Asian Journal of Chemistry Vol. 18, No. 3 (2006), 2261–2268

Synthesis and Characterization of Holmium Oxide Doped Zinc Lead Borate Glasses

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Holmium doped zinc-lead borate glasses were prepared from melting in appropriate proportions of ZnO, PbO_2, H_3BO_3 and (1–2 mol %) Ho_2O_3 mixture in the temperature range of 800–850°C. The density of glass samples was measured using Archimedes' principle. The infrared spectra of the glasses in the range of 4000–400 cm^{-1} showed their structure systematically. No boroxol ring formation was observed in the structure of these glasses but the conversion of three-fold to four-fold coordination of boron atoms in the structure of glasses was observed. Glass transition studies were done through differential scanning calorimetry. Optical analysis was done by using Judd-Ofelt theory.

Key Words: **Holmium, Zinc, Lead borate glasses.**

INTRODUCTION

Many inorganic substances may be formed not only in crystalline form but also in a glassy state, when their structure lacks the long-range crystallographic order. The majority of elements and inorganic compounds can be transformed into state using techniques such as ultra-quick under cooling of the melt to the solid state. Nowadays the chemical composition of technical glasses is varied. Almost all of the chemical elements can be used; however, oxide glasses are the most widely used[1].

According to Stoch[2, 3], expression glass is a solid body with a flexible random structure. The construction and uniformity of the structure depends on the chemical composition, the origin and the history of glass preparation.

The structure of the majority of oxide glasses has a polymeric, three-dimensional, continuous, geometrically disordered network composed of coordination tetrahedra ($[SiO_4]$, $[AlO_4]$, $[BO_4]$, $[PO_4]$). Part of the oxygen bridges combining these tetrahedra is broken by cations of uni- or bivalent metals (modifiers) coordinated by six, eight or even more oxygens to form structures such as Zacharriasen's glass model.

Several glasses have discontinuous polymeric network made up of chains or rings of tetrahedra linked by the surrounding cations (some phosphate and borate glasses).

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A number of glasses have non-polymeric structure. Some of them are made up of halides with small dispersed islands of coordination polyhedra of oxide or other components. These belong to the super ionic conducting glasses based on silver halide and phosphorus, boron, silicon, arsenic oxides as stabilizing admixtures. Their structure is interpreted as "a cluster and tissue pseudo phase model"[4]. 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 in borate glasses and also of scientific interest because of the occurrence of boron anomaly[5]. Up to now the study of oxide glasses has received considerable attention due to their structural peculiarities. 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 formulation and its related doped systems. In borate glasses B^{3+} ions are triangularly coordinated by oxygen atoms and the triangle units are corner bonded in a random configuration[6].

Infrared spectroscopy and Raman scattering are two of the mostly used spectroscopic techniques applied to characterize vitreous materials like oxide glasses[7–9]. The synthesis and study of lanthanum borate[10], aluminum borate whiskers and borate glasses, in particular, has been the subject of numerous infrared studies due to their structural peculiarities[11, 12].

With the development of fibre optic communication, up-conversion and laser, there has been much research into new optical glasses. Since the particular 4*f* electronic configuration of trivalent rare earth ions in numerous hosts leads to absorptions and emissions from ultraviolet to infrared, studies on rare earth doped glasses have gained much interest[13–16]. Moreover, rare earth borate glasses have attracted much attention due to their high transparency, low melting point, easily-shaped and cost-effective properties[17].

In the present paper, the synthesis and characterization of zinc-lead borate glasses doped with holmium oxide will be discussed with the help of UV-Vis and infrared spectroscopy. IR spectroscopy has been used to determine the structure of lead borate glasses containing varying amounts of ZnO and Ho_2O_3.

EXPERIMENTAL

Holmium ions doped lead-zinc borate glasses were prepared using AnalaR grade H_3BO_3, PbO_2, ZnO and Ho_2O_3 in the composition range $XPbO_2\cdot(50\text{-}x\text{-}y)ZnO\text{-}50H_3Bo_3\cdot yHo_2O_3$ where x = 30 and y = 0, 1, 2. The glasses' compositions are given in Table-1 for various samples.

TABLE-1

COMPOSITION OF Ho^{3+} DOPED ZINC-LEAD BORATE GLASSES

No.	Sample	Composition
1.	ZPB0	$30PbO_2\cdot 20ZnO\cdot 50B_2O_3$
2.	ZPB1	$30PbO_2\cdot 19ZnO\cdot 50B_2O_3\cdot Ho_2O_3$
3.	ZPB2	$30PbO_2\cdot 18ZnO\cdot 50B_2O_3\cdot 2Ho_2O_3$

The appropriate amounts of chemicals were weighed using Shimadzu AW 220 balance and thoroughly mixed using mortar and pestle. Each composition was taken in an open silica crucible and kept in a Kerr 666 electric furnace for heat treatment. Initially, the samples were maintained at about 450–550°C for 1 h to decompose boric acid and then the temperature was raised up to 850°C and maintained for 2 h.

The crucibles were shaken frequently for homogeneous mixing of all the constituents. Then, the molten liquid was poured between two stainless steel mould plates kept at room temperature to form a glassy composition of required shape. The quenched glasses were yellow in colour.

X-ray diffraction

The glassy nature of the samples was confirmed by XRD studies using D5000 (Siemens, Germany) with Cu-K_α line of wavelength $\lambda = 1.5418$ Å at the scanning rate of 2°/min and 2θ was varied from 4° to 70°.

DSC thermogram

The glassy nature of prepared glasses ($30PbO_2 \cdot 20ZnO \cdot 50B_2O_3$ and $30PbO_2 \cdot 19ZnO \cdot 50B_2O_3 \cdot Ho_2O_3$) was confirmed by differential thermal studies using Shimadzu DSC60 differential scanning calorimeter (DSC) in the temperature range 30–410°C at the heating rate of 10°C/min in air.

Infrared spectra

Infrared spectroscopy studies were used to get essential information about the arrangement of the structural units of glass samples. The FTIR transmission spectra in the region 400–4000 cm^{-1} were recorded for all the samples using FTIR (Nexus, Holland) 670 by KBr pellet technique.

Density measurement

The density of glass samples was measured using Archimedes' principle. The measurements were carried out using Aw 200 balance (Shimadzu, Japan) and xylene as an inert immersion liquid. The density was obtained using the equation

$$d(g/cm^3) = [a/(a-b)]x \qquad (1)$$

where x is the density of xylene, a is the weight of the glass sample in air and b is the weight of the glass sample when immersed in xylene. The density of xylene[18] is 0.865 (g/cm^3). The physical properties of 1 mol% Ho_2O_3-doped zinc-lead borate glass is given in Table-2.

TABLE-2

PHYSICAL PROPERTIES OF 1 mol % Ho^{3+} IONS DOPED ZINC-LEAD BORATE GLASS

Physical properties	
Average molecular weight (g)	131
Density (g/cm^3)	5.38
Refractive index	1.95
Reflection loss R (%)	10.20
Dielectric constant	3.80

Optical spectrum

The optical spectrum was recorded using UV-1650 PC spectrometer (Shimadzu-Japan) in the wavelength range of 400–1000 nm at room temperature.

RESULTS AND DISCUSSION

X-ray diffraction

The X-ray diffraction pattern of Ho_2O_3-doped zinc-lead borate glasses shows no sharp peaks indicating the absence of crystalline nature. This confirms the amorphous nature of the glasses.

Thermal analysis

The DSC thermograms of $30PbO_2{\cdot}20ZnO{\cdot}50B_2O_3$ and $30PbO_2{\cdot}19ZnO{\cdot}50B_2O_3{\cdot}Ho_2O_3$ glasses are shown in Fig. 1. From this figure it is observed that the glass transition temperature of the first sample is 392°C and doping Ho^{3+} causes an increase of about 5°C in the glass transition temperature of the second sample.

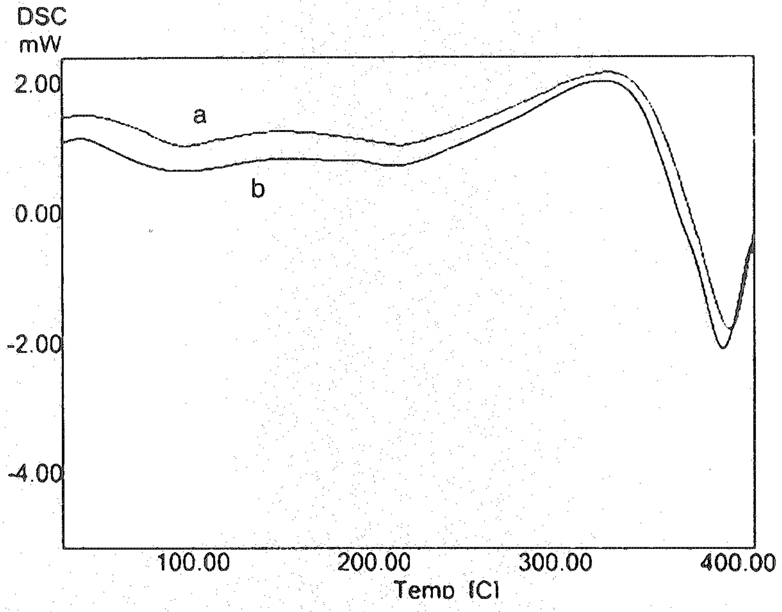

Fig. 1. The DSC curves of the glasses heated at a rate of 10°C/min in air: (a) $30PbO_2{\cdot}20ZnO{\cdot}50B_2O_3$; (b) $30PbO_2{\cdot}19ZnO{\cdot}50B_2O_3{\cdot}Ho_2O_3$

FTIR and Raman analysis

The broad composite bands extending from 3600–3200 cm^{-1} are attributed to hydroxyl or water groups[19, 20]. In Fig. 2, it can be seen that there is no effect of composition on the types of structural groupings in the present case. This may be due to the presence of symmetric $(BO_3)^{3-}$ triangles, $(BO_4)^{4-}$ tetrahedral and asymmetric $(BO_3)^{3-}$ units (non-bridging oxygen) in each sample of PbO_2-ZnO-B_2O_3 glasses. Furthermore, it seems that in the spectra containing different concentrations of Ho_2O_3 the structure is not changed.

According to the Krogh-Moe's model[21], the structure of boron oxide glass consists of a random network of planar BO_3 triangles with a certain fraction of

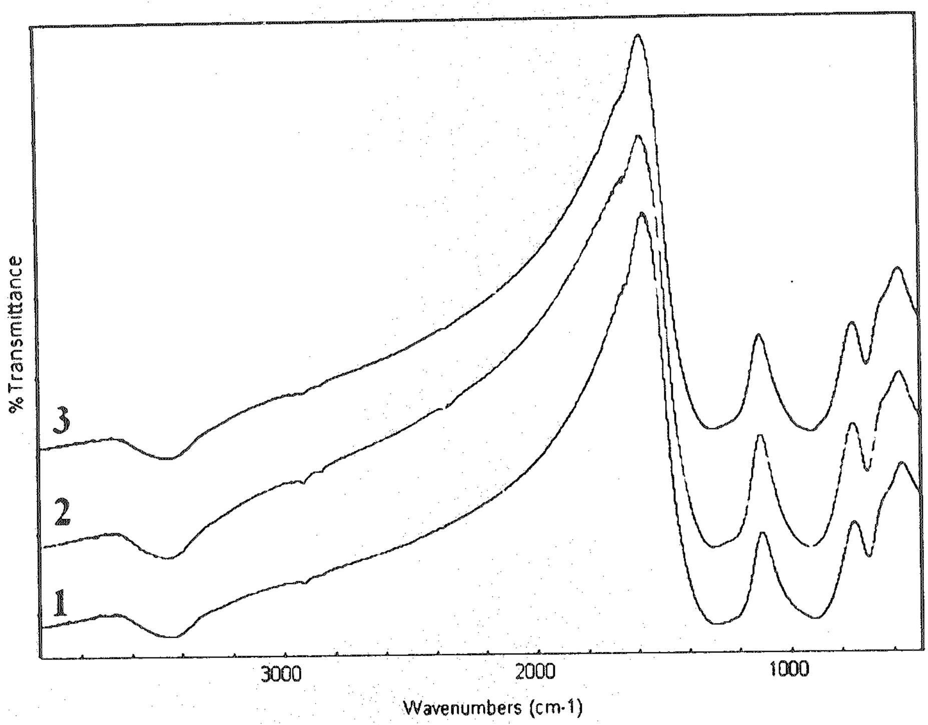

Fig. 2. FTIR spectra of $XPbO_2(50\text{-}X\text{-}Y)ZnO\cdot 50B_2O_3\cdot YHo_2O_3$: (1) X = 30, Y = 0; (2) X = 30, Y = 1; (3) X = 30, Y = 2

six-membered (boroxol) rings. X-ray diffraction data suggest that the 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[22, 23]: (i) the first group of bands which occur at 1600–1200 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, most 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 system 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 a random network. This corresponds to the progressive substitution of boroxol rings by BO_3 and BO_4 groups. This type of behaviour is observed in B_2O_3-Li_2O glasses[24–26]. 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[27]. On passing from boron trioxide to borate glasses the coordination number of boron takes place. In these glasses, boron is tetrahedrally surrounded by four oxygen atoms[28]. The band around 1292 cm^{-1} is due to B—O asymmetric stretching of BO_3 unit[29]. The shoulder at 1234 cm^{-1} may arise from B—O stretching vibrations of $(BO_3)^{3-}$ unit in metaborate chains and orthoborates[30]. Similarly, the band at 1005 cm^{-1} is due to vibration of some atoms attached to non-bridging oxygen in the form of BO_4 vibration[31]. The absorption around 1000 cm^{-1} indicates the formation of diborate groups in present glasses. The shoulder at 1021 cm^{-1} can be referred to stretching vibrations of tetrahedral BO_4. In IR spectra of $Na_2O\cdot B_2O_3\cdot SiO_2$ 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 assumed to be 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 $50Pb_2\cdot 50B_2O_3$ glass system the absorption band at 828 and 1130 cm^{-1} was reported by Doweidar *et al.*[32]. In the present $PbO_2\cdot ZnO\cdot B_2O_3$ glasses, it is found that the bands are absent. Probably this may be due to substitution of ZnO for a 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 Zn (*i.e.*, ZnO_4) is absent[33].

Optical analysis

The optical absorption spectrum of 1 mol % Ho_2O_3-doped zinc-lead borate glass in the wavelength range of 400–1000 nm is shown in Fig. 3. The optical spectrum of 2 mol % Ho_2O_3 doped zinc-lead borate glass shows no change in the barycenter.

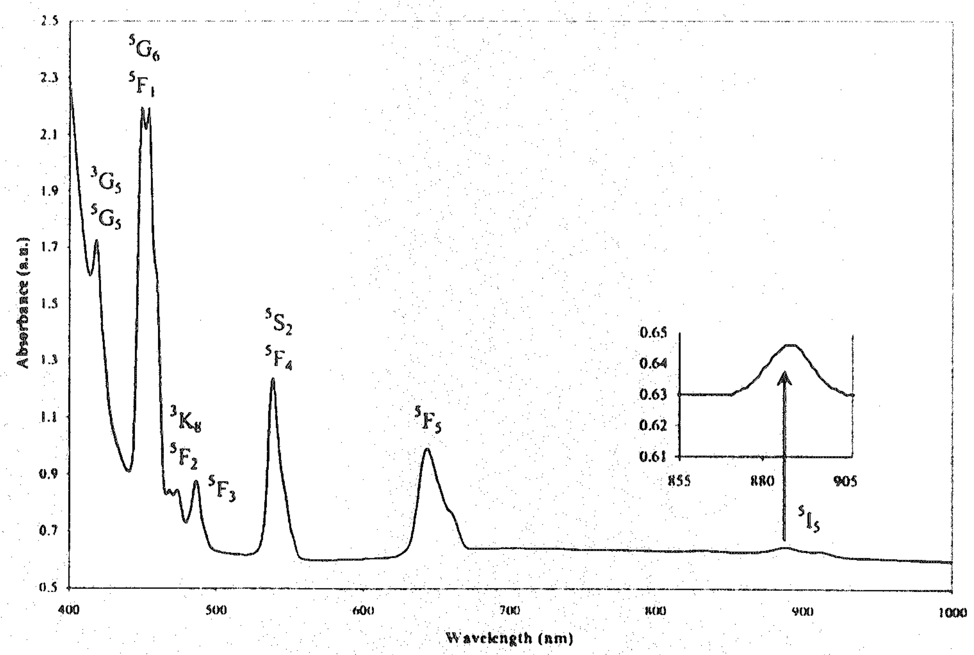

Fig. 3. UV-Vis spectra of $XPbO_2$ (50-X-Y)CdO·$50B_2O_3\cdot YHo_2O_3$ (X = 30; Y = 1)

However, the intensity of the bonds observed is higher than that of the spectrum of 1 mol % Ho_2O_3. The following transitions are observed in the 400–1000 nm spectral region, from the $^5I_8$ ground state to the $^5I_5$, $^5F_5$, $^5F_4 + {}^5S_2$, $^5F_3$, $^5F_2 + {}^3K_8$, $^5G_6 + {}^5F_1$, $^5G_5 + {}^3G_5$ excited states. The assignments of these transitions have been made on the basis of Carnall *et al.*[35].

The experimental oscillator strength was calculated from the absorption by using the equation

$$f_{meas} = 4.32 \times 10^{-9} \int_{\nu_2}^{\nu_2} \varepsilon(\nu)d\nu \qquad (2)$$

where $\varepsilon(\nu)$ is the molar extension coefficient. According to Judd-Ofelt theory[36, 37], the oscillator strength of a transition between an initial J manifold (S, L)J and a final manifold (S′, L′)J′ is given by

$$f_{calc}(aJ, bJ') = \frac{8\pi^2 m\nu}{3h(2J+1)} \times \left[\frac{(n^2+1)^2}{9n} S_{ed} + nS_{md}\right] \qquad (3)$$

where $$S_{ed}[(S, L)J : (S', L')J'] = \sum_{\lambda = 2, 4, 6} \Omega_\lambda \left|\langle (S, L)J \| U^{(\lambda)} \| (S', L')J' \rangle\right|^2 \qquad (4)$$

and S_{nd} is the magnetic dipole line strength. The bonds which are produced by the magnetic dipole mechanism will have very low spectral intensity magnitude compared to those of electric dipole bonds and hence S_{md} has not been considered. $|\langle (S, L)J \| U^{(\lambda)} \| (S', L')J' \rangle|^2$ is the reduced matrix element and n is the refractive index of the medium. The very weak bands are not included in the analysis, because of the uncertainties in the area determination. From the optical absorption spectrum, it is observed that the hypersensitive transition ($^5F_1 + {}^5G_6 \leftarrow {}^5I_8$: 446 nm) is shifted to the higher wavelength region of 451 nm. This is due to the nephelauxetic effect[38] which indicates the presence of Ho—O covalence in the glass system.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the Council of Tabriz University and the Management and Planning Organization of the Islamic Republic of Iran.

REFERENCES

1. L. Stoch and M. Sroda, *J. Mol. Struct.*, **511–512**, 77 (1999).
2. L. Stoch, *High Temp. Mater. Processes*, **10**, 245 (1992).
3. ———, *Glasstech. Ber. Glass Sci. Technol.*, **67C**, 239 (1994).
4. A. Paul, Chemistry of Glass, Chapman & Hall, London, p. 174 (1982).
5. D.L. Griscon, Borate Glasses, Materials Science Research, Plenum, New York, p. 36 (1978).
6. S.S. Yawale, S.P. Yawale and C.S. Adgaonkar, *Indian J. Engg. Mater. Sci.*, **7**, 150 (2000).
7. D.D. Martino, L.F. Santos, A.C. Marques and R.M. Almeida, *J. Non-Cryst. Solids*, **293**, 394 (2001).
8. A.K. Hassan, L.M. Torell, L. Borjesson and H. Doweidar, *Phys. Rev. B*, **45**, 12797 (1992).
9. Y.D. Yiannopoulos, G.D. Chryssikos and E.I. Kamitsos, *Phys. Chem. Glasses*, **42**, 164 (2001).
10. Y. Hinatsu, Y. Doi, K. Ito, M. Wakeshima and A.A. Alemi, *J. Solid State Chem.*, **172**, 438 (2003).

11. S.G. Motk, S.P. Yawale and S.S. Yawale, *Bull Mater. Sci.*, **25**, 75 (2002).
12. E.I. Kamitsos and M.A. Karakassides, *J. Phys. Chem. Glasses*, **30**, 19 (1989).
13. R. Reisfeld, H. Minti, A. Patra, D. Ganguli and M. Graft, *Spectrochim. Acta*, **54A**, 2143 (1998).
14. B. Jacquir, *J. Alloys Comp.*, **225**, 15 (1995).
15. M. Bettinelli, G. Ingletto and P. Polato, *Phys. Chem. Glasses*, **37**, 4 (1996).
16. K. Tonooka, F. Maruyama and N. Kamata, *J. Lumin.*, **62**, 69 (1994).
17. L. Huang, X. Wang and H. Lin, *J. Alloys Comp.*, **316**, 256 (2001).
18. B. Karthikeyan and S. Mohan, *Physica B*, **334**, 298 (2003).
19. R.V. Adams and R.W. Douglas, *J. Soc. Glass Technol.*, **43**, 147 (1959).
20. H. Scholzelt, *Glass: Nature, Structure and Properties*, Springer-Verlag, New York (1991).
21. U.K. Moe, *J. Phys. Chem. Glasses*, **6**, 46 (1965).
22. E.I. Kamitsos, M.A. Karakassides and G.D. Chryssikos, *J. Phys. Chem. Glasses*, **91**, 1073 (1987).
23. N.A. Ghoneun, H.A. El-Batul, N. Shafi Abdel and Azooz, Proceedings of Egyptian Conference of Chemistry, p. 162 (1996).
24. A.R. Kulkarni, H.S. Maiti and A. Paul, *Bull. Mater. Sci.*, **6**, 207 (1984).
25. F.L. Galeener, G. Lucovsky and J.C. Mikkelsen, *Phys. Rev.*, **B22**, 3983 (1980).
26. M.A. Kanehisa and R.J. Elliot, *Mater. Sci. Engg.*, **B3**, 163 (1989).
27. V.G. Chekhovskii, *Fisika I. Khimiya Stekla* (English Translation), **11**, 24 (1985).
28. J. Biscoe and B.E. Warren, *J. Am. Ceram. Soc.*, **21**, 287 (1938).
29. H.M. Heaton and H. Moore, *J. Phys. Chem. Glasses*, **28**, 203 (1987).
30. E.I. Kamitsos, A.P. Patsis, M.A. Karakassides and G.D. Chryssikos, *J. Non-Cryst. Solids*, **126**, 52 (1990).
31. Y. Ito and K. Miyauchi, *J. Non-Cryst. Solids*, **57**, 389 (1983).
32. H. Doweidar, M.A. Abouzeid and G.M. El-Damrawi, *J. Phys. D, Appl. Phys.*, **24**, 2222 (1991).
33. S.P. Yawale, S.V. Pakade and C.S. Adgaonkar, *Indian J. Pure Appl. Phys.*, **33**, 35 (1995).
34. J.W. Robinson, Practical Handbook of Spectroscopy, CRC Press, Inc., USA, p. 533 (1991).
35. W.T. Carnall, P.R. Fields and K. Rajnak, *J. Chem. Phys.*, **49**, 4412 (1968).
36. B.R. Judd, *Phys. Rev.*, **126**, 750 (1962).
37. G.S. Ofelt, *J. Chem. Glasses*, **11**, 46 (1970).
38. M.B. Saisudha and J. Ramakrishna, *Phys. Rev. B*, **53**, 6186 (1996).

(*Received*: 3 November 2005; *Accepted*: 3 March 2006) AJC-4711