strength of cations.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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