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Physical Characterization of Sb_2O_3-M_2O-MoO_3 (M = Li, K) New Glasses

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New heavy metal oxide glasses involving Sb_2O_3 have been investigated. By using classical routes (melting--casting), glasses synthesized in silica crucibles were obtained in the combination of ternary systems Sb_2O_3-M_2CO_3--MoO_3 (M = Li and K). Characteristic temperatures such as glass transition T_g, and onset of the crystallization T_x, have been measured using differential scanning calorimeter. Ultrasonic velocities were measured by using pulse echo method to determine the elastics parameters, such as elastic modules (E, G, K, L). Other physical properties were measured, such as density and optical transmission window in far infrared spectra using KBr pellets. Influence of composition on these physico-chemical properties is discussed and correlated to the glass structure.

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1. Introduction

Sb_2O_3 glasses emerge as one major family of heavy metal oxide glasses [1, 2] and appear promising for potential applications in non-linear optical devices like ultra-fast optical switches, power limiters [3] and broad band optical amplifiers operating around 1.5 μm using antimony–silicate glass fiber [4, 5]. Among the various experimental methods available for studying structure--property relations, the elastic properties of glasses are very significant. The knowledge of the elastic modules in combination with differential scanning calorimetry (DSC) measurements, molar volume and Fourier transform infrared (FTIR) spectra seems to be a useful tool for understanding the nature of bonding in the solid state and glass network compactness and dimensionality of the glass structure.

In this paper we present new glasses in the Sb_2O_3--M_2O-MoO_3 systems where M = Li or K. The study of such glass system seems to be very interesting in the sense of the theory of the continuous random network established by Zachariassen, since these glasses were made by using Sb_2O_3 as the unique glass former, Li_2O and K_2O as a glass modifier and MoO_3 as an intermediate oxide. However, so far, to our knowledge, no work is carried out to explore the structural properties of antimony glasses using ultrasonic technique. Selected glass sample has been prepared to measure density and ultrasound velocities. The calculated elastic parameters, and molar volume are correlated to the glass composition and some interpretations on the glass structure have been deduced.

2. Experimental procedures

These glasses were synthesized by conventional method [1] in the ternary system (80-x)Sb_2O_3-20M_2O-$x$$MoO_3$. Thermal characteristics including temperatures for glass transition, T_g and onset of crystallization T_x, have been measured with an estimated error on the temperature ± 2°C. They are determined by DSC using SEIKO S 220 Instruments. Assessment of glass stability is made from semi-empirical parameters: the value of the stability range $\Delta T = T_x - T_g$. The density, accurate to $\pm 0.05\%$, was determined by Micromeritics Accupyc pycnometer under helium pressure. For ultrasonic measurement, good glass samples (without defects, crystallites or air bubbles) are required and should be cut into perfectly parallel faces with diameters greater than the size of the ultrasound transducers to reduce the edge effect. A high power ultrasonic pulse receiver (Olympus NDT, 5900 PR, USA) using respectively X-cut and Y-cut quartz transducers each of frequency 10 MHz and a digital storage oscilloscope (Lecroy, Wave Runner 104 MXi 1 GHz, USA) were used for recording ultrasonic signals. FTIR spectra were recorded in the range 400–4000 cm^{-1} using KBr pellets and carried out with a Shimadzu 8400S.

3. Results and discussion

The characteristics temperature, density and molar volume of synthesized glasses in the ternary system (80-x)Sb_2O_3-20M_2O-$x$$MoO_3$ are collected in Table I. As expected the density of lithium containing glasses are larger than those containing potassium. Adding MoO_3 instead of Sb_2O_3 may decrease the density and the molar volume due to the large size of Sb_2O_3 molecule.

T_g and ΔT of both series of glasses were found to increase when MoO_3 is added up to 20 (mol.%) and decrease for more molybdenum added. For stable glasses, sizeable samples can be obtained with ΔT large than 100, however less stable glasses should be rapidly quenched and hence ΔT takes small values. The non-linear evolution of T_g may be related to the structural role of MoO_3 in the glass matrix of antimony glasses.

TABLE I

T_g, T_x, glass stability ΔT, density ρ, molar volume V_m, longitudinal velocity V_l and transverse velocity V_t for Sb_2O_3-M_2O-MoO_3 glasses.

Glass composition	Code	T_g	T_x	ΔT	ρ	V_m	V_l	V_t
		[°C]			[g/cm^3]	[cm^3/mol]	[m/s]	
$80Sb_2O_3$-$20K_2O$	K0	254	411	157	4.6	53.84	3089	1681
$70Sb_2O_3$-$20K_2O$-$10MoO_3$	K10	277	370	93	4.55	48.61	–	–
$60Sb_2O_3$-$20K_2O$-$20MoO_3$	K20	282	380	98	4.46	44.85	–	–
$50Sb_2O_3$-$20K_2O$-$30MoO_3$	K30	248	397	141	4.372	40.97	3109	1638
$40Sb_2O_3$-$20K_2O$-$40MoO_3$	K40	245	344	99	4.283	37.47	2994	1655
$80Sb_2O_3$-$20Li_2O$	L0	273	–	–	4.961	49.97	3060	1738
$70Sb_2O_3$-$20Li_2O$-$10MoO_3$	L10	281	409	128	4.783	48.74	2894	1713
$60Sb_2O_3$-$20Li_2O$-$20MoO_3$	L20	289	442	153	4.701	46.46	2874	1710
$50Sb_2O_3$-$20Li_2O$-$30MoO_3$	L30	274	403	129	4.572	44.54	3067	1769

The structure of Sb_2O_3 based glasses is always made using the similarity from its crystalline variety form valentinite as reported elsewhere [6]. The structure is formed by double chains of triangular based [SbO_3] pyramids sharing corners with Sb^{3+} 3-coordinated and the lone pair opposed to the base of triangle. As established by Zachariassen, MoO_3 as an intermediate oxide, leading to a glass former with Mo^{6+} ion when linked to four or six oxygen forming [MoO_4] tetrahedral or [MoO_6] octahedral structural units [7] or as a modifier with Mo^{5+}. The increase in T_g is related to the rigidity and connectivity of the glass structure by the formation of more coordinated [MoO_6] units instead of trigonal [SbO_3] units. For more than 20 (mol.%) of MoO_3 added it can be suggested that tetragonal [MoO_4] units with low coordination are formed instead of the hexagonal units.

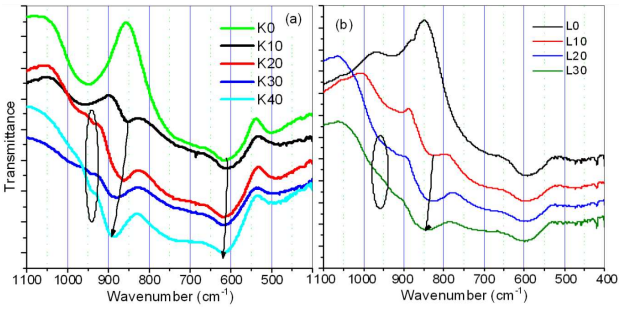

Fig. 1. FTIR spectra of (80-x)Sb_2O_3-$20M_2O$-$xMoO_3$ (x = 0, 10, 20, 30, and 40) glasses. (a) M = K, (b) M = Li.

The FTIR spectra of (80-x)Sb_2O_3-$20M_2O$-$xMoO_3$ glasses are drawn in Fig. 1a and b. They present the same bands, however, the intensity of the absorption bands for glasses containing potassium oxide are stronger than lithium containing glasses. This is may be due to the strong ionic character of K as compared to Li ion. The bands situated at 486, 600, and 710 cm^{-1} are related to the symmetric bending and stretching vibration of [SbO_3] unit. However, the band located at 960 cm^{-1} is related to external impurities (such as Si, H_2O and OH^- groups) rising from experimental synthesis of glasses [5].

When MoO_3 is introduced, glasses containing Li or K show new bands at 867 and 823 cm^{-1}. They are related to the vibration mode of oxygen in Mo–O–Mo of [MoO_6] units. The observed shift to longer wave number of these two bands can be related to the conversion from hexagonal [MoO_6] to tetragonal [MoO_4] units and the vibration of isolated [MoO_4] units could interfere with the shoulder at about 895 cm^{-1} [7, 8]. The shift of the 600 cm^{-1} band to longer wave number with the increase of MoO_3, more viewed for potassium containing glasses, can be related to the formation of Sb–O–Mo linkages with a modifying role of Mo ions.

TABLE II

Elastic modules L, G, E and Poisson number ν of Sb_2O_3-Li_2O-MoO_3 glasses.

Glasses composition	Code	L	G	E	ν
		[GPa]			
$80Sb_2O_3$-$20Li_2O$	L0	4.65	1.50	3.78	0.26
$70Sb_2O_3$-$20Li_2O$-$10MoO_3$	L10	4.00	1.40	3.45	0.23
$60Sb_2O_3$-$20Li_2O$-$20MoO_3$	L20	3.88	1.37	3.37	0.22
$50Sb_2O_3$-$20Li_2O$-$30MoO_3$	L30	4.30	1.43	3.58	0.25

The measured longitudinal V_l and transverse V_t ultrasonic velocity were found related to the glass composition. Both velocities decrease when the amount of MoO_3 increases up to 20 mol.% and a slow increase is observed for more MoO_3 content. The same trend was observed for the calculated Young (E), shear (G) and longitudinal modules (L) shown in Table II. This behavior can be explained by the increasing number of non-bridging oxygen's involved by the increasing number of $[MoO_4]^{2-}$ isolated units. These tetrahedra should be surrounded by antimonite units and alkaline elements K or Li. Then, the charge compensations of the $[MoO_4]^{2-}$ are achieved by Sb^{3+}, K^+ or Li^+ cations. The Poisson ratio ν is considered as good indicator of the glass structure and its value indicates directly the glass network dimensionality. ν is equal to 0.4, 0.3, or 0.15 for glass networks having

a dimensionality of one, two, or three, respectively [8]. νg ecreases when the amount of MoO_3 increases up to 20 (mol.%) and increases for more MoO_3 added. This behavior is consistent with the formation of more coordinated structural $[MoO_6]$ units at low molybdenum content and the conversion of hexagonal units to low coordinated $[MoO_4]$ units at high MoO_3 content.

4. Conclusions

New glasses in the (80-x)Sb_2O_3-20M_2O-$x$$MoO_3$ have been synthesized and characterized. MoO_3 was found to play the former role by the formation of hexagonal units $[MoO_6]$ and isolated $[MoO_4]$ units for low MoO_3 content. $[MoO_4]^{2-}$ units may compensate the charge balance induced by the alkaline elements K^+ and Li^+. For more than 20 mol.% of MoO_3, a possible conversion from hexagonal to tetragonal units occurred. These results are supported by FTIR spectra and ultrasonic modules.

Acknowledgments

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