

Acoustic study of nano-crystal embedded PbO–P₂O₅ glass

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Abstract. Nano-crystal embedded PbO–P₂O₅ glass has been prepared and characterized by XRD and TEM measurements. The ultrasonic velocity and attenuation measured within the temperature range 80–300 K show significant structure and interesting feature with the presence of nano-crystalline region. The glass samples were prepared by melt-quench method and nano-crystals of different sizes were produced by heat treatment of the glasses for different durations of heating. All the processes were carried out at or above glass transition temperature. A theoretical model that takes account of the effects of thermally activated relaxation, anharmonicity as well as microscopic elastic inhomogeneities arising out of fluctuations has been successfully applied to interpret the variation of ultrasonic velocity and attenuation data. An interesting outcome of this application has been to propose a method for the determination of the size of nano-crystals from the ultrasonic attenuation data.

Keywords. Glasses; acoustical properties; nanostructured materials; glass ceramic.

1. Introduction

During the last two decades, studies of different physical properties of nano-crystal embedded glass matrix have attracted attention of technologists as well as scientists for fabrication of glass ceramic through controlled crystallization. The studies usually involve X-ray diffraction measurement (XRD) (Komatsu *et al* 1991; Balaya and Sunandana 1993), electrical conductivity measurement (Chatterjee and Chakravorty 1990; Maity *et al* 1996), optical (Kraevskii and Solinov 2003) and thermal (Balaya and Sunandana 1993) properties measurements etc. In addition, the differential scanning calorimetry measurements give us information about the mechanism of crystallization and activation energy for crystal growth in glass. Further, we may also mention that after different thermal treatments, crystallization behaviour of TeO₂–LiNbO glasses by determining the phases using X-ray diffraction was reported (Komatsu *et al* 1991). The magnetization measurement of vitroceraamics containing lithium ferrite crystal showed closed link to the crystal sizes by annealing of LiFe₅O₈ glass (Chaumont and Benier 1983). The effects of crystallization on electrical conductivity of 30Li₂O·70TeO₂ glass were also studied (Balaya and Sunandana 1993). The main aspects of such studies of nano particles are two folds, viz. (i) to observe the change of different physical properties due to nano size of the materials and (ii) to develop various processes of tuning these properties with

various sizes of particles. Heat treatment of glassy materials at or above glass transition temperature is relatively an easy process to produce nano-crystals within the glass matrix. In this process one can control the size of the produced nano particles by controlling the heat treatment temperature and duration of thermal treatment. A large number of workers have generated nano-crystals by this process and studied their different physical properties.

But ultrasonic characterization of such materials is yet to be done. In this communication, we present the different phases with varying sizes of nano-crystals developed during heat treatment of (PbO)_{0.5}(P₂O₅)_{0.5} glass and investigate the variation of ultrasonic velocity and attenuation with the size of nano-crystals and finally propose an empirical relation between attenuation parameter and size of nano-crystals.

2. Experimental

The (PbO)_{0.5}(P₂O₅)_{0.5} glass samples were prepared by melt quench method as described earlier (Mukherjee *et al* 1993; Maiti *et al* 1996; Paul *et al* 1997, 1998). The glass transition temperatures (T_g) of the samples were estimated from differential thermal analysis (DTA). The glass ceramic phases were developed within the samples by heat treatment. For this purpose, two temperatures were considered, one the glass transition temperature, 443 K and the other, 30 K above the glass transition temperature i.e. 473 K. Keeping the temperatures fixed at 443 K and 473 K, the samples were heated for different durations of time:

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30 min, 1 h and 90 min. The development of crystal phases was confirmed from XRD. To ensure the complete formation of crystal phases one of the glass samples was heat-treated for a period of 2 h at 673 K which is above the crystallization temperature. It was then taken as the reference polycrystalline sample for a comparison of particle size and degree of crystallization by transmission electron microscopy (TEM) and XRD, respectively of the samples undergoing different heat treatments. Figure 1 shows XRD pattern of all the samples including the reference polycrystalline one. TEM micrographs were also taken for all glass ceramic samples and are presented in figure 2. For ultrasonic measurements bulk samples with exactly parallel and polished opposite faces are prepared. Ultrasonic velocity and attenuation measurements were carried out at a frequency of 10 MHz in the temperature range 80–300 K. The polycrystalline sample was very much fragile and so the ultrasonic measurements could not be performed. Details of the experimental setup and procedure for measurements are given elsewhere (Mukherjee *et al* 1993; Maiti *et al* 1996; Paul *et al* 1997, 1998).

3. Results and discussion

From TEM micrographs we observed nano sized crystals developed by heat treatment within the glass matrix for all the samples excepting the one heat treated at 443 K for 30 min. The average sizes of the nano-crystals have been calculated from TEM micrographs. The particle sizes of the samples heat treated at different temperatures are given in table 1. From the data it is clear that the size of the crystals increases with the duration of heat treatment. Again the XRD spectra show a hump around $2\theta = 25^\circ$ for the samples undergoing heat treatment up to 1 h at different fixed temperatures. But when the heat treatment time is 90 min, a large number of crystalline peaks indicating

aggregate formation have been observed. XRD data, however, do not lead to any conclusive information about the structure of the nano aggregates formed. The XRD profiles S3 and S6 indicate the presence of P_2O_5 in the studied samples. Thus, in addition to entering into the aggregate formation, P_2O_5 exists also in the unreacted form. Obviously XRD data do not suggest any definite composition. Characteristic features of the composition and related structural details by suitable methods may reveal the true picture. Variations of longitudinal ultrasonic velocity and attenuation coefficient with temperature have been presented in figures 3 and 4, respectively. The variation of longitudinal velocity with temperature of all the samples shows a negative slope. The value of ultrasonic velocity is almost same at different temperatures for all the samples except the one heat treated at 473 K for 90 min in which case it is slightly lower. A broad peak has been observed for all the samples in the temperature variation of ultrasonic attenuation. The peaks become more flat and the values become lower than that of the sample heat-treated at 443 K for 30 min where no crystals were observed.

To explain the variation of ultrasonic velocity and attenuation with temperature for nano-crystal embedded glass, we consider a model which includes the effects of thermally activated relaxation in a double well created by the glassy disorder, anharmonicity as well as microscopic elastic inhomogeneities generated by freezing of different natural fluctuations. The scenario envisaged by the model is that due to inherent disorder in glass, atoms or a group of atoms constituting localized structural defects can have different configurational states and may move in a double well potential having two minima corresponding to two local equilibrium configurations. At low temperature these particles can only move from one well to the other by quantum mechanical tunneling. At high temperature (range of our study) the two defect configurations should actually be treated as two thermodynamical states involving a thermodynamical average over some vibrational degrees of freedom and the double well description is interpreted as free energy curve rather than potential energy curve. When a sound wave passes through such material, the strain field causes a relative change in free energy of the two states corresponding to the two possible configurations and thus produces thermal disequilibrium. The change in free energy due to the strain field is characterized by a deformation potential, D , which may be defined as the relative energy shift of the two states for a strain field of unit strength. A relaxation process follows to restore the equilibrium configuration by surmounting the barrier height via a thermally activated process.

We can calculate the change, dv , of the sound velocity due to relaxation effect from its value in absence of relaxation (i.e. at 0 K) and the dissipation factor, often called internal friction, Q^{-1} (related to the attenuation coefficient, a , by $Q^{-1} = 2a v/w$) arising from the relaxation effect and obtained the following expressions (Jäckle *et al* 1976)

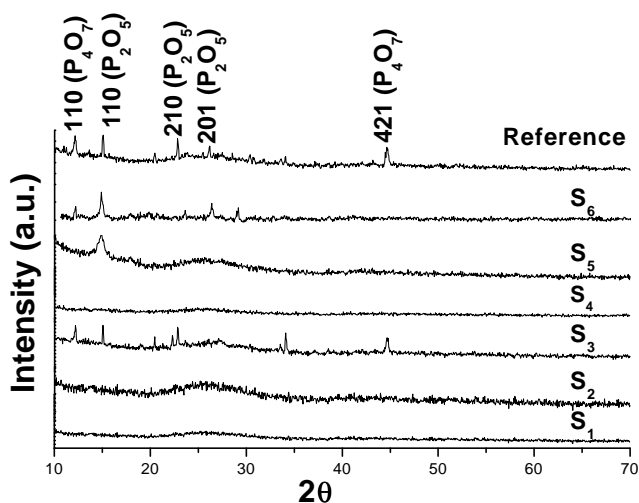


Figure 1. XRD spectra of the glass ceramic samples.

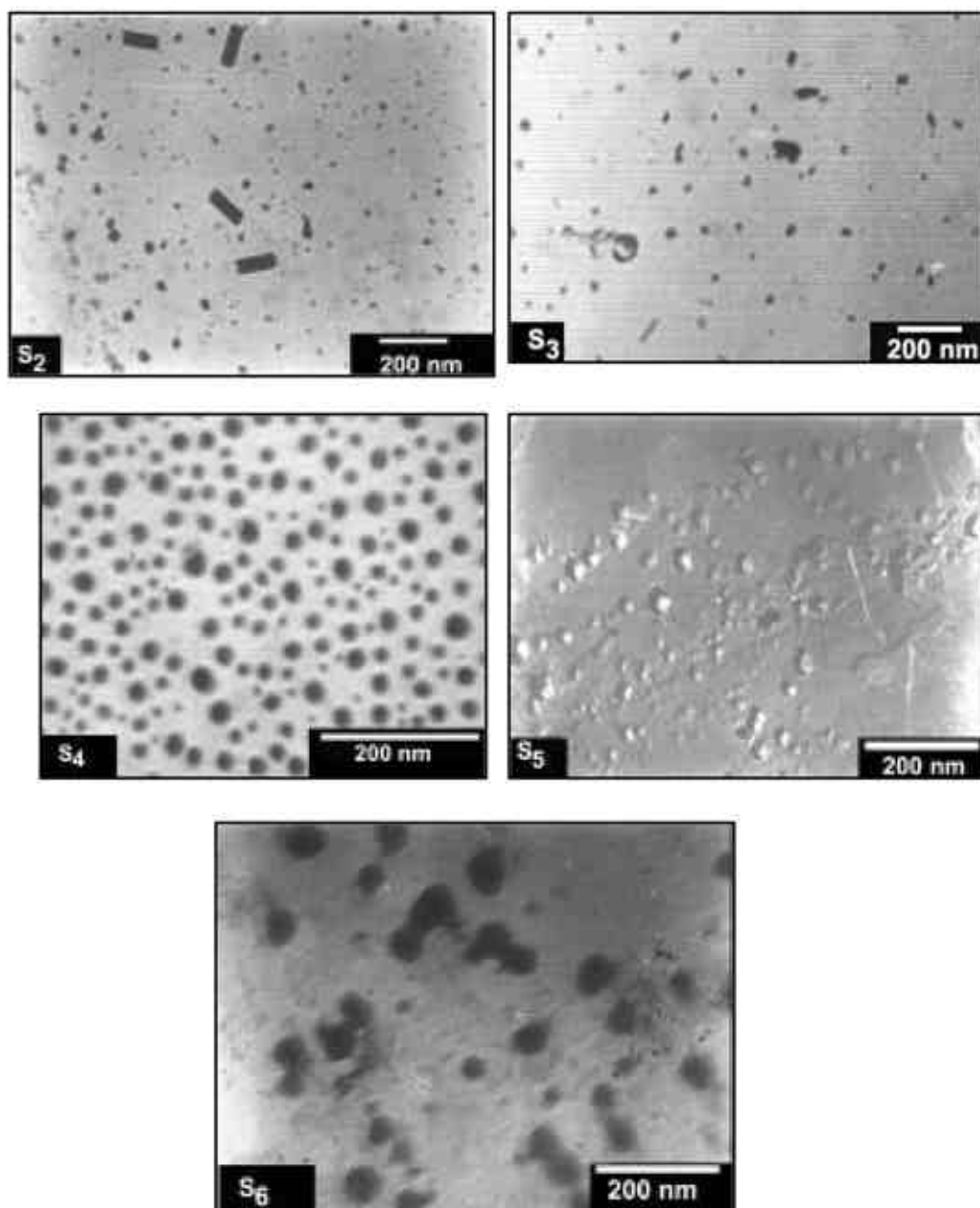


Figure 2. TEM micrographs of glass ceramic samples.

Table 1. Sample specifications and particle size of the nano-crystals.

Sample name	Temperature of heat treatment (K)	Duration of heat treatment	Particle size as obtained from TEM (nm)
S1	443	30 min	
S2	443	1 h	13.6
S3	443	90 min	17
S4	473	30 min	14
S5	473	1 h	20
S6	473	90 min	49

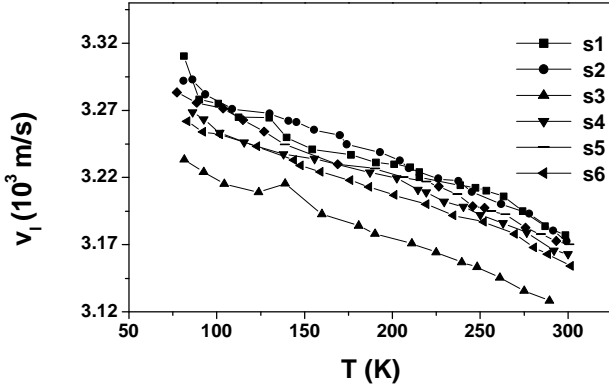


Figure 3. Variation of longitudinal ultrasonic velocity with temperature (The solid lines are fit to aid the eye).

$$\frac{dv}{v_0} = -\frac{nD^2}{8rv_0^2kT} \frac{1}{1+w^2t^2}, \quad (1)$$

$$Q^{-1} = \frac{nD^2}{4rv_0^2kT} \frac{wt}{1+w^2t^2}, \quad (2)$$

where t (relaxation time) = $t_0 e^{V/kT}$, n the number of relaxing particles per unit volume, r the density of material, v_0 the sound velocity in absence of relaxation (i.e. at 0 K) and D the deformation potential. The above relations refer to one kind of defect particle only with a single value of t and D . In glass there will be several kinds of defects having several values of t (hence different values of activation energy, V , i.e. barrier height between the two wells in a double well) and different values of deformation potential, D . The asymmetry parameter, Δ , is defined by the difference in energy of the minima of the two wells. The distribution of Δ represented by $f(\Delta)$ is considered to be constant (denoted by f_0) (Gilroy and Phillips 1981), an assumption valid below the glass transition temperature. Further the distribution of V is taken in the form, $g(V) = 1/V_0 \exp(-V/V_0)$, where V_0 is the energy value of the order that corresponds to T_g (Gilroy and Phillips 1981). Introducing the above distributions in (1) and (2), an approximate solution in closed form is obtained as follows (Gilroy and Phillips 1981)

$$\frac{dv}{v_0} = -\frac{D^2}{4rv_0^2} f_0 [1 - (wt_0)^{kT/V_0}], \quad (3)$$

$$Q^{-1} = \frac{D^2}{4rv_0^2} f_0 p \frac{kT}{V_0} (wt_0)^{kT/V_0}. \quad (4)$$

The theory described above, which accounts for the attenuation behaviour, is found to be inadequate to explain the velocity variation with temperature. It should be noted

that $wt_0 \ll 1$ and from (3) dv decreases as T increases. Evidently, the relaxation effect alone cannot explain the high temperature variation of sound velocity in some glasses where the velocity rises after attaining a minimum. For such cases an improvement can be made by introducing the effect of anharmonicity as well as the microscopic elastic inhomogeneities that exist in glass. Using an extension of the quasiharmonic continuum model of Garber and Granato (1975) to isotropic material (Clayton and Sladek 1978), the anharmonic effect on elastic constant, C , at any temperature, T , can be expressed as

$$C = C_0 [1 - \Gamma F(T/\Theta)], \quad (5)$$

where C_0 is the elastic constant at 0 K, the factor Γ determines the anharmonic effect, Θ the Debye temperature at 0 K and the function, $F(T/\Theta)$, is given by

$$F\left(\frac{T}{\Theta}\right) = \left[3 \left(\frac{T}{\Theta}\right)^4 \int_0^{\Theta/T} \frac{x^3 dx}{e^x - 1} \right]. \quad (6)$$

Then the anharmonic effect of sound velocity is immediately obtained using (5) as follows

$$v_T = v_0 \left[1 - \frac{1}{2} \Gamma F\left(\frac{T}{\Theta}\right) \right]. \quad (7)$$

The microscopic inhomogeneities referred to earlier are associated with the freezing of natural fluctuation of the order parameter of liquid glass at temperature close to T_g during glass formation. When the rate of cooling is high for glass formation the order fluctuations are not dispersed but are frozen at T_g and are retained in the solid state. Details of the calculation are given in our earlier works (Paul *et al* 1998, 1999). Considering the effect of relaxation, anharmonicity and frozen-in fluctuation, the expression for velocity variation becomes

$$R = \frac{v_T - v_{80}}{v_{80}} = \frac{\frac{f_0 D^2}{4rv_0^2} [P_{80} - P_T] + \frac{1}{2} \Gamma [H_{80} - H_T]}{\frac{1}{2r} \left[\frac{\frac{A}{v_0^2} S_{80} + \frac{B}{v_0^2} S_{80}^2}{1 - \frac{f_0 D^2}{4rv_0^2} P_{80} - \frac{1}{2} \Gamma H_{80}} - \frac{\frac{A}{v_0^2} S_T + \frac{B}{v_0^2} S_T^2}{1 - \frac{f_0 D^2}{4rv_0^2} P_T - \frac{1}{2} \Gamma H_T} \right]} = \frac{1 - \frac{f_0 D^2}{4rv_0^2} P_{80} - \frac{1}{2} \Gamma H_{80} - \frac{1}{2r} \left[\frac{\frac{A}{v_0^2} S_{80} + \frac{B}{v_0^2} S_{80}^2}{1 - \frac{f_0 D^2}{4rv_0^2} P_{80} - \frac{1}{2} \Gamma H_{80}} \right]}{1 - \frac{f_0 D^2}{4rv_0^2} P_T - \frac{1}{2} \Gamma H_T - \frac{1}{2r} \left[\frac{\frac{A}{v_0^2} S_T + \frac{B}{v_0^2} S_T^2}{1 - \frac{f_0 D^2}{4rv_0^2} P_T - \frac{1}{2} \Gamma H_T} \right]}, \quad (8)$$

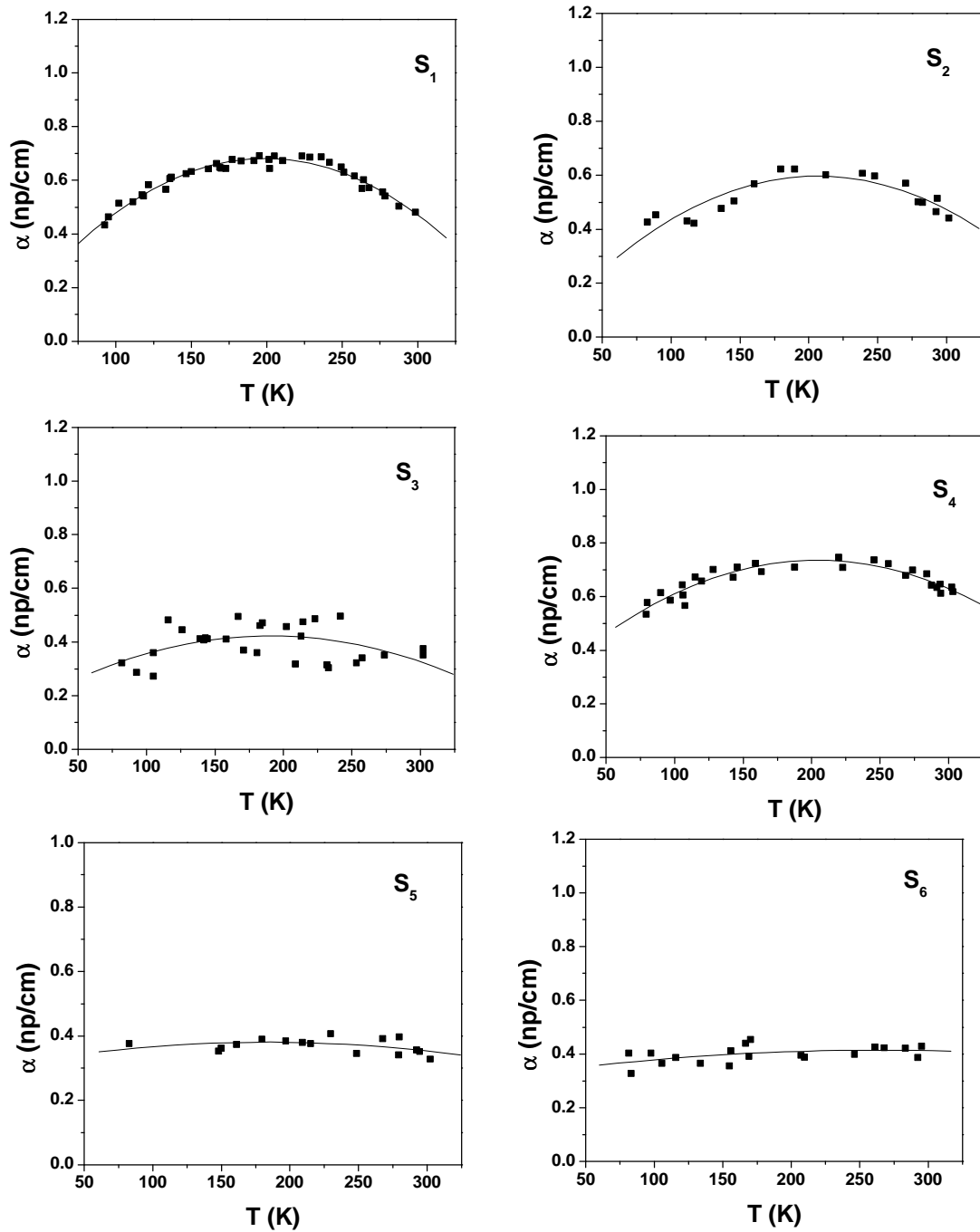


Figure 4. Variation of longitudinal ultrasonic attenuation coefficient with temperature (The solid lines are fit to aid the eye).

Table 2. Values of the theoretical parameters for different glass ceramic samples.

Sample	t_0 (s)	V_0 (10^{-23} J)	$f_0^2 D^2 / v_0^2$ ($10^3 \text{ Jm}^{-5} \text{ s}^2$)	Γ	A/v_0^2 (10^{-5})	B/v_0^2 (10^{-7})	Q_s
S2	10^{-13}	3000	1.20	0.100	83	1	0.8923
S3		3000	1.00	0.100	0.99	29	0.9799
S4		3000	1.50	0.100	37	19	0.9938
S5		3000	0.79	0.100	6.99	37	0.9859
S6		3000	0.70	0.100	64	10	0.9893

where $P_T = 1 - (wt_0)^{K_B T/V_0}$, $P_{80} = 1 - (wt_0)^{K_B 80/V_0}$, $H_T = F(T/\Theta)$; $H_{80} = F(80/\Theta)$, $S_T = (T_g - T)$ and $S_{80} = (T_g - 80)$.

We would like to mention here that in case of attenuation the major contribution comes from the thermally activated relaxation process. In an earlier communication we have estimated the contribution of anharmonicity and the frozen-in fluctuation towards attenuation and have shown that these are negligible (Paul et al 1999). Transforming our attenuation data into internal friction, Q^{-1}

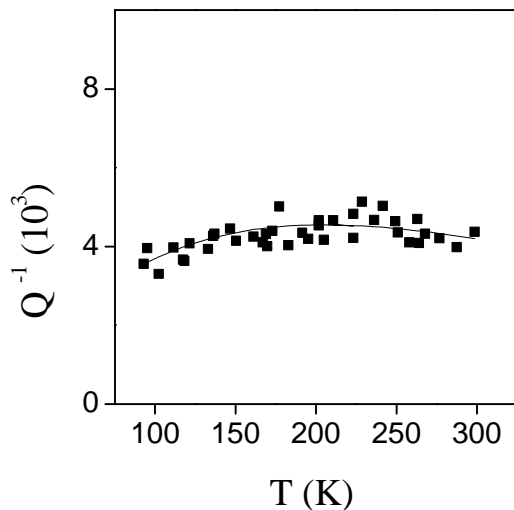


Figure 5. Theoretical curve (solid line) of Q^{-1} (longitudinal) against temperature and experimental points (■) are also shown for the sample, S4.

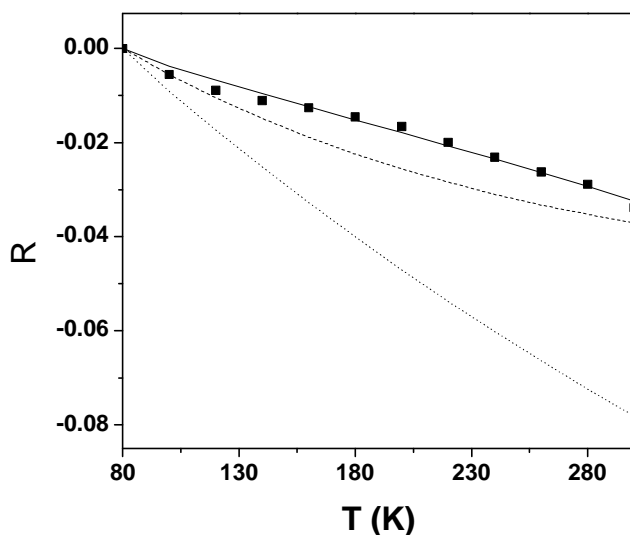


Figure 6. Fit to the relative change in longitudinal sound velocity (dashed line), theoretical curve considering the relaxation process alone; (dotted line), theoretical curve considering the relaxation and anharmonicity; (solid line), theoretical curve considering the relaxation and anharmonicity and frozen-in fluctuation and (■), experimental points of the sample, S4.

and taking $(f_0 D^2/v_0^2)$, t_0 and V_0 of (3) and (4) as parameters, we fit the experimental data by similar procedure as elaborated in our earlier publications (Paul et al 1997, 1999). Besides the parameters $(f_0 D^2/v_0^2)$, t_0 and V_0 already evaluated from attenuation data we treat Γ , A/v_0^2 and B/v_0^2 in (8) as additional parameters to fit the velocity data. The evaluated parameters are given in table 2. Figures 5 and 6 show a representative fit of experimental data with the theory for attenuation and velocity, respectively.

It is expected that the mechanical stress at the crystal glass interface is likely to influence sound propagation. Also, the wave propagation will depend on crystalline fraction and the number of nano-crystals formed. However, the changes in the ultrasonic velocities for the samples, S1 to S5, throughout the range of temperature studied are rather small and do not appear to follow a regular order. While the marked change is observed for sample 6 there is overlap between the curves of other samples, so with this limited observation the analysis of the velocity data is not attempted.

From the analysis of the Q^{-1} data it was found that V_0 is the same for all the samples whereas the values of $f_0 D^2/v_0^2$ go on decreasing with the size of the nano-crystals as shown in figure 7. The constant value of V_0 indicates that the distribution of barrier height has not been affected by the presence of small quantities of nano-crystals. The change in the values of the ultrasonic velocities of different samples is very small throughout the entire range of temperature studied, so it is expected that the change in v_0 is also small for all the samples. This implies that the change in deformation potential, if any, is too small to be perceptible. Hence the change in values of the parameter, $f_0 D^2/v_0^2$, is mostly due to the change in the values of f_0 alone, from sample to sample. As the duration of heat treatment increases the size of the nano-crystals increases

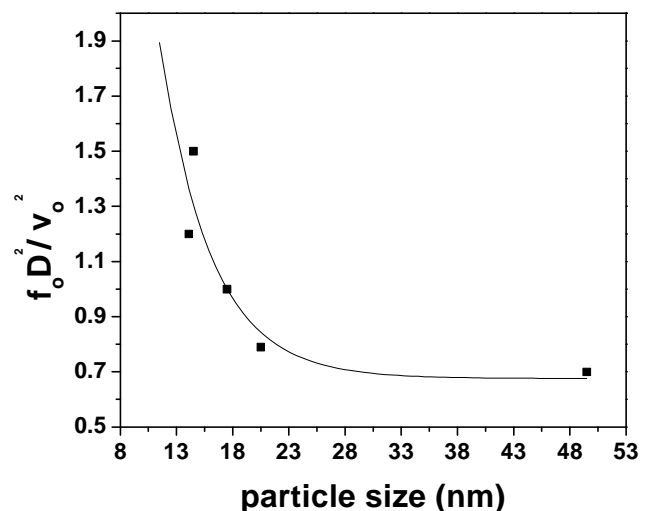


Figure 7. Variation of the parameter, $f_0 D^2/v_0^2$, with particle size of the nano-crystals.

in the system, and the parameter, $f_0 D^2/v_0^2$, shows a decreasing trend. It is found with the increasing size of the nano-crystals the value of the parameter, $f_0 D^2/v_0^2$, decreases exponentially and follows the relation

$$y = y_0 + A \exp [-x/b],$$

where y_0 , A and b are constants (see figure 7). For this glass system, $y_0 = 0.67578$, $A = 13.72105$ and $b = 4.54247$. We could expect that once we evaluate the values of these constants for a particular glass system in which nano-crystals are embedded, the size of the crystals within the glass matrix can be evaluated from the attenuation data. Hence this method may be used to determine size of nano-crystals using ultrasonic as a tool.

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