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Mechanical Properties Enhancement due to Network Modification by different Alkali Ions at Equal Concentration Doped in Borate Glasses-An Ultrasonic Investigation at 10MHz on the Phenomenon "Mixed Alkali Effect"

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Abstract: The host alkali metal ions can influence longitudinal and transverse ultrasonic velocities when doped in pure borate glasses. The glass family represented by the general formula A Na_2O -B K_2O- [1-A-B] B_2O_3 are well studied .by varying total alkali ion concentration[A+B] from 5% to 45%.
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 highlights 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. The ultrasonic attenuation at 10 MHz is also measured . Micro-hardness of these samples are also measured.
The temperature variation of C_{11} and C_{44} are measured form 293K to403K .The results obtained are interpreted on the basis of random network model [6]
Keywords: Mixed alkali effect [MAE], Pulse echo overlap, elastic constants micro hardness, molar volume

I. INTRODUCTION

The glass formation tendency of B_2O_3 is high peaked [7].The most important property of amorphous material is they are transparent in the visible spectrum. The dopant alkali metal ions [Na+, K+, Li+] or alkaline earth metal ions [Zn2+, Pb2+,.Ba2+] enhances the network. Due to this reason Mechanical and optical properties undergoes variations with increase in dopant concentration. In the present work we are giving prime importance for investigation of the mentioned properties.
The spectroscopic reals that these ions can act as a network former and network modifier. The non-linear variations of ultrasonic velocities and micro-hardness and optical properties are. collectively named as "Mixed alkali effect" [8,9,10 11,12,13,14,15 16].The modulation of these properties are the main attraction during the past years and many authors gave explanation of MAE [17]. When the glasses are doped with Er^{3+}ions can be used in fibre amplifiers, laser materials, [17] and in solid state batteries fuel cells and chemical sensor[A] High bond strength and low cationic size make the borate glasses as a suitable material for dielectric.[18]
In the present work involves the study of structural variation inside the sample keeping the concentration of alkalies equal and velocities and attenuation are measured at high frequency 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 Na_2O and K_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 K_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 A Na_2O -B K_2O- [1-A-B] B_2O_3 glasses with larger variations in total alkali concentration Ultrasonic tools are very important for characterizing materials 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]

A. Sample Preparation and Experimental Technique

Glasses with the general formula A Na_2O -B K_2O-[1-A-B] B_2O_3 are prepared by melt quenching technique.TheH_3BO_3 and K_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 475^0 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 7mm are obtained. The sample is then subjected to annealing 370^0C for two hours so that thermal strain are 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 at 10MHz which is already mentioned above.

The “Mc Skimin 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 Y and K and σ are calculated from the following equations given below

$$C_{11} = d\, V_L^{2}$$

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

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

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

Poisson’s ratio $q = [C11\text{-}2Cc44]/2\,[C11\text{-}C44]$

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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 Kg m^{-3}	V_l ms^{-1}	V_t ms^{-1}	C_{11} GPa	C_{44} GPa	Y GPa	K GPa	q
NHB5 2.042	4205	2210	36.07	9.96	26.09	22.79	0.3091
NHB10 2.112	4415	2310	41.13	11.25	29.51	26.13	0.3117
NHB15 2.15	4607	2457	46.26	13.16	34.27	28.71	0.3010
NHB20 2.190	4878	2508	53.53	13.90	36.82	34.99	0.3246
NHB25 2.221	5012	2620	55.77	15.23	39.96	35.46	0.3122
NHB28 2.263	5259	2812	62.51	17.87	46.45	38.68	0.3000
NHB30 2.291	5358	2952	65.74	19.96	51.27	38.93	0.2765
NHB32 2.312	5402	2980	67.40	20.51	52.53	40.05	0.2826
NHB33 2.36	5489	2997	71.11	21.20	54.59	42.44	0.2856
NHB35 2.391	5210	2791	64.87	18.62	48.36	40.04	0.2987
NHB40 2.414	5184	2780	64.76	18.63	48.36	39.92	0.2980
NHB45 2.434	5015	2723	61.11	18.01	46.50	37.09	0.2910

The values of V_L, V_T, C11, C44, Y, K and Poisson's Ratio, given in the the table are plotted against alkali concentration in mol% [Fig.1, Fig.2, Fig.3, Fig.4]

Fig:1 Fig:2

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40 50

Fig:3

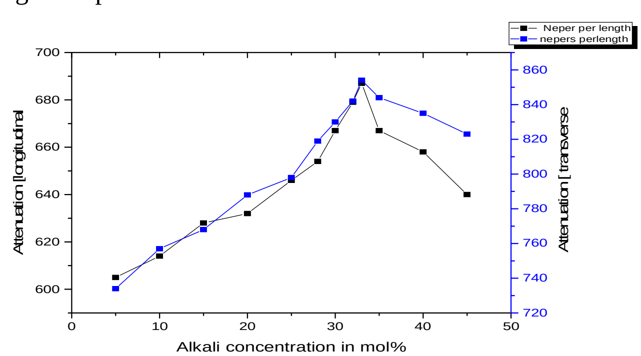
Fig:4

The values of longitudinal ultrasonic velocity and transverse velocity increases up to the total alkali concentration 33% and there after decreases slowly. 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 to0.33% 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. 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.

A. Ultrasonic Attenuation Measurements

Values of ultrasonic attenuation in these samples are measured at high frequency 10 MHz by measuring amplitudes of successive echoes and making an exponential fit. The values increase up to maximum alkali concentration 33% and there after decreases. The measured values are in Neper per unit length are plotted below



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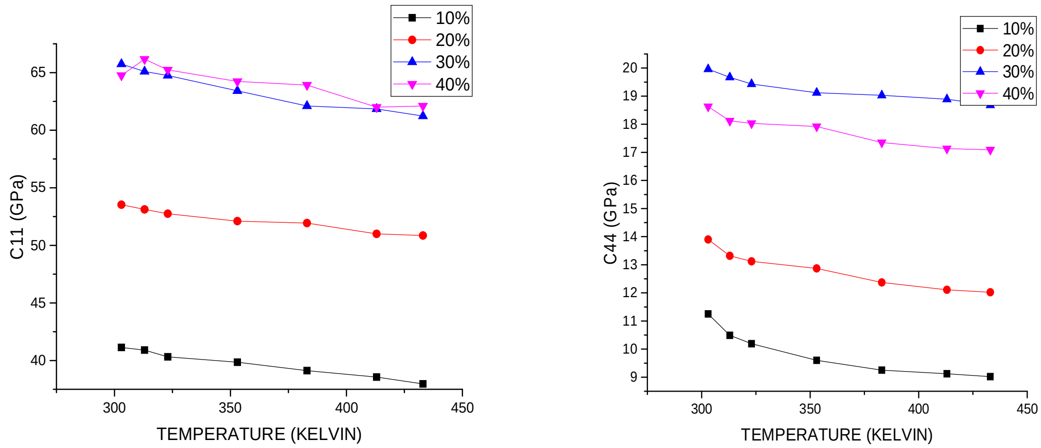
B. Variation of Elastic Constants with Temperature

The variation of elastic constants with temperature are keeping the sample inside a thermostat and controlling currents through the coil the increase of temperature can be achieved. The leads from the thermostat are connected to the MATEC MODEL7700.The variation of elastic constants C_{11} and $C_{44}$with temperature for alkali concentrations 10%, 20%.,30%,40% are plotted [fig 4,fig5] . The values of C11 and C44 are found to be decreasing with increase of temperature. The reason for this behaviour is the an-harmonic properties of the glass sample. The bending and stretching properties of B-O-B changes due to the decrease in interatomic forces.

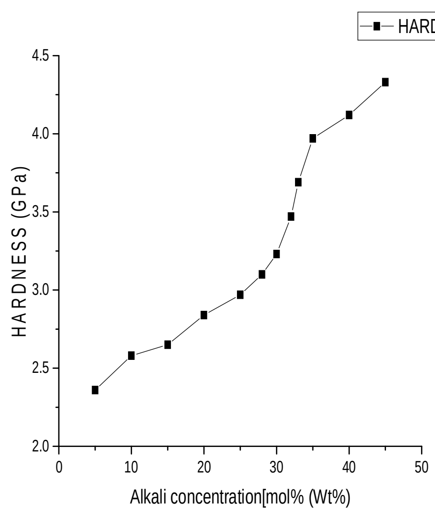


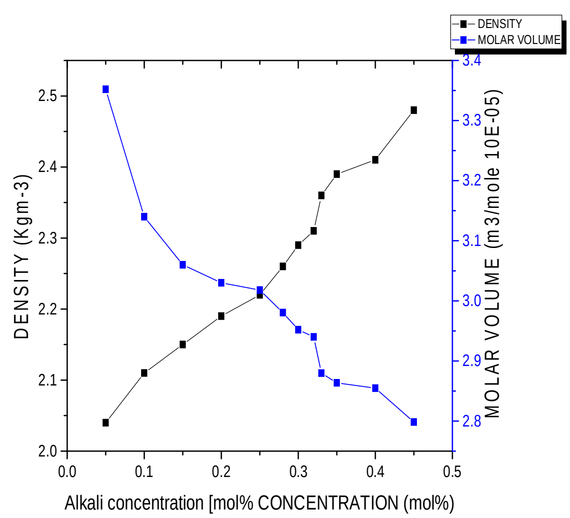
Variation of C11 and C44 with temperature

The decrease of elastic constantsC_{11} and is due to an-harmonicity produced due to temperature variations inside the sample and is plotted The variation is almost similar inC44

C. Measurement of Micro-hardness of the Sample

The values of micro hardness increases with increase in total alkali concentration and is due to increase of density of the samples. The increase of density of the sample is due to decrease in molar volume. Both of them are plotted.





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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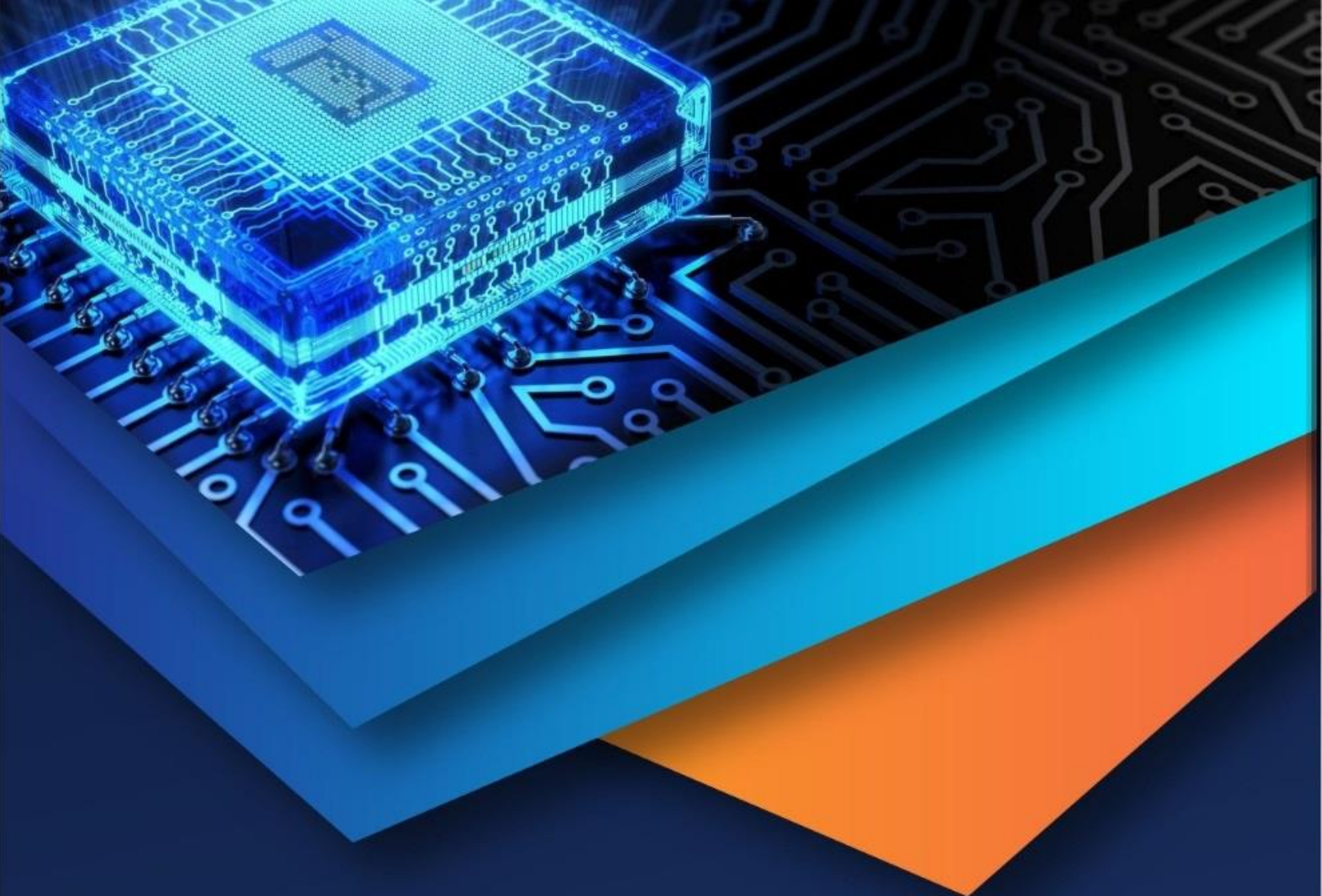

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