

Study of Elastic Properties of Potassium Borate Glasses Doped With Barium Oxide

R. Ezhil Pavai, M. Indhira

Department of Physics, Annamalai University, Annamalainagar, Tamil Nadu, India

ABSTRACT: The ternary glass system of B_2O_3 - K_2O - BaO with different concentrations of BaO (5 to 20 mol. %) were prepared by melt-quench technique. The longitudinal and shear ultrasonic velocities were measured for all the glass samples at room temperature and at 10 MHz frequency. The amorphous nature of the samples was checked by X-ray diffractometry. Density of the samples was measured using relative measurement method. Elastic moduli, Poisson's ratio, acoustic impedance and Debye temperature were calculated from velocity and density data. Compositional dependence of ultrasonic velocities and related parameters are discussed to understand the rigidity and compactness of the glass system studied.

KEYWORDS: Density, ultrasonic velocity, XRD, elastic moduli.

I. INTRODUCTION

The study of elastic properties plays a significant role in understanding the forces between the atoms or ions, in interpreting the bond nature existing in the solid materials. Since the elastic property measurement yields valuable information, they are suitable for portrayal of glass structure as a function of composition. Borate glasses containing alkali or alkaline earth oxide exhibit high mechanical strength and are relatively moisture-resistant when compared with the pure borate glass. Some of their applications include phosphors, solar energy converters and optical devices [1].

The conventional method, for studying the microstructure, phase changes, mechanical properties and elastic properties of glasses is the ultrasonic non-destructive testing [2-4]. The ultrasonic pulse echo technique is one of the most useful techniques available for the characterization of glasses. The measurements of ultrasonic velocity and attenuation as a function of composition, temperature and frequency can furthermore play a significant role in understanding the structural characteristics of glass network. These parameters produce information about the microstructure and the dynamics of glasses, because they are directly related to microscopic properties through the behavior of the network former and modifier. Mitsuru Kawashima et al. [5] studied the elastic properties of alkali borate glasses discussed the formation of 4-coordinated boron atom.

Alkali borate glasses containing divalent oxides such as BaO have attracted many researchers as they can be used as solid-state electrolytes in the fabrication of solid-state batteries and various technical and industrial applications [6]. The insulating property of borate glasses turns into a semiconducting or electronic or ion conducting nature when metal oxides such as alkali and alkaline earth oxides are added to them [7-9].

The present study is aimed to investigate the elastic properties of the ternary $60B_2O_3-(40-x)K_2O-xBaO$ (where $x=10, 15, 20, 25$ and 30 mol %) glass system, using ultrasonic technique. The elastic moduli, Poisson's ratio, acoustic impedance and Debye temperature have been calculated using ultrasonic and density data which will give further insight into the rigidity of the glass under investigation.

II. EXPERIMENTAL PROCEDURE

Glass Preparation

In this research work, samples of formula B_2O_3 - K_2O - BaO were prepared by the melt-quench technique. A gradual increase in the concentration of BaO was done from 0 to 20 mol% while K_2O concentration was decreased from 35 to 20 mol%. The raw materials of boron trioxide (B_2O_3), potassium oxide (K_2O) and barium oxide (BaO) were

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

mixed together by grinding to obtain a fine powder. The obtained mixture was melted in a silica crucible for 3 hours in a muffle furnace at 900 °C until a bubble free liquid is formed. The melt was poured into a brass mould to form samples of dimensions 10mm diameter and 6mm thickness. Glass samples were annealed at 420 °C for 2 hours 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. The obtained samples of two parallel sides were polished using a polishing machine in order to obtain a suitable sample for the ultrasonic measurements.

The amorphous nature of glasses was determined by X-ray diffraction technique using GE-Inspection technology 3003TT model made in Germany, copper target at operating voltage 40 Kv and 300 mA current rates. The densities of the glasses were determined by Archimedes principle with water as a floatation medium. Ultrasonic velocity measurements have been carried out using Pulse-Echo overlap technique at a frequency of 10 MHz at room temperature. By measuring the thickness of the sample (d), the ultrasonic velocities were calculated using the relation

$$U = 2d/t,$$

where t is transit time taken by ultrasonic waves to propagate through the glass samples.

The molar volume, elastic moduli, acoustic impedance, Poisson's ratio and Debye temperature have been calculated using the following relations,

(i) Molar volume $V_m = \frac{M}{\rho}$

(ii) Longitudinal modulus $L = \rho U_\ell^2$

(iii) Shear modulus $G = \rho U_s^2$

(iv) Bulk modulus $K = L - \left(\frac{4}{3}\right)G$

(v) Young's modulus $E = (1 + \sigma) 2G$

(vi) Acoustic impedance $Z = U_t \rho$

(vii) Poisson's ratio $\sigma = \left(\frac{L - 2G}{2(L - G)}\right)$

(viii) Debye temperature $\theta_D = \frac{h}{K} \left(\frac{9N}{4\pi V_m}\right)^{1/3} U_m$

where h, K, N and V_m are the Planck's constant, Boltzmann's constant, Avogadro's number and molar volume of the sample respectively. The mean sound velocity U_m is given by

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

$$U_m = \left[\frac{1}{3} \left(\frac{2}{U_s^3} + \frac{1}{U_\ell^3} \right) \right]^{-1/3}$$

The nominal compositions in mol. % of glasses are presented in Table 1.

Table 1
Nomenclature and the composition of glass samples

Nomenclature	Composition (Mol %)		
	B ₂ O ₃	K ₂ O	BaO
BKBa05	60	35	5
BKBa10	60	30	10
BKBa15	60	25	15
BKBa20	60	20	20

III.RESULTS AND DISCUSSION

X-ray diffraction

Fig. 1 shows XRD spectra of BKBa 05 and BKBa 20 glass samples. The spectra did not show any sharp peaks and this confirms the fact that glass samples are amorphous in nature [10].

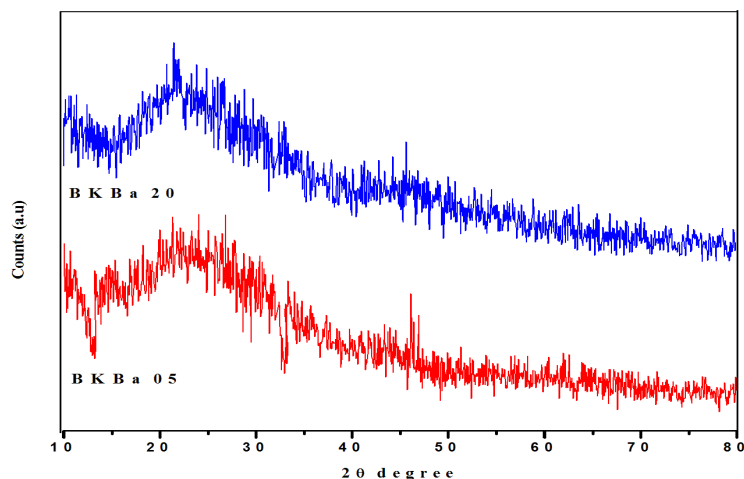


Fig.1 XRD patterns of BKBa 05 and BKBa 20 glasses

Density and molar volume

The density is one of the effective tools to explore the degree of structural compactness and reflects the underlying atomic arrangements in a quantitative manner [11]. In the present system, density increases while the molar

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

volume decreases with the increase of BaO concentration (Table 2). On addition of BaO, the oxide dissociation occurs on account of additional oxygen obtained and causes a conversion from trigonal boron atoms BO_3 to four-fold BO_4 coordinated boron atoms. Thus formed units are liable for the increase in connectivity of the glass network. Therefore, the structure of glass depends on the nature of BaO entering in the network and hence the density of the glass [12].

Table 2 Values of density, molar volume, longitudinal velocity and shear velocity of BKBa glass system

Name of the Glass	Density (ρ) $\times 10^{-3}$ kgm^{-3}	Molar volume (V_m) cm^3/mol	Ultrasonic velocity ms^{-1}	
			Longitudinal (U_l)	Shear (U_s)
BKBa 05	2.4416	33.75	4797.2	2581.0
BKBa 10	2.6303	32.45	4825.3	2691.1
BKBa 15	2.7691	31.90	4905.6	2867.7
BKBa 20	2.9590	30.85	5031.7	2998.2

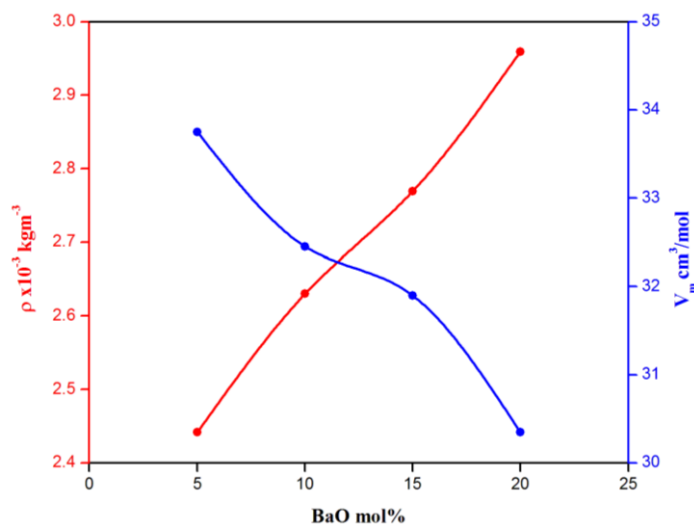


Fig.2.1. Variation of density and molar volume with BaO mol%

In general, it is expected that the density and the molar volume should show opposite behaviour to each other. Here, the molar volume decreases from 33.75 to 30.85, indicating that BO_4 units are preferentially included in the six-membered rings of penta borate groups which are transformed from boroxol rings. Moreover the decreases in molar volume causes decrease in interatomic spacing and hence increase in packing density [13, 14].

Ultrasonic and elastic behaviour of BKBa glasses

In general, the acoustic properties of a glass depend upon its composition and to a considerable extent upon its structure. It can be observed from the Table 2 that the longitudinal velocity and shear velocity increase almost linearly with the increase in concentration of BaO, but the rate of increase of U_l is greater than that of U_s . The increase in ultrasonic velocity has been attributed to an increase in packing density because of transformation of coordination of boron ion. Due to this increase in packing density, the rigidity of the glass system increases and hence the ultrasonic velocity and elastic constant.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

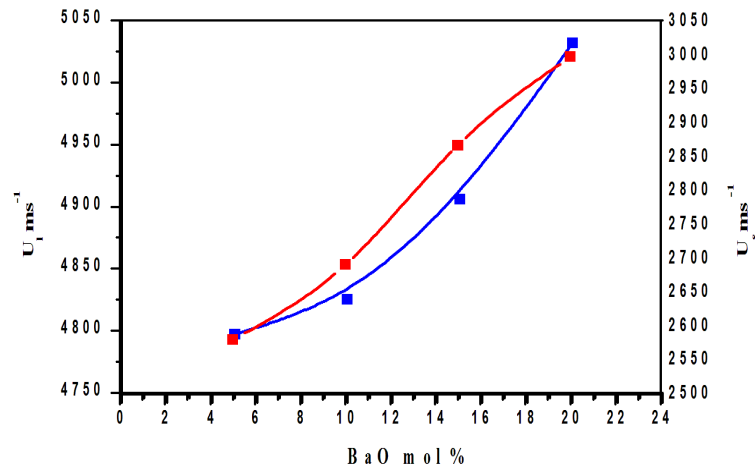


Fig. 2.2. Variation of longitudinal and shear velocity with BaO mol%

Table 3 shows the values of longitudinal, shear, bulk and Young's moduli for increase in mole percentage of BaO. The increase in the elastic constants has been attributed to the increasing packing density and the rigidity of the glass network [15]. The large difference between L and G arises from volume effect. The change in volume due to compressions and expansions involved in longitudinal strain is pronounced while no change in volume is involved in shear strain [16].

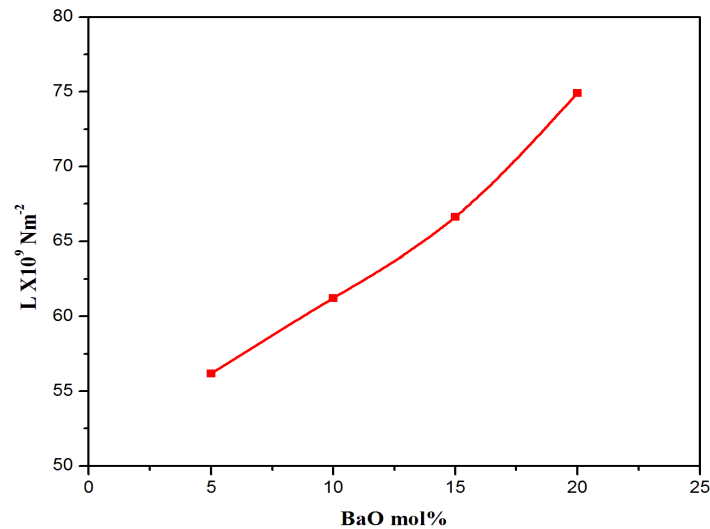


Fig. 2.3. Variation of longitudinal modulus with BaO mol%

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

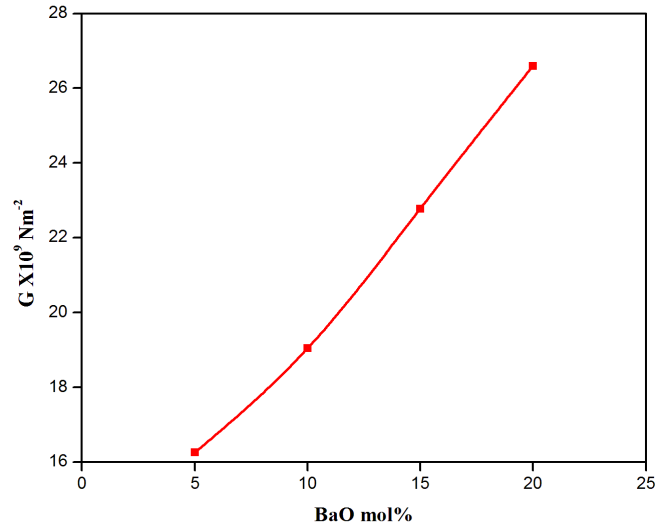


Fig. 2.4. Variation of shear modulus with BaO mol%

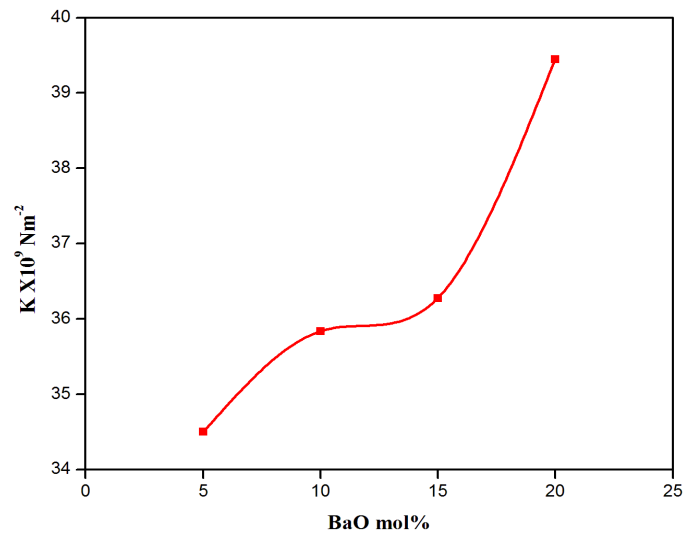


Fig. 2.5. Variation of bulk modulus with BaO mol%

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

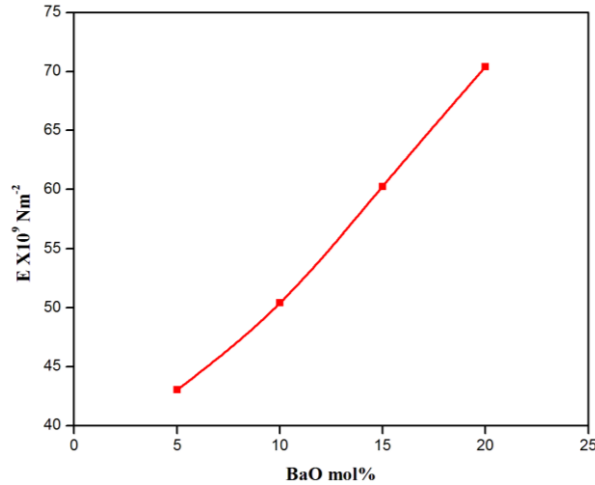


Fig. 2.6. Variation of Young's modulus with BaO mol%

Table 3 Values of longitudinal, shear, bulk and Young's moduli, Poisson's ratio, acoustic impedance, Debye temperature of BKBa glass system

Name of the Glass	Longitudinal modulus $L \times 10^9 \text{ Nm}^{-2}$	Shear modulus $G \times 10^9 \text{ Nm}^{-2}$	Bulk modulus $K \times 10^9 \text{ Nm}^{-2}$	Young's modulus $E \times 10^9 \text{ Nm}^{-2}$	Poisson's ratio (σ)	Acoustic impedance $Z \times 10^{-7} \text{ kgm}^{-2} \text{ s}^{-1}$	Debye temperature $\theta_D \text{ K}$
BKBa 05	56.19	16.26	34.50	43.04	0.2963	1.1713	320.97
BKBa 10	61.24	19.05	35.84	50.41	0.2743	1.2692	338.14
BKBa 15	66.64	22.77	36.28	60.26	0.2404	1.3584	360.91
BKBa 20	74.92	26.60	39.45	70.39	0.2247	1.4889	380.88

Poisson's ratio is the ratio of the transverse and linear strains for a linear stress. Poisson's ratio has also been discussed in terms of the dimensionality of glass network. As it can be seen from Table 3, that the Poisson's ratio is decreased with increase in concentration of BaO, these composition dependence of Poisson's ratio may be due to the change in the structure of the glass network and this suggests that there is no formation of BO_3 groups with NBOs [17].

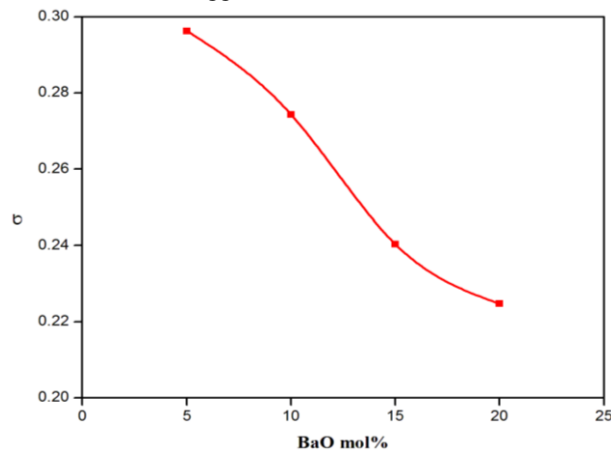


Fig.2.7. Variation of Poisson's ratio with BaO mol%

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

The acoustic impedance increases with increase in mol% of BaO content in the glass system confirming the increase in rigidity of the structure of the glass. The results are further confirmed by another parameter, the Debye temperature (θ_D) which plays an important role in solid materials in the determination of elastic moduli and atomic vibrations. It is known that Debye temperature depends directly on the mean ultrasonic wave velocity. Debye temperature increases with increase in mol. % of BaO content in BKBa glass system. The continuous increase of Debye temperature also suggests that the compactness and structure leading to increase in mean sound velocity [18].

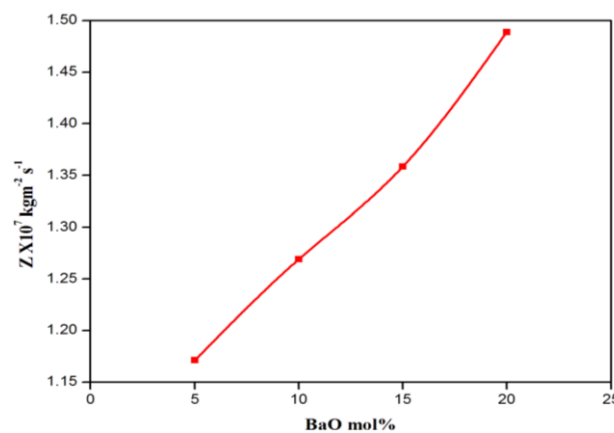


Fig. 2.8. Variation of acoustic impedance with BaO mol%

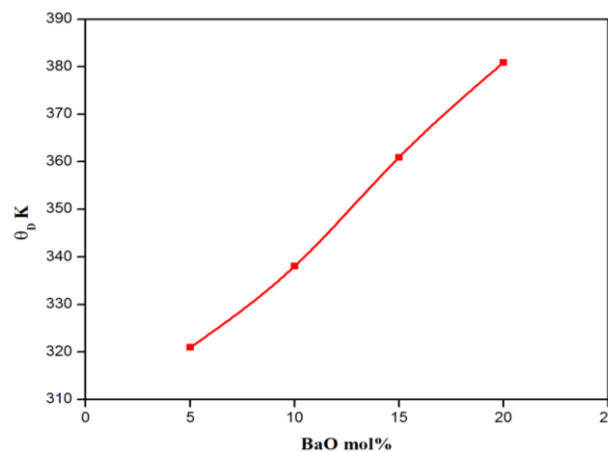


Fig. 2.9. Variation of Debye temperature with BaO mol%

IV. CONCLUSION

The $\text{B}_2\text{O}_3\text{-K}_2\text{O-BaO}$ glasses were prepared and characterized. Based on the results obtained, it is demonstrated that the density increases as the molar volume decreases with respect to the increase of BaO concentration. The ultrasonic velocities (U_l and U_s) were measured at room temperature using the pulse-echo method. The elastic moduli, Poisson's ratio, acoustic impedance and Debye temperature have been evaluated. The increase in the values of ultrasonic velocity, elastic moduli, acoustic impedance and Debye temperature has been attributed to an increase in the packing density and rigidity of glass samples. The Poisson's ratio values shows opposite trend. However, the BKBa series of glasses possess higher rigidity, strength and compactness of the glass network.

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 8, August 2015

REFERENCES

1. D.L. Griscom, Borate Glasses: Structure properties and applications. Plenum. Newyork. 1978.
2. A. Abd El-Moneim, Quantitative analysis of ultrasonic attenuation in TiO_2 . doped $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses. *Mat. Chem. & Phys* 98: 261-266, 2006.
3. L. Abd El-Moneim and Abd El- Latif , Theoretically calculated elastic moduli of tellurite, phosphate and silicate glasses. *Phys. Chem. Glasses* 44(6): 446-453, 2003.
4. T. Uchino, and T.Yoko, Sodium and lithium environments in single- and mixed-alkali silicate glasses. *J. Phys. Chem. B* 103 1854-1858, 1999.
5. Mitsuru Kawashima, Yu Matsuda and Seiji Kojima. Temperature dependence of elastic properties in alkali borate binary glasses. *J. Mole. Struc* 993:155-159, 2011.
6. L. Balachandera, G. Ramadevudub, Md. Shareefuddina, R. Sayannac, and Y.C Venudharc, IR analysis of borate glasses containing three alkali oxides. *Science Asia* 39: 278–283, 2013.
7. N. Nagaraja, T. Sankarappa, M., Prashant Kumar, P. Santosh Kumar, and J. Sadashivaiah, Dielectric relaxation studies in single and mixed alkali doped cobalt-borate glasses. *Optoelectronics & Advanced Materials – Rapid Communications* 2(1) 22 – 25, 2008.
8. D.W. Kim, D.G. Lee and K.S. Hong, Low-temperature firing and microwave dielectric properties of BaTi_4O_9 with Zn-B-O glass system. *Mater. Res. Bull* 36(3-4) 585-595, 2001.
9. R. Palani, and G. Srinivasan, Elastic properties of Ba^{2+} and Mn^{2+} metal iron doped lithium borate glasses using pulse echo technique. *Int. J. Rec. Sci Res* 3(11): 992-996, 2012.
10. J. Krogh Moe, Interpretation of the IR spectra of boron oxide and alkali borate glasses. *Phys. Che. Glasses* 6(2): 46-54, 1965.
11. F. A. Khalifa, Z. A. El-Hadi, F.A. Moustaffa and N. A. Hassan, Density and molar volume of some sodium silicate, lead borate and lead silicate glasses. *Indian J. Pure Appl. Phys* 27(6): 279-281, 1989.
12. Mitsuru, Kawashima, Yu matsuda, Synsuke, Aramomi and Seiji Kojima, High temperature Brillouin scattering of potassium borate glasses. *Proceeding of symposium on ultrasonic electronics* 30:433-434, 2009.
13. Mitsuru Kawashima, Yu Matsuda, Yasuteru Fukawa, Seiichi Mamiya, Masao Kodama and Seiji Kojima, Elastic properties of potassium borate glass in a wide composition range studied by Brillouin scattering. *Japanese J. of Appl Phys* 48: 07-03, 2009.
14. Mitsuru Kawashima, Yu Matsuda and Seiji Kojima, Temperature dependence of elastic properties in alkali borate binary glasses. *J. Mole. Struc* 993: 155–159, 2011.
15. Y. Fukawa, Y. Matsuda, Y. Ike, M. Kodama and S. Kojima, Glass Transitions and Elastic Properties of Lithium Borate Glasses over a Wide Composition Range Studied by Micro-Brillouin Scattering . *Jpn. J. Appl. Phys* 47: 3833-3835, 2008.
16. Yasuteru Fukawa, Yu Matsuda, Mitsuru Kawashima, Masao Kodama and Seiji Kojima, Brillouin scattering study of elastic properties of sodium borate binary glasses. *Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. B* 50 (3): 149–152, 2009.
17. A. Ramesh Babu, Ch. Rajyasree, P. Vinaya Teja, M. Yusub and S.P. Krishna Rao, Influence of manganese ions on spectroscopic and dielectric properties of $\text{LiF-SrO-B}_2\text{O}_3$ glasses. *J. Non - Crys. Solids* 358: 1391, 2012.
18. M.A. Sidkey, A.M Abd-El Fattah, L. Abd-El Latah and R.I. Nakhla, Ultrasonic studies on some sodium borate glasses. *J. Pure & Appl Ultrason* 12:93-97, 1990.