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Electrical, dielectric, and optical properties of Sb_2O_3–Li_2O–MoO_3 glasses

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ABSTRACT

Temperature and frequency dependencies of DC and AC conductivities, dielectric response, static permittivity, optical absorption edge, infrared absorption spectrum, density, and temperatures of glass transition and crystallization for lithium molybdenum–antimonite glasses, $(80 - x)Sb_2O_3$–$20Li_2O$–$xMoO_3$, where $x = 0$–40, are measured and discussed. The DC conductivity increases with increasing concentration of MoO_3. At 150 °C, it ranges from 5×10^{-11} S/m up to 3×10^{-8} S/m. Polaron hopping between Mo^{5+} and Mo^{6+} ions contributes, probably, to the DC conductivity. Ionic conductivity by Li^+ ions is also present. The conduction activation energy monotonously decreases from 1.15 eV, at $x = 5$, down to 0.91 eV, at $x = 40$. In all glasses with $x > 0$, the conduction activation energy is close to a half of the indirect allowed optical gap. The pre-exponential factor, σ_0, goes through a sharp maximum close to the composition ($x = 20$) with both the highest glass transition temperature and the largest thermal stability range. The frequency dependence of the AC conductivity is composed of three components — the DC conductivity and two AC components. For $x = 35$ and 40, the activation energy of electrical relaxation is equal to 0.954 ± 0.008 eV and the pre-exponential factor of relaxation times is equal to $(4 \pm 1)\ 10^{-14}$ s. The static relative permittivity ranges from 17.4 to 23.0. Strong extrinsic absorption bands in infrared region originate from hydroxyl ions, CO_2 impurities, and silicon–oxygen vibrations. The UV–visible indirect allowed absorption edge shifts from 2.6 eV to 2.1 eV with increasing MoO_3 content. With increasing MoO_3 content the glasses darken, from a light yellow color, at $x = 0$, to a deep brown color, at $x = 40$.

1. Introduction

Antimonite glasses form a major and important family of heavy metal oxide glasses [1–5]. They are attractive for their low phonon energy, broad transmission spectrum, and high refractive index. Their broad thermal stability range appears promising for fiber drawing [3]. They have potential applications in non-linear optical devices and in broad band optical amplifiers. The large nonlinearity of antimonite glasses is attributed to the high polarizability of Sb^{3+} ions due to contributions from the bound electrons and lone electron pairs [6,7]. Sb_2O_3 is a heavy metal oxide glass former with a relatively low liquidus temperature [1,2]. An increase of the thermal stability and resistance against crystallization can be achieved by adding MoO_3 in the glass matrix [1]. It exhibits also some glassforming ability in multicomponent systems. Alkali metal oxides, e.g. Li_2O, are added to enlarge the glassforming region and to enhance the stability of the glass [1,2].

Antimony oxide participates in the glass network with trigonal pyramidal [:SbO_3] structural units sharing corners which can be viewed as tetrahedrons with the oxygen at three corners and a lone pair of electrons at the fourth corner [8,9]. Such structural unit can be also considered as pseudo-tetrahedral unit with one vertex occupied by the lone pair of electrons [8]. Antimony ions exist not only in the Sb^{3+} state but also in the Sb^{5+} oxidation state. In the Sb^{5+} state, ions participate in the glass network as octahedral [SbO_6] units [8] or as singly positive $[Sb^{5+}O_4]^+$, 4-coordinated structural units [10,11]. The $MoO_3 \rightarrow Sb_2O_3$ substitution brings an excess of anionic oxygen which increases the number of non-bridging oxygen [9,12]. Molybdenum ions exist in two states as Mo^{5+} and Mo^{6+} [10]. Mo^{6+} ions participate in the glass network with [MoO_4] tetrahedrons; in MoO_3-rich region, [MoO_6] octahedrons are also present. These octahedrons are linked to [MoO_4] tetrahedrons via bridging oxygen and in this way they increase the network connectivity [12]. The Mo^{6+} ions act as network formers with $[MoO_4]^{2-}$ structural units [13–15]; the Mo^{5+} ions form $[Mo^{5+}O_3]^-$ complexes which act as network modifiers [12].

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Table 1
Compositions, colors, DC conduction activation energies, E_σ, pre-exponential factors, σ_0, and corresponding correlation coefficients, r, of $(80-x)Sb_2O_3$–$20Li_2O$–$xMoO_3$, SLMx, glasses.

	Sb_2O_3 [mol%]	Li_2O [mol%]	MoO_3 [mol%]	Color	E_σ (main temperature ranges) [eV]	σ_0 [S/m]	r
SLM00	80	20	0		0.78 ± 0.09 (194–220 °C) 1.161 ± 0.003 (125–170 °C) 0.48 ± 0.04 (40–100 °C)	$(5.11 \pm 0.02) \times 10^{-4}$ $(5.9 \pm 0.5) \times 10^{3}$ $(8.7 \pm 0.9) \times 10^{-6}$	−0.99978 −0.99697 −0.9967
SLM05	75	20	5		1.151 ± 0.003 (110–220 °C)	$(2.9 \pm 0.1) \times 10^{3}$	−0.99974
SLM10	70	20	10		1.136 ± 0.002 (110–220 °C)	$(5.3 \pm 0.2) \times 10^{3}$	−0.99989
SLM15	65	20	15		1.108 ± 0.001 (85–220 °C)	$(6.9 \pm 0.2) \times 10^{3}$	−0.99993
SLM20	60	20	20		1.092 ± 0.001 (95–220 °C)	$(1.35 \pm 0.01) \times 10^{4}$	−0.99999
SLM25	55	20	25		1.069 ± 0.001 (80–220 °C)	$(1.69 \pm 0.02) \times 10^{4}$	−0.99997
SLM30	50	20	30		1.016 ± 0.001 (80–220 °C)	$(7.5 \pm 0.1) \times 10^{3}$	−0.99996
SLM35	45	20	35		0.962 ± 0.001 (40–210 °C)	$(3.8 \pm 0.05) \times 10^{3}$	−0.99996
SLM40	40	20	40		0.914 ± 0.001 (55–205 °C)	$(2.68 \pm 0.04) \times 10^{3}$	−0.99996

Last years an intensive attention was given to antimonite glasses because of their similar physical properties to widely used tellurite glasses without specific problems related to tellurium toxicity [1–10,16–18]. They have a broad thermal stability range and so they are also suitable for fiber drawing [3]. This paper deals with the new glassy system Sb_2O_3–MoO_3–Li_2O. This system represents an interesting combination of glass-forming, intermediate, and modifying oxides. Only few papers dealing with this system appeared up to now. These papers were dealing with absorption spectra in the Urbach's rule region [19], FTIR spectra, elastic properties, and some basic parameters of this system [20]. However, the system is also interesting from the point of view of its electrical conduction and relaxation as it represents a mixed ionic–polaronic conductor. Therefore, we have studied the influence of composition on its thermal, electrical, dielectric, and optical properties and we also examined relations between the composition, glass structure, and these properties.

2. Experimental

The starting composition used in this study is a ternary system: $(80-x)Sb_2O_3$–$20Li_2O$–$xMoO_3$, SLM_x, where $x = 0$–40. Materials used are Sb_2O_3 ≥99% (Acros), Li_2O ≈99% (Alfa Aesar), and MoO_3 ≈99 +% (Acros). Synthesis is carried out in several steps. Batches, around 10 g in weight, are made from thoroughly mixed powders. The mixture is introduced into a silica tube, around 10 mm in diameter and 10 cm in height, and heated by burner flame until a clear liquid is obtained. After that the melt is cast onto a brass plate preheated to approximately 200 °C. Estimated cooling rate ranges from 10 °C/s to 100 °C/s. It results in samples a few millimeters in thickness which are afterwards polished for experimental purposes.

The samples for measurements of electrical and dielectric properties (thickness of 2.6 ± 0.3 mm) are coated with a conductive graphite layer on contact surfaces. DC conductivity is measured at a constant voltage of 10 V using Novocontrol Concept 90, in the temperature range from −50 °C up to 225 °C. The current is measured by picoammeter Keithley 6517B. The temperature is measured using a Pt/PtRh thermocouple, with an accuracy of ±1 °C. Temperature dependencies of the DC conductivity are measured at increasing temperature, with a heating rate of 5 °C/min [17]. The combined uncertainty of DC conductivity measurements is equal to 7% [21].

AC measurements (from 20 °C up to 200 °C) are done using LCR Hi-tester Hioki 3522-50 at frequency range 100 Hz–100 kHz. Measurements are done in steps of 10 °C, after 20 min tempering at chosen temperatures. For the evaluation of the bulk DC conductivity the frequency dependence of the AC conductivity is used. To avoid the influence of electrode polarization effects and for better understanding of the electrical relaxation, the modular spectroscopy concept is used [22]. The static relative permittivity is determined using both the modular spectroscopy [9,10,22] and Kramers–Kronig relations.

At electrical and dielectric measurements, the temperature or frequency dependences are fitted to the experimental data using Levenberg–Marquardt iteration. Regression coefficients, r, are given in corresponding tables and figures for all dependences.

The glass composition is analyzed using scanning electron microscope and energy dispersive X-ray spectrometer (SEM-EDSJSM 6400 Jeol and Oxford link ISIS). Crystalline materials are used as standard references. Experimental error depends on the selected element, as signal to noise ratio is smaller for lighter atoms. It is estimated to be 1% for Sb and Mo and 5% for Li and oxygen.

Thermal properties are measured by differential scanning calorimetry (DSC 2010 from TA Instruments) with a heating rate of 10 °C/min. Small bulk samples are used; they are 5 to 10 mg in weight and set in aluminum sealed pans. With sensitivity better than 0.1 °C, the estimated

Table 2
Glass transition temperature, T_g, temperature of crystallization, T_x, thermal stability range, T_x–T_g, density, d, relative static permittivity, ε_{rs}, and indirect optical gap, E_g, with corresponding correlation coefficients, r, of SLMx glasses.

	T_g [°C]	T_x [°C]	T_x–T_g [°C]	d [g/cm^3]	ε_{rs}	r_ε	E_g [eV]	r_E
SLM00	273	385	112	4.916	19.5 ± 0.3	−0.95815		
SLM05	277	405	128		18.7 ± 0.3	−0.98544	2.57 ± 0.05	0.99895
SLM10	281	409	128	4.783	17.4 ± 0.2	−0.99181	2.52 ± 0.05	0.99943
SLM15	288	433	145		19.9 ± 0.2	−0.99696	2.48 ± 0.05	0.99943
SLM20	289	442	153	4.701	19.2 ± 0.2	−0.99826	2.42 ± 0.04	0.99944
SLM25	281	423	142		21.3 ± 0.2	−0.9982	2.36 ± 0.03	0.9997
SLM30	274	403	129	4.572	17.4 ± 0.2	−0.99839	2.26 ± 0.03	0.99982
SLM35	268	396	128		23.0 ± 0.2	−0.99877	2.20 ± 0.04	0.99951
SLM40	259	378	119	4.438	22.2 ± 0.2	−0.99898	2.10 ± 0.02	0.99987