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Synthesis and characterization of cadmium doped lead–borate glasses

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Abstract. **Cadmium doped lead–borate glasses were prepared from the melts in appropriate proportions of PbO_2, H_3BO_3 and (15–40 mol%) CdO mixture in the temperature range 700–950°C. The infrared spectra of the glasses in the range 400–4000 cm^{-1} show their structures. No boroxol ring formation was observed in the structure of these glasses. Furthermore, doped cadmium atoms were not seen in tetrahedral coordination. But the conversion of three-fold to four-fold coordination of boron atoms in the structure of glasses was observed.**

Keywords. **Cadmium; lead borate glasses.**

1. Introduction

Infrared spectroscopy and Raman scattering are two important spectroscopic methods applied in the structural investigation of the local order characterizing vitreous materials like oxide glasses (Hassan *et al* 1992; Martino *et al* 2001; Yiannopoulos *et al* 2001). B_2O_3 is one of the most common glass formers and is present in almost all commercially important glasses. It is often used as a dielectric material and borate glasses possess scientific interest because of the occurrence of boron anomaly (Griscon 1978). Synthesis and study of lanthanum borate (Hinatsu *et al* 2003), aluminum borate whiskers (Alemi and Hinatsu) and borate glasses, in particular, have become subjects of great interest for infrared studies, due to their structural peculiarities (Kamitsos and Karakassides 1989; Motke *et al* 2002). In borate glasses, B_2O_3 is a basic glass former because of its higher bond strength, lower cation size and smaller heat of fusion, so the structural investigation of boron in these glasses is one of the most attractive points of borate glass formation and related doped systems. In borate glasses, B^{3+} ions are triangularly coordinated by oxygen atoms and the triangle units are corner bounded in a random configuration (Yawale *et al* 2000). PbO and ZnO can enter the glass network both as a network former and also as a network modifier and due to this the structure of this glass is expected to be different from that of alkali borate glasses. The structure of borate glasses is completely different from other glasses such as phosphate glasses and silicate glasses.

In the present paper, synthesis and characterization of lead borate glasses, doped with cadmium oxide are studied with the help of infrared and Raman spectroscopy to determine the structure of borate glasses containing varying amounts of PbO_2 and CdO.

2. Experimental

2.1 *Sample preparation*

Cadmium doped lead–borate glasses were prepared from analar grade powders of H_3BO_3, PbO_2 and CdO which were thoroughly mixed in the composition range of $x$$PbO_2$–(50–$x$)CdO–$50B_2O_3$, where $x = 10$, 15, 20, 25, 30 and 35 mol%. The appropriate amount of chemicals were mixed and heat treated in open porcelain crucible on a kerr 666 electric furnace. Initially, the samples were maintained for 1 h at the temperature range from 450–550°C for decomposition of boric acid. Then the temperature was raised up to 750–900°C and maintained for 2 h and the melt was poured between two stainless steel mould plates. Samples were quenched at 250°C in order to prevent crackings on the glasses and these glasses were yellow in colour.

2.2 *X-ray diffraction*

The glassy nature of the samples was confirmed by XRD studies using D5000 Siemens with Cu–K*a* line of wavelength *l* = 1·5418 Å at the scanning rate of 2 /min and 2 *q* was varied from 4–70°.

2.3 *DSC thermogram*

The glassy nature of prepared glass ($30PbO_2$–20CdO–$50B_2O_3$) was confirmed by the differential thermal studies using Shimadzu DSC60 differential scanning calorimeter (DSC) in the temperature range from 30–500°C with a heating rate of 10°C/min under nitrogen atmosphere.

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2.4 *Infrared spectra*

In the present work, the FTIR transmission spectra in the region 400–4000 cm^{-1} were recorded for all the samples using FT–IR Nexus 670 by KBr pellet technique.

2.5 *Density measurement*

The density of glass samples was measured using Archimedes's principle. The measurements were done using Shimadzu Aw 200 balance and xylene as an inert immersion liquid. The density was obtained from the relation

$$d(\mathrm{g/cm^3}) = [a/(a-b)]x(\text{density of the xylene}),$$

where a is the weight of the glass sample in air and b the weight of the glass sample when immersed in xylene. The density of xylene is 0·865 (g/cm^3) (Karthikeyan and Mohan 2003).

2.6 *Refractometer*

The refractive indices of the prepared glasses were measured on a microscope (ARL–ZEISS 4685266) and luxmeter.

3. Results and discussion

3.1 *X-ray diffraction*

The X-ray diffraction pattern of CdO-doped lead–borate glasses show no sharp peaks indicating amorphous nature.

3.2 *Thermal analysis*

The DSC thermogram of $30PbO_2$–20CdO–$50B_2O_3$ glass is shown in figure 1. From this figure it is observed that the glass transition temperature of the sample is 370°C.

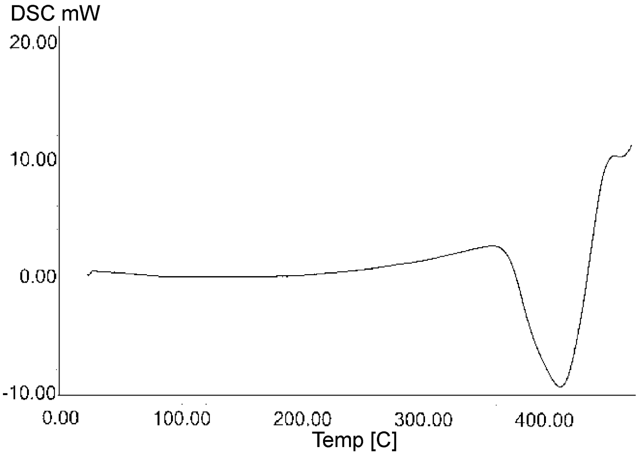

Figure 1. DSC thermogram of $30PbO_2$–20CdO–$50B_2O_3$ glass.

3.3 *FTIR and Raman analysis*

The FTIR spectra of doped glasses were obtained using KBr pellet technique in the range 400–4000 cm^{-1}. The broad composite bands extending from 3200–3600 cm^{-1} are attributed to hydroxyl or water groups (Adams and Douglas 1959; Scholzelt 1991). In figure 2, it can be seen that there is no effect of composition on the types of the structural groupings. This may be due to presence of symmetric $(BO_3)^{3-}$ triangles, $(BO_4)^{4-}$ tetrahedral and asymmetric $(BO_3)^{3-}$ units (non-bridging oxygen) in each of the samples of PbO_2–CdO–B_2O_3 glasses. Furthermore, it is noticed that in the spectra containing different concentrations of CdO, the structure is not changed.

According to the Krogh Moe's model, the structure of boron oxide glass consists of a random network of planar BO_3 triangles with a certain fraction of six membered (boroxol) rings (Moe 1965). X-ray diffraction data suggest that glass structure consists of a random network of BO_3 triangles without boroxol rings. The vibrational modes of the borate network are seen to be mainly active in three infrared spectral regions, which are similar to those reported by several workers (Kamitsos *et al* 1987; Ghoneun *et al* 1996): (i) the first group of bands which occur at 1200–1600 cm^{-1} is due to the asymmetric stretching relaxation of the B–O band of trigonal BO_3 units, (ii) the second group lies between 800 and 1200 cm^{-1} and is due to the B–O bond stretching of the tetrahedral BO_4 units and (iii) the third group is observed around 700 cm^{-1} and is due to bending of B–O–B linkages in the borate networks. The infrared spectra of these glasses show seven to eight absorption peaks. The peaks are sharp, medium, weak and broad. The broad bands are exhibited in the oxide spectra, probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples. In the present glass, the absence of absorption peak at 806 cm^{-1} indicates the absence of boroxol ring formation. The progressive substitution of boroxol rings by triborate and tetraborate groups is observed. In pure B_2O_3 glass, the 806 cm^{-1} frequency is a characteristic of boroxol ring. The vanishing of 806 cm^{-1} means no boroxol ring in the glass structure; ultimately it consists of BO_3 and BO_4 groups. These groups may be attached in the form of random network. This corresponds to the progressive substitution of boroxol ring by BO_3 and BO_4 groups. This type of behaviour is observed in B_2O_3–Li_2O glasses (Galeener *et al* 1980; Kulkarni *et al* 1984; Kanehisa and Elliot 1989). The absorption band at 1307 cm^{-1} is associated with B(III)–O–B(IV) stretching vibrations. The band around 1357 cm^{-1} is assigned to B–O stretching vibrations of trigonal $(BO_3)^{3-}$ units in metaborates, pyroborates and orthoborates (Chekhovskii 1985). On passing from boron trioxide to borate glasses in the coordination number, boron takes place. In these glasses, the boron is tetrahedrally surrounded by four oxygen atoms (Biscoe and Warren 1938). The band around 1292 cm^{-1} is due to B–O

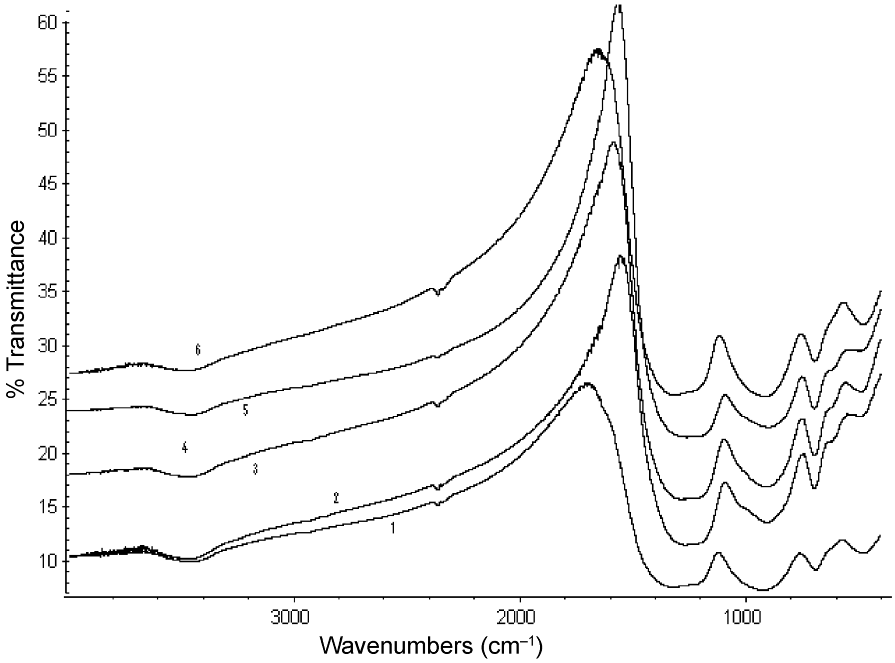

Figure 2. FTIR spectra of xPbO$_2$–(50–x)CdO–50B$_2$O$_3$ (1: $x = 10$, 2: $x = 15$, 3: $x = 20$, 4: $x = 25$, 5: $x = 30$, 6: $x = 35$).

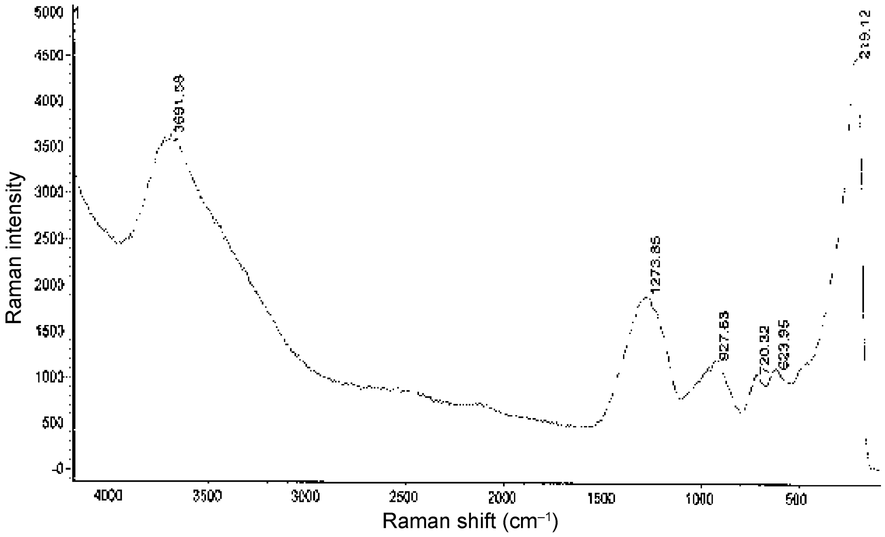

Figure 3. Raman spectrum of 30PbO$_2$–20CdO–50B$_2$O$_3$ glass.

Table 1. Physical properties of cadmium doped lead–borate glass.

No.	Physical properties	
1	Density (g/cm^3)	5·81
2	Dielectric constant	3·71
3	Reflection loss (*R*%)	10
4	Refractive index	1·925

asymmetric stretching of BO$_3$ unit (Heaton and Moore 1987). The shoulder at 1234 cm^{-1} may arise from B–O stretching vibrations of (BO$_3$)$^{3-}$ unit in metaborate chains and orthoborates (Kamitsos *et al* 1990). Similarly the band at 1005 cm^{-1} is due to vibration of some atoms attached to nonbridging oxygen in the form of BO$_4$ vibration (Ito and Miyauchi 1983). The absorption around 1000 cm^{-1} indicates formation of diborate groups in the present glasses. The shoulder at 1021 cm^{-1} is due to stretching vibrations of tetrahedral BO$_4$. In IR spectra of Na$_2$O–B$_2$O$_3$–SiO$_2$ glasses the band at about 995 cm^{-1} is attributed to a stretching vibration of B–O–Si linkage. Similarly the presence of the band at 992 cm^{-1} in the spectra may be assigned to a stretching vibration of B–O–M (B–O–Pb) linkage where M represents a metal ion. The absorption band at 696 cm^{-1}

is due to combined vibration of BO_4 and PbO_4 groups. The band around 699 cm^{-1} indicates that oxygen bridges two trigonal boron atoms. In $50Pb_2$–$50B_2O_3$ glass system the absorption band at 828 and 1130 cm^{-1} was reported by Doweidar *et al* (1991). In present PbO_2–CdO–B_2O_3 glasses, it is found that the bands are absent. Probably this may be due to substitution of CdO for fraction of PbO_2 contents. The absorption at region 840 cm^{-1} is not observed in these glasses, which suggests that the formation of tetrahedral coordination of Cd (i.e. CdO_4) is absent (Yawale *et al* 1995). Figure 3 indicates the Raman spectrum of $30PbO_2$–20CdO–$50B_2O_3$ glass which has a strong absorption band in the region 200–300 cm^{-1} which corresponds to Cd–O vibrational modes (Robinson 1991). The other absorption bands have been discussed in its FTIR spectra.

3.4 *Refractive index*

Refractive index has been measured using a Luxmeter. The transition coefficient (T_n) and its relations with Furnel coefficient was also used to calculate the amount of refractive index. The physical properties of cadmium doped lead borate glass is shown in table 1.

Transition coefficient,

$$T_n = \frac{\text{Intensity of transmitted light}}{\text{Intensity of incident light}} \qquad T_n = 0{\cdot}9,$$

$$T_n = \frac{n_2}{n_1} t_{12}^2, \text{ Furnel transition coefficient, } t_{12}^2 = \frac{2n_1}{n_1 + n_2},$$

$$T_n = \frac{n_2}{n_1}\left[\frac{2n_1}{n_1+n_2}\right]^2 = \frac{n_2}{1}\left[\frac{2}{1+n_2}\right]^2,$$

the refractive index of the air, $n_1 = 1$,

$$0{\cdot}9 = \frac{n_2}{1}\left[\frac{2}{1+n_2}\right]^2 \Rightarrow n_2 = 1{\cdot}925.$$

The measured refractive index has been 1·92 for the glasses by using direct optometry with a microscope and agreed well in both the approaches.

4. Conclusions

We conclude that the structure of cadmium doped lead borate glasses consists of BO_3 and BO_4 groups which are connected randomly. The structures of present glasses are independent of their compositions. The small changes occurring in the absorption bands do not account for major structural changes.

Acknowledgements

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