Original Paper

Relaxation of ultrasonic waves in ternary $TeO_2-V_2O_5-Sm_2O_3$ glasses

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Studies were carried out on the attenuation of longitudinal ultrasonic waves in tellurite glasses containing vanadium and samarium oxides with different concentrations, using the pulse echo technique. Glass samples were prepared in the form (composition in mol%): $65 TeO_2-(35 - x) V_2O_5-x Sm_2O_3$, where $x = 0.1, 0.5, 1.0, 2.0, 3.0, 4.0$ and 5.0 mol%. The temperature dependence of the attenuation at ultrasonic frequencies of 2, 4, 6, and 10 MHz in the temperature range 150 to 280 K was proved. The shape of the loss peaks, i.e. the relaxation spectra, showed the presence of well-defined peaks at various temperatures depending upon glass composition and operating frequency. It was observed that these loss peaks shift to higher temperatures with increasing frequency suggesting some kind of relaxation process. Activation energies of the relaxation process, and deformation potential were calculated. Results showed that activation energies are strongly dependent on the samarium oxide content. Deformation potential is also frequency- and composition-dependent. Discussion of the results obtained in this study is reported.

Relaxation von Ultraschallwellen in ternären $TeO_2-V_2O_5-Sm_2O_3$-Gläsern

Mittels der Pulsecho-Methode wurde die Dämpfung von longitudinalen Ultraschallwellen in Telluritgläsern, die Vanadium- und Samariumoxid in unterschiedlichen Konzentrationen enthielten, untersucht. Die Glasproben hatten folgende Zusammensetzung (in Mol-%) $65 TeO_2-(35 - x) V_2O_5-x Sm_2O_3$ (mit $x = 0,1; 0,5; 1,0; 2,0; 3,0; 4,0$ und $5,0$). Die Temperaturabhängigkeit der Dämpfung bei Ultraschallfrequenzen von 2, 4, 6 und 10 MHz im Temperaturbereich von 150 bis 280 K wurde festgestellt. Die Form der Dämpfungsverluste, d.h. der Relaxationsspektren, zeigte die Anwesenheit von gut definierten Peaks bei unterschiedlichen Temperaturen in Abhängigkeit von der Glaszusammensetzung und Arbeitsfrequenz. Es wurde beobachtet, daß diese Dämpfungsverluste sich mit ansteigender Frequenz zu höheren Temperaturen verschieben, was auf einen Relaxationsprozeß hinweist. Die Aktivierungsenergien des Relaxationsprozesses und das Deformationspotential wurden berechnet. Die Ergebnisse zeigen, daß die Aktivierungsenergien stark von dem Samariumoxid-Gehalt abhängig sind und daß das Deformationspotential von der Frequenz und der Zusammensetzung abhängt. Die in dieser Untersuchung erzielten Ergebnisse werden abschließend diskutiert.

1. Introduction

The study of ultrasonic attenuation in all glasses so far investigated revealed the presence of absorption peaks, in the attenuation versus temperature curve, occurring in the temperature range between 20 and 300 K [1 to 5]. The position and characteristics of these peaks depend on the glass composition and the frequency of the applied ultrasonic waves. The absorption peaks occurring in most inorganic oxide glasses have long been attributed to loss mechanisms of the standard linear solid type with low dispersion and a broad distribution of Arrhenius-type relaxation time [6]. The loss has been ascribed to the presence of particles or group of particles moving in

double-well potentials, and experimental values of activation energy and attempt frequency suggest that the particle dimensions are of atomic order of magnitude [6].

In silicate glasses, the peak occurred around 50 K, while in GeS_2 glass, the peak occurred at about 200 K, for 20 MHz longitudinal ultrasonic frequency [7]. EL Mallawany et al. [8] observed an absorption peak in the temperature dependence of the attenuation coefficient in TeO_2-MoO_3 glasses lying in the temperature range 150 to 250 K. Sidkey and his coworkers [9] reported the existence of absorption peak in $TeO_2-V_2O_5$ glass in the range 230 to 245 K and its position depends upon the composition of the glass and the applied frequency (2 to 10 MHz). In a recent study [10] on relaxation of ultrasonic waves in $TeO_2-V_2O_5-ZnO$ and $TeO_2-V_2O_5-CeO_2$

ternary glasses, the absorption loss peaks were observed at low temperature in the range between 150 and 230 K. Carini and his coworkers [11] reported an unusually high peak lying between 200 and 300 K in $x \, \mathrm{AgI} = (1 = x) \, (\mathrm{Ag_2O} = \mathrm{B_2O_3})$ superionic glass.

The work under report aims to study the ultrasonic relaxation process in the ternary glass system $65 \, \mathrm{TeO_2} - (35 = x) \, \mathrm{V_2O_5} - x \, \mathrm{Sm_2O_3}$ in the temperature range 150 to 280 K and applied ultrasonic frequencies of 2, 4, 6, and 10 MHz.

2. Experimental

Glass samples were prepared in the form (composition in mol%): $65 \, \mathrm{TeO_2} - (35 = x) \, \mathrm{V_2O_5} - x \, \mathrm{Sm_2O_3}$, where $x = 0.1, 0.5, 1.0, 2.0, 3.0, 4.0$ and 5.0 mol%. The preparation method was described in detail in a previous article [12]. Pieces of 1.5 cm in length were lapped and polished on the ends and used as specimens. Nonparallelism of the end faces was less than 0.01 mm. A cryostatic arrangement with liquid air as cryogen was used to set the sample at a desired temperature between that of liquid air and room temperature. The glass sample with the bonded transducer (Nona stopcock grease which proved to be a satisfactory couplant) was mounted on a suitable sample holder and placed inside the cooled chamber. The temperature of the sample was measured using a thermocouple placed in direct contact with the sample. Ultrasonic attenuation measurements were made by using an ultrasonic flaw detector USM3 (Krautkrämer, Köln (Germany)). The pulse echo technique was the method used, and the same transducer acted as the transmitter and receiver simultaneously. The heights of the successive echoes were measured accurately, and the attenuation coefficient was then calculated according to the equation:

$$a = \left(\frac{20}{2\,d}\right) \lg \left(\frac{A_1}{A_2}\right) \tag{1}$$

where d is the thickness of the sample, and A_1 and A_2 are the heights of the first and second echo, respectively.

3. Results and discussion

Longitudinal ultrasonic attenuation, at room temperature in the investigated glasses with different $\mathrm{Sm_2O_3}$ contents, was measured at ultrasonic frequencies of 2, 4, 6, and 10 MHz, and plots of the data are shown in
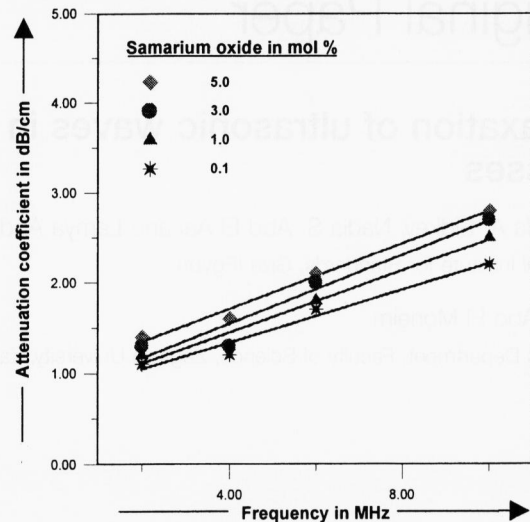

Figure 1. Variation of absorption coefficient with applied frequency for different contents of samarium oxide.

figure 1. All curves can be represented by straight lines indicating a nonzero extrapolated absorption at zero frequency. The data for all measurements can be expressed by the relation

$$a = g(T, x)f + a_\mathrm{r} \tag{2}$$

where g is temperature and composition dependent, x is the concentration of the modifier (mol% $\mathrm{Sm_2O_3}$), and a_r is the residual attenuation. The magnitude of g increases from 0.137 to 0.175 when the $\mathrm{Sm_2O_3}$ content increases from 0.1 to 5.0 mol%, while values of a_r range between 0.825 and 1.055 dB/cm. The ultrasonic attenuation in these glasses is strongly dependent on the concentration of $\mathrm{Sm_2O_3}$, the lower value of a was observed in $65 \, \mathrm{TeO_2} - 34.9 \, \mathrm{V_2O_5} - 0.1 \, \mathrm{Sm_2O_3}$ glass, while the maximum value was observed in $65 \, \mathrm{TeO_2} - 30 \, \mathrm{V_2O_5} - 5 \, \mathrm{Sm_2O_3}$ glass.

The temperature dependence of the attenuation coefficient for longitudinal ultrasonic waves at four frequencies namely 2, 4, 6, and 10 MHz for all glass samples are reported. Figures 2a and b show this dependence for 0.1, and 5.0 mol% $\mathrm{Sm_2O_3}$ content. It can be seen from these figures that the peak temperature, T_p, at which maximum attenuation occurs shifts towards higher temperature as the applied frequency is increased. Besides, the peak temperatures are shifting to higher temperature with increasing $\mathrm{Sm_2O_3}$ content.

The inverse of the peak temperatures against the logarithm of the applied frequency is plotted and shown in figure 3. The plots yielded straight lines satisfying Arrhenius equation of the form

$$f = f_0 \, \mathrm{e}^{-E/(KT)}. \tag{3}$$

Figures 2 and 3 suggest that there is some kind of relaxation process and the origin of the absorption loss lies in

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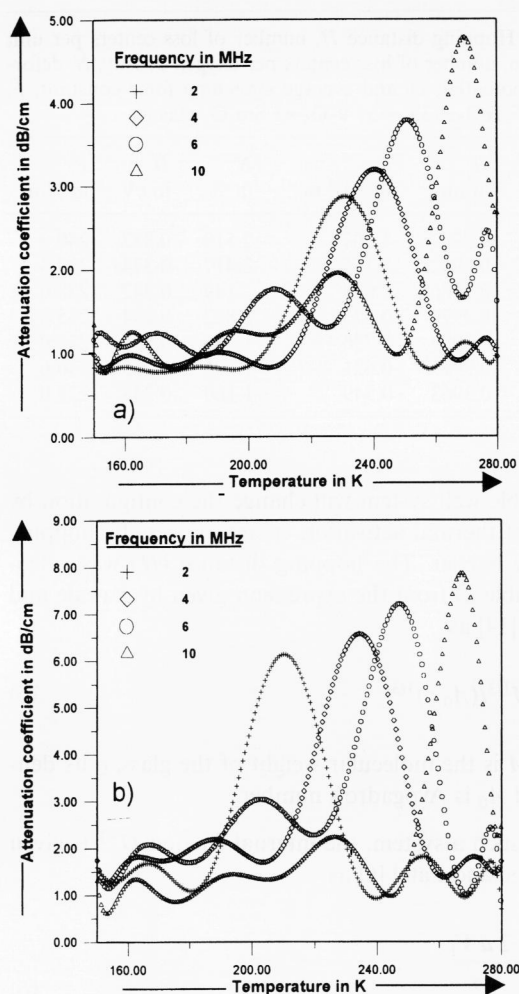
Figures 2a and b. Variations of absorption peaks with temperature for a) 0.1 mol% samarium oxide, and b) 5.0 mol% samarium oxide.
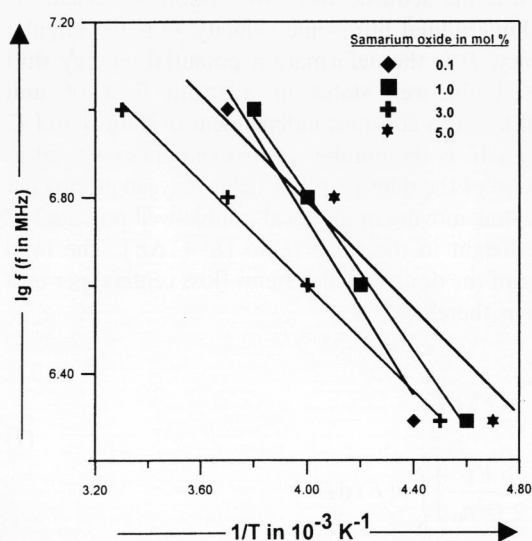

Figure 3. Variation of lg (f) versus inverse temperature ($1000/T$).

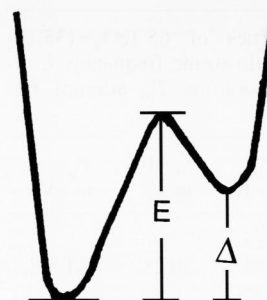a thermally activated relaxation process. This relaxation process can be ascribed to a particle moving in asymmet-

Figure 4. Asymmetric double-well potential of barrier height E and asymmetry Δ.

ric double-well potential, of atomic dimensions, figure 4, corresponding to two-equilibrium configurations arising from a defect structure in the amorphous network. The ultrasonic waves disturb the equilibrium and produce a relative energy shift between the minima of the double-wells by an amount $\Delta E = D \varepsilon$ in a strain field of magnitude ε. The deformation potential D expresses the energy shift of the relaxing states in a strain field of unit strength. Thus, the ultrasonic waves produce thermal inequilibrium, and a relaxation process is set up to restore the equilibrium again. The particle can surmount the barrier between the double-wells in a thermally activated process.

The experimental low-temperature loss peaks obtained in this study are too wide to be explicable in terms of a single relaxation process, and this makes the usual well-known relaxation time in the form

$$\tau = \tau_0\, e^{E_p/(KT)} \qquad (4)$$

an inadequate description. Thus, the activation energies (E_p) obtained in this study (table 1) are in fact spread of values around the fixed value obtained in crystalline tellurium-vanadium-samarium glass. The loss peak has to be analyzed in terms of distribution of relaxation times with each relaxing element moving in the double-well potential [13] of the form shown in figure 4. Also, there will be a distribution in the value of the anion-cation spacings and these spacings are smaller than the equilibrium (crystalline) value for bond angles acuter than normal, while they are larger for bond angles straighter than normal. It follows that the variability of $Te-O-Te$, $Te-O-V$, $Te-O-Sm$, $V-O-Sm$, and $Sm-O-Sm$ bond angles means that there is a spread of the atomic ring size in these glasses as shown in figure 5. Here, we can consider a distribution of double-well systems of vibrating particles will arise from a spread of cation-anion spacing with a distribution of barrier heights for both longitudinal and transverse motions of the anion for all kinds of bonds. It is also acceptable to just speak about the motion of oxygen atoms, as the vibrating particles, since tellurium, vanadium, and samarium atoms have relatively larger masses.

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Table 1. Low-temperature properties of $65\,TeO_2-(35\, - x)\,V_2O_5-x\,Sm_2O_3$ glasses; applied ultrasonic frequency, f, attenuation coefficient, α, peak temperature, T_p, attempt frequency, f_0, and activation energy, E_p

x in mol%	f in MHz	α in dB/cm	T_p in K	$f_0 \cdot 10^8$ in s^{-1}	E_p in eV
0.1	2	2.9	225		
	4	3.2	239	80.28	0.1308
	6	3.7	245		
	10	4.7	267		
0.5	2	3.4	209		
	4	3.6	219	43.62	0.1243
	6	4.13	229		
	10	4.3	231		
1.0	2	3.75	220		
	4	3.87	241	11.39	0.1089
	6	4.25	250		
	10	4.87	267		
2.0	2	3.93	212		
	4	4.07	218	5.34	0.0867
	6	4.5	239		
	10	5.16	253		
3.0	2	4.18	223		
	4	4.43	252	3.09	0.0835
	6	5.35	265		
	10	5.89	308		
4.0	2	5.9	162		
	4	6.31	192	2.76	0.0742
	6	6.77	225		
	10	7.3	249		
5.0	2	6.2	211		
	4	6.73	237	193	0.0671
	6	7.17	242		
	10	7.9	263		

Table 2. Hopping distance H, number of loss centers per unit volume, n, number of loss centers per oxygen density, N, deformation potential, D, and average stretching force constant, $\bar{F}$, [13] of $65\,TeO_2-(35\, - x)\,V_2O_5-x\,Sm_2O_3$ glasses

x in mol%	H in nm	n in 10^{27} m^{-3}	N in %	D in eV	$\bar{F}$ in N/m
0.1	0.3992	1.207	2.519	0.387	240.3
0.5	0.3992	1.155	2.417	0.374	239.3
1.0	0.3986	1.029	2.149	0.342	238.0
2.0	0.3976	0.873	1.822	0.294	235.5
3.0	0.3983	0.736	1.556	0.287	233.0
4.0	0.3959	0.621	1.296	0.265	230.6
5.0	0.3963	0.549	1.160	0.248	228.0

the double-well system will change the configuration by means of thermal activation energy process by hopping over the barrier. The hopping distance (H) was calculated (table 2) from the expression given by Yawale and Pakade [14] as

$$H = M^{1/3}/(A_0\,\varrho)^{1/3} \tag{5}$$

where M is the molecular weight of the glass, ϱ its density, and A_0 is Avogadro's number.

For such a system, the internal friction Q^{-1} is given by Bridge and Patel [6] as

$$Q^{-1} = \frac{2\,a\,V_1}{\omega}$$
$$= \frac{D^2\,2\,n_0}{\varrho\,V_1^2} \int_0^\infty \frac{\omega\,\tau\,n(E)\,\mathrm{d}E}{1 + \omega^2\,\tau^2} \tag{6}$$

where a is the acoustic wave absorption coefficient, V_1 is the longitudinal ultrasonic velocity, ω is the angular frequency, D is the deformation potential (energy shift of the double-well states in a strain field of unit strength), n_0 is a constant independent of both Δ and E, and $n(E)\,\mathrm{d}E$ is the number of loss centers expressed as a function of the number of particles (oxygen atoms) per unit volume moving in identical double-well potential of barrier height in the range E to $(E + \Delta E)$. The total number of the double-well systems (loss centers) per unit volume is therefore

$$n = \int_0^\infty n(E)\,\mathrm{d}E$$
$$= \left[\frac{\varrho\,V_1^2}{2\,D^2\,n_0}\right] \int_0^\infty c(E)\,\mathrm{d}E \tag{7}$$

where the integral $c(E)\,\mathrm{d}E$ is the area under the curve relating to a and T (figure 2).

Gilroy and Phillips [12] have proposed that for asymmetric double-well potential, $n(E)$ takes the form
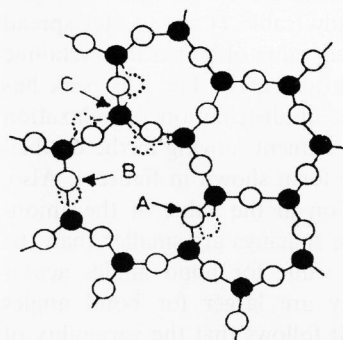

Figure 5. Schematic representation of glassy quartz structure with three possible types of two-state defects in the glass (A, B and C).

For any one of the double-well systems $O-A-O$, further oxygen atoms situated to the left and the right of A cation will generally be situated at sites slightly at different distances from the latter. Thus, a distribution of asymmetries Δ will appear as a second order effect. At peak temperature, T_p, the oxygen atoms comprising

$$n(E) = \frac{1}{E_p} \exp\left(\frac{-E}{E_p}\right) \qquad (8)$$

where E_p is an energy related to T_g which determines the shift of the loss peaks.

Assuming $n_0 = E_p^{-1}$ where E_p is the activation energy at which maximum absorption occurs [12], i.e. at T_p, equation (7) can take the form

$$n = \left[\frac{\varrho}{2}\frac{V_l^2}{D^2} E_p\right] \int_0^\infty c(E)\, dE. \qquad (9)$$

The integral $c(E)\, dE$ was computed by performing a computer program and the total number of loss centers per oxygen density N in % were calculated and given in table 2.

It is clear from table 1 that the increase in Sm_2O_3 content is accompanied by a decrease in both activation energy E_p, the number of loss centers n, and the deformation potential D. Thus activation energy E_p follows predominantly the trend of the stretching force constant F. For a given $A-O-A$ bond angle, the $A-A-$ separation would be directly proportional to the stretching force constant of the network. Thus, as the $A-O-A$ bond force constant decreases, the energy required to produce a given degree of bond angle or length distortion will decrease leading to a decrease in activation energy. Moreover, the decrease in the number of loss centers and the deformation potential will affect the activation energy of the relaxation process.

From the above, we can conclude that the absorption, in the measuring temperature range, is thought to be thermally activated and is attributed to particles $-$ probably oxygen atoms $-$ moving in double-well potential with a broad distribution of barrier height.

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