

INFRARED SPECTRA OF LITHIUM BORATE GLASSES DOPED WITH MODIFIER IONS

CEPHAS JOHN LYOBHA

Department of Physics,
The University of Dodoma,
Tanzania,
East Africa

E-Mail: lyobhacephas@yahoo.com,
+255-757251022

J. ANJALIAH

Department of Physics,
The University of Dodoma,
Tanzania. & Department of Physics,
Geethanjali College of Engineering
& Technology, Keesara

E-Mail: anjaiah.juluru@gmail.com,
+91-9441230077

C. LAXMIKANTH

Department of Physics,
The University of Dodoma,
Tanzania,
East Africa

E-Mail: htnakimxal@gmail.com,
+255 658121299

ABSTRACT

The aim of this study is to investigate the infrared spectra of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses doped with modifier ions ZnO , CaO and CdO . Glasses with composition 30 Li_2O -10 MO -60 B_2O_3 doped Modifier ions (where $\text{MO}=\text{ZnO}$, CaO and CdO) were prepared by using the melt quenching technique. Differential scanning calorimetry in the temperature range 30-750 °C reveals that homogenous glasses are formed and glass forming ability is more in ZnB glass samples. FTIR spectra in the wavelength range 400-4000 cm^{-1} reveals the presence of BO_3 and BO_4 units in the glass network by introduction of modifier ions.

Keywords: Differential scanning calorimetry, Infra-red spectra, Borate glasses, melt quenching method.

INTRODUCTION

Glasses are super cooled liquids, transparent, and amorphous in nature. They are inorganic product of fusion which has cooled to a rigid condition without any crystallization. The main distinction between glass and crystals is the presence of long-range order in the crystal structure [1]

The credit of first successful attempt to categorize the materials into glass formers and non-glass formers goes to Zachariasen [2]. He prepared the glasses with five oxide materials which were the only known glass formers by themselves: SiO_2 , GeO_2 , B_2O_3 , As_2O_3 and P_2O_5 . In addition, these oxides can also form glasses when mixed up with other oxides (up to certain percentage) which were not by themselves glass formers. Basing on these glasses Zachariasen proposed certain rules which an oxide should obey if it has to form a glass. The latest rules after Cooper [3] objections to original rules are

- A high proportion of glass network forming cations is surrounded by oxygen tetrahedra or triangles.
- The oxygen polyhedra share only corners with each other.
- Some oxygen atoms are linked to only two cations, and do not form additional bonds with any other cations.

Basing on these rules, a continuous random network for a glass can be constructed. As per these rules, the oxides of the type AO , A_2O should not form glasses, and the rules are satisfied only for oxides of the type A_2O_3 , AO_2 and A_2O_5 . Presence of oxides such as A^+ (example Li^+ , Na^+ , K^+ etc.),

A^{2+} (example Ca^{2+} , Pb^{2+} , Zn^{2+} , Cd^{2+} etc.) other than A^{3+} and A^{4+} are known as network modifiers. Li_2O , Na_2O , K_2O , ZnO , CaO , CdO are some of the basic examples of modifiers in glass network. These modifiers break up the continuous network by introducing non-bridging oxygens. A third group of oxides known as intermediate class of oxides also exist which by themselves not readily form glasses but do so when mixed with other oxides; such oxides are known as network modifiers. The examples of this group are TeO_2 , WO_3 , MoO_3 , Ge_2O_3 , Al_2O_3 , Ga_2O_3 and V_2O_5 . Excellent reviews and articles on the topology of the glass by Vanvotert [4], Elliott [5], Polk [6], Egamin [7], give the useful information.

During the last few decades a large variety of inorganic glasses have been developed with an attempt to achieve suitable electrical and optical characteristics. These characteristics are associated with the improved physical properties such as electrical resistance, mechanical strength, glass transparency, IR transmission performance and their ability to accept more rare-earth ions as luminescent centers for their use in glass laser technology. Work along these lines was carried out on a number of glasses giving valuable information [8-15]. Investigations on electrical properties such as dielectric properties and dielectric breakdown strength of glasses help to have an idea over their insulating character. Investigations on the optical properties such as optical absorption, IR spectra, and luminescence can be used as probes to throw some light on the structure of these glasses.

The boric acid (B_2O_3) is used in the present study since it is one of the good glass formers and can form glass alone with good transparency, high chemical durability, thermal stability and good rare-earth ion solubility [16]. Among the three modifier oxides chosen to mix in the present glass system, viz., CaO , ZnO and CdO ; ZnO is expected to shorten the time taken for solidification of glasses during the quenching process. Both ZnO and CdO are thermally stable and appreciably covalent in character [17]. Addition of alkaline-earth oxide CaO into these glass matrices is expected to increase the resistance of the glasses to the moisture [18]. The glass containing Li_2O as network modifier was seen as bubble free, highly stable and moisture resistant, suitable for a systematic analysis [19].

Infrared spectroscopy (IR) is an important tool for understanding the structure and dynamics of amorphous materials. It is also used to assign the observed absorption peaks to the proper vibration of the atoms in geometric

grouping. The spectra of many solids variables can affect the absorption peaks, and the assignment of vibration peaks of the atoms is very difficult. Usually, the method of repeated occurrence is followed in analyzing the IR spectrum of solid materials [20,21]. In this spectroscopy, the nature of the light matter interaction is not same as in Raman spectroscopy, and the fundamental differences of the two processes determine the selection rules, which control Raman or IR activity of normal mode of vibrations. Interaction of IR radiation with a normal mode of vibration only occurs when the electric field of radiation oscillates with same frequency as instant dipoles caused by atomic vibrations. A normal vibration is therefore, IR active only if a change in the dipole moment of the vibration occurs and is a one photon process, as only photon is absorbed [22].

I. MATERIALS AND METHODS

The following modifier ion doped glasses in mole% are prepared by using standard melting and quenching techniques and used for the present study. [23-25].

ZnB : 30 Li₂O-10 ZnO-60 B₂O₃,

CaB : 30 Li₂O-10 CaO-60 B₂O₃, and

CdB : 30 Li₂O-10 CdO-60 B₂O₃,

Appropriate amounts of raw materials ZnO, CaCO₃, CdO, H₃BO₃ and Li₂CO₃ were thoroughly mixed and grounded in an agate mortar and melted in a platinum crucible. The chemicals used in the work were of high purity (99.9%). These compositions were heated in a PID temperature controlled furnace at 450 °C for 2 hour for the decarbonization from CaCO₃ and Li₂CO₃ and then the temperature maintained within the range 1000-1050 °C and kept the melt at this temperature for an hour till a bubble free liquid was formed. The crucibles were shaken frequently for the homogeneous mixing of all the constituents. The resultant melt was poured on a rectangular brass mould held at room temperature. The samples were subsequently annealed at glass transition temperature in another furnace to remove mechanical stress and were polished.

The density 'ρ' of these glasses was determined by the standard density of Archimedes' using xylene (99.99% pure) as the buoyant liquid. The glass transition temperatures T_g and crystallization temperature T_c of these glasses were determined (to an accuracy of ± 1 °C) by differential scanning calorimetry (DSC) traces, recorded using universal V23C TA differential scanning calorimeter with a programmed heating rate of 15 °C per minute in the temperature range 30-750 °C.

Infrared transmission [IR] spectra for these glasses were recorded using a Perkin Elmer Spectrometer in the wavenumber range 400-4000 cm⁻¹ by KBr pellet method.

II. RESULTS

The density and the average molecular weight \bar{M} values of all samples were measured and presented in the Table 1.

Table 1
Various physical properties of Li₂O-MO-B₂O₃ glasses

Property/ Glass	ZnB	CaB	CdB
Refractive index, n_d	1.517	1.519	1.523
Density, ρ (g/cm ³)	2.181	2.415	2.799
Average molecular weight, \bar{M}	46.001	46.017	46.028

Our visual examination, absence of peaks in X-ray diffraction spectra, existence of glass transition temperature T_g and crystallization temperature T_c in differential thermal analysis curves, indicate that the glasses prepared were of amorphous in nature.

Fig.1 represents the thermograms of pure Li₂O-MO-B₂O₃ glasses; the glass samples ZnB, CaB and CdB exhibits an endothermic effect due to the glass transition temperatures T_g at 553 °C, 544.7°C, 537 °C respectively. Presence of single transition temperature T_g in each glass sample indicates homogeneity of the glasses. At still higher temperatures an exothermic peak T_c due to the crystal growth followed by an endothermic effect due to the re-melting of the glass symbolized by T_m are observed. The glass forming ability (Hruby's) parameter $K_{gl} = (T_c - T_g)/(T_m - T_c)$ is calculated, which gives the information about the stability of the glass against devitrification [26,27] are evaluated and presented in Table 2.

Fig. 2 represents IR spectra of the pure Li₂O-MO-B₂O₃ glasses. The infrared transmission spectra of pure Li₂O-MO-B₂O₃ glasses exhibit three groups of bands: (i) in the region 1336-1378 cm⁻¹, (ii) in the region 939-992 cm⁻¹ and (iii) a band at about 710 cm⁻¹. It is well known that the effect of introduction of alkali oxides into B₂O₃ glass is the conversion of sp² planar BO₃ units into more stable sp³ tetrahedral BO₄ units and may also create non-bridging oxygens. Each BO₄ unit is linked to two such other units and one oxygen from each unit with a rare earth ion and the structure leads to the formation of long tetrahedron chains. The second group of bands is attributed to such BO₄ units whereas the first group of bands is identified as due to the stretching relaxation of the B-O bond of the trigonal BO₃ units and the band at 710 cm⁻¹ is due to the bending vibrations of B-O-B linkages in the borate network [28-31]. When the glasses are doped with MO, the intensity of the second group of bands (band due to the trigonal BO₄ units) is found to increase at the expense of first group of bands (bands due to tetrahedral BO₃ units) with the increase of atomic number of modifier ions with the shifting of meta-centres of first and second group of bands, respectively towards slightly lower and higher wave number for all the glasses. The summary of the data on the positions of various bands in the IR spectra of Li₂O-MO-B₂O₃ glasses are presented in Table 3.

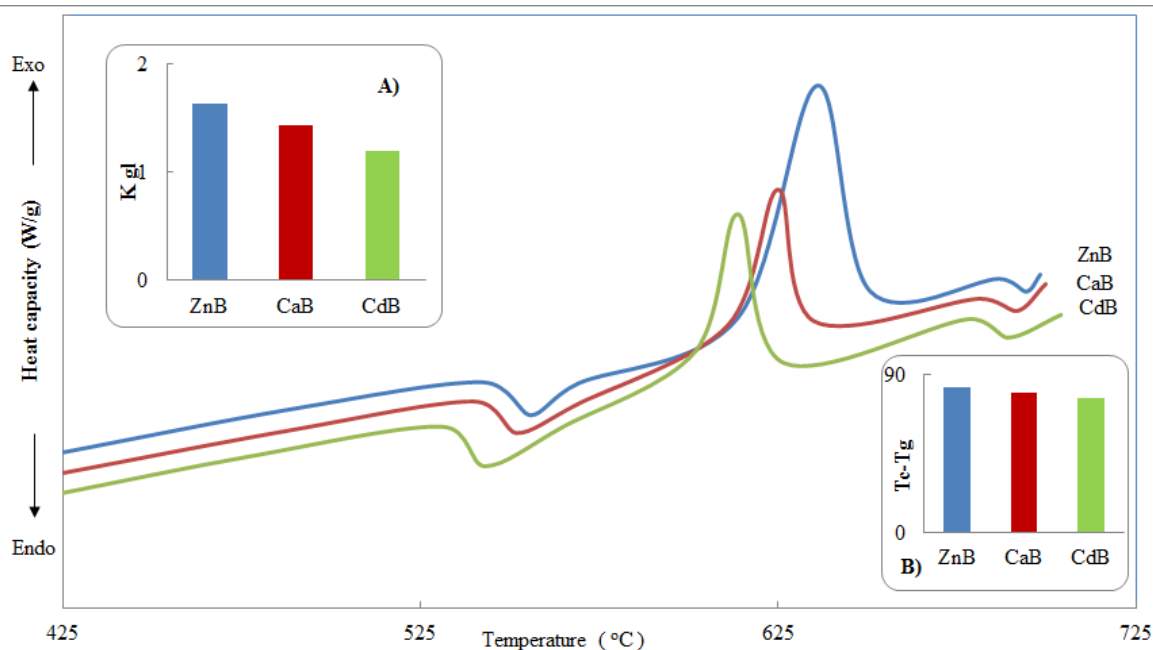


Figure 1: Regular CSLA Circuit

Table 2 Data on differential scanning calorimetric studies of $\text{Li}_2\text{O-MO-B}_2\text{O}_3$ glasses.							
Glass	T_g ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)	T_g/T_m	(T_c-T_g) ($^{\circ}\text{C}$)	$(T_c-T_g)/T_m$	K_{gl}
ZnB	553.0	636	686.7	0.805	83.0	0.121	1.637
CaB	544.7	625	681	0.800	80.3	0.118	1.434
CdB	537.0	613.8	678	0.792	76.8	0.113	1.196

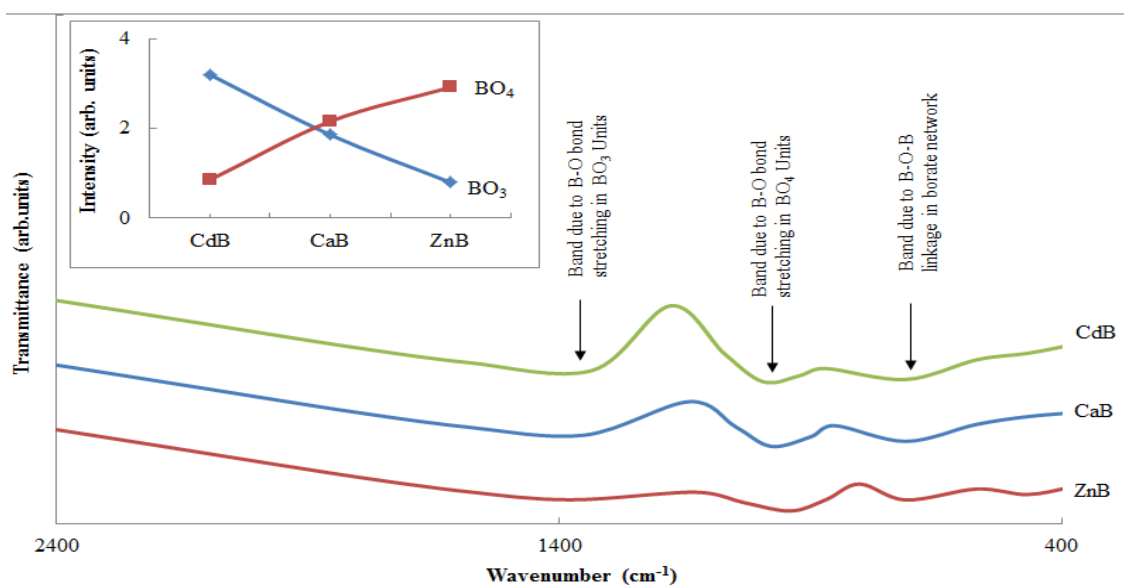


Figure 1: Regular CSLA Circuit

Table 3 Peak positions (cm^{-1}) of IR spectra of Ln^{3+} doped $\text{Li}_2\text{O-MO-B}_2\text{O}_3$ glasses.			
Glass	Band due to B-O bond stretching in BO_3 units	Band due to B-O bond stretching in BO_4 units	Band due to B-O-B linkage in borate network
ZnB	1378	939	710
CaB	1352	979	710
CdB	1336	992	710

IV DISCUSSION

The Li^+ ions have closed structure, do not have energy levels within 10 eV of the ground state and hence these ions do not participate directly in luminescence but may act as activator ions [32]. The action of X-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electrons may traverse in the glass network depending upon their energy and the composition of the glass and are finally be trapped, thus forming color centers (or alternatively they may form excitations with energy states in the forbidden gap). The trapping sites may be the modifier ions which constitute the glass structure, ions of admixtures to the main composition and the structural defects due to impurities in the glass. Thus this process leads to the formation of 1) boron electron centers, 2) non-bridging oxygen hole centers and 3) boron oxygen hole centers [33-35].

It is well known that the effect of introduction of alkali oxides into B_2O_3 is the conversion of sp^2 planar BO_3 units into more stable sp^3 tetrahedral BO_4 units and may also create non bridging oxygens. Each BO_4 unit is linked to two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long chain tetrahedron. The presence of such BO_4 units in the present glasses is evident from the IR spectral studies.

V. CONCLUSIONS

Finally our studies on properties of $\text{Li}_2\text{-B}_2\text{O}_3$ glasses doped different modifier ions indicate that i) Differential scanning calorimetric studies indicate high glass forming ability is for CdB glass. ii) The IR spectral studies indicate relatively less disorder in ZnB glass network.

REFERENCES

- [1]. M. Yamane and Y. Asahara, Glasses for Photonics, Cambridge University Press, Cambridge, UK, 2000
- [2]. Zachariasen W.H., J. Am. Chem.Soc. 54 (1932) 3841.
- [3]. Cooprr A.R., Phys. Chem. Glasses. 19 (1978) 60.
- [4]. Vanvotert L.G., J. Appl. Phys. 50 (1979) 8052. De Nenfvile J. P. & Rockstan H. K., Proc. 5th Int. Conf. on Amorphous and Liquid semiconductors (1974).
- [5]. Elliott S.R., Physics of Amorphous Materials (Longmann Sci.& Tech. Essex) 1990.
- [6]. Polk D.E., Scripta metall. 4 (1970) 117.
- [7]. Egami T. & Waseda Y., J. Non - Crystal. Sol. 64 (1984) 113.
- [8]. Music S., J. Mat. Sci. (U.K.) 29 (1994) 1227.
- [9]. Hayakovea S., J. Ceram. Soc. Jpn. 102 (1994) 522.
- [10]. Dimitrov V., J. Non - Crystal. Solids 180 (1994) 51.
- [11]. Wei - Jin, Kaljia R.K., Phys. Rev. Lett. (USA), 71 (1993) 3146.
- [12]. Horton M., Phys. Chem. glasses (U.K), 34 (1993) 238.
- [13]. Yen W. M., Optical Spectroscopy of Glasses, (ed : I. Zschokke) (D. Reidel Pub. Co., Dordrecht 1986)
- [14]. Zhang J.C., Boine B., Pedrini C., Parent C. and Flem G., J. Phys. Chem. Sol. (1992) 56.
- [15]. Kanvar Jit Singh, Singh D.P. and Bhatti S.S., J. Pure Appl. Ultrason., 14 (1992) 56.
- [16]. YAN ZHANG, CHUNHUA LU, LIYAN SUN, ZHONGZI XU, YARU NI, INFLUENCE OF Sm_2O_3 ON THE CRYSTALLIZATION AND LUMINESCENCE PROPERTIES OF BOROALUMINOSILICATE GLASSES, MAT. RES. BULL. 44 (2009) 179.
- [17]. J.D.Lee, Concise Inorganic Chemistry, Oxford: Blackwell Science (1996).
- [18]. A. Brahmaiah, S. Bala Murali Krishna, M. Kondaiah, T. Bala Narendra Prasad, D. Krishna Rao, Influence of chromium ions on dielectric and spectroscopic properties of $\text{Na}_2\text{O-PbO-B}_2\text{O}_3$ glass system, Mat. Sci. and Engg. 2 (2009) 012028.
- [19]. T.V.R. Rao, R.R. Reddy, Y. Nazeer Ahammed, M. Parandamaiah, Luminescence properties of Nd^{3+} : $\text{TeO}_2\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Li}_2\text{O}$ glass, Infrared Phys. & Tech. 41 (2000) 247.
- [20]. S. Anderson, R. L. Bohon, and I. D. Kimpton J, "Infrared spectra and atomic arrangement in fused boron oxide and soda borate glasses," Journal of the American Ceramic Society, vol. 38, no. 10, pp. 370-377, 1955.
- [21]. J. Wang and C. A. Agell, Glass Structure By Spectroscopy, chapter 7, Dekker, New York, NY, USA, 1976.
- [22]. B. Schrader, Infrared and Raman Spectroscopy, John Wiley and Sons, London, UK, 1995.
- [23]. A. Paul, Chemistry of glasses, London: Chapman & Hall. (1982).
- [24]. S.R. Elliot, Physics of amorphous materials, London: Longman. (1990).
- [25]. J. F. Shackl Ford, Introduction to Materials Science for Engineers, New York: Macmillan. (1985).
- [26]. A. Dietzel, Glass structure and glass properties, Glasstech Ber. 22 (1968) 41-50.
- [27]. A. Hruby, Evaluation of glass-forming tendency by means of DTA, Czechoslovak J. Physics B. 22 [11] (1972) 1187-1193.
- [28]. R.P. Tandon, & S. Hotchandani, Electrical conductivity of semiconducting tungsten oxide glasses, Physica Status Solidi (a). 185 (2001) 453-460.
- [29]. Hong-Hua QIU, Hidetsugu MORI, Hironobu SAKATA, Toru HIRAYAMA, Electrical conduction of glasses in the system $\text{Fe}_2\text{O}_3\text{-Sb}_2\text{O}_3\text{-TeO}_2$, J. Ceramic Society of Japan. 103(1) (1995) 32- 38.
- [30]. F.A. Khalifa, H.A. El Batal & A. Azooz, Infrared absorption spectra of gamma irradiated glasses of the system $\text{Li}_2\text{O-B}_2\text{O}_3\text{-Al}_2\text{O}_3$, Ind. J. Pure & App. Phys. 36(6) (1998) 314-318.
- [31]. A.A. Ahmed, N. Abd ElShafi, M. R. ElTohamy, Infrared study of glasses in the system $\text{B}_2\text{O}_3\text{-PbO-CuO}$ in relation to their structure, Ind. J. Pure & App. Phys. 36 (1998) 335-341.
- [32]. A. Van Der Ziel, Solid State Physics Electronics, New Delhi: Prentice-Hall of India. (1971).
- [33]. W.M. Pontusuchka, S. Isotani, A. Piccini, Optical and thermal bleaching of x-irradiated barium aluminoborate glasses, The Amer. Ceramic Soc. 70(1) (1987) 59-64.
- [34]. S.M. Del Nery, W.M. Pontusuchka, S. Isotani, C.G. Rouse, Luminescence quenching by iron in barium aluminoborate glasses, Phys Rev B. 49 (1994) 3760.
- [35]. M.S.F. da Rocha, W.M. Pontusuchka, A.R. Blak, Radiation induced capacitance in barium aluminoborate glasses, J. Non-Cryst. Solids 321(2003) 29.