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EVALUATION OF BULK MODULUS AND RING DIAMETER OF SOME TELLURITE GLASS SYSTEMS

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Bulk modulus (K_{bc}) and Poisson's ratio (σ_{cal}) for 25 glass compositions of the following five tellurite glass series $TeO_2 – WO_3 – PbO$, $TeO_2 – V_2O_5 – Bi_2O_3$, $TeO_2 – WO_3 – K_2O$, $TeO_2–Nb_2O_5–ZnO$ and $TeO_2–Nb_2O_5–ZnO–Er_2O_3$ have been evaluated using bond compression model. Structural parameters like: number of bonds per unit volume, average stretching force constant, ratio of calculated bulk modulus to experimental bulk modulus (K_{bc}/K_e), atomic ring size of the glass network "ring diameter" and average crosslink density have been evaluated.

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Keywords: Tellurite glasses; acoustic properties; bulk modulus and Poisson's ratio; Atomic ring size.

1. Introduction

In materials engineering design prediction and understanding over the physical properties are essential to develop new class of functionalized materials. The modification of properties induced by the addition of transition metal oxides (TMO) or rare earth oxides (REO) into host glass matrix like tellurite glasses have attracted a lot of attention due to their physical properties and applications [1-14].

In the present work, theoretical bulk moduli K_{bc} will be calculated and the ratio of the calculated bulk modulus K_{bc} to the collected experimental bulk modulus K_e will be evaluated. Also, ring diameter ℓ, average stretching force constant $\overline{F}$, number of bonds per unit volume, average crosslink density $\overline{n_c}$ and Poisson's ratio σ_{cal} for every glass composition were evaluated and discussed. Such studies are helpful for understanding the medium range structure of tellurite glasses.

2. Theoretical Background

The structure of oxide glasses can be described in terms of bond compression model [15,16]. The model was based on two assumptions:
(i) The elastic moduli depends only on the "connectivity" of the network (number of bonds per cation) and on the average force constant. According to this model calculated bulk modulus K_{bc} and the first-order stretching-force constant *f*, can be estimated using the relations;

$$K_{bc} = \sum_i n_b r^2 f_i / 9 \qquad \text{(GPa)} \qquad (1)$$

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In Eq. (1), the number of bonds per unit volume n_b of glass is given as,

$$n_b = n_f N_f = n_f \rho N_A / M \quad (2)$$

where N_f is the number of formula units per unit volume , x_i is the mole fraction of the i_{th} oxide, n_f is the number of network bonds per glass formula unit, r_i is the bond length, ρ is the density of the glass, N_A is the Avogadro's number and M is average glass molecular weight. The stretching force constant f_i of every bond present in the glass network is calculated [16] using

$$f_i = 1.7/r_i^3 \quad (3)$$

Accordingly, the average bond stretching-force constant $\overline{F}$ for a three-dimensional poly-component oxide glasses can be estimated [16] using

$$\bar{F} = \sum_i x_i n_i \; f_i \; / \sum_i x_i n_i \quad (4)$$

(ii) The ratio between the calculated bulk moduli and the experimental one (K_{bc}/K_{exp}) is assumed to be directly proportional to the atomic ring size ℓ. The atomic ring size is defined as the ring perimeter (number of bonds times bond length divided by π) and is given by the relation [15];

$$\ell(nm) = \left[0.0106 \frac{\bar{F}}{K_{\exp}} \right]^{0.26} \quad (5)$$

where K_e is the experimental bulk modulus and F_b is the bond bending force constant of the glass, to the first approximation, may be taken as proportional to the average bond stretching force constant $\overline{F}$. The average crosslink density per unit formula of glass is given as,

$$\overline{n_c} = \frac{1}{\eta} \sum_i x_i (n_c)_i (N_c)_i \quad (6)$$

Where $\bar{n}_c$ is the number of crosslink density per cation which equals the number of bridging bonds per cation minus 2 [8], N_c is the number of cations per glass formula unit and η is the total number of cations per glass formula unit. The calculated Poisson's ratio will be calculated according to the next equation [16]

$$\delta_{th} = 0.28(\overline{n}_c)^{-0.25} \quad (7)$$

3. Discussions

Values of number of bonds per unit volume of glass n_b, average bond stretching-force constant $\overline{F}$, calculated bulk modulus K_{bc} and ratio (K_{bc} /K_e) for each glass composition are also presented in **Table 1** for 25 glass compositions of the following five tellurite glass series TeO_2 – WO_3 – PbO, TeO_2 – V_2O_5 – Bi_2O_3 , TeO_2 – WO_3 – K_2O, TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3 by using Equ.1 to Equ. 5. The discussions will as follows

Table 1: Number of bonds per unit volume (n_b), calculated bulk modulus K_{bc}, experimental bulk modulus Ke , ratio (K_{bc} /K_e), Average atomic ring diameter (ℓ), Average stretching force constant (F) $TeO_2 – WO_3 – PbO$, $TeO_2 – V_2O_5 – Bi_2O_3$, $TeO_2 – WO_3 – K_2O$, $TeO_2–Nb_2O_5–ZnO$ and $TeO_2–Nb_2O_5–ZnO–Er_2O_3$ glasses.

No.	Glass compositions									n_b x10^{28} (m^{-3})	K_{bc} GPa	K_e GPa	(K_{bc} / K_e)	ℓ (nm)	F^- (N/m)	n^-_c	σ_{cal}^-
	TeO_2	WO_3	V_2O_5	Nb_2O_5	ZnO	PbO	K_2O	Bi_2O_3	Er_2O_3								
1	1.00									7.699	72.71	31.70 Ref.20	2.294	5.023	213	2.000	0.235
2	0.70	0.20				0.10				8.581	79.82	39.98 Ref.17	1.996	4.685	205	2.833	0.216
3	0.675	0.20				0.125				8.798	81.41	44.42	1.833	4.542	202	2.875	0.215
4	0.65	0.20				0.15				8.846	81.43	47.39	1.718	4.450	200	2.917	0.214
5	0.625	0.20				0.175				9.091	83.25	49.36	1.687	4.388	197	2.958	0.213
6	0.60	0.20				0.20				9.133	83.22	51.77	1.607	4.319	194	3.000	0.213
7	0.50		0.45					0.05		7.125	67.85	31.80 Ref.18	2.134	5.054	218	3.333	0.207
8	0.50		0.40					0.10		7.253	68.60	33.50	2.048	4.961	214	3.333	0.207
9	0.50		0.35					0.15		7.322	68.77	34.60	1.987	4.895	210	3.333	0.207
10	0.50		0.30					0.20		7.442	69.40	35.80	1.939	4.826	206	3.333	0.207
11	0.50		0.25					0.25		7.512	69.55	36.70	1.895	4.769	202	3.333	0.207
12	0.80	0.15					0.05			8.435	78.70	33.02 Ref.19	2.384	4.931	206	2.300	0.228
13	0.80	0.10					0.10			8.030	73.90	29.70	2.489	5.032	201	2.200	0.230
14	0.80	0.05					0.15			7.668	69.70	27.57	2.527	5.091	194	2.100	0.233
15	0.80	0.00					0.20			7.389	66.30	25.12	2.638	5.173	189	2.000	0.236
16	0.90			0.10	0.0					8.192	76.52	42.50 Ref.13	1.800	4.619	207	2.364	0.226
17	0.85			0.10	0.05					8.555	79.91	38.50	2.075	4.739	206	2.455	0.224
18	0.80			0.10	0.10					8.861	82.77	38.10	2.173	4.752	206	2.545	0.222
19	0.75			0.10	0.15					9.261	86.51	37.10	2.332	4.785	206	2.636	0.220
20	0.75			0.10	0.15				0.00	9.261	86.51	36.70 Ref.20	2.357	4.799	206	2.636	0.220
21	0.75			0.095	0.15				0.005	9.305	86.87	39.10	2.222	4.718	206	2.645	0.220

22	0.75			0.09	0.15				0.01	9.336	87.11	38.80	2.245	4.726	206	2.655	0.219
23	0.75			0.085	0.15				0.015	9.343	87.12	39.30	2.217	4.709	206	2.664	0.219
25	0.75			0.08	0.15				0.02	9.380	87.42	39.60	2.208	4.698	205	2.673	0.219
25	0.75			0.075	0.15				0.025	9.531	88.77	43.20	2.055	4.591	205	2.682	0.219

a- Values of the number of bonds per unit volume n_b (calculated by equation 2) increased from 8.581 to 9.133, from 7.125 to 7.512 m^{-3} from 8.192 to 9.261 m^{-3}, from 8.192 to 9.261 m^{-3} and from 9.261 to 9.531 m^{-3} for $TeO_2 - WO_3 - PbO$, $TeO_2 - V_2O_5 - Bi_2O_3$, TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3 glasses as the content of the last component increases respectively. While it decreases from 8.435 to 7.389 m^{-3} for $TeO_2 - WO_3 - K_2O$ glasses. Recently, it has been found that n_b = 8.680, 9.550, 9.499, 9.648 and 9.684 for 80(TeO_2)-5(TiO_2)-(15 - x)(WO_3)-(x)A_nO_m, (x)A_nO_m = 0.01Nb_2O_5, 5Nb_2O_5, 3Nd_2O_3, 5Nd_2O_3 and 5Er_2O_3 mol%[11],

b- The stretching force constant $\overline{F}$ (calculated by equation 4) has been decreased from 205 to 194, from 218 to 202 and from 206 to 189 N/m, from 207 to 206 N/m and from 206 to 205 N/m for $TeO_2 - WO_3 - PbO$, $TeO_2 - V_2O_5 - Bi_2O_3$, $TeO_2 - WO_3 - K_2O$, TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3 glasses respectively,

c- The calculated bulk modulus K_{bc} (calculated by equation 1) increased from 79.82 to 83.22 GPa , from 67.85 to 69.55 GPa, from 76.52 to 86.51 GPa and from 86.51 to 88.77 GPa for $TeO_2 - WO_3 - PbO$, $TeO_2 - V_2O_5 - Bi_2O_3$, TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3 glasses respectively and decreased from 78.70 to 66.30 GPa for $TeO_2 - WO_3 - K_2O$ glasses. Values of K_{bc} for TeO_2 glass was 72.71 GPa [20] and the behavior of the calculated bulk modulus has the same trend as that of the experimental bulk modulus for each tellurite glass series,

d- The atomic ring size ℓ (calculated by equation 5) has been decreased from 4.685 to 4.319 nm, from 5.054 to 4.769 nm and from 4.799 to 4.591 nm for $TeO_2 - WO_3 - PbO$, $TeO_2 - V_2O_5 - Bi_2O_3$ and TeO_2–Nb_2O_5–ZnO–Er_2O_3 glasses respectively. But it increased from 4.931 to 5.173 and from 4.619 to 4.785 nm for $TeO_2 - WO_3 - K_2O$ and TeO_2–Nb_2O_5–ZnO glasses,

e- Variation of ratio of (K_{bc}/K_e) with the calculated ring diameter ℓ has been shown in Fig.1 shows that the ratio (K_{bc}/K_e) range ≤ 2.0 (PbO tellurite glass series), ≈ 2.5 (K_2O tellurite glass series), ≈ 2.0 (Bi_2O_3 tellurite glass series), ≥ 2.0 (ZnO tellurite glass series), ≈ 2.3 (Er_2O_3 tellurite glass series) and calculated ring diameter $\ell \leq 5.0$ nm indicating that elastic constants of tellurite glasses calculated using equations 1 to 5 are nearly in agreement with those measured by ultrasonic method and consistent with the ratio of pure TeO_2 glass [20]. The figure shows that high values of both (K_{bc}/K_e) and atomic ring size ℓ for $TeO_2 - WO_3 - K_2O$ glasses are responsible for very open three dimensional structure with respect to pure TeO_2 glass. Due to lower values of the calculated atomic ring size ℓ and ratio of (K_{bc}/K_e) for $TeO_2 - V_2O_5 - Bi_2O_3$, $TeO_2 - WO_3 - PbO$, TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3 glasses have closer three dimensional structure than pure TeO_2 glass. The $TeO_2 - WO_3 - PbO$ glasses show the low values of the ratio (K_{bc}/K_e) while $TeO_2 - WO_3 - K_2O$ glasses have the high values of (K_{bc}/K_e) against ring diameter. The atomic ring size ℓ of TeO_2 glass was 5.0 nm [20]. Recently, it has been found that (K_{bc}/K_e) =2.46, 2.69, 2.44, 2.22 and 2.09 while the atomic ring size ℓ = 0.491, 0.500, 0.486, 0.472 and 0.463 nm [8] for $TeO_2 - PbO - WO_3$ glasses. Previously, the ratio (K_{bc}/K_e) = 2.3 has been calculated for pure TeO_2 glass [20, 9]. This result also indicates that tellurite glasses can be considered as dense packing structure,

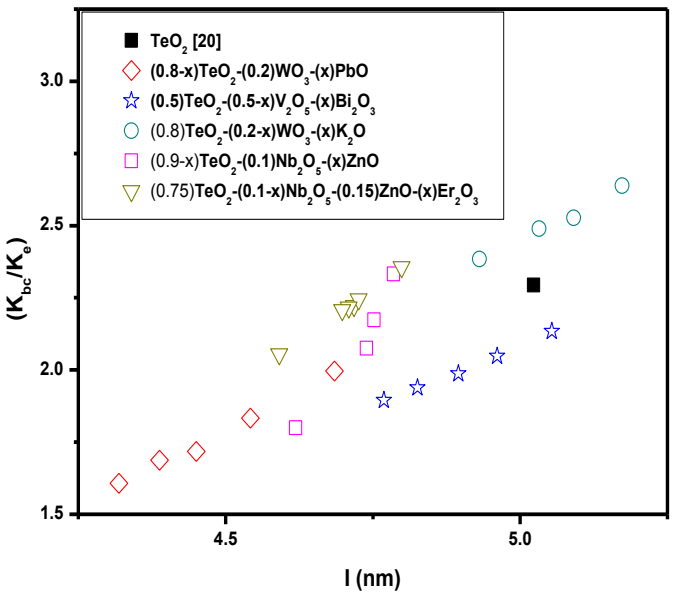

Fig.1 : Variation of ratio of (K_{bc}/K_e) with the calculated ring diameter ℓ for TeO_2 – WO_3 – PbO, TeO_2 – V_2O_5 – Bi_2O_3 , TeO_2 – WO_3 – K_2O, TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3.

f- The average crosslink density $\overline{n_c}$ and Poisson's ratio ($\int_{cal}$) for the 25 tellurite glass compositions have been calculated by using Equ.6 and 7. The average crosslink density $\overline{n_c}$ increased from 2.833 to 3.00 from 2.364 to 2.636, from 2.636 to 2.682 and calculated Poisson's ratio decreased from 0.216 to 0.213, from 0.226 to 0.220, 0.220 to 0.219 for TeO_2 – WO_3 – PbO, TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3 glasses and it has a fixed value at 3.333 and calculated Poisson's ratio at 0.207 for TeO_2 – V_2O_5 – Bi_2O_3 glass. While it decreased from 2.300 to 2.000 and calculated Poisson's ratio increased from 0.228 to 0.236 for TeO_2 – WO_3 – K_2O glass. The average crosslink density of TeO_2 glass 2.00 and calculated Poisson's ratio 0.235.

Based on the above arguments, it is possible to presented the probable illustrations of three dimensional structural fragmentations as illustrated in Fig.2-a for pure TeO_2 glass networks with TeO_4 (tbp) structural units, Fig.2-b for glass network with tetrahedral tungsten ions , Fig.2-c for TeO_2 glass network with octahedral tungsten ions. Fig.2-d for TeO_2 glass network with tetrahedral niobium ions, Fig.2-e for TeO_2 glass network with octahedral niobium ions, Fig.2- f forTeO_2 glass network with BiO_3 structural units and Fig.2-g for TeO_2 glass network with octahedral bismuth ions. Regarding Er_2O_3, the coordination number Er^{3+} in general varies from 8-12 and hence it is difficult to show in the form of structures. Similarly in the case of vanadium ions these ions participate in the glass with (VO^{2+}), called as vanadyl complexes and hence it is also difficult to show in the diagram. However, in case of lead ions they participate both in tetrahedral and in octahedral positions like tungsten ions in the glass network.

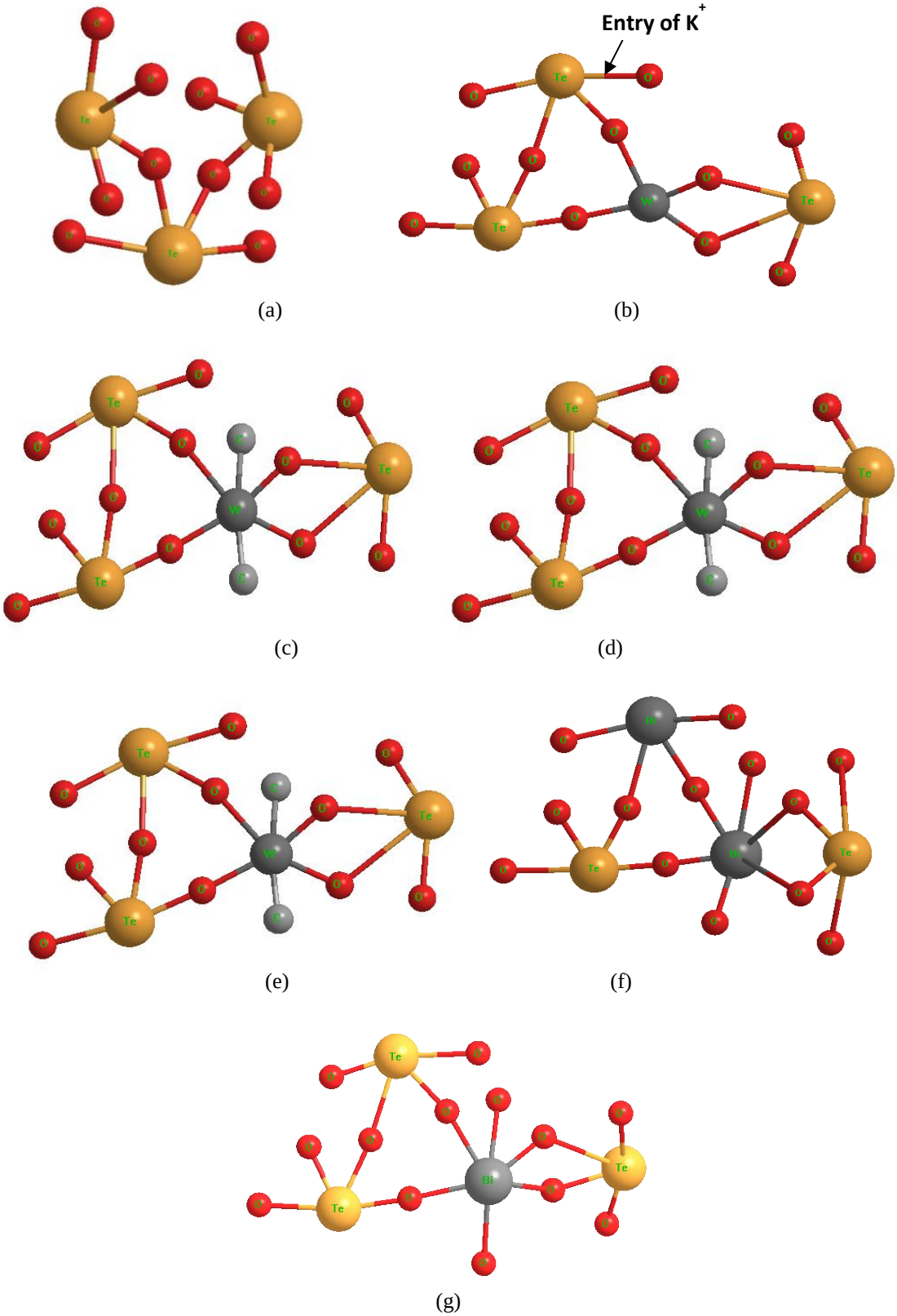

Fig.2: Illustrations of structural fragments of various TeO_2 glass networks. Pure TeO_2 glass network with TeO_4 structural units (b) TeO_2 glass network with tetrahedral tungsten ions (c) TeO_2 glass network with tetrahedral tungsten ions. (d) TeO_2 glass network with tetrahedral niobium ions (e) TeO_2 glass network with octahedral niobium ions (f) TeO_2 glass network with BiO_3 structural units (g) TeO_2 glass network with octahedral bismuth ions.

4.Conclusion

Medium range structure parameters of the five families of tellurite glasses (of 25 compositions) of TeO_2, $TeO_2 - WO_3 - PbO$, $TeO_2 - V_2O_5 - Bi_2O_3$, $TeO_2 - WO_3 - K_2O$ TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3 have been deduced. From the calculated atomic ring size ℓ and ratio of (K_{bc}/K_e) is has been found that:

- $TeO_2 - WO_3 - PbO$, $TeO_2 - V_2O_5 - Bi_2O_3$, TeO_2–Nb_2O_5–ZnO and TeO_2–Nb_2O_5–ZnO–Er_2O_3 glasses have closer three dimensional structure than pure TeO_2 glass,
- TeO_2-WO_3-K_2O glass has more open three dimensional structure than pure TeO_2 glass.

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