Compositional dependence of thermal, optical and mechanical properties of oxyfluoride glass

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Abstract. Tungsten oxyfluoride glasses are characterized by low phonon energy. This is due to the presence of fluoride ions that have low phonon energy and formation of low phonon energy WO6 units. Oxyfluoride glasses based on WO3–BaF2–RF, where RF= LiF, NaF or mixed (LiF–NaF) have been prepared by melt quenching technique. The density and molar volume of the prepared glasses show a decrease with the increase of RF instead of WO3 content. The glass transition temperature Tg is found to decrease with increasing RF content. The refractive index increases with the addition of heavy polarizable fluorides. The decrease of the elastic moduli and microhardness of these glasses may be due to the decrease in density and the depolymrization effect. The Poisson's ratio increases with increasing RF content due to the structural changes and formation of (NBOs) and (NBF) units. The aim of this work is to prepare a glass host with low phonon energy to be an efficient host with good luminescence properties, when doped with rare earth ions, and to study its structural, thermal, optical and mechanical properties.

1. Introduction

Glasses containing tungsten ions are considered to be very important technological glasses [1]. This is due to their specific thermal, chemical, mechanical and optical properties [1,2]. The addition of WO_3 to the glass enhances its network connectivity [3,4] and this increases its thermal and chemical stability. With their different structural units (WO_4 tetrahedral and WO_6 octahedral units), tungsten ions have a great influence on optical and electrochemical properties of the glasses in which they are incorporated [5-7]. Having different oxidation states (W^{4+}, W^{5+} and W^{6+}), tungsten ions impart specific photo-, thermo- and electrochromic properties to the glass in which they are incorporated so that it could be used in different optoelectronic devices and as a sensor [8]. Addition of WO_3 to glass decreases its phonon energy due to the formation of WO_6. This provides the glass with interesting optical properties such as photochromic and linear absorption effect, and imparts efficient luminescent properties to the glass when it is doped with rare earth ions [9]. At high concentrations of WO_3, WO_6, structural units are linked together through W-O-W bonds that result in the formation of highly polarizable clusters responsible for optical properties [10,11]. Addition of fluoride content affects glass formation and structure and makes promising optical materials for laser hosts. It also helps to decrease the phonon energy, non-radiative losses, reduces the OH content and increases the

transparency in the visible region [12]. Rare earth doped tungsten glasses and crystals have excellent properties to be used in different applications such as waveguides, amplifiers, and lasers [13,14].

2. Preparation and measurements

Anhydrous fluorides are commercial products: BaF2 and LiF from Prolabo, NaF from Ridel de Haen and WO_3 from Strem. Calculated amounts of starting materials were mixed and heated up to the melting temperature which is about 650–700 ^{o}C. Melting was carried out in a platinum crucible for 30–45 min. Then the melt was poured into a brass mold preheated up to about 200–250 ^{o}C. The samples were annealed at near the glass transition temperature for one hour.

The densities of the prepared samples were measured by the Archimedean method using CCl_4 as an immersion liquid. The molar volume was calculated by the equation $V_m = (M/\rho)$, where ρ is the density (g/cm^3) and M is the molecular weight of the glass sample (gm). The error of the density measurements was not more than ± 0.001 gm/cm^3.

The characteristic temperatures of the glass (e.g., glass transition temperature T_g, onset crystallization temperature T_x and crystallization temperature T_c) were measured by a differential scanning calorimeter SEIKO DSC 220 at a heating rate of 10 ^{o}C.min^{-1} under controlled atmosphere N_2. The average values of the thermal expansion coefficient α were measured by using TMASII Seiko 5200 instrument. Bar samples with a thickness of about 3 mm were used in the measurements. The measurements were performed in the temperature range from 50 ^{o}C to near the glass transition temperature of the chosen samples. Then the average values of thermal expansion coefficient were determined in the temperature range of 100–150 ^{o}C. The uncertainty of the obtained values was $\pm 3 \times 10-7$ ^{o}C^{-1}. Heat capacity C_p was measured by a differential scanning calorimeter, DSC-7 PerkinElmer. The samples for heat capacity measurements with a mass of 30–50 mg were enclosed in crimped Al DSC pans. The C_p values of the test glasses were measured from 70 ^{o}C to near the glass transition temperature region at 4 K min^{-1} heating rate.

Ultrasonic velocities were measured using KARL DEUTSCH Echograph 1080 ultrasonic flow detector. The ultrasonic longitudinal velocity (VL) was measured using normal longitudinal probe Krautkramer, 5 MHz, and the ultrasonic shear velocity (VS) was measured using normal shear probe Olympus, 2.25 MHz. The velocity was obtained by dividing the round trip distance by the elapsed time. The relative error in the determined values of these velocities was roughly about ± 30 m/s.

3. Results and discussion

The obtained data show that the density and molar volume decrease with increasing LiF, NaF and the mixture (LiF-NaF), see Table. 1. The decrease of the density is due to the smaller molecular weight of the added alkali fluorides (LiF=25.94, NaF=41.99) than that of WO_3 (231.85) and also the packing density, V_t, (V_t was calculated according to our previous works [15, 16] and their values are given in Table 1). The decrease in the molar volume is due to the change of the W–O bond length. In addition, the change in the molar volume is the result of the creation of non-bridging oxygen (NBO) and fluorine (NBF). The variation in the density and molar volume with the addition of RF content were attributed to the change of the coordination state of Li^+ and Na^+ ions. It was proposed that at higher concentration Li^+ ion can be coordinated by six F^- ions and behave as a glass-modifier region, and Na^+ ion is coordinated by six F^- ions and acts as a glass-modifier [17].

The transition temperature of the present glasses decreases with increasing LiF, NaF and mixed (LiF-NaF) instead of WO_3 (see Table 1). This is due to weakening of the glass structure. Alkali fluorides have lower T_g which varies inversely with the ion size. Therefore, LiF has unexpectedly most effect in view of its higher bond strength. The decrease of T_g with increasing RF content can be attributed to the breaking of linkages in the glass structure. It may also be due to the replacement of O^{2-} ions with F^- ions that leads to depolymerization of the oxide and as a result, T_g decreases [18]. As previously discussed [19], the structure of the present glass consists of tetrahedral WO_4 and WO_6 octahedral group chains cross-linked by Ba^{2+} or Li^+ and Na^+ ions. The replacement of the transition

ion (W) by alkali ion (Li or Na) decreases the degree of cross-linking and thus renders the glass more fluid, therefore the glass transition temperature decreases.

Table 1. The composition, density, molar volume V_m, packing density V_t, cross link density $\overline{n_c}$, F/O ratio, glass transition temperature T_g, crystallization temperature T_c, thermal stability (T_c-T_g), activation energy of crystallization E_a and average linear thermal expansion α of WO_3-BaF_2-RF glass.

Sample Name	WO_3	BaF_2	LiF	NaF	$\square$ g.cm^{-3}	V_m cm^3	V_tx10^{-6} m^3	T_g ^oC	T_c ^oC	T_c-T_g ^oC	$\square$x10^{-7o}C^{-1}
			Mol %								
WBL-1	42	30	28		5.83	26.97	0.6151	314	375	61	142
WBL-2	40	30	30		5.77	26.54	0.6141	309	369	60	
WBL-3	38	30	32		5.73	26.00	0.6157	299	346	47	150
WBL-4	36	30	34		5.63	25.73	0.6109	271	382	111	
WBL-5	34	30	36		5.56	25.32	0.7105	263	421	58	163
WBN-1	46	30		24	5.83	29.05	0.6044	352	433	81	152
WBN-2	44	30		26	5.78	28.63	0.6043	343	432	89	
WBN-3	42	30		28	5.73	28.23	0.6037	336	403	67	160
WBN-4	40	30		30	5.67	27.86	0.6024	326	386	60	170
WBNL-1	42	30	10	18	5.78	27.70	0.6094	322	398	76	142
WBNL-2	40	30	10	20	5.70	27.43	0.6059	315	404	89	
WBNL-3	38	30	10	22	5.65	26.99	0.6063	309	375	66	179
WBNL-4	36	30	10	24	5.52	26.94	0.5978	294	357	63	
WBNL-5	34	30	10	26	5.48	26.45	0.5991	293	348	55	193

The decrease in T_g with increasing RF content could be due to the disruption of the network and weakening of the W–O bonds as suggested by the density explanation. Also, the decrease in T_g with the increase in RF content instead of WO_3 content may be due to the decrease in packing density.

The activation energy of crystallization was determined by Chen's equation [20],

$$\ln\left(\frac{T_C^2}{\alpha}\right) = \frac{E_a}{RT_C} \tag{2}$$

where Tc is the crystallization temperature, α is the heating rate (10 Ks^{-1}), E_a is the activation energy of crystallization and R is the universal gas constant. The values of E_a were calculated and given in Table 1. Thermal stability was determined according to:

$$S = T_c - T_g \tag{3}$$

The values of S are given in Table 1. The structure of the present glasses is deformed from WO_4 tetrahedra and WO_6 octahedra group disorderly packs by means of corner-sharing or edge-sharing to form the skeleton of the glass. Ba^{2+}, Li^+ and Na^+ are incorporated into the vacancies of the skeleton and center on the WO_4 and WO_6 anions. The addition of the alkali fluorides RF results in the system of F$^-$ anions which form non-bridging fluorides at one or two corners of the metal oxide polyhedra. This increases the spatial freedom linking between the polyhedral and hence the stability of the glasses is improved. As seen from Table 1, the average thermal expansion increases with the increase of alkali fluoride and mixed alkali fluoride. As RF increases instead of WO_3, the units of each glass become more disconnected. The non-bridge fluorine will be formed at one or two corners of the polyhedral in metal oxide. So that when the sample is heated, the unit volume of each glass expands with increasing RF, which is also confirmed by the decrease in the glass transition temperature T_g as discussed before. In addition, this could be due to the disruption of the network and weakening of W–O bonds that was suggested by density and glass transition temperature. Also, the excess of RF content result in the

formation of W–F–W bonds, which provide weak points in the vitreous network, that results in decreased T_g and increased thermal expansion coefficient. The data on specific heat C_P of the present glasses versus temperature during heating in the temperature range from 70 ^{o}C up to 170 ^{o}C at a rate of 4 ^{o}C/min is shown in Figure 1. C_P increases with increased temperature. The C_P values of these glasses are higher than those of oxide glass due to the low vibration frequencies in the oxyfluoride glass, which means that their Debye temperature is also low. It was found that at different temperatures C_P decreases with increasing LiF and the mixed (LiF-NaF), while it increases in case of NaF contents. This is due to the change of the glass structure as mentioned before. The refractive index is one of the interesting optical parameters to design glass for optical devices. The refractive index is changed as follows: n(Na-Li)< n(Na)< n(Li). This may due to the difference in the refractive potential for each alkali fluoride component in the glasses. The larger its value, the larger the contribution to the refractive index of the glass, for example, these values are 0.221, 0.244 for NaF and LiF, respectively [21]. When RF increases instead of WO₃, the denser nature of the glass relatively decreases, which leads to decrease the refractive index [22].
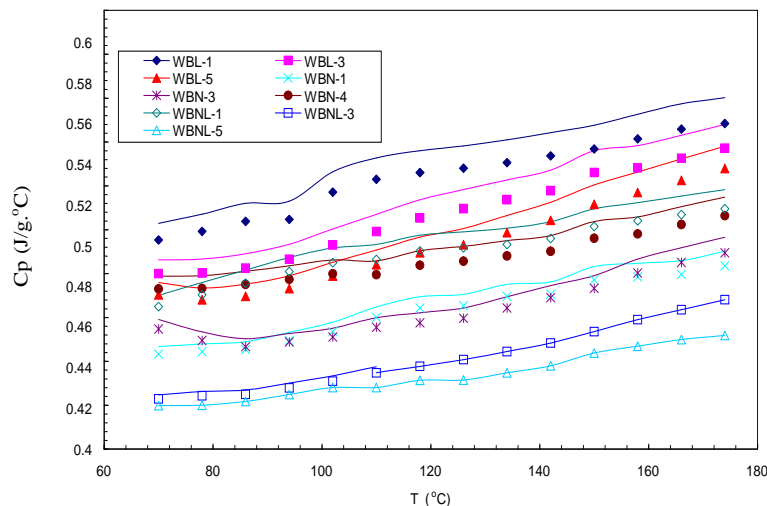

Figure1. Dependence of specific heat Cp on temperature of the prepared glasses.

The addition of heavy polarizable fluorides increases the refractive index and molar refractivity. [23]. This suggests that when the lighter alkali metal is incorporated into the present oxyfluoride glass, the refractive index and molar refractivity will reduce as shown in Figure 2. However, different cations in the glass have different structural effects; those with higher electrical changes and small coordination and bond ionicity due to strong polarization and their refractivities and volumes in fluoride glasses are very different from those in crystals. For alkali substituting, the effect of substitution of an ion with a slightly smaller ionic refractivity is outweighed by a relative decrease in the molar volume [24], ionic refraction of Li$^+$, Na$^+$, W^{6+}, O^{2-} and F$^-$ is 0.1, 0.8, 2.6, 3.8 and 2.0, respectively [25].

Finally, the refractive index is decreased due to substitution of alkali contents instead of the present oxide. As a result, lower ionic refractivity in alkali and decreased molar volume of the glass can be observed.
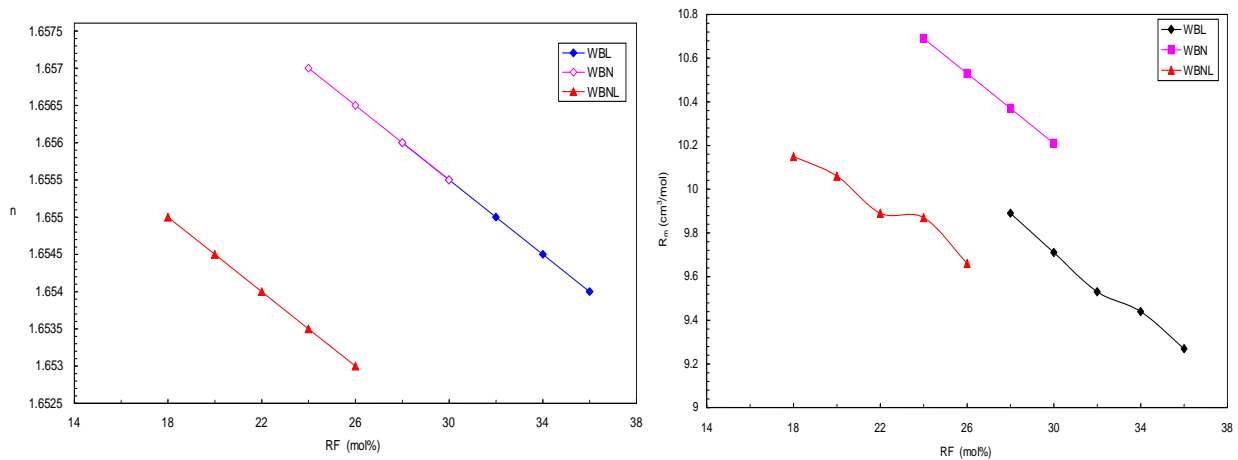
Figure 2. Variation of n & R_m with composition for the prepared glasses.

The elastic moduli such as longitudinal L, shear S, Young's modulus E, bulk modulus B and Poisson's ratio σ can be determined as follow:

$$L = \rho V_L^2, \quad S = \rho V_s^2, \quad E = \rho V_s^2 \frac{(3V_L^2 - 4V_s^2)}{(V_L^2 - V_s^2)}, \quad B = \rho(V_L^2 - \frac{4}{3}V_s^2), \quad \sigma = \frac{(V_L^2 - V_s^2)}{2(V_L^2 + V_s^2)} \quad (11)$$

where V_L, V_S are longitudinal and transverse velocities of the prepared glasses and ρ is the glass density.

Then the mean ultrasonic velocity (V_{mean}) and the microhardness (H) can be calculated according to:

$$V_{mean} = \left[\frac{(\frac{1}{V_L^3} + \frac{2}{V_S^3})}{3} \right]^{-\frac{1}{3}}, \quad H = \frac{(1 - 2\sigma)E}{6(1 + \sigma)} \quad (12)$$

The longitudinal L, shear S, Young's modulus E, bulk modulus B and themicrohardnessof the prepared glass samples show a decrease with increasing RF content, while the poisson's ratio increases with increasing RF content, see table2.

This may be due to the decrease in density and depolymerisation effect occurred in the glass network with increasing RF content. The increase in the Possion's ratio can be attributed to the structural changes and the formation of nonbridging oxygen units (NBOs) and (NBF) with increasing RF content.

Table 2. Longitudinal modulus, L (GPa), Young's modulus, E (GPa), bulk, B and shear moduli, S (GPa), Poisson's ratio and micro hardness of the present glasses:

Sample Name	L GPa	S GPa	E GPa	B GPa	σ	H GPa
WBL-1	91.085	25.17313	65.905	57.521	0.309	3.205
WBL-2	88.303	24.65226	64.408	55.433	0.306	3.183
WBL-3	84.097	23.06419	60.477	53.344	0.311	2.905
WBL-5	85.219	24.2634	63.132	52.868	0.301	3.219
WBN-1	83.52	22.793	59.825	53.129	0.312	2.852
WBN-2	82.543	21.686	57.331	53.62809	0.322	2.576
WBN-3	78.105	22.981	59.363	47.463	0.292	3.194
WBN-4	77.033	24.238	61.587	44.715	0.270	3.709
WBNL-1	76.422	24.2634	55.668	48.022	0.307	2.743
WBNL-3	81.142	22.769	59.42727	50.78184	0.305	2.961
WBNL-4	79.750	24.609	62.84413	46.93807	0.277	3.661
WBNL-5	76.365	22.895	58.88197	45.8386	0.286	3.268

4. Conclusion

The decrease in density and the molar volume with increasing alkali and mixed alkali fluoride instead of WO_3 is due to the lighter molecular weight of the added LiF and NaF as compared to that of WO_3 and the increase of W–O bond length. The decrease of glass transition temperature, specific heat at constant pressure and the increase of average linear thermal expansion with the increase of alkali and mixed alkali fluoride content are due to the weakening of the glass structure. The refractive index also decreases due to the lower ionic refractivity of the alkali content and the decrease of the molar volume of the prepared glasses. Formation of (NBOs) and (NBF) increases the Possion's ratio for the prepared glasses and the observed decrease in the elastic module and microhardness may be also due to the decrease in the density and the depolymerisation effect that occurred in the glass network with increasing RF content. These glasses have acceptable values of the glass transition, average linear thermal expansion, specific heat and refractive index. As a result, it may be used in many optical and electrical applications.

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