

Influence of molybdenum oxide on structural, optical and physical properties of oxychloride glasses for nonlinear optical devices

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ABSTRACT

The unconventional Heavy Metal Oxide Glasses (HMOG) are characterized by a low phonon energy, large infrared range transmission, high refractive index and nonlinear optical properties. Ternary glasses have been synthesized and studied in the Sb_2O_3 – MoO_3 – ZnCl_2 system. Further, the glass formation compositional limits are reported and some glass samples with the formula: $(90-x)\text{Sb}_2\text{O}_3$ – $x\text{MoO}_3$ – 10ZnCl_2 ($10 \leq x \leq 50$, mole%) were elaborated. Thermal properties have been measured and indicating that the glass transition temperature decreases with increasing proportions of molybdenum oxide. The evolution of density, microhardness and elastic modulus has been studied as functions of parameter x and Raman spectra measurements have been shown the partial conversion of MoO_6 octahedral units into MoO_4 tetrahedral.

1. Introduction

Over the past few years, several researches have been carried out on antimony glasses. Binary and ternary Sb_2O_3 -based glasses have been studied, including various oxide [1–6], oxysulphide [7,8] and oxychloride systems [9,10]. These glasses are used in nonlinear optical devices particularly in broadband optical amplifiers functioning about $1.5\text{ }\mu\text{m}$ [11].

Molybdenum oxide is considered as a glass former that requires the presence of other elements to form a glass. Molybdate glasses are obtained by introducing another network-forming oxide such as Sb_2O_3 , P_2O_5 , TeO_2 ...etc. The molybdate glasses are used for high-density memories, light modulation, large area display devices like smart windows and other electrochromic systems [12,31,32]. The different oxidation states of molybdenum are: Mo^{6+} , Mo^{5+} , Mo^{4+} and Mo^{3+} . In the molybdate glasses, different works suggest the existence of molybdenum in the Mo^{6+} form which is the most stable [13]. Rada et al. [14] suggest that a part of the Mo^{6+} ions is converted into Mo^{3+} and Mo^{5+} ions. This process causes the depolymerisation of host glass network. The molybdenum oxide is formed in the glass by different structures, like structural units of octahedron and tetrahedron units such as MoO_6

and MoO_4 respectively. Krapchanska et al. [15] showed a partial conversion of MoO_6 to MoO_4 units in the MoO_3 – TiO_2 – Bi_2O_3 system. Subcik et al. [16] also showed that the incorporation of MoO_3 units in the ZnO – B_2O_3 – P_2O_5 glasses revealed the increase of the $\text{MoO}_6/\text{MoO}_4$ ratio.

Sb_2O_3 contributes in the glass network with SbO_3 structural units and it appears tetrahedra with the oxygens to be found at three corners and the lone pair of electrons of antimony Sb^{3+} at the fourth corner localized in the third equatorial direction of the Sb atom. There may be a possibility of existence of antimony ions in the Sb^{5+} state and participate in the glass network forming with Sb^{5+}O_4 structural units may enhance the nonlinear optical properties [11]. In Sb_2O_3 based glasses the addition of transition metal oxide MoO_3 improves functionality of glasses for their desired optical applications. Particularly, MoO_3 shows interesting optoelectronic features and can control phase separation in glasses [43].

The aim of this paper is focuses on the elaboration of a new antimony oxychloride glass from the Sb_2O_3 – MoO_3 – ZnCl_2 system. We are interested by molybdenum rates incorporated into the glass, its effect on the different physical properties that have been measured, and especially in the structural study by Raman measurements. Physical

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Table 1

Composition and some experimental properties of SMZ glasses.

Glass	Nominal composition					Analyzed composition						Hv N/mm ²	ρ g/cm ³	V _m cm ³ /mol
	Cation %			Anion%		Cation%				Anion%				
	Sb	Zn	Mo	O	Cl	Sb	Zn	Mo	Si	O	Cl			
SMZ10	88.9	5.55	5.55	93.1	6.9	86.55	6.42	6.63	0.4	79.5	20.5	172	5.038	11.031
SMZ20	82.35	5.88	11.77	93.1	6.9	82.65	5.1	11.63	0.6	85.09	14.91	194	4.97	10.78
SMZ30	75	6.25	18.75	93.1	6.9	72.34	6.83	19.73	1.1	92.01	7.99	206	4.892	10.48
SMZ40	66.66	6.67	26.27	93.1	6.9	58.95	6.8	33.75	0.5	84.86	15.14	223	4.814	10.2
SMZ50	57.15	7.14	35.71	93.1	6.9	55.87	8	35.43	0.7	95.56	4.44	229	4.722	9.96

properties such as: density, energy dispersive spectroscopy (EDS), differential scanning calorimetry (DSC), optical transmission, micro-hardness and elastic moduli have also been considered in terms of molybdenum influence.

2. Experimental

In this present study, the starting materials $\text{Sb}_2\text{O}_3 \geq 99\%$ (Acros), $\text{ZnCl}_2 \geq 99.8\%$ (Merck) and $\text{MoO}_3 \approx 99\%$ (Acros) are used for the synthesis of the glass samples. Melt-quenching is the process of synthesis. The powders are mixed thoroughly in a mortar with the mean batch weight around 5 g. The mixture is inserted into a silica glass tube, about 10 mm in diameter and then subjected to a flame until a clear liquid obtaining. The bath of fusion is cast in a mould under preheated brass plate around 200 °C. The samples obtained (thickness of a few millimetres) are placed in the furnace at a temperature lower than the temperature of vitreous transition with a slow heating rate. After annealing, the samples were polished for physical measurements.

The glass composition was analyzed by the (EDS) energy dispersive spectroscopy (JSM 6400 Jeol and Oxford link ISIS). With the help of crystalline materials references, experimental error is estimated to be 1% for Sb, Mo and Zn, 2% for Cl and 5% of oxygen. Density was determined using a helium pycnometer (Micromeritics, AccuPyc 1330) with ± 0.001 g/cm³ accuracy.

Thermal properties of the samples were measured by the differential scanning calorimetry (DSC 2010 from TA Instruments) at the heating rate of 10 K / min with the sensitivity better than 0.1 °C. The estimated accuracy is ± 2 K for the glass transition temperature T_g , crystallization temperature T_x and ± 1 K for the temperature of the crystallization of peak. T_x - T_g provides the stability against devitrification. The DSC signals showed no crystallization peaks indicating that these glasses are having a very low tendency to crystallization and exhibiting extremely high thermal stability. Thermal stability is the important property of glasses and gives the measure of the degree of disorder of glassy state.

The analysis of the vitreous samples was carried out by the Raman spectroscopy in the range of 1100 cm⁻¹ to 100 cm⁻¹ by Sentra- Bruker. Varian Cary 5 spectrometer was used to record the optical transmission in the UV-visible spectrum between 400 and 800 nm and Bomem Michelson 100 IR spectrometer was employed for the infrared spectrum in between 500 and 4000 cm⁻¹.

The Matuzawa MXT 70 digital microhardness was used with 100 g as load to measure the microhardness values. Ultrasonic measurements were taken by the pulse –echo method using a Panametrics model 5800 pulser/receiver with a quartz transducer. Both X-cut transducer and Y-cut transducer (with 10 MHz frequency) were employed for both longitudinal and shear modes. A Hewlett-Packard model 54502A oscilloscope recorded the pulse transient. Young's modulus E, bulk modulus K, and shear modulus G were measured by the following equations [33]:

$$E = \frac{\rho V_T^2 (3V_L^2 - 4V_T^2)}{(V_L^2 - V_T^2)} \quad (1)$$

$$K = \frac{\rho (3V_L^2 - 4V_T^2)}{3} \quad (2)$$

$$G = \rho V_T^2 \quad (3)$$

where ρ = Density of the glass sample

V_T = Transversal ultrasonic velocity

V_L = Longitudinal ultrasonic velocity

The uncertainty is estimated to be about $\pm 2\%$ for elastic modulus.

3. Results and discussion

3.1. Physical properties

Chemical composition, some experimental properties of SMZ glasses are provided in Table 1. Fig. 1 shows the Oxy-halogenated glass area for ternary system. The glass matrix Sb_2O_3 - MoO_3 - ZnCl_2 was characterized by its extensive glass area and exceptional thermal stability. We have chosen to vary the molybdenum oxide, which is an excellent effect in heating homogenization [17,18]. It is used for its electrochromic properties [19] and especially for improving the conductivity by the ionic and electronic input [20,21]. A series of ternary system bulk samples were prepared for the physical measurements and were represented by the lines in Fig. 1 with the formula: $(90-x) \text{Sb}_2\text{O}_3$ - $x\text{MoO}_3$ - 10ZnCl_2 ($10 \leq x \leq 50$) called "SMZ". The molar concentration of MoO_3 is given by the number that follow the letters SMZ.

Glass compositions of the prepared samples were studied by the EDS spectra. Fig. 2 shows the chemical composition spectra of the sample SMZ20. In Table 1 it is clear from the chemical composition of the glasses that the differences between the nominal and analyzed

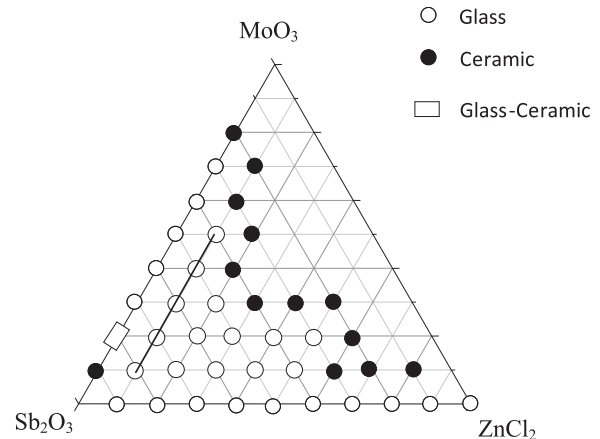


Fig. 1. Glass formation in the Sb_2O_3 - MoO_3 - ZnCl_2 system.

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