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CORRELATION BETWEEN SOME PHYSICAL PROPERTIES FOR TRI-COMPONENT TELLURITE GLASSES AND LOW TEMPERATURE ULTRASONIC RELAXATION

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Theoretical analysis of ultrasonic wave absorption and elastic moduli for TeO_2-V_2O_5-Sm_2O_3 glass system is presented. A correlation between low temperature ultrasonic relaxation parameters and other physical (elastic) properties for this glass system was achieved according to a model presented by Bridge and Patel. Correlation coefficients greater than 96% were obtained indicating that correlations between ultrasonic attenuation and activation energy at low temperatures and the bulk modulus of this glass system at room — temperature (through the two crucial structural parameters, number of anions and anion-cation force) exist.

1. Introduction

Based on the great deal of experimental information about the physical properties of tellurite glasses (which have been obtained from ultrasonic investigations) it is generally accepted that in almost all binary and ternary tellurite glass systems, the composition is a decisive factor [1–8]. The elastic constants (bulk modulus), experimental ring size, and the mean stretching force constant, calculated at room temperature, are strongly compositional dependent. The change in these parameters with the increase of the modifier mol percent content is mainly due to progressive strengthening of the network with more crosslinks between the units of the structure introduced by the increase of the modifier. On the other hand, the position and overall shape of the loss peaks (peaks of the temperature dependence of ultrasonic absorption occuring at low temperature), number of loss centers per oxygen atom, and activation energies of the relaxation process are also strongly composition sensitive. The relaxation spectra have been attributed to loss mechanisms of the standard linear solid type, and a broad distribution of Arrhenius-type relaxation times. This is caused by thermal motion of particles in two-well potentials of atomic dimensions, with a distribution of barrier heights, [2, 5, 7]. The number of loss centers per oxygen atom (vibrating particles in thermal motion) control the loss occured in double-well potential which is a property of the vitreous network. The activation energy of the relaxation process (activation energy of the anion atoms in the double-well system) depends on the value of the cation-anion forces.

Bridge and Patel [9] proposed a model of correlation between low temperature ultrasonic relaxation parameters and other physical properties for oxide glasses. Their study was carried out with gradual and wide ranging changes in the glass composition in order to understand the microscopic origin of the relaxation mechanisms of the vitreous system Mo-P-O. The model assumed that, in almost all glass systems, there is a distribution of the thermally averaged cation-anion-cation spacings about the equilibrium values, and correspondingly a distribution of cation-anion-cation angles because straight bond angles are rare and not necessarily equal to 180°. It follows that there will exist two-well systems with a distribution of barrier heights, for both longitudinal and transverse motions of the anions with all kinds of bonds. The longitudinal and transverse double-well potentials are associated with elongated and contracted cation-anion-cation angles. In another article [10], Bridge and Patel tried to apply the model developed from the study of the MoO_3-P_2O_5 system to explain the differences in the low temperature acoustic loss behaviour in different oxide glass systems. A theoretical analysis of ultrasonic wave attenuation and the elastic moduli of tellurite glasses was reported by El Mallawany [11]. His treatment of the peak loss (maximum absorption coefficient of ultrasonic waves) and the bulk modulus for TeO_2-MoO_3 networks is based on the fact that the total number of two-well systems per unit volume (number of loss centers) is proportional to the oxygen density, and the average activation energy is proportional to the mean first-order stretching force constant. He reported correlations between the ultrasonic absorption coefficients and the activation energy at low temperatures, on the one handside, and the bulk modulus of the glasses at room temperature, on the other side. The correlations were achieved through two crucial structural parameters: the number of anions and the anion-cation force.

The work under report aims to apply the model presented by Bridge and Patel [9] to the ternary glass system TeO_2-V_2O_5-Sm_2O_3 in order to examine its validity for this glass system.

2. Model

Bridge and Patel [9] noted that there is a distribution in thermally averaged cation-anion-cation spacings about the equilibrium values, and correspondingly a distribution of cation-anion-cation angles. Furthermore, the authors noted that, the longitudinal and transverse double-well potentials are associated with a spread of bond length and spread of cation-cation spacings. Therefore, there exist double-well systems with a distribution of barrier heights for all kinds of bonds. They also reported that the total number of loss centers (n) is proportional to oxygen density [O], and it increases with the mean atomic ring size (ℓ). The activation energy (E_p) increases with the average stretching force constant (F), and it also increases with the mean atomic ring size (ℓ). Quantitatively, they proposed the following empirical equations:

$$n = c_1[\mathrm{O}]\,\ell^m, \tag{1}$$

$$E_p = c_2 F \ell^m, \tag{2}$$

where [O] is the oxygen density that can be calculated from the chemical composition of the glass according to the following relation [11]:

$$[\mathrm{O}] = (c/D)(N_\mathrm{A}/16), \tag{3}$$

where c is the total amount of oxygen in 100 g of the glass, D is the volume of 100 g of the glass, N_A is Avogadro's number, c_1 and c_2 are constants, and m is a high positive power.

The total number of two-well systems per unit volume (n) is also given by:

$$n = \frac{\rho V_\ell^2 E_p}{2D} \int\limits_0^\infty C(E)\,dE, \tag{4}$$

where ρ is the density of the glass, V_ℓ is the longitudinal ultrasonic velocity, E_p is the activation energy of the relaxation process, D is the deformation potential (energy shift of the two-well states in a strain field of unit strength), and the integral $C(E)\,dE$ is the area under the curve relating between absorption and temperature. The average stretching force constant $\overline{F}$ for a network is calculated from the relation given by HIGAZY and BRIDGE [12] as

$$F = \frac{\sum(xn_f f)_i}{\sum(xn_f)_i}\,, \tag{5}$$

where x is the mole fraction of component oxide, n_f is the coordination number of cations (number of network bonds per formula unit), and f is the first order stretching force constant of the oxide (values of stretching force of each cation-anion pair, or mean force constant for respective types of the network bond).

BRIDGE *et al.* [13] argued that the average ring sizes could be obtained for the oxide network by

$$K = c_3 F/\ell^n, \tag{6}$$

where K is the bulk modulus, and n is a high positive power. Taking $c_3 = 0.0106$, $n = 3.84$, F is in Nm^{-1}, ℓ in nm, and K in GPa, they obtained a correlation factor of 99%. Then by eliminating (ℓ) between equations (1), (2), and (6) Bridge and Patel found

$$N = c_4(F/K)^{m/n}, \tag{7}$$

$$E_p = c_5 F(F/K)^{m/n}, \tag{8}$$

where N is the number of two-well systems per unit volume expressed as a percentage of the number of oxygen atoms. From inspection of Eqs. (7) and (8), Bridge and Patel observed that (F) can in fact be eliminated to yield the relation

$$E_p = c_6 N^{(1+n/m)} K. \tag{9}$$

They tested their model on the Mo-P-O glass system and after performing linear regression on $Ln(N)$ and F/K, they obtained the relationship

$$N = 0.589(F/K)^{0.576} \tag{10}$$

with a correlation coefficient of 80%. A linear regression performed on E_p and $F(F/K)$ yielded the relation

$$E_p = 6.92 \times 10^{-5} F(F/K)^{0.576} \tag{11}$$

with a correlation coefficient of 98%. However, apart from the correlation coefficient, the most important feature of Eqs. (7) and (8) is the fact that they predict correctly the general character of the compositional dependence of (N) and (E_p).

3. Results and discussion

In previous published articles by the authors [6, 7], the results of studies on low-temperature ultrasonic relaxation and physical properties for ternary tellurite glass system TeO_2-V_2O_5-Sm_2O_3 were reported. The authors observed that, the calculated bulk modulus (K) increases from 28.87 GPa to 32.47 GPa with increasing Sm_2O_3 from 0.1 to 5.0 mol %. Both the atomic ring size (ℓ) and average stretching force constant (F) decrease from 0.532 to 0.509 nm, and from 240.3 to 228.0 N/m respectively, as the Sm_2O_3 content increases indicating a change in the glass structure given in Table 1. On the other hand, as Sm_2O_3 mol % increases, both the activation energy (E_p) and total number of loss centers $(N\,\%)$, decrease from 0.197 to 0.106 eV and from 5.88 to 3.54, respectively, as given in Table 1. It was also observed that, the total number of loss centers $(N\,\%)$ decreases with the decrease in the atomic ring size (ℓ). The activation energy (E_p) also decreases with the decrease of the stretching force constant (F), Table 1. Moreover, the total number of two-well systems per unit volume per oxygen atoms $(N\,\%)$ was found [7] to be proportional to the oxygen density (i.e. to the reciprocal of the volume per gram atom of oxygen). Moreover, the average activation energy (E_p) was found [7] to be proportional to the mean atomic ring size (ℓ) and the average stretching force constant (F). These observations show clearly the strong composition dependence of both the physical properties at room temperature, and of the acoustic loss parameters at low-temperature for the studied tellurite glass system TeO_2-V_2O_5-Sm_2O_3.

Table 1. Values of the experimental bulk modulus (K), average stretching force constant (F), ring diameter (ℓ), and the oxygen density (O).

Glass Composition			K	F	ℓ	$O\times10^{28}$
TeO_2	V_2O_5	Sm_2O_3	(GPa)	(N/m)	(nm)	(m^{-3})
65	34.99	0.1	28.87	240.3	0.532	4.79
65	34.95	0.5	29.04	239.3	0.531	4.78
65	34.00	1.0	29.45	238.0	0.528	4.788
65	33.00	2.0	30.30	235.5	0.523	4.79
65	32.00	3.0	30.66	233.0	0.520	4.73
65	31.00	4.0	31.83	230.6	0.513	4.79
65	30.00	5.0	32.47	228.0	0.509	4.74

Table 2. Values of the experimental number of loss centers (N_{exp} %), theoretically calculated number of loss centers (N_{th} %), experimental activation energy (E_{exp}), and theoretically calculated activation energy (E_{th}).

Glass Composition			N_{exp} %	N_{th} %	E_{exp} (eV)	E_{th} (eV)
TeO_2	V_2O_5	Sm_2O_3				
65	34.99	0.1	5.88	1.363	0.197	0.197
65	34.95	0.5	5.63	1.355	0.172	0.195
65	34.00	1.0	5.37	1.340	0.153	0.192
65	33.00	2.0	4.72	1.310	0.144	0.186
65	32.00	3.0	4.33	1.294	0.139	0.181
65	31.00	4.0	3.72	1.259	0.115	0.175
65	30.00	5.0	3.54	1.236	0.106	0.169

Taking the values of $n = 3.84$ and $c_3 = 0.0106$ [13] and the value of $m = 2.21$, as obtained from a close fit of equation (2) to the data given in Table 1, and performing a linear regression on $Ln(N)$ and (F/K) we obtained

$$N = 0.402(F/K)^{0.576}, \tag{12}$$

with a correlation factor of 99.8%.

The linear regression was performed on E_p and $F(F/K)$ fitting equation (8) to the experimental values of average activation energy for our glass system; we obtained

$$E_p = 2.42 \times 10^4 F(F/K)^{0.576} \tag{13}$$

with the correlation factor of 95.8%.

The linear regression was also performed on $Ln(E_p/K)$ and $Ln(N)$. It results in

$$E_p = 6.7 \times 10^4 N^{1.374} \cdot K \tag{14}$$

with a correlation factor of 98%.

Apart from the correlation coefficients, the important feature of equations (12) and (13) is the fact that they predict correctly the general character of the compositional dependence of N and E_p, Table 1. Thus, as the Sm_2O_3 mol% increases from 0.01 to 5.0 mol%, the number of loss centers expressed as a function of the number of oxygen atoms per m^3, (N_{th} %), which was predicted from Eq. (12), decreases from 1.363 to 1.236 showing the same trend as found from the experimental data (N_{exp} %) which decreases from 5.88 to 3.54. This is shown in Fig. 1. In the case of the average activation energy (E_p), the values of the theoretically calculated data (E_{th}) predicted from equation (13) decrease from 0.197 to 0.106 eV, Fig. 2.

The decrease in both the activation energy (E_p), stretching force constant (F) and the increase in the bulk modulus (K) fulfill equation (13). The relations are shown in Figs. 3 and 4.

From an inspection of the ring size values (ℓ) given in Table 1, it can be observed that the decrease in the average ring size (ℓ) with decreasing activation energy (E_p) obeys the first principal given in Eq. (2) and shown in Fig. 5.

The decrease of the oxygen density [O] from 4.79 to 4.74 × $10^{28}\,\mathrm{m}^{-3}$ with increasing modifier content means that the number of loss centers decreases at a high Sm_2O_3

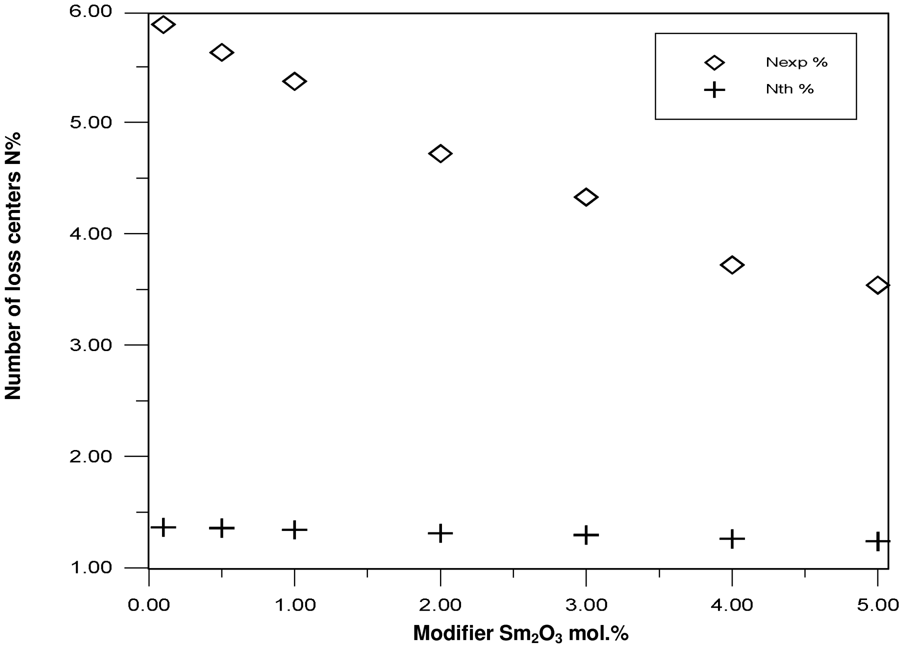

Fig. 1. Compositional dependence of the number of loss center N expressed as a function of oxygen atoms per cm^3 (TeO_2-V_2O_5-Sm_2O_3 glasses). N_{exp} and N_{th} (predicted theoretically by Eq. (12)).

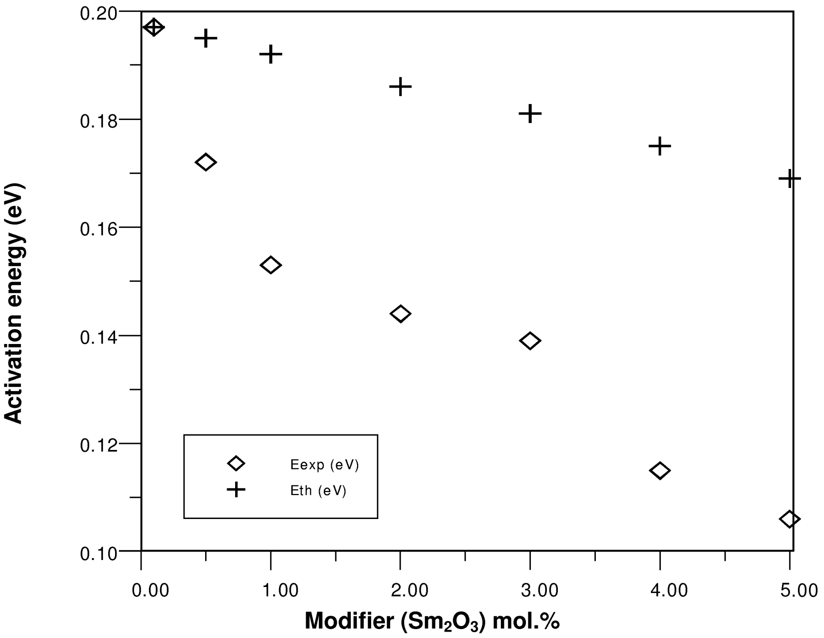

Fig. 2. Compositional dependence of the average activation energy E_{exp} (experimental) and E_{th} (theoretically predicted by Eq. (13)).

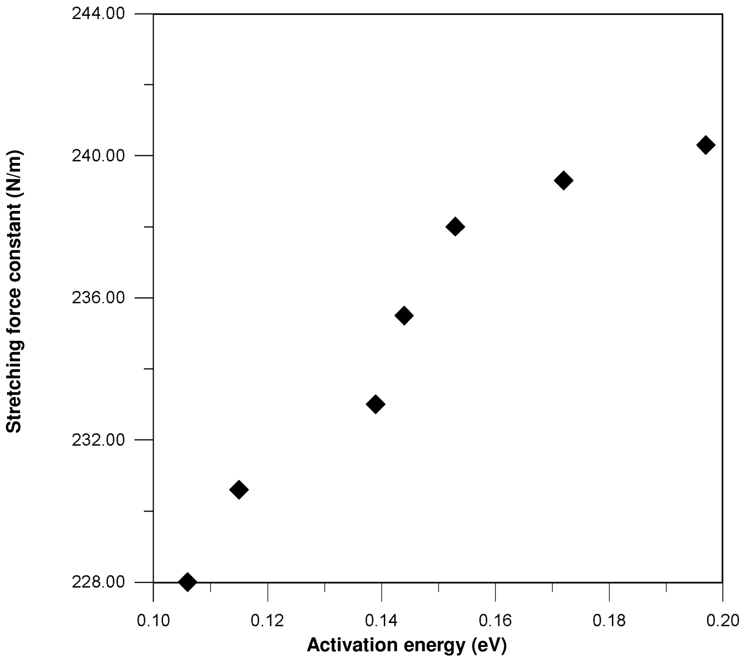

Fig. 3. Variation of the average stretching force constant with activation energy.

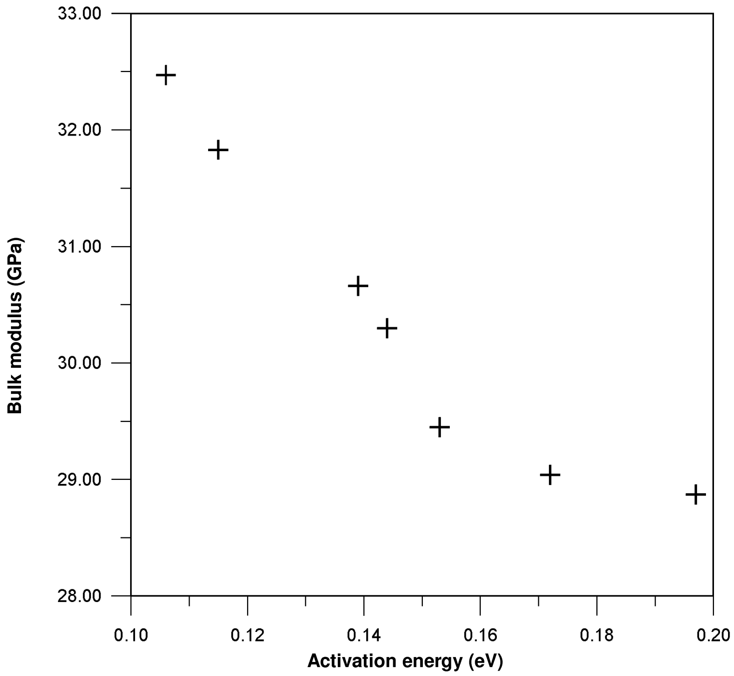

Fig. 4. Variation of experimental bulk modulus with activation energy.

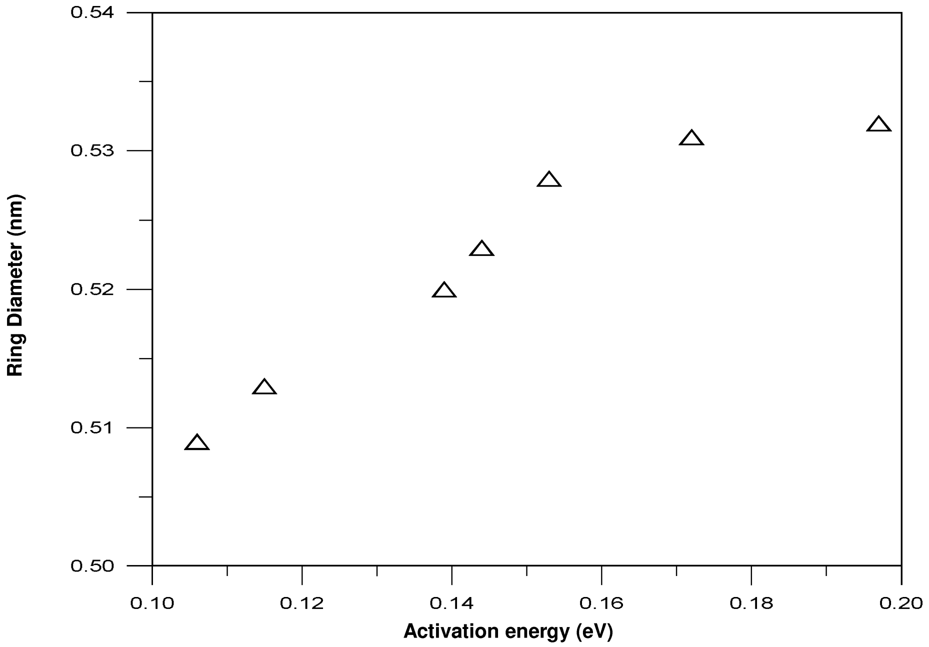

Fig. 5. Variation of the ring diameter with the activation energy.

content, that is added on the expense of V_2O_5. Since the number of loss centers is a fraction of the oxygen density. Therefore, this decrease will cause a decrease in the average activation energy and this fits Eq. (9).

The discussion, under report explains the role of Sm_2O_3 on tellurium-vanadium glasses. The behaviour of Sm_2O_3 in these glasses can be explained as follows; the activation energy (E_p) of the ternary TeO_2-V_2O_5-Sm_2O_3 glass system decreases due to the decrease of both the average stretching force constant (F), and the number of loss centers ($N\,\%$) (oxygen atoms per unit volume) on one hand side and the increase in bulk modulus (K) on the other side.

4. Conclusion

The correlation between some physical properties for tri-component tellurite glasses (bulk modulus K measured at room temperature and low temperature ultrasonic relaxation parameter, i.e. the activation energy E_p) was achieved through the two structural parameters: the number of anions (N) and the anion-cation stretching forces (F).

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