Thermal properties of new molybdenum oxyfluoride glasses

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New oxyfluoride glasses were prepared in the form MoO_3-BaF_2-xRF where RF is alkali fluoride (LiF, NaF and mixed NaF—LiF) with $x = 5, 10, 15, 20, 25, 30$ and 35 mol%. The densities of the studied glasses were measured and the molar volumes were calculated. Thermal properties like glass transition temperature T_g, the onset of crystallization temperature T_x, crystallization temperature T_c and melting temperature T_m were determined by using the differential scanning calorimetry (DSC) technique and from which the glass stability S and the glass forming tendency K_g were calculated. Values of thermal expansion coefficient α and specific heat C_p of the present glasses were also measured. All the above properties are correlated with composition alkali fluoride RF content and structure of the glass. © *2002 Kluwer Academic Publishers*

1. Introduction

Studies of oxyfluoride glasses have concentrated on; glass forming behavior, thermal and optical properties [1–3]. The oxyfluoride and fluorozirconate glasses are relatively more dense than most silicate glasses, e.g., the density $= 4.51$ gm/cm^3 for ZBLAN glasses [4]. This was attributed to the high values of atomic weight of their cations. The fluorine ion packing fraction is fundamentally much higher than that of oxygen ions in silicates, since the fluorine ions were found to occupy 0.75 of the available space in ZBLAN glass whereas in vitreous silica, oxygen ions can fill only 0.44 of the volume [4].

The alkali metal fluorides lower the vlaues of glass transition temperature, T_g, by an amount that varies inversely with ion size, e.g., the LiF has an unexpected effect in decreasing T_g values appreciably inspite of its high bond strength. The OH content can affect not only T_g values but also the glass tendency, i.e., as its content increases, it decreases T_g and facilitates crystallization [5]. Also, the incorporation of OH groups renders the structure more open and weak which leads to decrease the glass transition temperature T_g [6].

Special requirements for thermal expansion coefficient matching are needed, e.g., for antireflection coating and vapour deposition of fluoride glass film with the substrate. In order to design glasses for specific applications, a method of predicting thermal expansion coefficient as a function of composition is very useful. The effects of composition have been systematically studied by Parker [7] but insufficient data are available

to define appropriate relationships in more than a few cases. Nevertheless, significant trends can be identified. Because the fluoride ion is singly charged, bond strengths are more lowest in halide glasses than that in silicate glasses. Consequently, intermediate potentials are more asymmetric and values of expansion coefficient are high. For typical heavy metal fluoride glasses these values range from 150 to 220×10^{-7}°C^{-1} while for SiO_2 and commercial soda-lime-silica glasses, the coefficients have the values 5 and 90×10^{-7}°C^{-1} respectively [7]. This is of practical importance since a great thermal shock susceptibility is implied [8].

The specific heats, C_p and C_v, of fluoride glasses has been measured by several authors [9, 10]. Trans *et al.* [11] pointed out that C_v values are approximately 3 percent lower those of C_p. When expressed on a molar basis the specific heats at room temperature are remarkably consistent for different glasses, being typically 21.3 J/(mol · K). These values are approximately 86 percent of the Dulong and Petit values of 3R (24.9 J/mol · K) for vibrational heat capacity. On the other hand, C_p and C_v values are near 55 and 70% of Dulong and petit for silicates.

In the present work it is intended; (i) To prepare three glass systems in the form $(y - x)MoO_3$-$zBaF_2$-xRF new oxyfluoride glasses, where RF represents the alkali fluoride (LiF, NaF and mixed NaF—LiF) with $y = 70$ mol% for glass systems containing LiF and the mixture LiF—NaF and 80 mol% for the glass containing NaF, $z = 30$ mol% for the glasses containing LiF and 20 mol% for the glasses containing NaF and the

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mixture (LiF—NaF) and $x = 5$, 10, 15, 20, 25, 30 and 35 mol%. The densities of the studied glasses will be measured and its molar volumes are calculated. (ii) The diffrential scanning calorimetry (DSC) technique employ in ordr to determine the thermal properties e.g., the glass transition temperature T_g, onset of crystallization temperature T_x, the crystallization temperature T_c and the melting temperature T_m. The glass stability S and the glass forming tendency K_g are calculated, and (iii) Determining the thermal expansion coefficient α and specific heat C_p of the present glasses. All these properties will be correlated with composition (alkali fluoride RF content) and structure of the glass.

2. Experimental
The glass preparation method was explained in our previously work [12]. Amounts of starting materials are weighed, mixed together in a deep platinum crucible and heated up to melting temperature which was around 550°C in a furnace open to the atmosphere for 30–45 min. Then the melt is poured in a brass mould to give bar samples of thickness 3 mm. Samples are annealed near their glass transition temperatures for one hour, then the furnace is switched off. The density is obtained by the Archmide's method by using CCl_4 as an immersion liquid. The uncertainty in the density value is ±0.01 gm/cm³. Molar volumes were calculated according to $V_m = M/\rho$ where ρ is the density and M is the molecular weight of the glass sample which is calculated as follows: $M = \Sigma_i (x_i)(w_i)$, where x_i and w_i are the mole fraction and molecular weight of the component i, respectively.

Glass transition temperature T_g, crystallization temperature T_c, the onset of crystallization temperature T_x and the melting temperature T_m were determined by using the recorded thermograms of the differential scanning calorimetry (Seiko DSC 220) at a 10 K/min heating rate. Temperatures are given with an accuracy of ±1°C. Thus, the glass stability S and the glass forming tendency K_g could be calculated.

The average values of thermal expansion coefficient α are measured by using TMA SII Seiko 5200 instrument. Bar samples of thickness about 3 mm were used in the measurements. Measurements were performed in the temperature range from 50°C to near the glass transition temperature of each worked glass. Then the average values of thermal expansion coefficient are determined in the temperature range 100–150°C. The uncertainty of the obtained values is ±3 × 10⁻⁷°C⁻¹.

Heat capacity, C_p, is measured by a differential scanning calorimeter (DSC-7 Perkin-Elmer) equipped with a computerized data acquisition and analysis system. Samples for heat capacity measurements were typically 30–50 mg in mass and enclosed in crimped Al DSC pans. The C_p values of tested glasses were measured from room temperature to near their glass transition temperatures region at 4 K/min heating rate.

3. Results and discussion
The vitreous area of the present new molybdenum oxyfluoride glasses is displayed in Fig. 1. Referring to this figure it is noted that the vitreous area of the system which contain the mixture LiF—NaF is greater

TABLE I Composition, density and molar volume of the MoO₃—BaF₂—RF oxyfluoride glasses

Sample no.	MoO₃ (mol%)	BaF₂ (mol%)	LiF (mol%)	NaF (mol%)	ρ (g/cm³)	V_m (cm³)
MBL1	65	30	5		4.58	32.21
MBL2	60	30	10		4.55	31.08
MBL3	55	30	15		4.53	29.94
MBL4	50	30	20		4.49	28.82
MBL5	45	30	25		4.46	27.77
MBL6	40	30	30		4.44	26.54
MBN1	75	20		5	4.40	32.99
MBN2	70	20		10	4.37	32.03
MBN3	65	20		15	4.32	31.21
MBN4	60	20		20	4.29	30.25
MBN5	55	20		25	4.26	29.28
MBN6	50	20		30	4.22	28.33
MBN7	45	20		35	4.20	27.25
MBNL1	65	20	10	5	4.34	30.72
MBNL2	60	20	10	10	4.32	29.66
MBNL3	55	20	10	15	4.27	28.82
MBNL4	50	20	10	20	4.24	27.86
MBNL5	45	20	10	25	4.21	26.79
MBNL6	40	20	10	30	4.17	25.86
MBNL7	35	20	10	35	4.11	24.99

than those of the others which include, both LiF and NaF. Also these glasses are brown in color. Compositions of the studied glasses as well as their densities and molar volumes are given in Table I. The density and the molar volume of each glass system are decreased with replacing the alkali fluoride RF content instead of that of MoO₃ as shown in Figs 2 and 3 respectively. The obtained values of the density of the present glasses are higher than those of most silicate glasses. This is because the higher values of molecular weights of the present constituent cations. Also the packing fraction of the fluorine ion is higher than that of the oxygen one. However, the observed decrease in the density and molar volume with increasing the alkali flurodie RF instead of MoO₃, viz Figs 2 and 3, may be attributed to the fact that molecular weights and volumes of added alkali fluorides which are relatively lower than those corresponding to that of MoO₃. Therefore by adding RF instead of MoO₃ yield some decreases in the density and molar volume.

The DSC thermograms of the present glasses exhibit a normal behaviour as shown in Fig. 4 for only, some of the prepared samples. The dependence of T_g on alkali fluoride content is illustrated in Fig. 5. Insepction of this figure reveals that, T_g is decreased with increasing RF content. However, the obtained values of T_g, T_x, T_c and T_m for tested glasses are given in Table II. The glass transition temperature T_g can be described by factors related to composition and structure. These factors are the average cross-link per cation, $\bar{n}_c$, and the average stretching force constant, F, of each glass system. It was found that, T_g is an increasing function of both of $\bar{n}_c$ and F [13],

$$T_g = f(\bar{n}_c, F) \qquad (1)$$

where

$$\bar{n}_c = \frac{1}{\eta}[(n_c)_1(N_c)_1 + (n_c)_2(N_c)_2 + \cdots] \qquad (2)$$
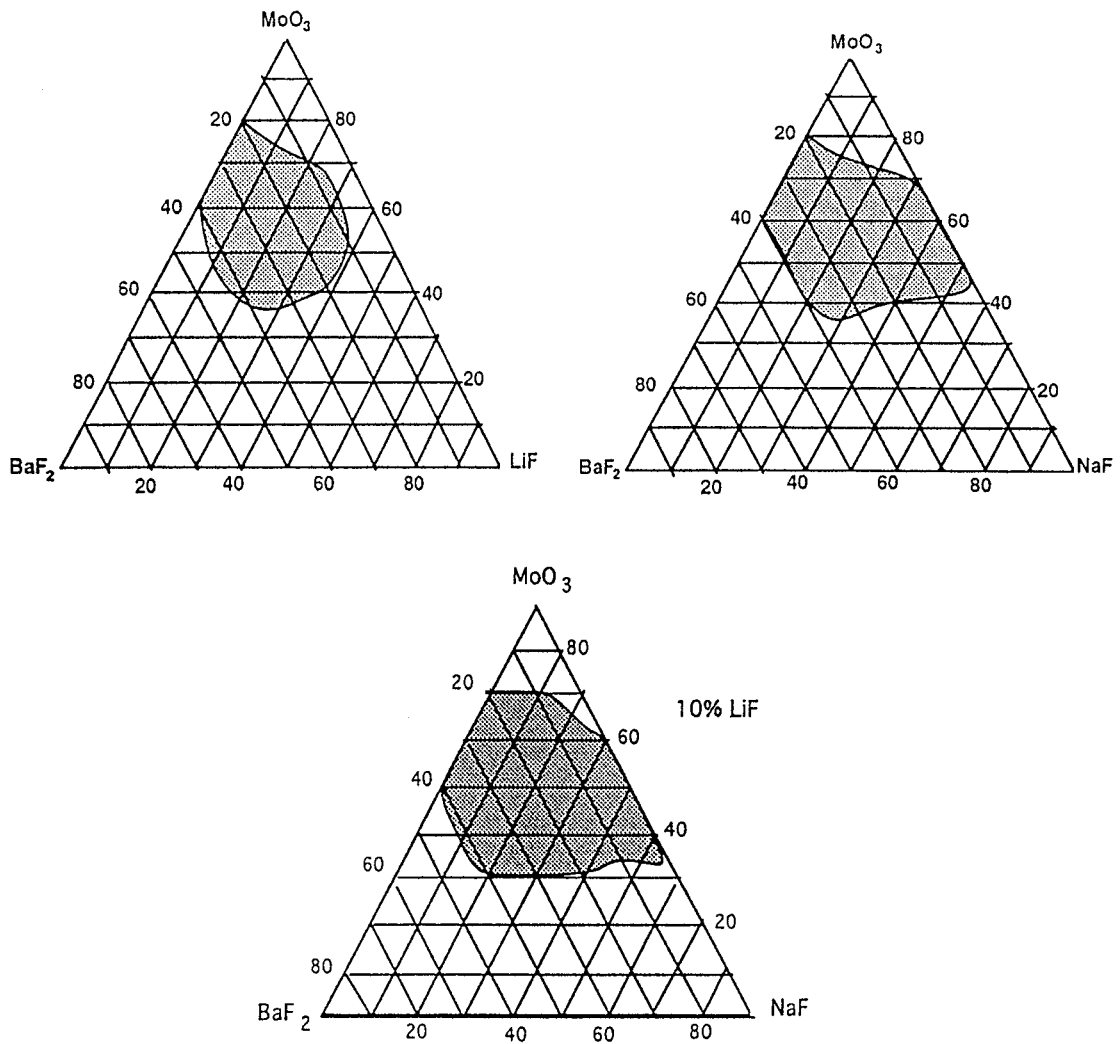
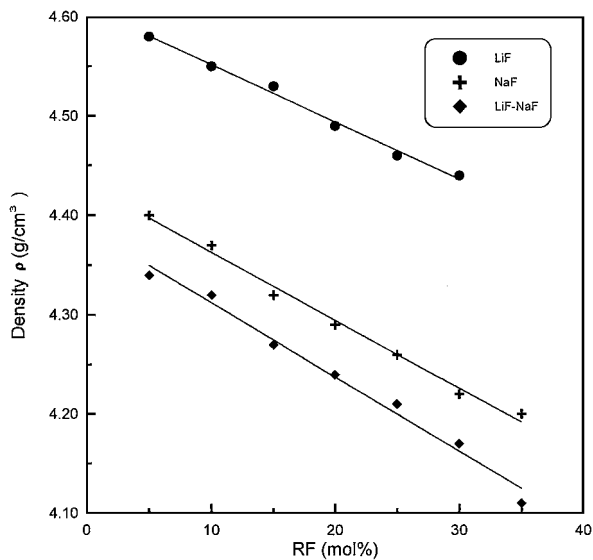Figure 1 The vitreous area of the MoO_3-BaF_2-RF system.

Figure 2 Variations of the density with the alkali fluoride RF of the present molybdenum oxyfluoride glasses.
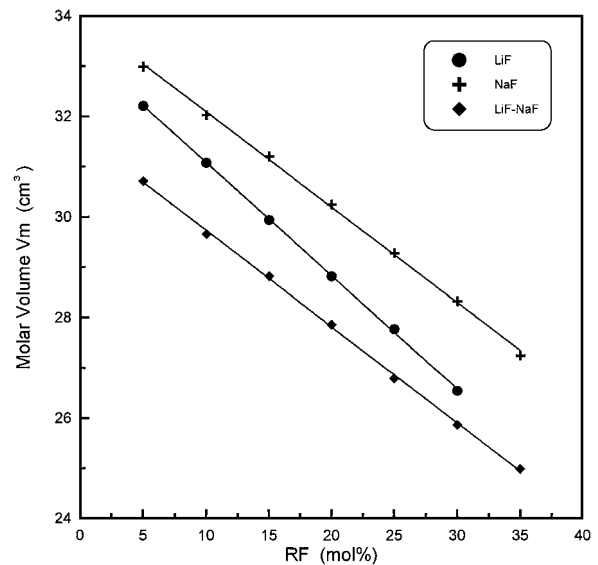

Figure 3 Variations of the molar volume with the alkali fluoride RF of the present molybdenum oxyfluoride glasses.

η = number of cations per glass formula unit.

$$\eta = \sum_i (N_c)_i$$

and $(N_c)_i$ is equal to the number of cations multiplied by the mole fraction of the i component and $n_c = n_f - 2$,

where n_f is the coordination number which equal to 6, 10, 7.5 and 7.2 for MoO_3, BaF_2, LiF and NaF respectively [14] and F = average stretching force consant of the glass.

$$F = \frac{[f_1(n_1)(N_c)_1 + f_2(n_2)(N_c)_2 + \cdots]}{[(n_1)(N_c)_1 + (n_2)(N_c)_2 + \cdots]} \quad (3)$$

TABLE II The glass transition temperature, T_g (°C), onset of crystallization temperature T_x (°C), crystallization temperature T_c (°C), glass stability $S = (T_x - T_g)$, thermal expansion coefficient α (°C^{-1}), glass forming tendency K_g and measured and calculated specific heat C_p (J/g·°C) at room temperature of the studied glasses

Sample no.	T_g (°C)	T_x (°C)	T_c (°C)	$S = (T_x - T_g)$ (°C)	K_g	$\alpha \times 10^{-7}$ (°C^{-1})	C_p meas. (J/g·°C)	C_p calc. (J/g·°C)
MBL1	268	358	369	90		162	0.528	0.496
MBL2	265	357	368	92				
MBL3	263	356	367	93	0.57	167	0.534	0.473
MBL4	252	353	367	101				
MBL5	241	330	345	89		177	0.559	0.4499
MBL6	240	344	345	104				
MBN1	282	359	361	77		124	0.516	0.500
MBN2	264	323	331	59				
MBN3	256	341	349	85	0.49	182	0.581	0.481
MBN4	242	344	361	102				
MBN5	241	334	345	91		199	0.596	0.462
MBN6	237	338	353	101				
MBN7	228	325	346	97				
MBNL1	254	325	330	71		167	0.516	0.477
MBNL2	243	349	369	106				
MBNL3	236	339	354	103	0.60	175	0.562	0.459
MBNL4	228	318	327	90				
MBNL5	219	330	343	111		216	0.871	0.439
MBNL6	218	327	340	109				
MBNL7	216	311	312	95				
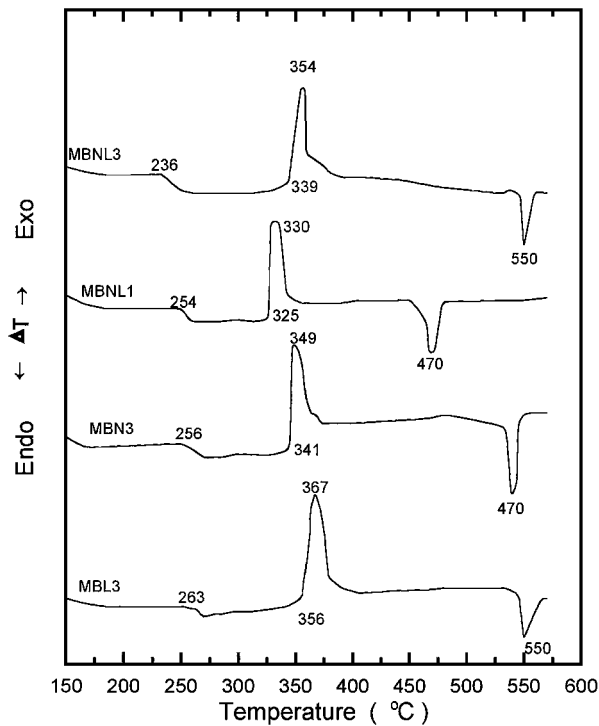
Figure 4 DSC curves of some of the MoO$_3$-BaF$_2$-RF glasses.

Figure 5 Variations of the glass transition temperature with the alkali fluoride RF of the present molybdenum oxyfluoride glasses.

where f_i is the first order stretching force constant which is calculated according to the empirical formula given by Gordy [15]

$$f = 5.28N \left[\frac{X_a X_b}{r^2} \right]^{\frac{3}{4}} + 30 \qquad (4)$$

r is the bond length in nanometer, N is the bond order i.e., the effective number of covalent or ionic bonds acting between the atoms a and b and X_a and X_b are the electronegativities of these two atoms respectively. These parameters are calculated for tested glasses and given in Table III.
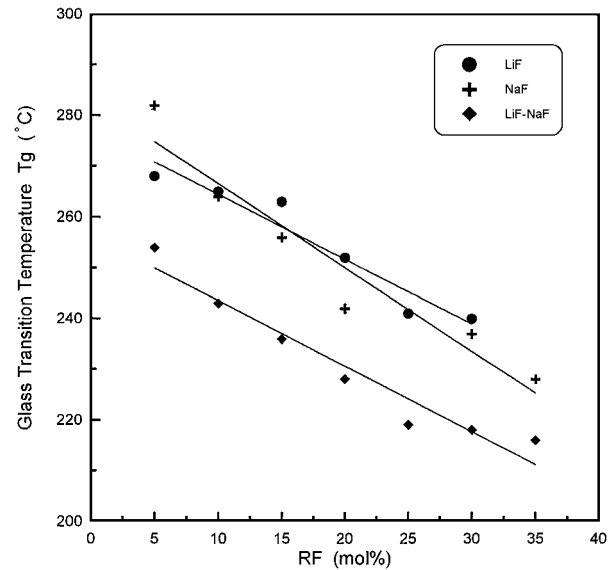
The minimum separation distance r between each cation-anion present in the glass materials can be determined as follows: if the glass has a component $x\%$ from A$_b$B$_c$ where A is the cation and B is the anion and x is in mol%, so the concentration n/cm^3 of ion A or B is given by

$$n(\text{A or B}) = \frac{(\text{b or c}) \cdot x \cdot N_A}{100 V_m^v} \qquad (5)$$

where N_A is the Avogadro's number and V_m is the glass molar volume. Therefore r is given by

$$r = \left(\frac{1}{n} \right)^{1/3} \qquad (6)$$

The calculated values of the minimum separation distance, r, are given in Table III. The average stretching

TABLE III The minimum separation distance, r, between the cation-anion (nm), average cross link density $\bar{n}_c$ and average stretching force constant F (N/m) of the MoO_3-BaF_2-RF glasses

| Sample no.	Mo—O (nm)	Ba—F (nm)	Li—F (nm)	Na—F (nm)	$\bar{n}_c$	F (N/m)
MBL1	0.218	0.218	0.511		5.275	177.5
MBL2	0.221	0.275	0.401		5.35	171.9
MBL3	0.224	0.275	0.346		5.425	157.7
MBL4	0.229	0.271	0.310		5.50	153.7
MBL5	0.230	0.268	0.280		5.575	152.7
MBL6	0.239	0.264	0.264		5.65	157.5
MBN1	0.209	0.325		0.515	4.86	193.8
MBN2	0.212	0.322		0.405	4.92	185.4
MBN3	0.215	0.319		0.351	4.98	177.8
MBN4	0.219	0.316		0.316	5.04	171.6
MBN5	0.223	0.312		0.289	5.10	166.4
MBN6	0.227	0.309		0.269	5.16	162.2
MBN7	0.233	0.305		0.253	5.22	159.3
MBNL1	0.214	0.317	0.399	0.503	5.01	177.1
MBNL2	0.217	0.313	0.395	0.395	5.07	169.5
MBNL3	0.222	0.310	0.391	0.342	5.13	162.6
MBNL4	0.226	0.307	0.387	0.307	5.19	157.1
MBNL5	0.231	0.303	0.382	0.281	5.25	152.9
MBNL6	0.238	0.299	0.377	0.262	5.31	149.7
MBNL7	0.246	0.296	0.373	0.246	5.37	147.4
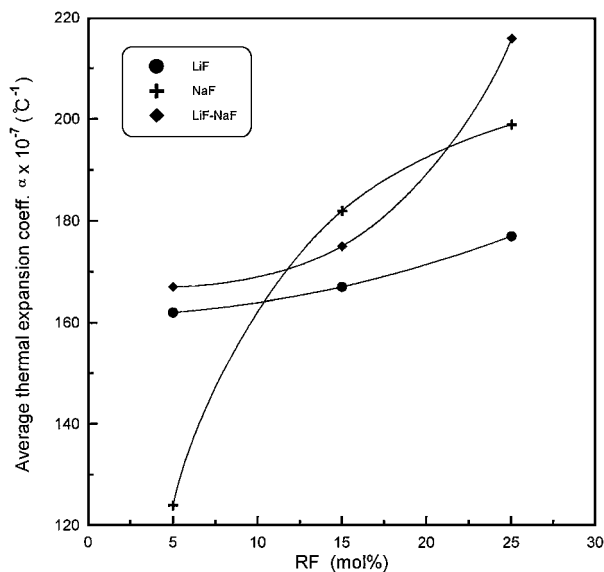
Figure 6 Variations of the stretching force constant with the alkali fluoride RF of the present molybdenum oxyfluoride glasses.
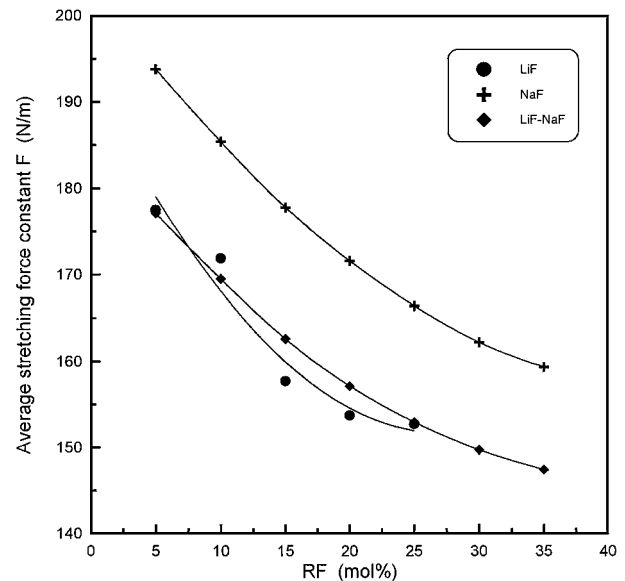

Figure 7 Variations of the thermal expansion coefficient α with the alkali fluoride RF of the present molybdenum oxyfluoride glasses.

force constant is decreased by replacement of MoO_3 by alkali fluoride content as shown in Fig. 6 and illustrated in Table III. From this table it is observed that the samples which contain nearly the same oxide and fluoride contents are having nearly equal average values of F. For example, values of average stretching force constant F of the sample MBL4 and MBNL4 (which contain 50 mol% oxide and 50 mol% fluoride) are 154 and 157 N/m respectively. Also, the values of F are 178 and 177 N/m for samples MBL1 and MBNL1 (which contain 65 mol% oxide and 35 mol% fluoride) respectively.

Since, the replacement of MoO_3 by the alkali fluorides decreases the average stretching force constant F, see Table III and Fig. 6, and thus the glass structure will be weakened and become open and renders the glass more fluid, then the glass transition temperature

T_g is decreased. This is in agreement with the previously reported fact [16] that the introduction of fluorine instead of oxygen in lead-fluorosilicate glasses will create non-bridging fluorine ions and the structure will be more open, so that the glass transition temperature is decreased.

The average value of thermal expansion coefficient of the studied glasses is found to be proportional to the RF content as in Fig. 7 and its values are given in Table II. These values are between 162–177, 124–199 and 167–216 $\times 10^{-7}{\circ}C^{-1}$ for MBL, MBN and MBNL glasses respectively. However, they are closed to that reported for the heavy metal fluoride glasses (150–220 $\times 10^{-7}{\circ}C^{-1}$) [7].

The correlation between the thermal expansion coefficient and alkali fluoride content is considered in different ways. Because the ionic charge is low for alkali

cations, thermal energy results in the larger increase of the M—F bond length by comparison with Ba—F bonding. From the structure point of view, a vitreous network of these oxyfluoride glasses is described as the association of MoO_4 tetrahedra and/or MoO_6 octahedra sharing corners [12]. Modifiers BaF_2 and RF (alkali fluorides) give their fluorine anion to the network while Ba^{++} and R^+ (R = Li or Na) cations are inserted in the network vacancies. Alkali incorporation results in weaker interaction between network and modifiers and increases variation of volume versus temperature. The replacement of MoO_3 by RF creates some Mo—F bonds and also non-bridging fluorine ions, which leads to a weaker network structure. Consequently, T_g is lowered and thermal expansion coefficient is increased as illustrated in Table II and Figs 5 and 7 respectively.

There some useful parameters used for investigating devitrification and stability of the glass. These parameters are the glass forming tendency K_g [17] and stability S which are given by the following equations:

$$K_g = \frac{T_c - T_g}{T_m - T_c} \tag{7}$$

$$S = T_x - T_g \tag{8}$$

Since, the higher values for K_g and S suggest that lower tendencies for glass devitrification. Therefore, for MBL3, MBN3 and MBNL3 glasses of the present work, the values of K_g are 0.57, 0.49 and 0.60 and those for S are 93, 85 and 103 respectively, are consistent in commonsense with the above Equations 7 and 8. This result is also confirmed in Fig. 1 which shows that the glass forming area of MBNL system containing the mixed alkali fluoride (NaF—LiF) is larger than those corresponding to MBL (which contain LiF) and MBN (which contain NaF) glass systems respectively. Figs 8–10 illustrate the variations of glass specific heat C_p with temperature in the range from room temperature to near the glass transition temperature for some of the prapared glasses. It is seen that C_p is increased with increasing the temperature, as well as, the mole per-
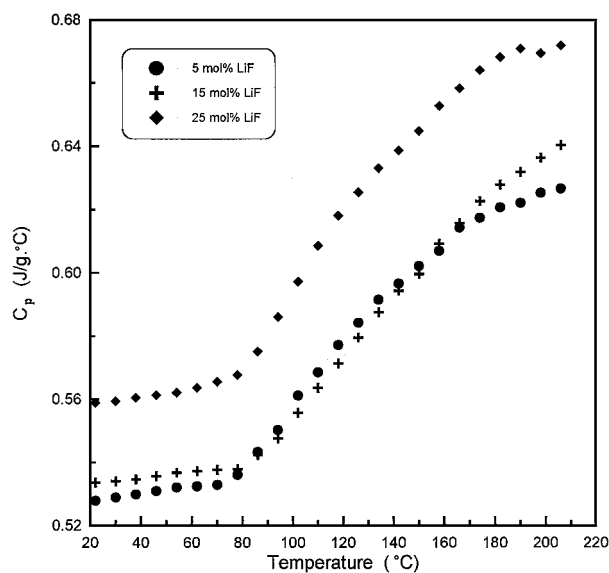

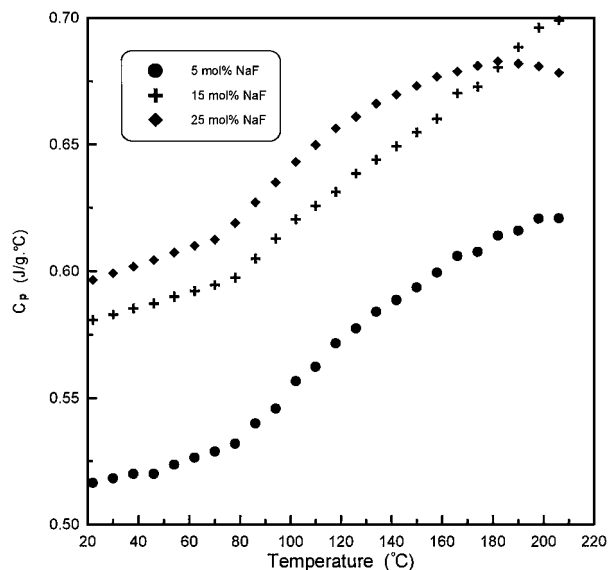*Figure 9* Variations of the specific heat C_p with temperature of MoO_3-BaF_2-NaF glass.
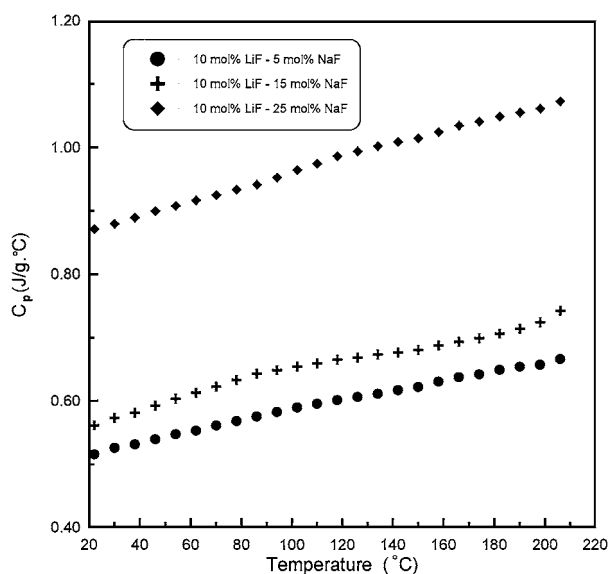

Figure 10 Variations of the specific heat C_p with temperature of MoO_3-BaF_2-LiF-NaF glass.

centage of the alkali fluoride added. The glass quasi lattice vibrational properties which are dependent on the structure, increase with increasing temperature. So, the specific heat C_p increases with increasing temperature. This explanation would suggest that differences in C_p should disappear at high temperatures where the vibrational heat capacity approaches the Dulong-Petit limit of 3R (24.9 J/g · atom). The compositional dependence of C_p is shown in Fig. 11 and reveals that C_p increases with increasing the RF content in the glass. This figure, shows also, that at 5 mol% RF, the specific heat C_p of the glass contains LiF is greater than those which contain NaF and the mixture (NaF—LiF) respectively. This is probably due to that, the average stretching force constant F of the glass containing LiF is lower than those which are containing NaF and the mixed alkali fluoride (NaF—LiF), see Fig. 6, i.e., a lower average stretching force constant F means a higher value of C_p is obtained for tested glass. At higher RF concentrations such as

Figure 8 Variations of the specific heat C_p with temperature of MoO_3-BaF_2-LiF glass.
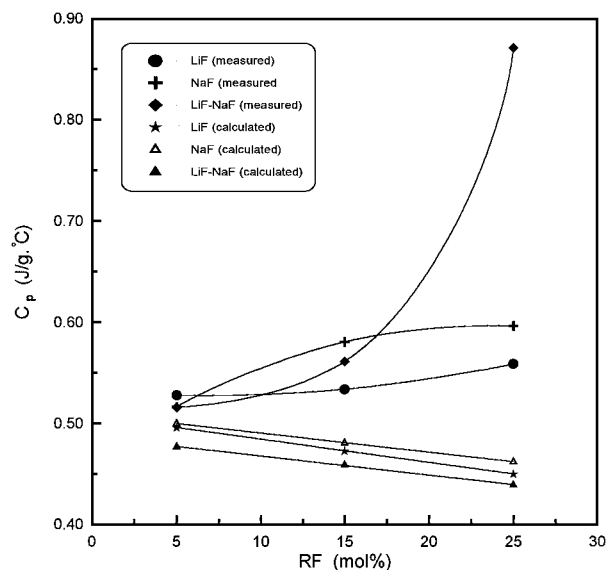
Figure 11 Variations of the measured and calculated specific heat C_p at room temperature with the alkali fluoride RF of the present molybdenum oxyfluoride glasses.

25 mol%, the C_p of the glass containing the mixed alkali fluoride content (NaF—LiF) is higher than that contains either NaF or LiF as in Fig. 11. The present observed non-linear variations of C_p of MBNL glass (which contain the mixed NaF—LiF) could be attributed to the mixed alkali effect as previously explained by many authors [18, 19].

The average specific heat of the present glasses at room temperature can be calculated from the C_p^* values of its crystalline constituents, according to this equation

$$C_p = \sum_i x_i C_{pi}^* \qquad (9)$$

where x_i is the mole fraction of the component i and C_{pi}^* its specific heat at room temperature. Since, the specific heat values of MoO_3, BaF_2, LiF and NaF are 17.92 cal/deg · mol (0.515 J/g · deg), 17.02 cal/deg · mol (0.489 J/g · deg), 9.94 cal/deg · mol (0.286 J/g · deg) and 11.20 cal/deg · mol (0.322 J/g · deg) respectively [20]. Then, values of the average specific heat C_p are calculated and given in Table II with its compositional dependence is illustrated in Fig. 11. It is seen that the compositional dependences of both the measured and calculated values of specific heat, C_p, at room temperature are inconsistent, i.e., the measured C_p increases with increasing RF but the calculated C_p decreases. The calculated average C_p values are smaller than those of the measured.

However, the observed deviation between the measured and calculated values suggests that Equation 9 is not applicable to the studied glasses.

4. Conclusion
From the present data of this work on molybdenum oxyfluoride glasses, it can be concluded that the replacement of the alkali fluoride RF instead of MoO_3 leads to decrease the glass transition temperature T_g while the average thermal expansion α and the specific heat are increased. These changes have been attributed to some structural changes, creation of non-bridging fluorine ions, which affects the produced structural to be weakened. Also, the glass forming area, the glass forming tendency, the stability, the average thermal expansion coefficient and the specific heat are all increased in value for the glass containing mixed alkali fluorides (LiF—NaF).

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