JOURNAL OF MATERIALS SCIENCE **35** (2000) 229–233

Temperature dependence of elastic and dielectric properties of $(Bi_2O_3)_{1-x}(CuO)_x$ oxide glasses

J. PHILIP, N. RODRIGUES
Department of Instrumentation, Cochin University of Science & Technology, Cochin—682022
M. SADHUKHAN, A. K. BERA, B. K. CHAUDHURI
Solid State Physics Department, Indian Association for Cultivation of Science, Calcutta—700032, India
E-mail: doinstr@md2.vsnl.net.in

Oxide glasses with the general formula $(Bi_2O_3)_{1-x}(CuO)_x$ have been prepared by quick quenching technique. Their longitudinal and shear elastic moduli have been determined by measuring the corresponding ultrasonic wave velocities between 300 and 470 K, which are well below the glass transition temperature of this system. Temperature variation of ultrasonic velocity and attenuation exhibit anomalies around 435 K in glasses with $x \geq 0.3$. A nonlinear behaviour is also reflected in the CuO concentration dependent dielectric constant curve around $x = 0.3$. These anomalies are interpreted in terms of a structural softening (or transformation) taking place in samples having CuO concentration above the critical value. The high dielectric constant of these glasses show very little increase with increase of temperature. Anomalies are also found in the temperature dependence of dielectric constant around 435 K. This behaviour is again considered to be associated with the softening of the glass network. © *2000 Kluwer Academic Publishers*

1. Introduction

Oxide glasses have been the subject of extensive research for several decades owing to their interesting properties and applications [1–4]. Various additives such as transition metal oxides are found to modify the properties of oxide glasses considerably. Bi_2O_3 glass is a popular member of the oxide glass family in which selected additives are found to modify its properties significantly.

Bi_2O_3 glass containing CuO are interesting materials which form an important constituent of high T_c superconducting glasses [5–7]. In the CuO-Bi_2O_3 system, it is found that Bi^{3+} ions participate in the network structure above 70 mol % of Bi_2O_3. In these glasses, network structure is formed with Bi_2O_3 pyramidal units as in the case of many other Bi containing glasses [8, 9]. Eventhough the thermal conductivity and heat capacity of many oxide glasses containing transition metal oxides have been measured over wide ranges of temperature from mK values to several hundred K, data on their elastic properties are comparatively less [10, 11]. Many of the transition metal containing glasses are semiconductors which exhibit threshold switching properties. The electrical and dielectric properties of various oxide glasses have recently been reviewed by Buchanan [12]. The electrical conductivity and dielectric constant of Bi_2O_3 glass with different concentrations of CuO have recently been measured as a function of temperature [13]. These measurements on pressed glass powders show that conductivity increases with CuO content and the results have been interpreted in terms of nonadiabatic small polaron hopping conduction mechanism. Optical absorption studies on CuO-Bi_2O_3 glassess indicate that addition of CuO improves electrical conductivity as well as optical properties [14]. Optical energy gap decreases with increase of CuO content, while the width of the localised states increase. It has also been shown that upto 30–40 mol % of CuO ($x = 0.3$–0.4), optical absorption is maximum and then it decreases. This has been explained by considering softening of the glass network structure with the addition of CuO.

In this paper we report the results of our measurements on the effect of addition of CuO on the elastic and dielectric properties of Bi_2O_3 glass. We have made measurements on pure Bi_2O_3 glass as well for comparison. We have determined the longitudinal and transverse elastic constants of $(Bi_2O_3)_{1-x}(CuO)_x$ glasses as a function of x, with x varying from 0 to 0.5, by measuring the corresponding ultrasonic velocities. Ultrasonic attenuation has also been measured as a function of temperature in the range (300–470 K) in all the glasses. Other related elastic properties such as Debye temperature (θ_D), Young's modulus (Y) and Poisson's ratio (σ) have also been determined and reported. The low frequency dielectric constant and its variation with temperature have been measured in all the glasses. The experimental techniques used, results obtained and a discussion of the results are given in the following sections.

2. Experimental method

2.1. Sample preparation and characterisation

$(Bi_2O_3)_{1-x}(CuO)_x$ glass samples with x ranging from 0 to 0.5 (0-50 mol% CuO) have been prepared by the quick quenching technique from the corresponding melts. Appropriate amounts of the two oxides, Bi_2O_3 and CuO (each of purity 99.99%), are well mixed in a mortar and heated at about 500 °C for 5 h. The preheated samples are ground and melted in platinum crucibles at 1000–1200 °C, for half an hour. Homogeneous glass samples are obtained by quenching the melts between two specially designed copper blocks. X-ray diffraction patterns of the prepared samples are recorded in a diffractometer . The scanning electron micrographs of the samples are taken in a scanning electron microscope, and the final compositions of the samples are determined by recording their atomic absorption spectra in a spectrometer. The density of the samples are measured at room temperature by Archemedes's principle method using benzene as the immersion liquid to an accuracy of ± 0.0005 g/cm^3. Differential scanning calorimetric analysis (DSC) has been performed in air using a Schimadzu thermal analyser at a heating rate of 10°/min. The samples have been cut in to cylindrical shapes with diameter approximately 10 mm and length 10 mm for ultrasonic measurements. The ends have been cut with a diamond wheel saw and polished by hand lapping so as to have plane parallel faces which are necessary for ultrasonic measurements. The nonparallelism of the end faces in all samples are estimated to be well within a degree. Thin slices of samples with thickness about 1mm have also been cut from the sample ingot for dielectric constant measurements.

2.2. Elastic constant measurements

Velocities of longitudinal and transverse ultrasonic waves propagating in each of the glass samples have been measured using the pulse echo overlap (PEO) technique using a MATEC 7700 pulse modulator and receiver system [15]. X and Y cut quartz ultrasonic transducers with resonant frequency 15 MHz have been bonded to the samples with silicon grease as the bond for generating longitudinal and transverse ultrasonic waves respectively. The samples have been placed inside a suitable temperature controlled oven to vary the temperature from 300 K (room temperature) to ≈470 K. For measuring the variation of velocity with temperature, the temperature has been increased in steps of 2° while keeping the temperature steady during measurements.

The McSkimin Δt criterion [16] has been applied to correct for the phase lag due to the bonding medium on RF echoes while making room temperature measurements on each sample. Once the correct overlap of echoes is identified at room temperature, variations in travel time can be monitored continuously as the temperature is varied. The PEO technique enables one to measure ultrasound transit time in the sample to an accuracy of a few tenth of a percent. Once the transit time is measured, the velocity can be evaluated knowing the length of the sample. The overall accuracy in measured velocity values is estimated to be of the order of ±1%.

Once the longitudinal and transverse velocities are measured, the corresponding elastic constants are determined from the relation $C_{ij} = \rho V^2$ where ρ is the density of the sample [17]. The ultrasonic attenuation in each sample has been measured by the pulse comparison technique from the exponentially decaying pulse pattern using the MATEC 2470B automatic attenuation recorder.

2.3. Dielectric constant measurements

The low frequency dielectric constant of all the samples have been measured using the capacitance technique after placing the sample inside a home made dielectric constant cell. The capacitance of a capacitor with the sample acting as the dielectric has been measured accurately using an HP 4170 impedance analyser. Variation of the dielectric constant with temperature has also been measured in selected samples using the same set up under temperature control.

3. Results

The X-ray diffraction patterns of the samples indicate diffuse scattering with broad peaks around $2\theta = 30°$ confirming the glassy nature of the samples. The scanning electron micrographs of the samples also indicate the absence of any microstructure. The DSC curve for sample with $x = 0.3$ is shown Fig. 1.

The variation of longitudinal and transverse elastic constant C_{11} and C_{44}, of $(Bi_2O_3)_{1-x}(CuO)_x$ glasses with x are shown in Fig. 2. The uncertainties in the data plotted, including uncertainties in density measurement, is less than 2%. As is evident from this figure, the elastic constants first decrease with addition of small amounts of CuO, the decrease being more in C_{11}. This indicates that the CuO ions reside in the Bi_2O_3 glass matrix as glass modifier without entering into the glass matrix. With further increase in CuO content, elastic constants increase as CuO ions start taking part in the formation of glass matrix. However, with further increase of CuO, a structural transformation occurs around $x = 0.3$ (30–40 mol% CuO) where the elastic constants show a minimum. However, C_{11} and C_{44} do not change significantly with the addition of CuO. The elastic constants tend to increase for $x > 0.3$ when

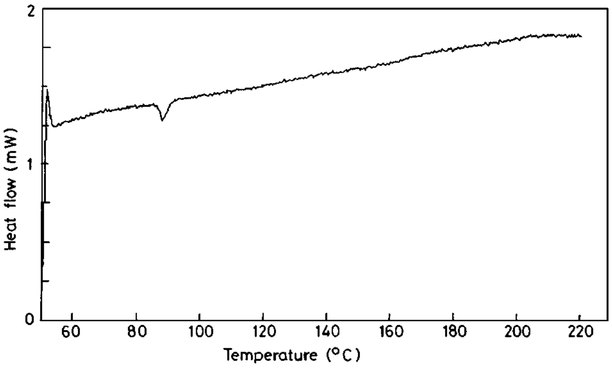

Figure 1 DSC curve of $(Bi_2O_3)_{0.7}(CuO)_{0.3}$ glass.

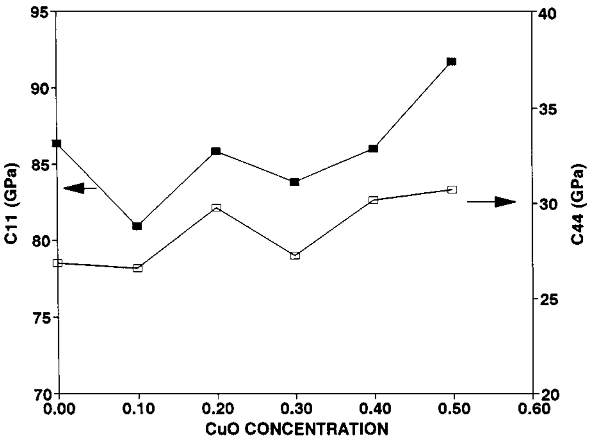

Figure 2 Variation of elastic constants C_{11} and C_{12} of $(Bi_2O_3)_{1-x}$ $(CuO)_x$ glasses with CuO concentration.

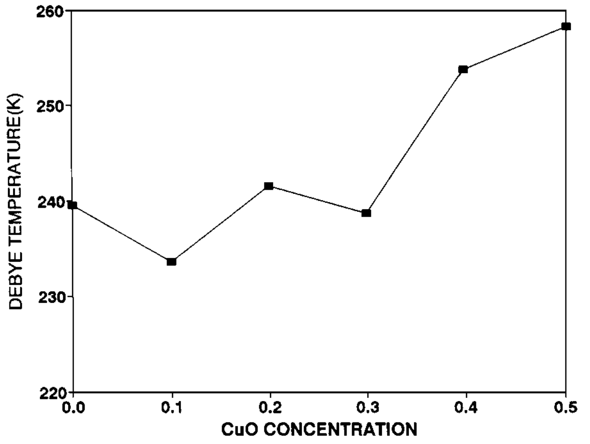

Figure 3 Variation of Debye characteristic temperature of $(Bi_2O_3)_{1-x}$ $(CuO)_x$ glasses with CuO concentration.

Cu ions enter in to the glass matrix substantially and a strong CuO–O bond stretching vibration would begin to occur. Here it should be mentioned that Bi_2O_3 is an unconventional glass and its characteristic features, which is not yet known completely, appear to be very different from other doped glasses. Therefore, CuO concentration dependent elastic constants really show some nonlinear behaviour between $x = 0.2$ and 0.3 which is also reflected in the CuO dependent dielectric properties presented later. The variation of the related elastic parameters, the Debye characteristic temperature, Youngs' modulus and Poisson's ratio with CuO concentration are shown in Figs 3 and 4. These figures also indicate some anomalous variation with CuO. As is expected the variation of these parameters follow the corresponding variations in the two basic elastic constants.

The temperature variation of longitudinal elastic constant C_{11} in glasses with $x = 0$ (pure Bi_2O_3) and $x = 0.1$ are shown in Fig. 5. Temperature variation of longitudinal velocity and C_{11} in pure Bi_2O_3 glass is almost featureless. However, the sample with $x = 0.1$ show some features around $T = 435$ K. The anomalous behaviour is more predominant for glasses with $x = 0.3$ and 0.5. Temperature variation of longitudinal elastic constant C_{11} in glass with $x = 0.3$ is shown in Fig. 6. A decrease in velocity can be noted around 435 K. Temperature variation of ultrasonic attenuation in glass with $x = 0.3$ is also shown in the same figure which exhibit a peak around the same 435 K. Glasses with $x = 0.4$ and 0.5 also show similar anomalies around 435 K. The velocity shows a minimum and attenuation exhibits a maximum around this temperature in all these glasses. Since the velocity and attenuation curves for glasses with $x = 0.4$ and 0.5 are similar to the ones for glass with $x = 0.3$, only the later curves are presented in the paper.

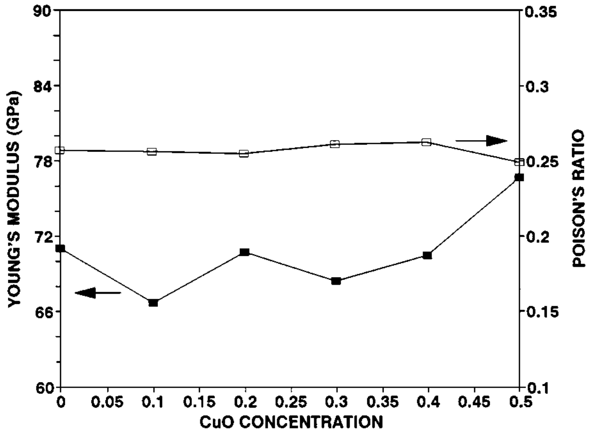

Figure 4 Variation of Young's modulus and Poissons ratio of $(Bi_2O_3)_{1-x}$ $(CuO)_x$ glasses with CuO concentration.

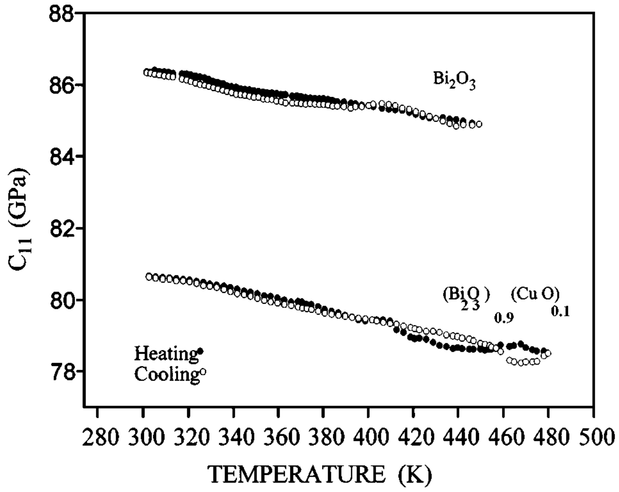

Figure 5 Temperature variation of longitudinal elastic constant C_{11} of (Bi_2O_3) and $(Bi_2O_3)_{0.9}$ $(CuO)_{0.1}$ glasses.

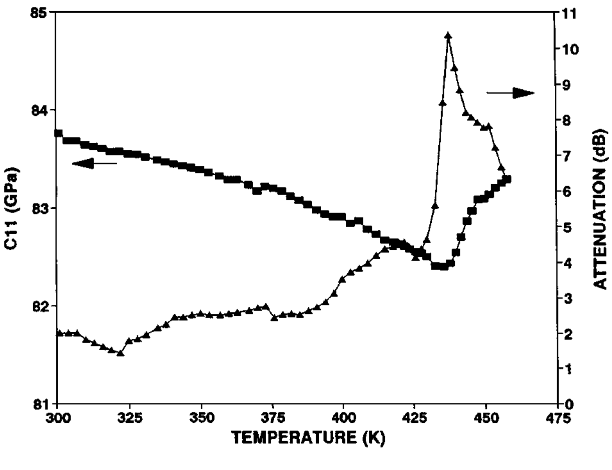

Figure 6 Temperature variation of longitudinal elastic constant C_{11} of $(Bi_2O_3)_{0.7}$ $(CuO)_{0.3}$ glass.

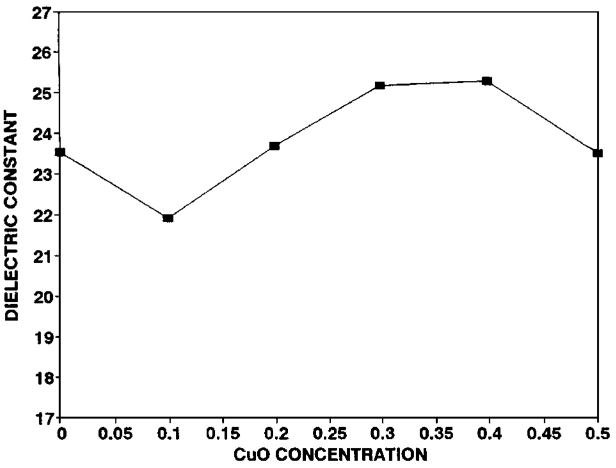

Figure 7 Variation of dielectric constant of $(Bi_2O_3)_{1-x}$ $(CuO)_x$ glasses with CuO concentration.

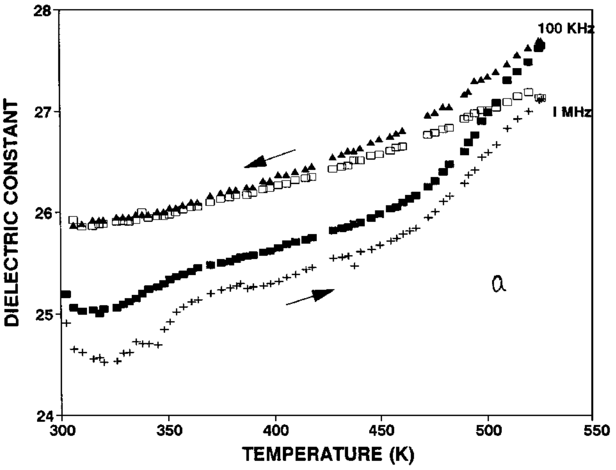

Figure 8 Temperature variation of low frequency dielectric constant of $(Bi_2O_3)_{0.7}$ $(CuO)_{0.3}$ glass.

In Fig. 7, we plot the variation of low frequency dielectric constant with CuO concentration. It may be noted that variation in dielectric constant with x more or less reflects the corresponding variation in elastic constants. The dielectric constant is found to show small increase with temperature for all samples as shown in Fig. 8, for glass with $x = 0.3$ at different frequencies. It can be noted that dielectric constant does not undergo any anomalous change at the temperature at which ultrasonic velocity and attenuation exhibit anomalous variations. Dielectric constant curves for other samples are not shown as they are similar to those shown in Fig. 8. It may be noted that the dielectric constant does not get back to original room temperature value upon cooling the sample to room temperature. This can be attributed to large relaxation behaviour of the dipoles. It is found that it takes a few hours for the dielectric constant to reach the original value after the sample has been taken through the heating cycle. This behaviour is rather unusual in transition metal oxide glasses.The temperature coefficients of the elastic and dielectric constants for a few selected compositions are tabulated in Table I. Linear regions of the corresponding variations have been used to determine the slopes.

TABLE I

Sample composition	$\frac{d\epsilon}{dT} \times 10^{-3}\ K^{-1}$	$\frac{-dC_{11}}{dT} \times 10^{-2}\ GPa\ K^{-1}$
Bi_2O_3	—	1.14
$(Bi_2O_3)_{0.9}$ $(CuO)_{0.1}$	—	1.62
$(Bi_2O_3)_{0.7}$ $(CuO)_{0.3}$	5.07	0.85
$(Bi_2O_3)_{0.6}$ $(CuO)_{0.4}$	—	0.79
$(Bi_2O_3)_{0.5}$ $(CuO)_{0.5}$	62.53	1.02

4. Discussion and conclusion

Our results indicate that the elastic properties of $(Bi_2O_3)_{1-x}(CuO)_x$ glasses marginally improve as CuO concentration increases. In these glasses Bi_2O_3 is the network former and CuO is a network modifier. During fusion of the glass mixture, a structural readjustment takes place such that the Bi—O—Bi bonds are broken and the bridging oxygens are converted into nonbridging oxygens. Such a rearrangement of atoms can be represented as

$$\text{Bi—O—Bi—} + \text{Cu—O} \rightarrow \text{Bi—O—Cu—O—Bi}$$

As the bond energy of Cu—O bonds is more than that of Bi—O bonds, the network becomes more rigid with addition of CuO giving rise to the observed increase in elastic constants.The multiphase nature of the samples could be the reason for the nonuniform variation of elastic constants with CuO concentration. This, combined with experimental uncertainties, results in the observed variations reported in Figs 2–4.

We have used the measured elastic constant values to determine the Debye temperature of the samples at room temperature. Obviously, we are assuming the wavelength to be large compared to the interatomic spacing and the lattice network to be a harmonic one. Since both C_{11} and C_{44} moduli vary more or less in the same manner with the addition of CuO, the Debye temperature should follow more or less the same variation. This discussion is applicable to the variation of Young's modulus with CuO concentration as well. As is well known, the Poisson's ratio of a polycrystalline or amorphous solid is related to the cross linking of the network. As can be seen from Fig. 4, Poisson's ratio remains more or less constant up to $x = 0.4$, beyond which it has a tendency to decrease. This could be due to the onset of a phase separation in the sample with the metal ions getting preferentially segregated in the discontinuous phase, causing a reduction in the number of bridging oxygens and hence reducing the cross linking of the network.

As more Cu atoms are added to the glass, fewer and fewer bridging oxygens remain. As is evident from Fig. 6, network with $x = 0.3$ undergoes a structural softening at around 435 K. Similar behaviour is shown by all glasses with $x \geq 0.3$. The anomaly in heat flow at around 88 °C or 361 K found in the DSC curve can be interpreted as due to the onset of the structural softening in the sample. As can be noted in Fig. 6, the elastic anomaly actually begins at 361 K and is complete at 435 K. This is reflected in the attenuation curve also.The sample undergoes a structural softening in a wide temperature range between 361 and 435 K indicating an anomaly in heat flow at the onset temperature. Since elastic constant is highly structure sensitive it shows maximum decrease when the softening is complete. This structural softening can be correlated to the number of nonbridging oxygens or Cu—O bonds present in the network. Our experiments show that the onset of the critical structure with optimum number of nonbridging oxygens occur for values of x lying between 0.2 and 0.3. As x increases, we can say that the network coherence decreases and it become easier for the metal ions to move through the network. When the network coherence goes below a critical value corresponding to a value of x between 0.2 and 0.3, the structure is such that it undergoes a softening between 361 and 435 K. A more detailed structural analysis and modeling would be required to confirm this and to give a quantitative footing for the above arguments. Besides these, there is chance for the occurrence of a gradual phase separation as transition metal ions could preferentially get segregated in the minor discontinuous phase. Such an effect is reflected in the dielectric constant as well as elastic constant values.

The observed tendency of the dielectric constant to decrease with increasing CuO content can be correlated to the increase in conductivity of the sample with the number of metal ions in the structure. The conductivity of oxide glasses is generally explained in terms of polaron hopping in non-adiabatic approximation [18, 19] and is found to increase with increase in the number of metallic ions [14]. This mechanism adequately explains the observed initial decrease in dielectric constant with CuO concentration shown in Fig. 7. As CuO concentration increases beyond $x = 0.1$, the sample gets phase separated leading to segregation of metal ions leading to a further decrease in conductivity or increase in dielectric constant . Addition of CuO beyond $x = 0.4$ leads to a sufficiently high density of metal ions going in to all possible vacant lattice sites leading to a further increase in conductivity or decrease in dielectric constant.The dielectric constant of glasses, as expected, decrease with increasing frequency. However, the variation over the wide range of frequencies is quite small. In general, ε increases slightly with increasing density of glasses. This is attributed to the fact that ε is a direct measure of polarizability per unit volume and that for a denser glass there are more electrons and ions to polarise. The increase in dielectric constant with temperature again follows the corresponding decrease in conductivity with temperature. In addition to this , at elevated temperatures the glass network relaxes and ionic motion becomes easier. This increase is also expected to be more pronounced at low frequencies because ions have more time to participate in the motion.

One important observation to be made in the temperature variation of dielectric constant is that it does not exhibit any anomaly around 435 K where ultrasonic velocity and attenuation exhibit anomalies. This indicates that the structure of the network is the origin of anomaly in elastic properties seen in glasses with $x \geq 0.3$. Probably a structural rearrangement of the network is taking place at this temperature which is reflected in ultrasonic properties. The real part of the dielectric constant is not that sensitive to detect this change. However, the elastic anomaly found in these glasses at higher temperatures may show up in dielectric loss measurements.

In conclusion, we report the variation of the longitudinal and transverse elastic constants with CuO addition in $(Bi_2O_3)_{1-x}(CuO)_x$ glasses. Ultrasonic velocity and attenuation are found to exhibit anomalies around 435 K in glasses with $x > 0.3$. We also report the low frequency dielectric constant in these glasses and their variation with temperature.

Acknowledgements

One of the authors (JP) thanks the Third World Academy Science (TWAS), Trieste, Italy for providing support for this work.

References

1. H. HIRASHIMA, Y, WATANABE and T. YOSHIDA, *J. Non-Cryst. Solids* **95&96** (1987).
2. Y. SAKURI and J. YAMAKI, *J. Electrochem. Soc.* **132** (1985) 512.
3. S. NAKAMURA and N. ICHINOSE, *J. Non-Cryst. Solids* **95&96** (1987) 512.
4. M. E. LINES, *J. Appl. Phys.* **69** (1991) 6876.
5. T. KOMATSU, R. SATO and K. MATUSUITA, *Appl. Phys. Lett.* **54** (1990) 170.
6. K. B. R. VARMA and K. J. RAO, *ibid.* **54** (1989) 69.
7. R. C. BAKER, W. M. HURNG and H. STEINFINK, *ibid.* **54** (1989) 371.
8. S. R. ELLIOT, "Physics of Amorphous Materials," 2nd ed. (Longman Scientific and Technical, 1990).
9. W. H. ZACHARIASEN, *J. Amer. Chem. Soc.* **54** (1932) 3841.
10. W. A. PHILLIPS (ed), "Amorphous Solids," (Topics in Current Physics) Vol. 24, (Springer-Verlag, 1981).
11. J. JACHLE, L. P. IICHE, W. ARNOLD and S. HUNKLINGER, *J. Non-Cryst. Solids* **20** (1975) 365.
12. R. C. BUCHANAN, "Ceramic materials for electronics," (University of Illinois Press, 1991).
13. D. K. BURGHATE, S. G. MOKE, W. J. GAWANDE, S. V. PAKADE and S. P. YAWALE, *Ind. J. Phys.* **68A** (1994) 141.
14. N. F. MOTT and E. A. DAVIS "Electronic processes in non. crystalline materials," 2nd ed. (Oxford University Press, 1971).
15. E. P. PAPADAKIS in "Physical Acoustics," Vol. 12, edited by W. P. Mason and R. N. Thurston (Academic Press, New York, 1976).
16. H. J. MC SKIMIN, *J. Acoust. Soc. Amer.* **33** (1961) 12.
17. E. SCHREIBER, O. L. ANDERSON and N. SOGA, "Elastic constants and their measurements," (Mc Graw Hill, New York, 1973).
18. I. G. AUSTIN and N. F. MOTT, *Advances in Physics* **18** (1969) 41.
19. N. F. MOTT, *J. Non-Cryst. Solids* **1** (1968) 1.

Received 28 May 1997
and accepted 4 May 1999