Behaviour of Ultrasonic velocities and elastic constants of xB_2O_3 - (75-x)PbO - $25P_2O_5$ and $xMoO_3$ - (75-x)PbO - $25P_2O_5$ glasses

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Abstract-Ultrasonic velocity and density measurements in B_2O_3 - PbO - P_2O_5 and MoO_3 - PbO - P_2O_5 composition glasses have been made at a temperature of 303 K by making use of Pulse Echo method. These measured values were used to evaluate elastic moduli such as longitudinal, Young's, bulk and shear, Poisson's ratio, acoustic impedance, micro hardness and Debye temperature. The structural and physical properties of th
e glass samples have been discussed in the light of the above parameters.

Index Term- longitudinal, Young's, bulk and shear, Poisson's ratio, acoustic impedance, micro hardness, Debye temperature.

1 INTRODUCTION

Interest in glasses has rapidly increased in recent years because of their diverse applications in electronics, nuclear and solar energy technologies, and acousto-optic devices. Among the various experimental methods available for studying structure- property relations, elastic properties of solid materials are of considerable significance. These measurement yields information concerning the forces that are operative between the atoms or ions in a solid. This is fundamentally important in interpreting and understanding the nature of bonding in the solid state. Therefore, the choice of the most appropriate material for particular application requires knowledge of its mechanical properties. Hence, elastic properties are suitable for describing the glass structure as a function of composition [1]. The propagation of ultrasonic waves in solids provides important information regarding the solid state motion in the material. The elastic moduli of glass are influenced by many physical parameters, which inturn may be studied by measuring the ultrasonic wave velocities. Significant work in this regard has been carried out for a number of alkaline-earth borate glasses [2-5]. Investigation of the elastic and acoustic properties of glasses is significant from the point of view of their applications in certain devices such as delay lines, light modulators and solid state sensors.

Phosphate based glasses find wide applications in various fields due to its varied physico-chemical properties. This glasses [6,7] have low melting and low softening temperature when compared with silicate and borate glass systems. Recently they have attracted considerable attention since they have great potential for using optoelectronic devices, (e.g., sealing materials for hybrid IC and PDP substrates).

Since B_2O_3 based glasses are important materials as thermal insulation (glass wool) and textile fiberglass (continuous filament), it is natural that recently, there have been reported many experiments regarding their structure from fundamental and practical applications points of view.

Lead borate glasses are highly transparent and exhibit very good glass formation over a large compositional region [8]. Moreover these glasses have desirable characteristics against irradiation since the naturally occurring stable boron isotope is a good absorber of thermal neutrons [9] and lead is known as a thick shielding material of γ – rays [10]. It is well known that the lead oxide (PbO) is

unique in its influence on the glass structure and is widely used in glasses because it enhances the resistance against devitrification, improves the chemical durability and lowers the melting temperature [11-15]. It can act both as a glass network former or modifier depending on its concentration of the glasses [16, 17].

Alkali borate glasses containing transition metal ions (TMI) have many technological applications owing to their important semi conducting and magnetic properties. Such properties depend mainly on the relative amounts of the different valence states of the doped TMI in the glass network [18, 19]. When glasses are doped with two different TMI, their technological applications become of high interest.

The present work aims to measure the ultrasonic velocity (both longitudinal and shear) and density for two series of glasses namely B_2O_3 - PbO - P_2O_5 (BPP) glasses and MoO_3 - PbO - P_2O_5 (MPP) glasses. These values have been used to evaluate longitudinal, Young's, bulk and shear moduli, Poisson's ratio, acoustic impedance, micro hardness and Debye temperature which will further insight into the rigidity and structure of glasses.

2 EXPERIMENTAL

2.1 Preparation of glass samples

The chemicals used for preparing the ten glass specimen were AR grade of B_2O_3, PbO, P_2O_5 and MoO_3. The required amount (≈10g) in mol% of different chemicals in powder form was weighed using single pan balance having an accuracy of ± 0.0001g. The homogenization of the appropriate mixtures of the components was effected by repeated grinding using a mortar. The homogenous mixture was put in a platinum crucible and placed in a muffle furnace. Melting was carried out under controlled conditions in the temperature range from 923K - 1173K and 823K - 973K for systems I and II respectively for 1 hour with occasional stirring. The molten sample was cast into copper mould having the dimension of 10mm diameter and 6mm height. Then the glass samples were annealed at 473K for two hours to avoid the mechanical strain developed during the quenching process. Thickness of the glass samples was measured using digital vernier calipers with an accuracy of 0.0001mm.

2.2 Measurement of Velocity

The ultrasonic longitudinal and shear velocities of the specimen were determined by using the conventional Pulse-Echo method. The pulser section generates electrical pulses, which are converted into ultrasonic signals using X-cut and Y-cut quartz transducers having the fundamental frequency of 5MHz. These transducers act as both transmitters and receivers of the ultrasonic pulse. The transducers were brought into contact with each of the ten samples by means of a couplant, in order to ensure that there was no air void between the transducer and the specimen. Couplant D-Gel type was used for longitudinal waves while resin was used for shear waves. By applying constant pressure on the probe the echo waveforms were obtained on the display unit and stored in the memory.

The computer controlled Pulse-Echo system used for the measurements had two softwares, one for storing the data as seen on the screen and the second for analysing the same. These softwares were programmed in such a way that by just feeding the thickness of the specimen and the frequency of the ultrasonic waves, the display unit will show the amplitude and velocity of the ultrasonic wave having the particular frequency and thickness. Ultrasonic velocity is obtained by the relation.

$$U = \frac{2d}{t}$$

where U, the velocity of the specimen (ms^{-1}), d, thickness of the specimen (mm) and t, transit time in micro seconds.

2.3 Measurement of density

The density of the glass samples was measured using Archimede's principle. Benzene was used as a buoyant liquid. The glass samples were weighed both in air and after immersing in benzene at 303K. The weight of the glass samples was measured using a single pan balance with an accuracy of 0.0001g. The density was calculated using the formula

$$\varrho = [w_1/(w_1 - w_2)]\ \varrho_B$$

where w1 and w2 are the weight of the glass samples in air and in benzene. ρ_B is the density of benzene at 303 K.

3 THEORY

The various elastic properties investigated were calculated using the following relations:

Longitudinal modulus $L = \rho U_\ell^2$

Shear modulus $G = \rho U_s^2$

Bulk Modulus $K = L-(4/3)G$

Poisson's ratio $\sigma = (L-2G)/2(L-G)$

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

Acoustic impedance $Z = U_\ell \rho$

Micro hardness $H = (1-2\sigma)[E/6(1+\sigma)]$

Debye temperature $\theta_D = (h/K)(9N/4\pi V_m)^{1/2}\ (1/U_\ell^3 + 2/U_s^3)^{-1/3}$

where ρ is the density, h the Planck's constant, K the Boltzmann constant, N the Avogadro number and Vm the molar volume of the sample.

4 RESULTS AND DISCUSSION

4.1 X-ray diffraction

X-ray diffraction is a useful method to detect readily the presence of crystals in a glassy matrix if their dimensions are greater than typically 100nm [20].The X-ray diffraction pattern of an amorphous material is distinctly different from that of crystalline material and consists of a few broad diffuse halos rather than sharp rings. All the samples were tested and the results showed the absence of crystalline characteristics.

Fig. (1 & 2) shows the typical X-ray diffraction patterns for these compositions. The patterns obtained do not reveal any crystalline phase in the glass.

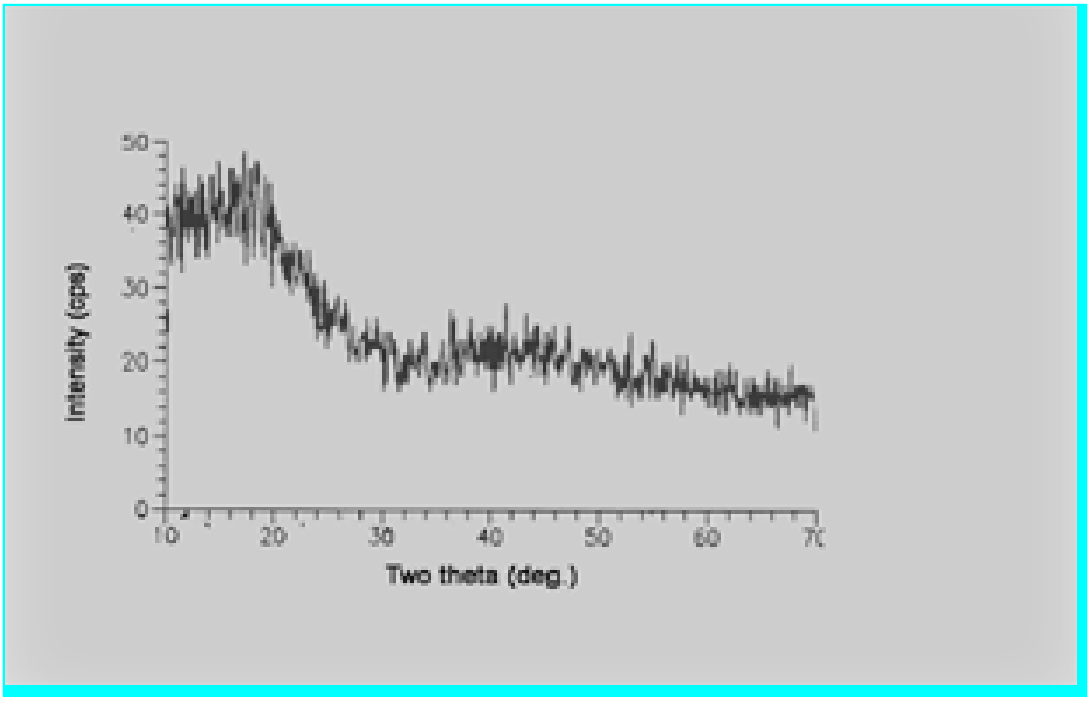

Fig. 1. XRD Spectrum of BPP glass

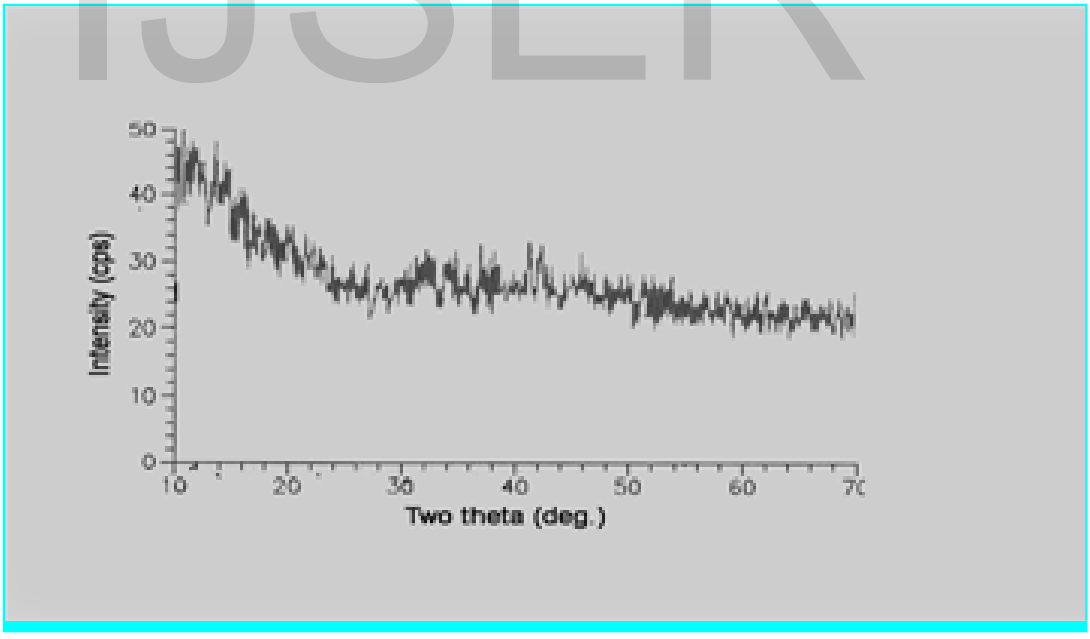

Fig. 2. XRD Spectrum of MPP glass

4.2 Density and Ultrasonic velocity

Series of glass samples and Nomenclature are given in Table 1.

TABLE 1 NOMENCLATURE

Series I [xB_2O_3 - (75-x)PbO - $25P_2O_5$]

Sample No.	Nomenclature	Composition in mol% B_2O_3 – PbO – P_2O_5	Remarks
1.	BPP1	50 – 25 – 25	
2.	BPP2	52 – 23 – 25	
3.	BPP3	54 – 21 – 25	Mol% of P_2O_5 is constant
4.	BPP4	56 – 19 – 25	
5.	BPP5	58 – 17 – 25	

Series II [$xMoO_3$ - (75-x)PbO - $25P_2O_5$]

Sample No.	Nomenclature	Composition in mol% MoO_3 – PbO – P_2O_5	Remarks
1.	MPP1	50 – 25 – 25	
2.	MPP2	52 – 23 – 25	
3.	MPP3	54 – 21 – 25	Mol% of P_2O_5 is constant
4.	MPP4	56 – 19 – 25	
5.	MPP5	58 – 17 – 25	

The values of density, longitudinal (U_ℓ), shear (U_s) velocity, longitudinal and shear modulus as well as elastic constants such as bulk modulus, Young's modulus and Poisson's ratio, micro hardness, acoustic impedance and Debye temperature are given in Table 2.

The density is an intrinsic property capable of casting the light on the short range order structure of a solid like glass. It is known that, B_2O_3 in its glassy form is a laminar network consisting of boron atoms three fold coordinated with oxygen upon modification with an alkali oxide the additional oxygen, obtained by the oxide dissociation, causes a conversion from the trigonal boron atoms BO_3 into four fold BO_4 coordinated boron atom. Each BO_4 structural group is negatively charged and four-oxygen are included in the network as bridging oxygen. Moreover, the transformation of molybdenum from six-fold coordination to four-fold coordination and the probable increase in the number of the non-bridging oxygen assist also the gradual increase of density [21]. These units are responsible for the increase in the connectively of the glass network.

The Values of density for series I increased from 2.9634 to 3.0121 kgm^{-3} and for series II increased from 3.0154 to 3.1573 kgm^{-3} with increase in mol% of B_2O_3 and MoO_3 respectively. Koudelka [22] showed that that the density increases linearly with mol% and they attributed this behaviour to an

increase in the rigidity of the glass. In the case of the glasses investigated the density value increase in the order from MoO_3 to B_2O_3.

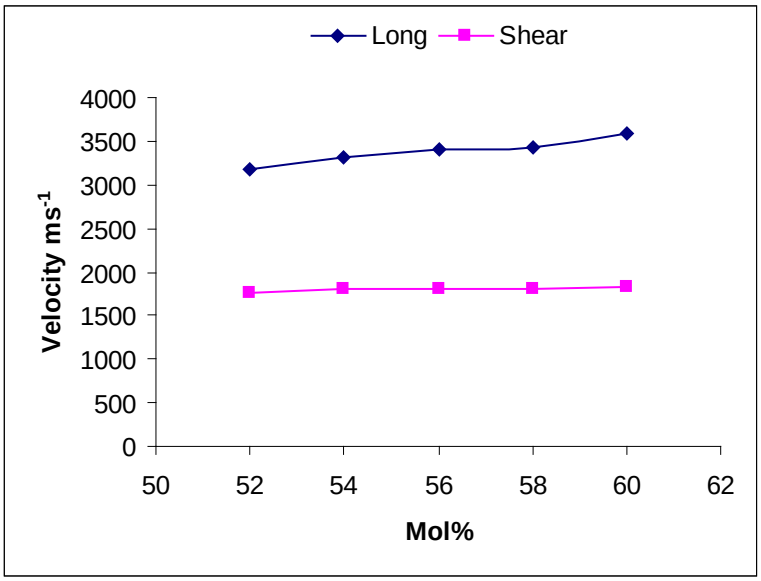

Fig.3 Composition (Mol % of B_2O_3) Vs Ultrasonic (Longitudinal and Shear) velocity for series I

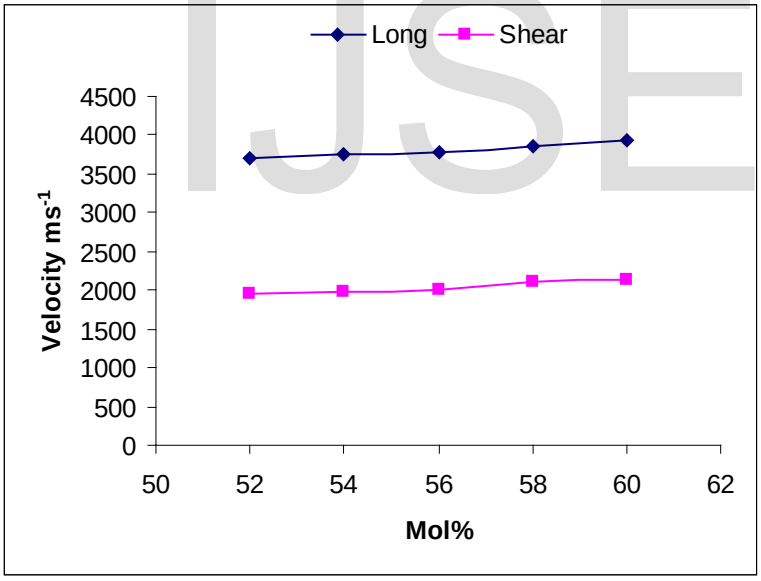

Fig.4 Composition (Mol % of MoO_3) Vs Ultrasonic (Longitudinal and Shear) velocity for series II

From the Table 2, it is found that both longitudinal and shear velocity increase almost regularly with the concentration of B_2O_3 and MoO_3 in both BPP and MPP glass systems, but the rate of increases of U_ℓ is greater than that of U_s for both system investigated (Figs. 3 & 4) . The increase in ultrasonic velocity has been attributed to an increase in packing density due to the transformation of co-ordination of boron from 3 to 4 and consequent occupation of the interstices by the alkali ions. But once BO_4 groups get saturated non-bridging oxygen start appearing producing a loose structure [23]. The increase of ultrasonic velocity is related to the increase in the connectivity and strength of the glass network [24-27].

4.3 Elastic moduli and Acoustic impedance

The elastic moduli (Figs. 5 & 6) such as longitudinal, shear, bulk and Young's modulus show a similar behaviour as that of density and velocity in both glass systems. Since the rigidity of the materials increases with their elastic moduli, it is therefore practical to assess the strength indirectly from their elastic properties. Simple combination of the measured ultrasonic velocities and density allow determination of the acoustic impedance (Z), elastic moduli (longitudinal (L), shear(s), bulk (K), and young's (E)) and Poisson's ratio (σ). One can note from Fig 8 that the acoustic impedance and all elastic moduli follow the same trend as ultrasonic velocities, i.e., increase in the order $MoO_3 > B_2O_3$. Xihuai and Pengnian [28] have made similar analysis in z value.

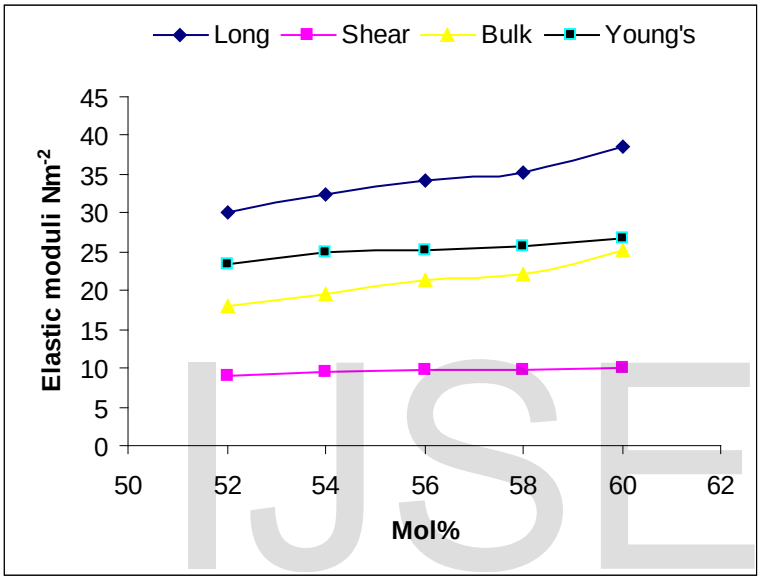

Fig.5 Composition (Mol % of B_2O_3) Vs Elastic moduli (Longitudinal, Shear, Bulk and Young's) for series I

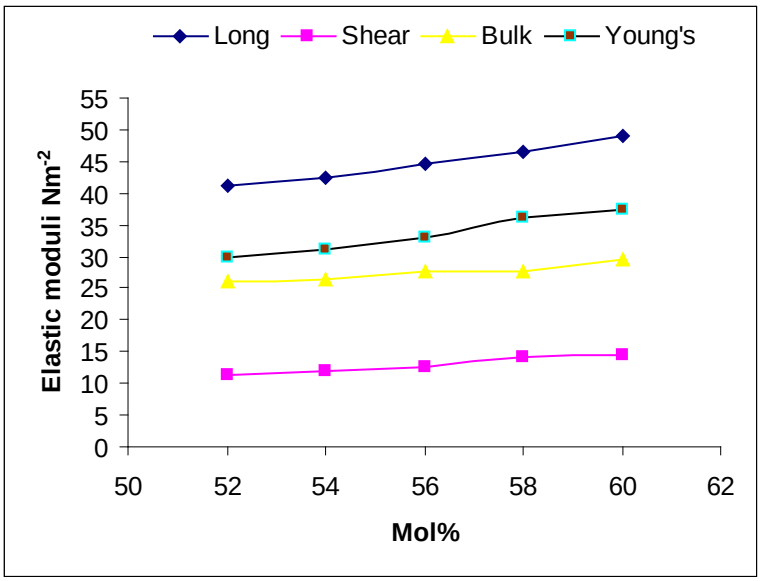

Fig.6 Composition (Mol % of MoO_3) Vs Elastic moduli (Longitudinal, Shear, Bulk and Young's) for series II

4.4 Poisson's ratio, Micro hardness and Debye temperature

Poisson's ratio (σ) is formally defined for any structure as the ratio of lateral to longitudinal strain produced when tensile forces are applied. In glasses, changes in Poisson's ratio reflect the dimensionality changes in the network. The value of Poisson's ratio (Fig.7) was found to increase with increase in B_2O_3 and MoO_3 concentration. This same trend is observed by Sidkey et al [23].

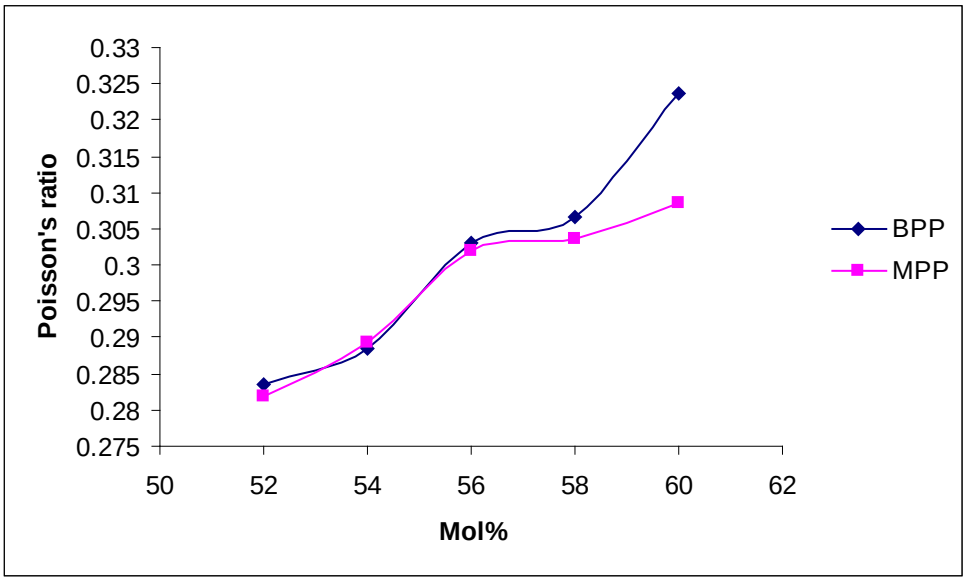

Fig.7 Composition (Mol % of B_2O_3 and MoO_3) Vs Poisson's ratio for series I and series II

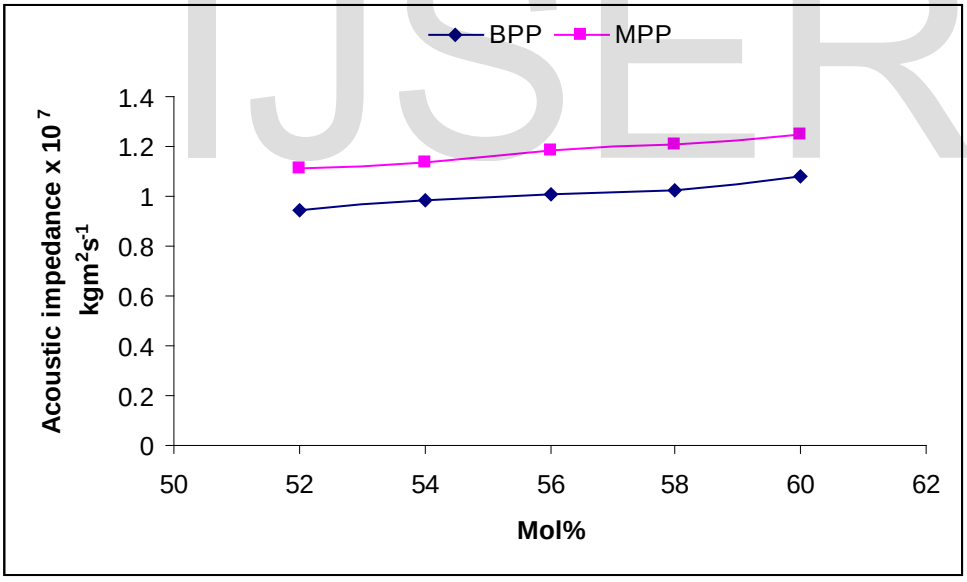

Fig.8 Composition (Mol % of B_2O_3 and MoO_3) Vs Acoustic impedance for series I and series II

TABLE 2 DENSITY (ρ), LONGITUDINAL VELOCITY (U_l), SHEAR VELOCITY (U_s), LONGITUDINAL MODULUS(L), SHEAR MODULUS(G), BULK MODULUS(K), YOUNG'S MODULUS(E), POISSON'S RATIO(Σ), ACOUSTIC IMPEDANCE(Z), MICRO HARDNESS(H) AND DEBYE TEMPERATURE(Θ_D)

Glass sample	Density ρ	Ultrasonic velocity ms^{-1}		Elastic moduli Nm^{-2}				Poisson's ratio σ	Acoustic impedance Z	Micro hardness H	Debye temperature θ_D
	$x10^{-3}$ kgm^{-3}	Long(U_l)	Shear(U_s)	Long(L)	Shear(G)	Bulk(K)	Young's(E)		$x10^7$ $kgm^{-2}s^{-1}$	$x10^9$ Nm^{-2}	K
Series I [xB_2O_3 - (75-x)PbO - $25P_2O_5$]											
BPP1	2.9634	3183.2	1750.2	30.02	9.07	17.92	23.30	0.2834	0.9433	2.1593	440.87
BPP2	2.9678	3304.5	1801.5	32.40	9.63	19.56	24.82	0.2886	0.9807	2.2543	452.58
BPP3	2.9718	3397.0	1805.7	34.28	9.68	21.37	25.25	0.3031	1.0093	2.1595	452.97
BPP4	2.9843	3434.5	1813.4	35.20	9.81	22.12	25.65	0.3067	1.0250	2.1591	465.34
BPP5	3.0121	3578.3	1826.9	38.56	10.05	25.16	26.62	0.3237	1.0778	2.0702	475.49
Series II [$xMoO_3$ - (75-x)PbO - $25P_2O_5$]											
MPP1	3.0154	3693.5	1943.4	41.14	11.39	25.95	29.80	0.2820	1.1137	2.4887	507.92
MPP2	3.0321	3742.1	1987.5	42.46	11.97	26.49	31.23	0.2892	1.1346	2.6656	508.92
MPP3	3.1232	3783.5	2015.3	44.71	12.69	27.80	33.03	0.3020	1.1817	2.8389	519.33
MPP4	3.1356	3845.2	2118.3	46.36	14.08	27.59	36.10	0.3035	1.2057	3.3630	531.04
MPP5	3.1573	3942.6	2147.0	49.08	14.55	29.67	37.52	0.3086	1.2448	3.3992	535.70

The micro hardness is seemingly another property characteristic of solids. It is defined as the resistance of a material to permanent indentation or penetration. As expected, the calculated H values (Fig.9) increase in the same order as elastic moduli. This confirms the increase in the stiffness (rigidity) of the glass network in the order $MoO_3 > B_2O_3$.

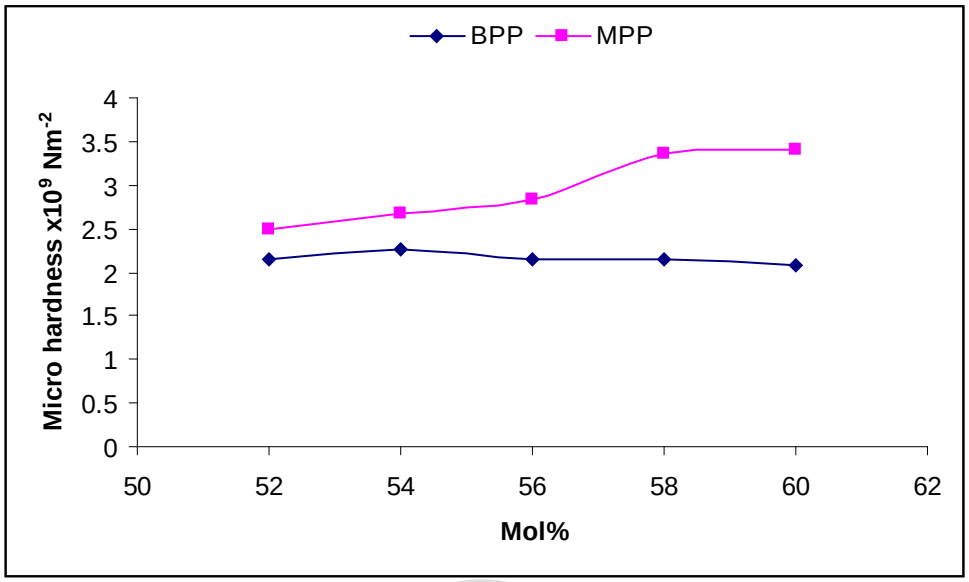

Fig.9 Composition (Mol % of B_2O_3 and MoO_3) Vs Micro hardness for series I and series II

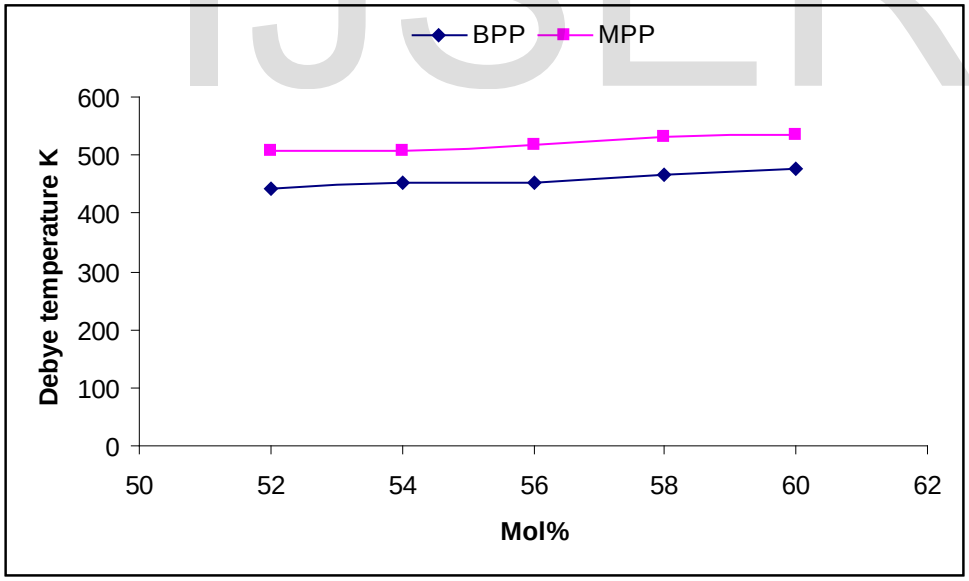

Fig.10 Composition (Mol % of B_2O_3 and MoO_3) Vs Debye temperature for series I and series II

Like other parameters, Debye temperature which is calculated from ultrasonic data is particularly sensitive with glass composition. The observed θ_D (Fig.10) in the glass network suggests the stiffness of the glass structure with incorporation of B_2O_3 / MoO_3 is the glass network. Similar increase in θ_D value were also observed by Rajendran et al [29].

5 CONCLUSION

Ultrasonic velocity of longitudinal and transverse waves has been measured in two ternary glass systems. The elastic constants and Poisson's ratio, acoustic impedance, micro hardness and Debye temperature have been evaluated. The increase in the values of ultrasonic velocity and elastic constants has been attributed to an increase in the packing density and rigidity of the glass samples when the concentration of B_2O_3 / MoO_3 in the two systems of glasses is increased. The composition dependences of density, ultrasonic velocity, elastic moduli and microhardness show that the rigidity of the glasses increases in the order $MoO_3 > B_2O_3$.

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