CHARACTERISTIC TEMPERATURES AND MICROHARDNESS OF $(ZnO)x-(AlF_3)y-(TeO_2)z$ TELLURITE GLASS SYSTEMS

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Glass transition temperature T_g and softening temperature T_s were measured by the differential thermogravimetric analysis DTA in the temperature range 300-850 K of ternary zinc oxyfluoro tellurite (ZOFT) with the composition $(ZnO)x-(AlF_3)y-(TeO_2)z$ where ($5 \leq x < 35$; $5 \leq y \leq 25$; $60 \leq z \leq 70$). Also, thermal expansion coefficient was measured by using a dilatometer over a range of 30°to 210°C. Acoustic Debye temperature θ_D, softening temperatures $T_{s(calc)}$ and microhardness $H_v$of ternary zinc oxyfluoro tellurite (ZOFT) have been calculated by using ultrasonic velocities data. The compositional dependence of these physical quantities were discussed to understand the rigidity and compactness of the glass system studied.

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1. Introduction

Tellurite glasses are very interesting glasses due to their unique physical properties and applications [1-10]. In recent years, the subject of glasses has rapidly increased because of their various applications in electronics and solar energy technologies [1,2]. Tellurite glass was applied at the back of amorphous silicon solar cells in combination with a rear reflector to improve the efficiency of the cell [1]. The propagation of ultrasonic waves in solids provides valuable information about the solid state motion in the material. The acoustic wave propagation in bulk glasses has been of considerable interest to understand their mechanical properties. Elastic properties provide information on the structures of solids which are directly related to the interatomic potentials.

The introduction of metal halides into the system could improve such properties and will decrease the their hygroscopic behaviour which limits the applications of many pure halides glasses. The main objective of the present work is to complete the previous of measuring ultrasonic velocities and elastic moduli by study the effect of concurrent ZnO addition and AlF_3 reduction on Debye, softening temperature and microhardness of zinc tellurite glass systems.

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2. Experimental work

Detailed preparation of these types of glasses is well documented as mentioned before [6]. Each of the glass compositions were checked by X-ray diffraction for their amorphous nature using X'Pert Pro Panalytical PW 3040 MPD X-ray powder diffractometer by employing Cr-Ka radiation. The density ρ of the glasses was determined by the Archimedes method with acetone as floating liquid. All the glasses were weighted with a digital balance ($\pm$ 0.0001 g accuracy). The thermal expansion coefficient was measured using L75D1250 dilatometer with the rectangular parallelepiped 3×3×6 mm^{3}of each glass composition and over a range of 30◦Cto 210◦C. The glass temperature T_g, and softening temperature T_s weredetermined by the differential thermogravimetric analysis(Setaram instrumentation Labsys DTA/6) at a heating rate of 20Kmin^{-1}. The accuracy in the measurement of T_g and $T_s$is $\pm$2◦C.The thermal expansion coefficient was measured by using a dilatometer over a range of 30◦to 210◦C according to relation 1,

$$\propto = \frac{\frac{\Delta L}{L}}{\Delta T} \quad (1)$$

Where L is the length of the sample, ΔL is the length increase and T is the temperature.

3. Results and discussions

The glass transition temperature of the ZOFT glass systems decreased from 664 to 647 K, 668 to 646 K and 670 to 635 K for Pn, Qn and Rn respectively as shown in Table 1. Fig. 1 shows the variation of T_g values in all series with the composition of ZnO mole fraction. All of the glasses in the series show a decrease in T_g with a decrease in AlF_3 content with the absence of anomalous behavior.

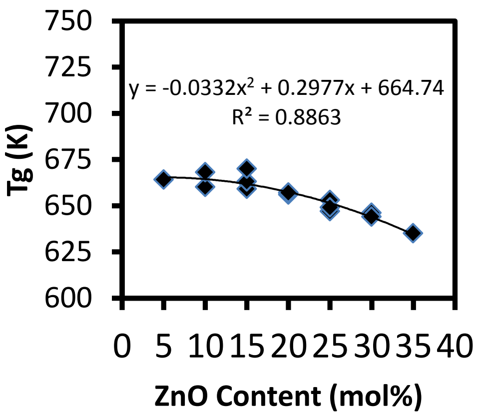

Fig. 1. Variation of glass transition temperature $T_g$with addition of ZnO for ZOFT glass series.

Table 1. Glass composition $x(ZnO)$-$y(AlF_3)$-$z(TeO_2)_z$, the glass temperature T_g, softening temperature T_s, thermal expansion and glass stability for ZOFT glass systems.

Sample Code	Glass Composition (mol%)			Temperature (K)		Thermal Expansion Coefficient ($\times 10^{-6}$ K^{-1})	Glass Stability (K)
	x	y	Z	T_g	T_s	α	
P1	5	25	70	664	802	9.88	138
P2	10	20	70	660	803	10.35	143
P3	15	15	70	659	811	10.30	152
P4	20	10	70	656	783	10.61	127
P5	25	5	70	647	755	11.51	108
Q1	10	25	65	668	794	10.73	126
Q2	15	20	65	663	787	10.24	124
Q3	20	15	65	657	777	10.55	120
Q4	25	10	65	653	767	11.66	114
Q5	30	5	65	646	725	10.76	79
R1	15	25	60	670	778	10.16	108
R2	20	20	60	657	759	9.97	102
R3	25	15	60	649	721	10.82	72
R4	30	10	60	644	723	11.32	79
R5	35	5	60	635	689	11.55	54

Softening temperature T_s of the prepared glasses decreased from 802 to 755K, 794 to 725K and 778 to 689 K for P_n, Q_n and R_n respectively as shown in Table 1. From Fig.2 for P1-P5 glass system, it can be seen that the softening temperature decreases from 802 to 755 K with increasing ZnO (decreasing AlF_3) content. The rest of glass samples show the same trend.The glass stability S(K) has been calculated by using relation 2,

$$S = T_s - T_g \qquad (K) \qquad (2)$$

The glass stability decreased from 138 to 108, from 126 to79 and from 108 to 54 K for the P_n, Q_n and R_n respectively. The glass stability decreased as the ZnO content increased, which could be attributed due to the loose packing structure has been noticed. Previously [10], Zn^{2+} and Al^{3+} ions may enter the glass network interstitially and the Te-O-Te bonds are broken and hence the formation of unstable bond may take place. The thermal expansion coefficient of the prepared glasses varied between 9.88 x $10^{-6}K^{-1}$ to 11.51 x $10^{-6}K^{-1}$, 10.73 x $10^{-6}K^{-1}$ to 10.76 x $10^{-6}K^{-1}$ and 10.16 x $10^{-6}K^{-1}$ to 11.51 x $10^{-6}K^{-1}$ as shown in Table 1 and Fig.2 for zinc oxyfluoro tellurite ZOFT code P_n, Q_n and R_n, respectively. Thermal expansion coefficient increases with the increase in ZnO content (decrease in AlF_3 content) as in Table 1. The present values of thermal expansion coefficient are slightly lower in the ZOFT glass system compared to binary zinc tellurite glass system [7]. Previously [8], addition of Al^{3+} into the glass network results in the structural rearrangement of the glasses due to the transfer of the bridging atoms.

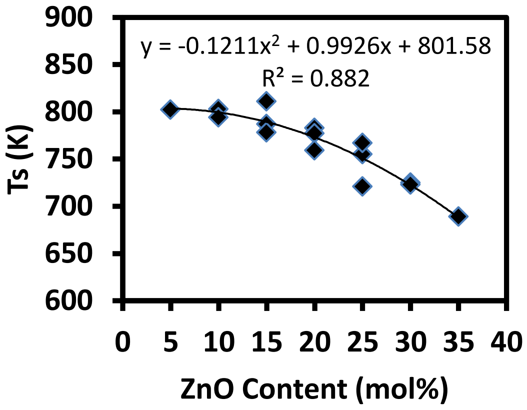

Fig. 2. Variation of glass softening temperature T_s, with addition of ZnO for ZOFT glass series.

The changes in the thermal properties of the ZOFT glass system could be attributed due to the number of bridging oxygen (BO) group decreases, which weaken the bond between each atom involved. So the bonds are much easier to break and hence the T_g of the ZOFT glass samples decreased. The Zn^{2+} is incorporated into the tellurite glass structure resulting in loose packing of the ZOFT glass structure and generally the ZOFT glass become thermally unstable. Replacing O^{2-} with F^- in the tellurite glass matrix causes the compositional dependence of the glass transition temperature. The fluorine ions tend to break up the strong TeO_2 covalent network of the glass by forming ionic, non-bridging Al-F bonds. All the current experimental data obtained from ZOFT glass series were analyzed using Microsoft Excel, by fitting nonlinear regression curves, with the results of the regression coefficients presented in Table 2. In Table 2, Y stands for the variables shown in the first column. As can be seen in previous figures, for most of the variables, a nonlinear curve ($Y=Ax^2+Bx+C$) gives the best fit.

Table 2.Nonlinear regression analysis of the variables ($y = Ax^2 + Bx + C$) for various physical and thermal propertiesof ZOFT glass series.

Variable	A	B	C	R^2
Density	-0.163	25.09	4527.1	0.89
Softening temperature, T_s	-0.121	0.993	801.58	0.88
Glass temperature, T_g	-0.033	0.298	664.74	0.89
Thermal Expansion, α	0.0008	0.020	9.92	0.57

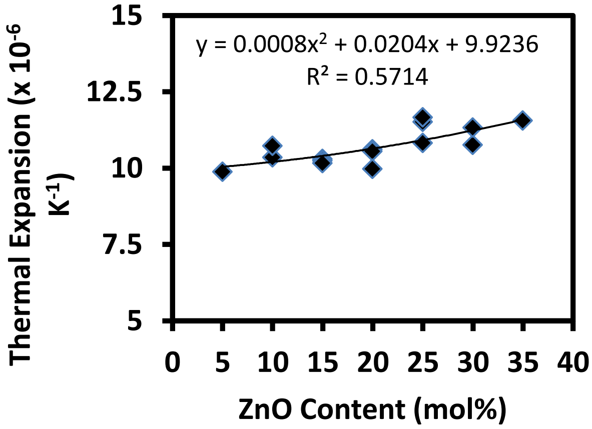

Fig. 3.Variation of glass thermal expansion with addition of ZnO for ZOFT glass series.

4. Calculations of characteristic temperatures and microhadness:

Recall the longitudinal, shear ultrasonic velocities and density values for the present glass systems as shown in **Table 3. Table 3** shows the composition of glass series of zinc oxyfluorotellurite (ZOFT) with an empirical formula of (ZnO)x-(AlF_3)y-(TeO_2)z , where (5 $\leq$x< 35; 5 $\leq$y$\leq$ 25; 60 $\leq$z$\leq$70) together with both densities and molar volumes [6]. Three systematic series of ZOFT glass system each denoted with Pn, Qn and Rn (n=1,..,5) have been successfully prepared previously. It was observed that the color of glass sample changes from semitransparent yellow to transparent yellow as more AlF_3 content is added to the ZOFT glass system [6]. Debye temperature θ_D was calculated using the equations 2 and 3.

$$\theta_D = \frac{h}{k}\left[\frac{9N}{4\pi V}\right]^{1/3} \upsilon_m \tag{2}$$

where

$$\upsilon_m = \left[\frac{(1/\upsilon_l^3) + (1/\upsilon_s^3)}{3}\right]^{-1/3} \tag{3}$$

where h Plank's constant, k Boltzman constant, υ_m is the mean ultrasonic velocity, and N the number of vibrating atoms per unit volume. If the Debye model is to represent all the vibrational modes (acoustic and optical), then N is equal to (PN_A), P is the number of atoms in the chemical formula and N_A is Avogadro's number. Calculated Softening temperature T_{SC} and microhardness H_v have been calculated by using equations 4and 5 as follows: Microhardness, H_v and softening temperature T_{SC} ,

$$T_{SC} = \left[\frac{M.w.}{\rho C}\right] v_s^2 \tag{4}$$

$$H_v = \frac{(1-2\sigma)E}{6(1+\sigma)} \tag{5}$$

Where

Where σ is Poisson's ration, M.W. is the molecular weight, E is Young's modulus and C is constant equal to 0.5074x10 cm/ $k^{1/2}$ s. Table 3 collected the values of microhardness, H_v, Debye temperature, θ_D (K) and softening temperature T_s(K) for the present zinc oxyfluorotellurite (ZOFT) with an empirical formula of (ZnO)x-(AlF_3)y-(TeO_2)z, where (5 $\leq$x< 35; 5 $\leq$y$\leq$ 25; 60 $\leq$z$\leq$70). Table 3 collects values of Debye temperature θ_D, softening temperatures T_s and microhardness H_v of some new ternary zinc oxyfluoro tellurite (ZOFT) with the composition (ZnO)x-(AlF_3)y-(TeO_2)z where (5 $\leq$x < 35; 5 $\leq$ y $\leq$ 25; 60 $\leq$ z$\leq$70).

Table 3 . Glass sample code, ultrasonic velocities, bulk density ρ , Poisson's ration σ , calculated Debye temperatureΘ_D,softening temperature, and microhadness of ZO(FT $(ZnO)_x(AlF_3)_y(TeO_2)_z$ glass systems.

Sample code	v_l (m/s) Ref.[6]	v_s (m/s) Ref.[6]	ρ (kg/m^3) Ref.[6]	σ Ref.[6]	Θ_D(K)	T_{SC}(K)	H_v(GPa)
P1	3669	2198	4670	0.220	292	802	4.21
P2	3618	2166	4840	0.221	289	803	4.23
P3	3576	2142	4910	0.220	284	811	4.20
P4	3482	2071	5010	0.226	270	784	3.92
P5	3390	1999	5130	0.233	263	755	3.64
Q1	3743	2201	4700	0.236	295	794	4.01
Q2	3585	2158	4860	0.216	289	787	4.29
Q3	3553	2110	4970	0.228	282	777	4.02
Q4	3478	2061	5040	0.229	274	767	3.86
Q5	3380	1970	5140	0.243	261	726	3.42
R1	3714	2194	4720	0.232	296	778	4.06
R2	3601	2134	4960	0.229	289	760	4.08
R3	3528	2046	5070	0.247	277	722	3.59
R4	3440	2014	5110	0.239	270	724	3.60
R5	3337	1931	5190	0.248	258	689	3.25

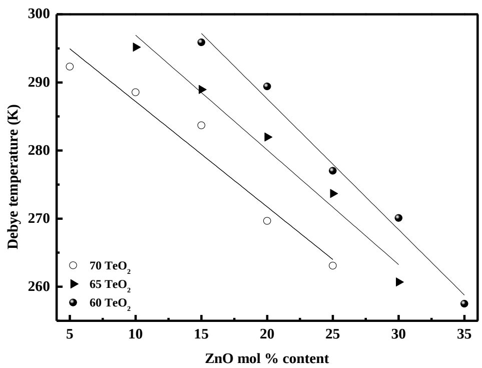

Fig.4 : Calculated Debye temperature of ternary zinc oxyfluoro tellurite (ZOFT) with the composition (ZnO)x-(AlF_3)y (TeO_2)z where (5 $\leq$x < 35; 5 $\leq$ y $\leq$ 25; 60 $\leq$ z$\leq$70).

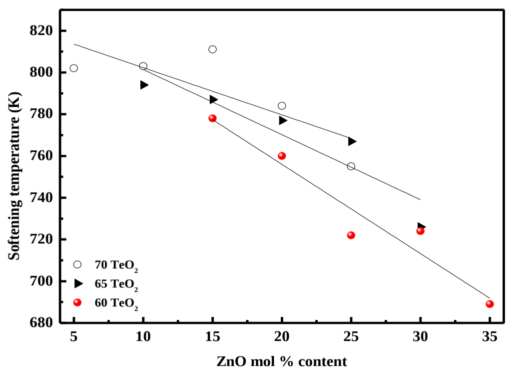

Fig.5: Calculated Softening temperature of ternary zinc oxyfluoro tellurite (ZOFT) with the composition (ZnO)x-(AlF_3)y (TeO_2)z where (5 $\leq$x < 35; 5 $\leq$ y $\leq$ 25; 60 $\leq$ z$\leq$70).

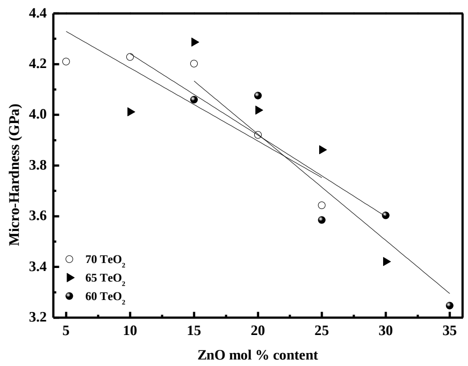

Fig.6 : Calculated Microhardness of ternary zinc oxyfluoro tellurite (ZOFT) with the composition (ZnO)x-(AlF_3)y (TeO_2)z where (5 $\leq$x < 35; 5 $\leq$ y $\leq$ 25; 60 $\leq$ z$\leq$70).

Fig.4 shows the variation of acoustic Debye temperature $\theta_D$as ZnO mol %present glass in the increases. As shown in Fig.4, it can be seen that in the glasses studied, Debye temperature decrease with ZnO addition to substitute the AlF_3 in the ZOFT glass system for all series.Debye temperature for P glass series (TeO_2:70) glass samples decreases from 292 to 263 K as the ZnO content increases from 5 to 25mol% and AlF_3 content decreases from 25 to 5mol%. Also, Debye temperature for both Q1 to Q5 and R1 to R5 (TeO_2:0.65 &TeO_2:0.60) glass samples decreases from 295 to 261 K and from 296 to 258 K as the ZnO content increases from 15 to 35 mol% and AlF_3 content decreases from 25 to 5mol%, respectively. Fig.5 shows the decrease of softening temperature $T_s$as ZnO mol %.or the three series of the present (ZnO)x-(AlF_3)y-(TeO_2)z where (5 $\leq$x < 35; 5 $\leq$ y $\leq$ 25; 60 $\leq$ z$\leq$70). Softening temperature decreases for P1 to P5, Q1 to Q5 and R1 to R5 (TeO_2:0.60 &TeO_2:0.65 &TeO_2:0.60) glass samples decreases from 802 to 755 K, from 794 to 726 K and from 778 to 689 K as the ZnO content increases from 5 to 25 mol%, from 10 to 30 mol% and from 15 to 35 mol% whereas AlF_3 content decreases from 25 to 5mol%, respectively.Fig. 6 shows the variation microhardness of ternary zinc oxyfluoro tellurite (ZOFT) with the composition (ZnO)x-(AlF3)y (TeO2)z where (5 <x < 35; 5 < y < 25; 60 < z<70). Microhardness shows a nonlinear decrease as more ZnO are added and substituting AlF_3 to the ZOFT glass system. Microhardness decreases for P1 to P5, Q1 to Q5 and R1 to R5 (TeO_2:0.60 &TeO_2:0.65 &TeO_2:0.60) glass samples decreases from 4.21 to 3.64 GPa, from 4.01 to 3.42 GPa and from 4.06 to 3.25 GPa as the ZnO content increases from 5 to 25 mol%, from 10 to 30 mol% and from 15 to 35 mol% whereas AlF_3 content decreases from 25 to 5mol%, respectively.As small quantity of AlF_3 is added into the TeO_2-ZnO glass network, a breaking of Te-O-Te takes place. F^- plays a role in decreasing the connectivity of the glass structure.

5. Conclusions

It is concluded that ternary zinc oxyfluoro tellurite ZOFT glass in the form x(ZnO)-y(AlF_3)-z(TeO_2), (5 $\leq$x < 35; 5 $\leq$ y $\leq$ 25; 60 $\leq$ z$\leq$70) has the following features:

- Both glass transition and softening temperatures decreases as ZnO increases,
- Thermal expansion coefficient increases as ZnO mole% increases,
- Calculated Debye temperature of the ZOFT glasses decreases as the ZnO content was added to substitute the AlF_3 content for ZOFT glass series while their molar volume decreases. The decrease in Debye temperature was due to decrease of molar volume as well as interatomic spacing,
- The observed decreased in calculated softening temperature and microhardness confirmed a substantial change in the glass structure. The concurrent of Zn addition and AlF_3 reduction in the tellurite glass matrix causes more ions being opened up in the network. Thus, weakening of the glass structure or reduction in the rigidity of the network takes place.

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