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Detailed Investigation of Phenomenon "MIXED ALKALI EFFECT" by Doping Alkali Ions with different Cationic Sizes with Equal Molar Concentration in Borate Glasses. An Ultrasonic Study at 10 MHz and Explanation by "Random Network Model"

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Abstract: The alkali metal ions with remarkable difference in ionic radii can cause variations longitudinal and transverse ultrasonic velocities when doped in pure borate glasses. The glass family represented by the general formula a Li_2O -b Na_2O- [1-a-b] B_2O_3 are well studied .by varying total alkali ion concentration[a+b] from 5% to 45%mol percentage. The velocities are measured using well known Pulse Echo Overlap method [1] using MATEC MODEL 7700 Pulse modulator and Receiver system at 10MHz using X cut and Y cut quartz transducers The "Mc Skimin Δt Criterion" [2] is applied so that velocities are accurate up to 0.01%. The results highlight the Phenomenon "Mixed Alkali Effect" [3,4,5]. Micro-hardness of these samples are also measured. The values are plotted against alkali ion concentration. The 'MAE' are found to get reflected in the values of elastic constants C_{11}, C_{44}, Young's modulus[Y], bulk modulus[K], Poisson's ratio. Micro-hardness of these samples are also measured. The temperature variation of C_{11} and C_{44} are measured form 293K to420K. The results obtained are interpreted on the basis of random network model [4]

Keywords: Mixed Alkali Effect, Pulse Echo Overlap, Mc Skimin Δt Criterion, Micro-hardness, random network model

I. INTRODUCTION

The B2O3 is a high glass former and different alkali ions or alkaline metal ions or transition metal ions can be easily doped in it, affecting its mechanical and optical properties. is high [6]. The enhancement of glass network can be achieved by doping the glass with alkali or alkaline earth metal ions. [Na+, K+, Li+] or alkaline earth metal ions [Zn2+, Pb2+.Ba2+]. In the present work we are giving prime importance for investigation of these above properties. The spectroscopic studies reveal that these ions can act as a network former and network modifier [7]. The non-linear variations of ultrasonic velocities and micro-hardness and optical properties are. collectively named as "Mixed alkali effect" [8,9,10 11,12,13,1415 16]. The modulation of these properties are the main attraction during the past years and attempted to give the explanation of MAE [17,18,19,20]. When the glasses are doped with Er^{3+}ions can be used in fibre amplifiers, laser materials,]

In the present work with alkali ion concentration equal we measured the values of Longitudinal velocity and Transverse velocity using quartz transducer at 10MHz Addition of various alkali modifiers like sodium oxide, lithium oxide, potassium oxide and alkaline earth metal ions like calcium, lead oxide, zinc oxide to the borate glasses brings drastic changes in the structural units. Lithium borate glasses have good ionic conductance properties. Since the addition of Li_2O and Na_2O to the borate glass adds extra oxygen atoms, which gets accommodated in the network, a transfer of some boron atoms from triangle BO_3 to tetrahedral BO4 occurs. In oxide glasses Li_2O and Na_2O are classified as glass network modifier. This means that, in borate glasses, they modify the borate network by forming either BO_4 units or non-bridging oxygen ions (NBOs), but they are not able to build any own structural units. It is found that alkali ion migration produces structural variations coordination of oxygen atoms are a successful in explain the non -linear shift B-O-B stretching and B-O-B bending frequencies. In the present work we studied the MAE in ***aLi_2O -bNa_2O- [1-a-b] B_2O_3*** glasses with larger variations in total alkali concentration Ultrasonic tools are very important for characterizing materi-als because they have many applications in chemistry, physics, engineering, biology, food industry, and medicine, etc. (7)

Ultrasonic technique similar to other techniques plays a significant role in understanding the structural characteristics of glass network. Ultrasonic characterization of materials is a versatile tool for the inspection of their microstructure and their mechanical properties [19] The measurement of ultrasonic parameters such as ultrasonic velocity and attenuation as a function of composition, temperature and frequency is of great interest in glass. The ultrasonic parameters besides density and molar volume as sensitive and informative about the changes occurred in the structure of glass network [20] The ultrasonic velocity, and hence, elastic properties are particularly suitable for describing glasses because they give some information about the microstructure and the dynamics of glasses. So, the ultrasonic study of the borate lithium glasses is very important as they can provide us with some idea about the glass structure [21]. For glasses, ultrasonic investigation is very useful as besides providing information on rigidity it also can indicate a structural modification of the glass network. The measurement of elastic properties of glasses by pulse-echo method becomes a more interesting subject, due to the non-destructive nature and the high precision of the technique. The measurement yields valuable information regarding the forces operating between the atoms or ions in a solid. Since the elastic properties describe the mechanical behaviour of the materials, so the study of these properties is of fundamental importance in interpreting and understanding the nature of bonding in the solid state [22] Hence, the elastic properties are suitable for describing the compactness of glass structure [23]

It is found that alkali ion migration produces structural variations coordination of oxygen atoms are a successful in explain the nonlinear shift B-O-B stretching and B-O-B bending frequencies. In the present work we studied the MAE in ***a*** Li_2O ***-b*** Na_2O***- [1-a-b]*** B_2O_3 glasses with larger variations in total alkali concentration

A. Sample Preparation And Experimental Technique

Glasses with the general formula ***a***Li_2O ***-b***Na_2O***- [1-a-b]*** B_2O_3 are prepared by melt quenching technique. The H_3BO_3 and Li_2O and Na_2O are collected from MERCK are off 99.9% pure. The total alkali concentration in mole percentage are varied as 5%,0%,15%,20%,25%,28%,30%,33%,35%,40% and 45%, weighed in The glasses appropriate quantities using digital balance having accuracy 0.0001 are taken and is mixed in an agate mortar so that so that samples have maximum homogeneity. The mixture is taken to a furnace and preheated up to a temperature of 500^0 C in order to remove all water content in the mixture. The sample is heated up to 875^0 C to 1000 ^{0}C and is well mixed and kept above temperature for 15-30 minutes for maximum fluidity. The melt is poured into a dye which is preheated, so that samples of diameter 12mm and thickness 8mm are obtained. The sample is then subjected to annealing 425^0C for two hours so that thermal strain is avoided. The end surfaces of samples are well polished and parallelism is assured by interference method. The densities of the samples are measured by using Archimedes method. The buoyant liquid is acetone.

The densities are calculated using the formula d= $\frac{w1}{w1-w0}$ d_a where $w_1$is weight in acetone and w_0 is the weight in air and d_a is the density of acetone The values of densities obtained are in good agreement with those measured using other techniques.

The longitudinal and transverse ultrasonic velocities inside the samples are measured using "PEO" method which is already mentioned above.

The "McSkimin Δt Criterion" is applied. The bonding material used for longitudinal measurements, Nonaque grease and for transverse measurements is Stopwatch grease. The bond correction is also applied. The values of C_{11} and C_{44} and Young's modulus Y, bulk modulus K, Poisson's ratio, bond connectivity and acoustic impedance and K and σ are calculated from the following equations given below

$$C_{11} = d\, V_L^2 \quad [1]$$

$$C_{44} = d\, V_T^2 \quad [2]$$

$$Y = \frac{C44\{3\,C11-4C44\}}{C11-C44} \quad [3]$$

$$K = \{3C11 - 4C44\}/3 \quad [4]$$

$$\sigma = [1 - Y/3K]/2 \quad [5]$$

$$F = 4\, C44/K \quad [6]$$

$$Z = V_l\, d$$

The refractive index is given by the square root of dielectric constant. The capacitance is measured by inserting the sample in between the plates of two metal sheets which forms a capacitor. The capacitance is measured by capacitance meter. The cell designed by me for this measurement is given in figure1 The capacitance that obtained is in the order of Picofarads. The distance between the metal plates can be varied by rotating a micrometre screw attached to the cell. The plate area is 10mm ^{2}.

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II. RESULTS AND DISCUSSION

The variations of longitudinal velocity and transverse velocity, the elastic constants, Young's modulus, and bulk modulus, and Poisson's ratio are given in the table below

Sample Identity density gm/cc	V_l ms^{-1}	V_t ms^{-1}	C_{11} GPa	C_{44} GPa	Y GPa	K GPa	σ	F	Acoustic Impedance Z_l $Kgm^{-2}s^{-1}$ 10^3
LNB5 2.122	6122	2767	79.45	16.23	43.83	57.81	0.3737	1.123	12.98
LNB[10] 2.161	6231	2967	83.86	19.04	52.17	58.18	o.3505	1.309	13.46
LNB15 2.232	6389	3277	91.03	23.95	60.92	59.09	0.3281	1.621	14.25
LNB20 2.283	6458	3348	95.09	25.56	67.38	61.01	0.3159	1.656	14.72
LNB25 2.322	6635	3577	101.25	29.42	76.21	62.02	0.2952	1.897	15.26
LNB30 2.335	6744	3722	105.97	32.27	82.68	62.94	0.2790	2.050	15.71
LNB32 2.351	6798	3768	108.60	33.29	85.15	64.21	0.2789	2.074	15.98
LNB33 2.388	6802	3799	110.12	34.35	87.46	64.32	0.2733	2.130	16.19
LNB35 2.392	6484	3552	98.38	29.52	72.05	59.02	0.2966	2.006	15.17
LNB40 2.400	6458	3440	98.42	27.93	72.72	61.18	0.3018	1.826	15.24
LNB45 2.412	6288	3281	93.71	25.52	67.01	59.71	0.3129	1.523	14.90

The values of V_L, $V_{T,}$ C11, C44, Y and K the table are plotted against alkali mol% [Fig.1, Fig.2, Fig.3, Fig.4, Fig.5]

Fig.1

Fig.2

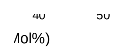

Fig.3

Fig.4

Fig.5

The values of longitudinal ultrasonic velocity and transverse velocity increases up to the total alkali concentration 33% and there after decreases slowly. The pronounced increase of longitudinal velocity is due to lithium ions are observed. The transverse also follows the same. The same type of variation is also followed by elastic constants C_{11} and C_{44} and Young's modulus and bulk modulus. The structure of B_2O_3 glasses consisting of BO_3 triangles. The addition of alkali ions creates BO_4 groups according to NMR results [14]. Critical dependence of mechanical properties like elastic constants are on the composition of BO4 groups. This is due to these units can enhance the dimensionality and network connectivity. As concentration of alkali ions increases from zero to 0.33% there happens a change of co-ordination number of boron atoms from 3 to 4. [14.15] and becomes maximum at total alkali concentration of 0.33mol%. If concentration of alkali ions are further increases the study of NMR reveals a cessation in the process of each added oxygen converting two boron atoms from BO_3 to BO_4 configuration [16]. The production of singly bonded oxygen atoms reduces the fourfold coordination significantly. In triangular arrangement requires for local charge density compensation by the modifying cation sample. So all singly bonded oxygen atoms are presumably associated with BO_3 triangles rather than BO_4 tetrahedron's causes decrease of elastic constants if total alkali concentration increases beyond 33%. The results establish the fact that the total alkali concentration value of 33% is more accurate other than the values reported by other authors as 30%.

Poisson's ratio can be explained on the basis of the effect of tensile stress on an oriented chain of atom or ions. If strain is lateral to the chain, its effect is maximum for lowest cross-links. Rajendran et al (23) reported that the Poisson's ratio is affected by the changes in the cross-link density of the glass network, and the structure with high cross-link density has Poisson's ratio in the order of 0.1-0.2, while structure with low cross-link density has Poisson's ratio in the order of 0.25- 0.5 [23] The experimental values of Poisson's ratio first decreases from the value0.3737 to0.2966 thereafter increases. The increase in Poisson's ratio is due to breaking of network linkages and formation of smaller structural units in the glass samples. Further, a low cross-link density leads to an increase in Poisson's ratio. while the fractal bond connectivity F decreases. Therefore, increasing of Poisson's ratio shows that the reducing of cross-link density due to more number of non-bridging oxygen. The Poisson's ratio values are increasing behaviour due to the increase in molar volume which means that the structure becomes more open. Therefore, the change in behaviour of Poisson's ratio as a sensitive tool for the glass compositions is attributed to the change in the type of bonding.

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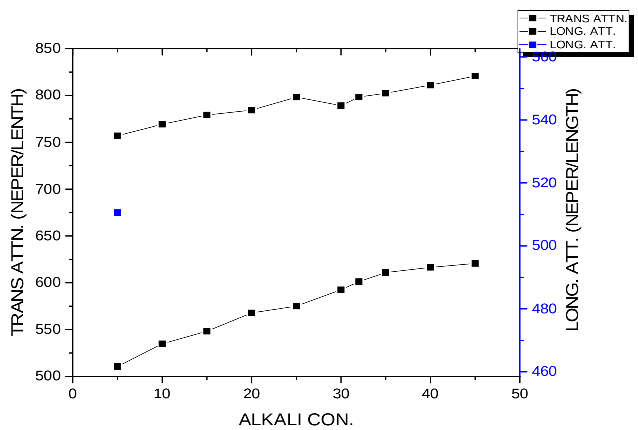
A. Measurement of Ultrasonic Attenuation at 10MHZ

The values of both longitudinal and transverse ultrasonic attenuation in the glass samples are measured by measuring the amplitudes of the successive echoes in the oscilloscope and making an Exponential fit. The values of ultrasonic attenuation increases as alkali concentration increases. The result is accurate up to 3% accuracy.

Name of sample	Transverse attenuation Nepers per unit length	Longitudinal attenuation Nepers per unit length
LNB[5]	510.6	756.9
LNB[10]	534.8	769.3
LNB[15]	548.3	779.1
LNB[20]	567.8	784.3
LNB[25]	575.1	798.2
LNB[30]	592.5	789.1
LNB[32]	601.2	798.2
LNB[33]	610.9	802.4
LNB[35]	616.5	811.0
LNB[40]	620.6	820.7



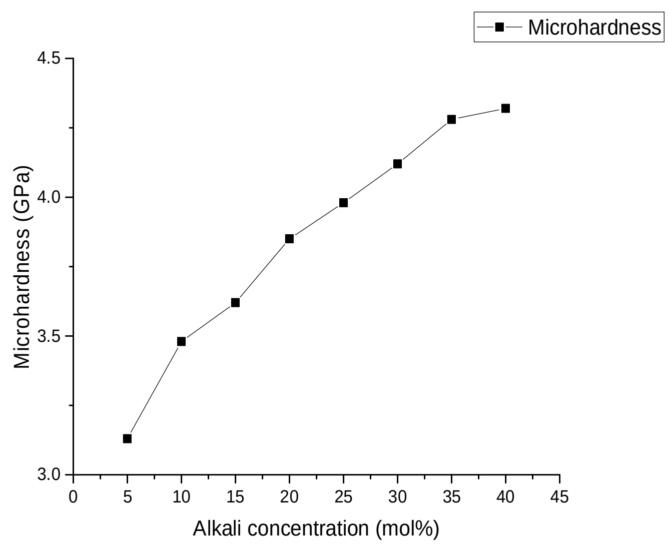
B. Temperature Variation of Elastic Constants

The samples are kept inside thermostat and temperature is varied from room temperature to 120^{0}C. It is found that as temperature increases both longitudinal and transverse velocities decreases. Samples LBK 20, LBK30, are selected for measurements. This is because other samples will follow the same type of variation

C. Microhardness Measurements

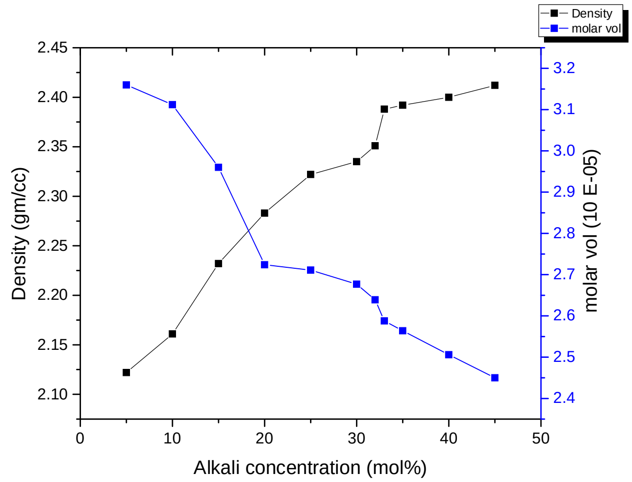
The microhardness of the samples is also measured and is shown in the table It is found the microhardness of the samples increases with increases of alkali ion concentration

SAMPLE NAME	MICROHARDNESS [GPa]
LNB5	3.13
LNB10	3.48
LNB15	3.62
LNB20	3.85
LNB25	3.98
LNB30	4.12
LNB35	4.28
LNB40	4.32



The increase of microhardness is due to increase in density with increase of alkali concentration. The molar volume decreases due to network enhancement corresponding an increase of density. The density and molar volume are given tin the table

SAMPLE NAME	DENSITY	MOLAR VOLME $10^{-5}m^3$per mol%
LNB[5]	2.122	3.160
LNB[10]	2.161	3.112
LNB[15]	2.232	2.963
LNB[20]	2.283	2.724
LNB[25]	2.322	2.711
LNB[30]	2.335	2.677
LNB[32]	2.351	2.639
LNB[33]	2.388	2.588
LNB[35]	2.392	2.564
LNB[40]	2.400	2.506
LNB[45]	2.412	2.450



III. CONCLUSION

The mechanical measurements like elastic constants, micro hardness clearly establishes the phenomenon Mixed Alkali Effect, and it is due to the network enhancement by the alkali ions in borate network. The measurements establish the fact that the mixed alkali effect causes increase in mechanical properties up to a total alkali concentration 33% mole and there after decreases. The network enhancement is well studied in this samples and the results highlights phenomenon "Mixed alkali effect."

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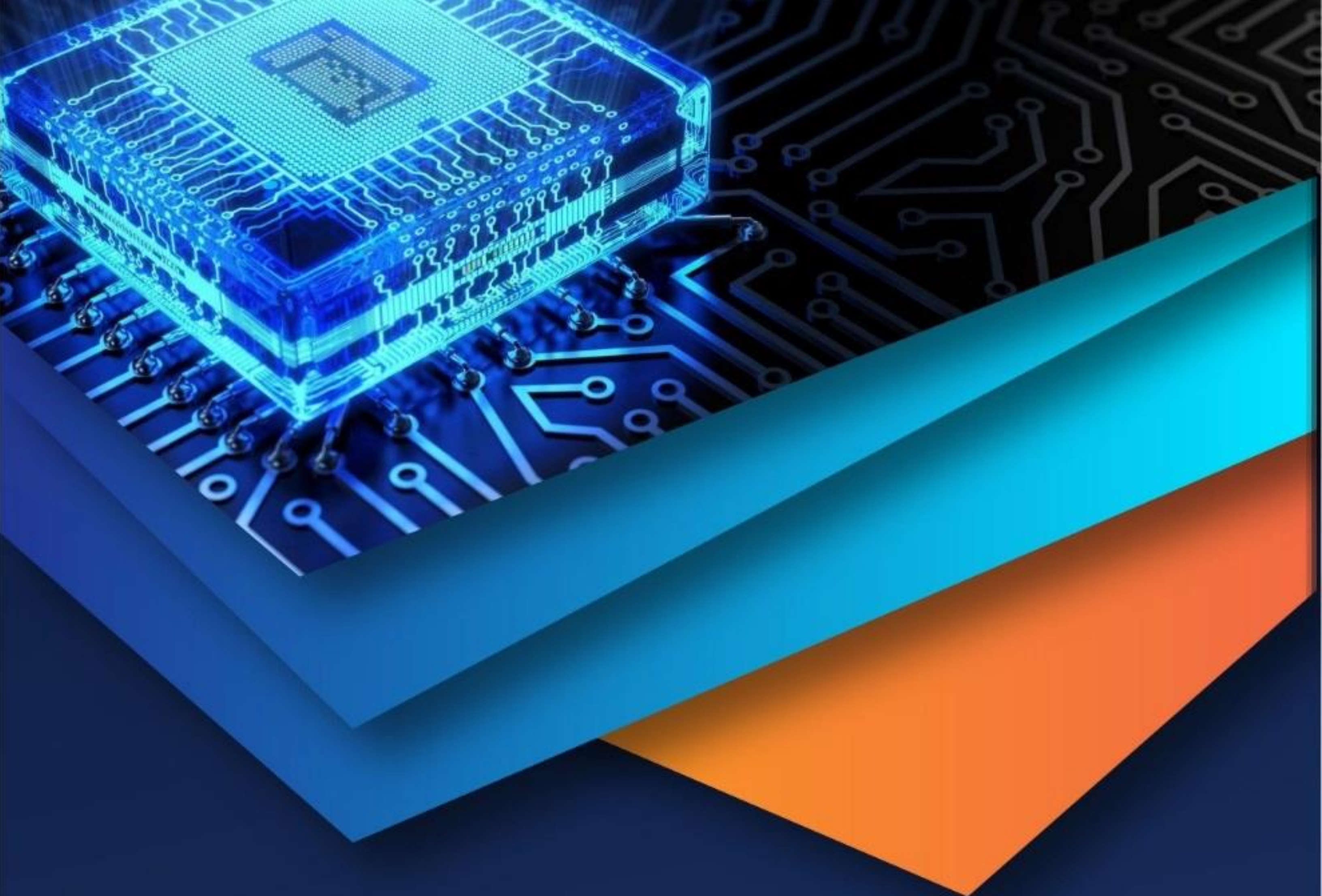

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