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DIELECTRICAL METHODS AS A POSSIBILITY TO INVESTIGATE THE STRUCTURAL CHANGES AND DEFECTS

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Abstract: *Measurement methods of temperature dependencies of direct electrical conductivity (dec) as well as frequency dependencies of complex permitivity (cp) and complex electrical modulus (cem), respectively, are perspective to search properties of in-ordered structures and also the macroscopic quantities which characterized studied material. Chemical and optical purities, the presence of physical (point) defects and defects of the larger dimension (micro-crystals, clusters etc.), the effect of admixtures and technology of production belong among them. Moreover they make possible to determine temperature and time stability of samples and to access their homogeneity and the application possibilities, as well.*

Key words: *Heavy Metal Oxide Glasses (HMOG), structure, electrical properties.*

1. INTRODUCTION

Heavy Metal Oxide Glasses (HMOG) are currently attracting interest for their specific optical properties. Oxide glasses free of silicon, boron and phosphorus have low phonon energy, which results in an extended transmission range in the infrared spectrum. This paper is centred upon oxide glasses based on antimony oxide Sb_2O_3 in association with lead halides or alkali oxide [1,2]. We will investigate electrical and dielectric properties in relation to chemical composition. Electrical properties may be more sensitive than other physical values to the incorporation of dopants and additives, which induce structural changes. Because antimony oxide content is always large, it is assumed that the structure of these glasses consists in a vitreous network based on the association of the antimony SbO_n polyhedral. Halide anions and alkali monovalent cations act as network modifiers [3].

2. EXPERIMENTAL PART

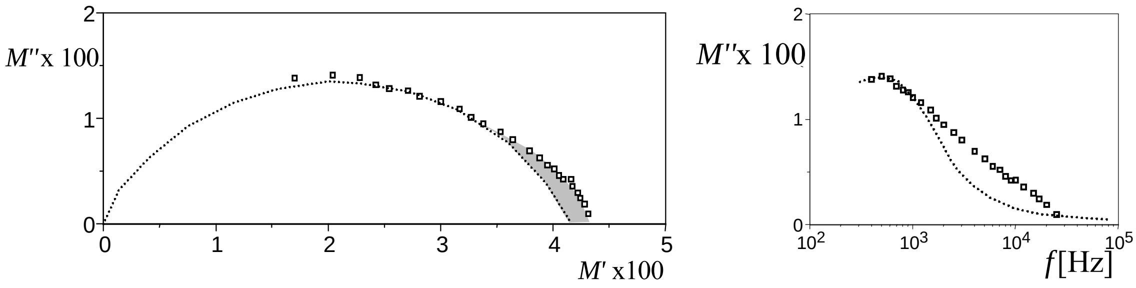
Oxide and oxyhalide glasses based on antimony oxide, lead halides and alkali oxides were prepared. Glass processing includes melting, fining, casting and annealing as main steps. Synthesis was performed in quartz or vitreous carbon tubes at room atmosphere [1]. The samples for the electrical measurements were coated with conductive layers deposited under vacuum and were small cylinders, 10 mm in diameter and 1 mm in height. The temperature dependencies of the direct conductivity were measured by the ratio method using the vibrating electrometer at 5 $K.mn^{-1}$ heating rate. Temperature and frequency dependencies of complex permitivity and complex electrical modulus, as introduced by Macedo et al. [4], were measured by bridge in the 0.2 - 100 kHz frequency range [5,6]. Absorption spectra were recorded by CARLZEISS JENA JENATECH spectrometer. X ray diffraction was used for investigation of defects in these glasses, wavelength was 1.79 A°.

Table 1. Values of direct electrical conductivity of vitreous samples at 200° C, transmittance and the sample appearance after measurement. *The different crucible was used during the glass processing.

Group of samples	Sample marks	Composition	*T* [%]	σdc(200° C) [$S.cm^{-1}$]	The microscope picture
SP	SP70Pt*	70 Sb_2O_3 – 30 $PbCl_2$	54	$8.21x10^{-09}$	The pure glass containing small crystals
	SP70*	70 Sb_2O_3 – 30 $PbCl_2$	67	$8.84x10^{-09}$	The pure glass containing small crystals
	SP85	85 Sb_2O_3 – 15 $PbCl_2$	13	$2.30x10^{-11}$	The glass contains amount of bubbles
	SP75	75 Sb_2O_3 – 25 $PbCl_2$	56	$6.35x10^{-10}$	The glass contains amount of bubbles and nonregular shapes
	SP55	55 Sb_2O_3 – 45 $PbCl_2$	23	$7.15x10^{-11}$	The glass contains nonregular shapes
	SP40	40 Sb_2O_3 – 60 $PbCl_2$	32	$6.74x10^{-07}$	The cloudy sample
SK	SK64	60 Sb_2O_3 – 40 K_2CO_3	51	$2.94x10^{-09}$	The destroyed sample

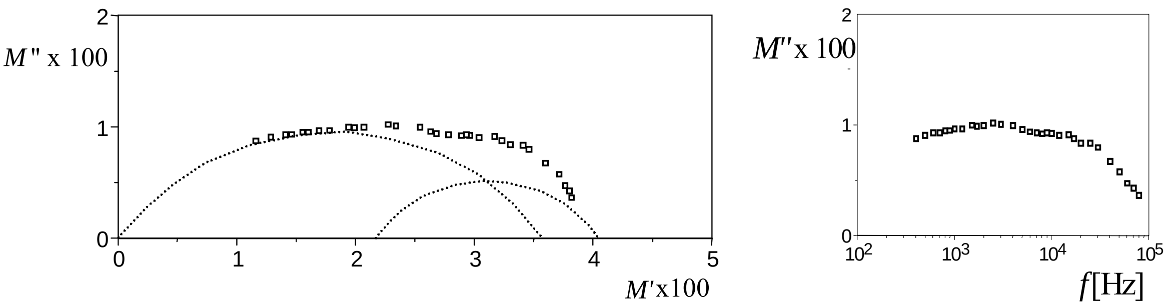
3. RESULTS

Dielectric measurements were performed for the sample SP 70 and SK 64. The experimental plots showed that the glass SP 70 is nearly monophasic but very inhomogeneous, as the centre of the half circle *M''* vs. *M'* is under axis *M'*. Simultaneously the tail and the evolution of *M''* vs. f is very wide at the high frequency, which suggests the occurrence of spectrum of relaxation times (Fig.1). The measured dependencies showed that the glass SK 64 had a biphasic structure (Fig.2). This indicates that the processing condition of the glass sample did not prevent partial crystallisation to occur, as it may been seen in the microscopically photo of the sample surface (Fig.3).



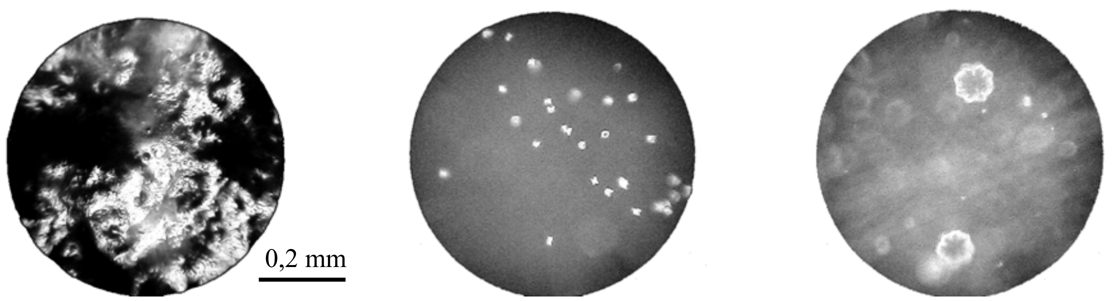
a) *b)*

Fig.1 *The measured dependencies for the glass SP 70 at the temperature of 210° C: a) Complex electrical modulus (M'' vs. M'). b) The frequency dependency of the imaginary part of complex electrical modulus (M'' vs. f).*



a) *b)*

Fig.2 *The dependencies for the glass SK 64 determined at the temperature of 210° C: a) M'' vs. M', b) M' 'vs. f.*



a) *b)* *c)*

Fig.3 *Microscope pictures made under polarised light for the glasses: a) SK 64, SP 70 Pt, c) SP 70.*

The upper limit of our electrical measurements was estimated to be close to 250 °C. At this temperature structural relaxation is still limited and repeated measurements on the sample SP 55 (Table 1) did not show evolution versus time as shown in figure 4. Activation energy of all measured samples is nearly equal [U_1 = (1.03 ± 0.05) eV] regardless the nature of the additives, their concentration and the chemical form of the cationic precursors ($PbCI_2$, $PbC0_3$, Na_2C0_3, etc.). The experimental dependency of the direct conductivity versus reciprocal temperature (σ_{dc} vs. 1/*T*) is linear tin a very large temperature interval. It means that one mechanism of transport dominant in this range. The change of activation energy U_2 = (3.75 ± 0.25) eV arises when the temperature goes beyond 260° C. This change can be ascribed to the evolution of the intrinsic conductivity in the vicinity of the glass transition (Fig.4). Conductivity values of individual glasses depend on their chemical composition. This appears clearly when conductivity is plotted at 200° C (Fig.5). The glasses of the system Sb_20_3-$PbCl_2$ were the most conductive. The monovalent admixtures reduced electrical conductivity (Fig. 5).

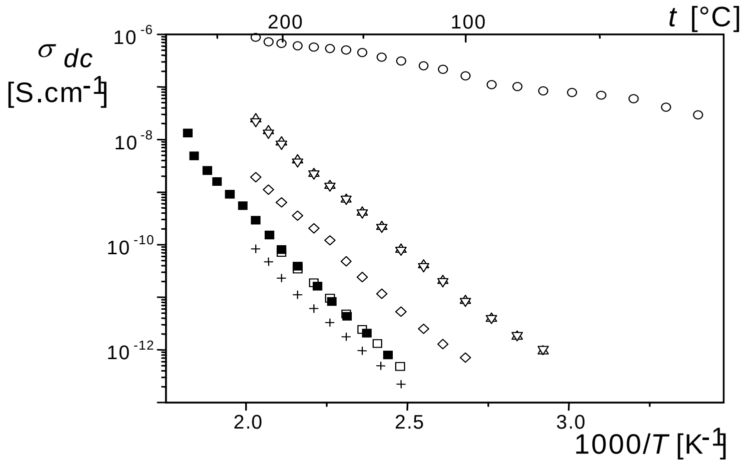


Fig.4 *Temperature dependencies of direct electrical conductivity for the glass Sb_2O_3 - $PbCl_2$ measured up to 220° C: ❍ - SP 40 (the cloudy sample), ☐ - SP 55, Δ - SP 70, ∇ - SP 70 Pt, ◇ - SP 75, + SP 85, ■ - the repeated measurement SP 55 up to 280°* C.

X ray diffraction analysis was using by samples SKP 640 and SP 70 Pt. This measurement acknowledge crystalline phase by sample SKP 64. This phase was identified as rhombohedral. In sample SP 70 Pt did not occur crystalline phase (Fig.6).

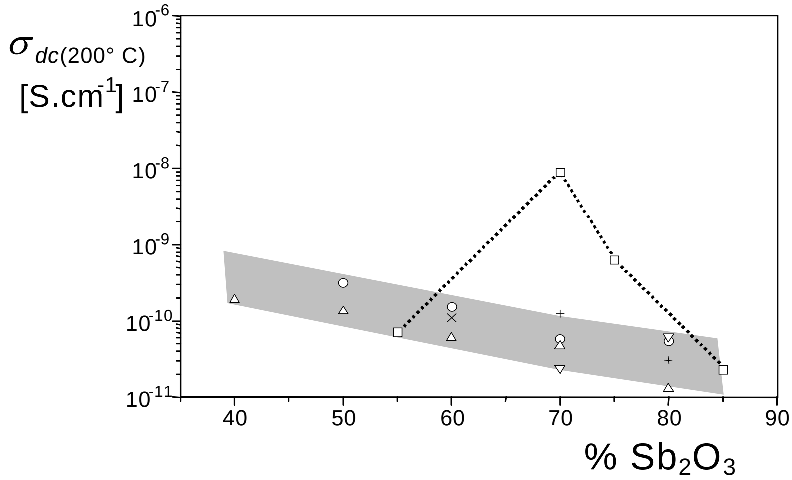


Fig.5 *The influence ofconcentracion of Sb_2O_3 for the values of direct electrical conductivity meaasured at the temperature of 200° C: □ the system SP (Sb_2O_3 – $PbCl_2$), ❍ - SNP1 (Sb_2O_3 – 10% Na_2CO_3 – $PbCO_3$), Δ - SNP2 (Sb_2O_3 – 20% Na_2CO_3 – $PbCO_3$), ∇ - SL (Sb_2O_3 – Li_2CO_3), + SK (Sb_2O_3 – K_2CO_3), ✕ - SKP 613(60% Sb_2O_3 – 10% Na_2CO_3 – 30% $PbCO_3$).*

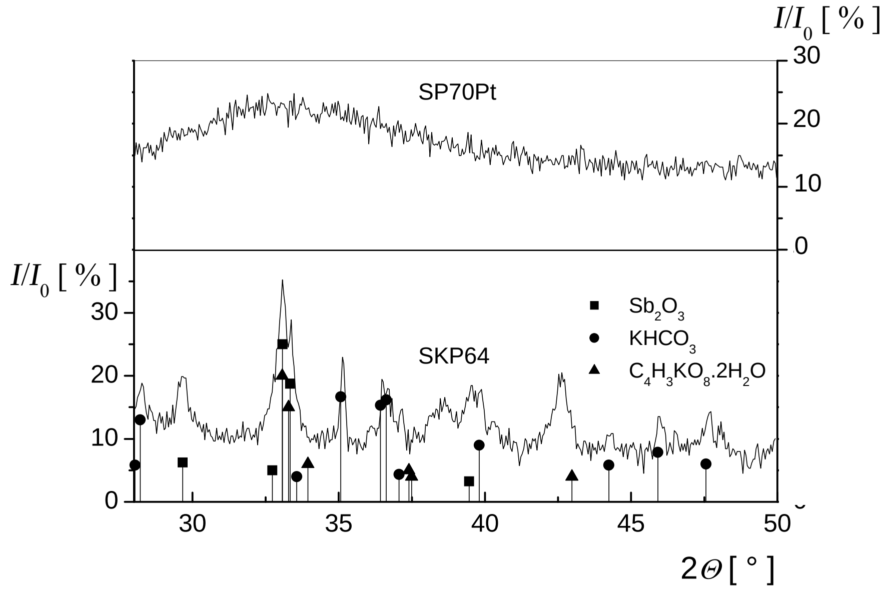


Fig.6 *Spectrum of X ray diffraction analysis for SKP 64 and SP 70 Pt.*

The optical quality of the glass samples may be assessed from the transmission factor in the transparency range. Maximal value is ruled by Fresnel losses, which are large, because refractive index is more than 2. The experimental transmission of these samples ranges from 13 to 71 %, exemplifying various scattering centres and defects. There is some correlation between transmission values - and consequently defect concentration - and direct conductivity (Table 1).

4.CONCLUSION

The preparation of the glasses of this study is difficult, leading to samples containing bubbles, inclusions, micro-crystals and scattering centres. These defects are clearly observed with an optical microscope (Fig.3). The electric measurements, especially complex electrical modulus, are also correlated to these defects. The first element is the existence of the "tail" of the half circle M'' vs. M' (Fig. 2). Also, the fact that the centre of the half-circle is located under the M' axis seems related to the large concentration of crystalline inclusions in the measured samples. Finally, the dependence of M'' vs. f is significantly wider with the several local maxims (Fig.2) for samples which contains defects. Temperature dependencies of direct electrical conductivity show considerable differences between glass samples from the same chemical system. The glasses SP 70 and SP 70 Pt had the highest values of conductivity. The type of the conductivity was not influenced by the presence of monovalent cations because activation energy was not changed. The change in the concentration of the charge carriers is attributed to the structural relaxation around glass transition temperature. The highest optical transparency was found out for the glass 70 Sb_2O_3 - 30 $PbCl_2$ (SP 70, SP 70 Pt) which had a limited concentration in scattering defects. These defects arise from improper glass processing. The sample SP 64 included rhombohedral crystalline phase. The study of the electrical and dielectric properties may appear as a useful tool for the optimisation of the synthesis technology.

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