RESEARCH PAPERS
FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA
SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

2011 Number 30

MONITORING THE INFLUENCE OF CHEMICAL COMPOSITION OF ELECTRICAL AND DIELECTRIC PROPERTIES OF SPECIAL GLASSES

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Abstract

The paper deals with the results of experimentally determined influence of the chemical composition change of pure Ge-Se-Te glasses systems with the rare earths elements additions (Pr, Er and Ho in oxide or pure metal form) on electrical and dielectric properties of the glasses. We used chalcogenide bulk glasses $Ge_{20}Se_{80-x}Te_x$ for $x \in (0, 5, 10, 15)$ prepared by systematic replacement of Se by Te. We wanted to find how electrical and dielectric properties of chosen chalcogenide glasses change with the change of content and form of rare earths. We carried out the measurements at different temperatures from 20 °C to 170 °C. Results show that the inhomogeneity and defects in the measured glasses have had an impact on the measured dielectric parameters.

Key words

special glasses, chalcogenide glasses, conductivity, rare earth elements, permittivity, electric module

Introduction

Ones of the subgroups of special glasses are chalcogenide glasses. They have favourable and excellent optical properties for different technical applications. They have been promising materials for telecommunications, integrated optics, biomedicine, and thermal imaging due to the relatively high transparency in a wide range of wavelengths of infrared spectrum, a high refractive index and low phonon energy. In terms of chemical, chalcogenide glasses are semi-conducting non-crystalline materials with covalent bond, which contain one or more chalcogenide elements (S, Se, Te) in combination with one or more elements of III a – V a subgroups of periodic system (III a – Ga, IV a – Si, Ge, V a – P, As, Sb, Bi) [1]. They can be classified into groups of non-oxide glasses. In comparison with oxide glasses (mainly based on SiO_2), they have different optical and electrical properties [2]. This paper is aimed at studying the impact of changes of the chemical composition of G e-Se-Te glass, both pure and

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with admixtures of rare earth elements (Pr, Er, Ho in oxide and metal form), on the values of selected electrical and dielectric parameters.

Theory

Chalcogenide glasses are substances prepared with high purity. In particular, impurities in the form of hydrides and oxides may be in a quantity exceeding the ppm, causing a significant decrease in transmittance, increased susceptibility of glass to create crystal phase and also reduce the value of the maximum solubility of rare earth elements. Increased emphasis is placed on preparing mixed selenium-telluride glasses [2, 3]. With increasing the content of tellurium, the range of wavelengths moves to higher values. The tendency to crystallization also increases. Therefore, the tellurium is replaced by selenium, while maintaining the area of transition radiation up to 15 μm with significantly reduced absorption at CO_2 laser wavelengths (10.6 μm).

Thermal stability of these glasses is good, and it therefore provides a broad commercial use of these substances for optical glass and for glass fibre [4]. Chalcogenide glasses crystallize easily and quickly, and they can be therefore used in the manufacture method of rapid cooling. Investigated glasses were prepared by cooling the melt in a sealed quartz ampoule evacuated to a vacuum 10^{-3} Pa at 850 to 950 °C during 15 to 20 hours.

Immersing the ampoule into water at room temperature, the melt cools down. The prepared ingots had a diameter of 10 mm and length from 50 to 80 mm [4, 5].

Experiment

In the evaluation of the measured results of observation glasses, we used the particular value of the complex electric module M^*, whose values are sensitive to changes in the volume of the sample and minimise the impact of contacts and the electrodes. Complex electrical module captures conductivity and polarization features, because a motion of bound and free charge carriers in the volume of material as it suppresses high-capacity effects in the electrodes and the emphasis on low-capacity volume effects. For the use in materials science, the measurement of complex electrical module is a more appropriate method. Complex electric module is defined as the inverted value of the complex permittivity (1).

$$M^* = \frac{1}{\varepsilon^*} = M' + \mathrm{i}M'' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + \mathrm{i}\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \quad , \tag{1}$$

where ε^* is determined by: $\varepsilon^* = \varepsilon' - \mathrm{i}\varepsilon''$. (2)

Real component of ε' is ideally identical with the frequency independence of the relative permittivity of material, ε'' is the imaginary component characterizing the electrical losses. M^* captures not only the conductivity, but also the polarization which occurs in the material structure.

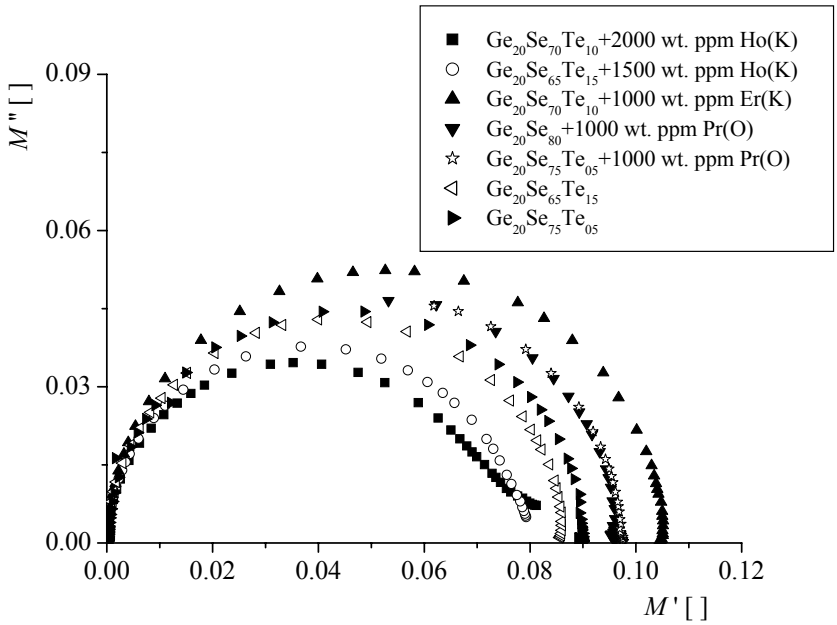

Fig. 1 *Dependence of complex electrical modules (M'' vs. M') measured at 70 °C for samples of glass containing praseodymium, holmium, erbium in the form of metal (K) or oxide (O) and without rare earth impurities.*

Measured complex electrical modules shown in the complex plane (Fig. 1) are consistent with theoretical predictions. Waveforms have the half-circular shape without perceptible distortion; it means that in the volumes of the samples there is no inhomogeneity, except for glasses $Ge_{20}Se_{65}Te_{15}$ with 1500 wt. ppm. Ho in the oxide form and $Ge_{20}Se_{70}Te_{10}$ with 2000 wt. ppm. Ho in metallic form. For each waveform, impact of adding the ingredients is visible and impact of the chemical forms of each ingredient is recognizable. The values of conductivity for different glasses are in accordance with Arrhenius law (3) (Fig. 4):

$$\sigma_{dc} = \sigma_0 \mathrm{e}^{-\frac{U}{kT}}, \tag{3}$$

where U is the activation energy for the formation of conductive electrical charge, k is Boltzmann constant, T is temperature, and σ_0 is the pre-exponential factor [3]. For the glasses with the presence of defects, the increase of peaks with increasing temperature was observed (Fig. 3). The defect can be due to oxides impurities, molecular water, OH groups, carbon and its compounds with hydrogen.

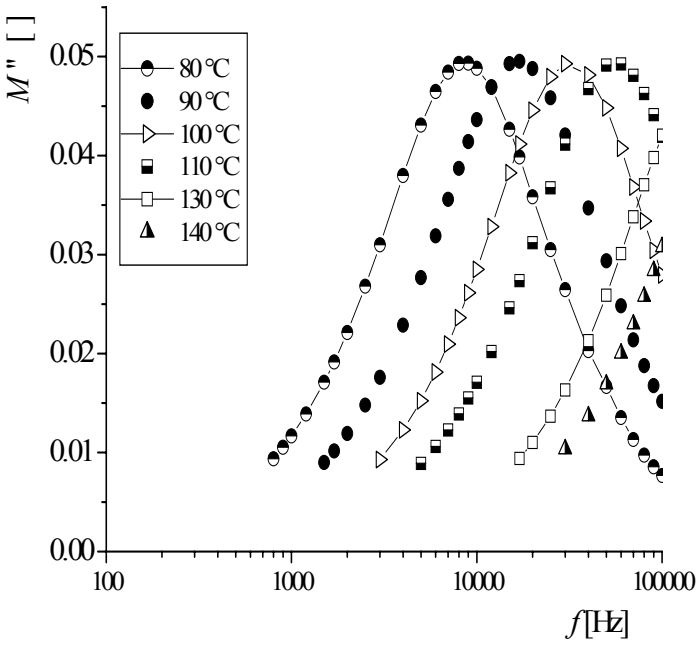

Fig. 2 *Frequency dependences of imaginary complex electrical module (M'' vs. f) at different temperatures for $Ge_{20}Se_{65}Te_{15}$+1000 wt. ppm Ho (as metal) glass*

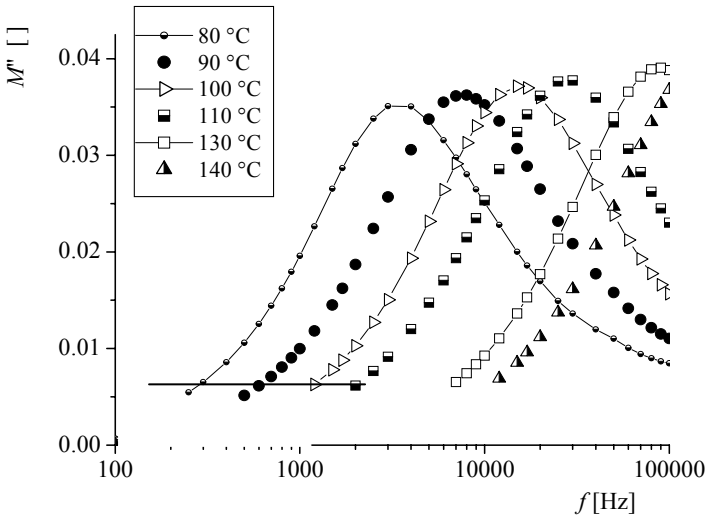

Fig. 3 *Frequency dependences of imaginary complex electrical module (M'' vs. f) at different temperatures for $Ge_{20}Se_{65}Te_{15}$+2000 wt. ppm Ho (as metal) glass*

When comparing the effects of rare earth elements, a significant impact of Er and Pr impurities is evident, while there is a less pronounced effect of Ho. In general, electrical conductivity values increase with increasing the concentration of tellurium in the glass. Impact of rare earth is strongest in the case of glasses without tellurium impurities, and values of conductivity significantly increase with admixture of rare earth.

Samples

The samples were prepared in the form of discs by grinding to the required size (diameter ~9 mm and thickness 1.5 mm). The fronts of the samples were coated with conductive layer of colloidal graphite. In the temperature range from 20 to 170 °C, the values of a DC electrical conductivity, the complex permittivity and complex electric module were determined. Based on the knowledge that the electrical and dielectric properties of glasses are dependent on their internal arrangement, usually signifies a change of their properties. DC electrical conductivity values are determined using the VA method by KEITHLEY 6487 apparatus at linearly increasing temperature. Values of other parameters were measured at a constant temperature every 10 °C by using Hioki 3522-50 instrument in the frequency interval of frequencies from 0.1 Hz to 100 kHz. Measurements were made in the measuring cell without protective atmosphere.

Conclusion

For $Ge_{20}Se_{80-x}Te_x$ glass system where $x \in \{0, 5, 10, 15\}$ with adding rare earth elements 1000 wt. ppm Er^{3+}, Pr^{3+} and Ho^{3+} either in the form of oxides or metals, the measurements of selected electrical and dielectric parameters were carried out. Results of the measurements of complex electrical module are slightly different from the characteristic dependence measured for an ideal dielectric with one relaxation time. The frequency dependences of imaginary part of a complex electrical module slightly differ from the Debye distribution shifted with increasing temperature (Fig. 2). In the case of glasses with higher doping rare earth elements, deviation from the behaviour of half circle distort display of complex electrical module in the complex plane at the high-frequency range can be observed.

The deformation of each dependency shows a higher tendency to crystallization of the glass in the case of adding Ho. The crystalline phase is skewed, confirmed by independent measurements (X-ray analysis). Measurements of DC electrical conductivity are characterized by dominant mechanism of transport of charge with the same value of activation energy in the whole temperature range. For these measurements, higher sensitivity to chemical composition as the formation of crystalline phase is noticeable. Glasses without tellurium and with adding rare earth elements show similar effect as tellurium. Temperature dependences of measured values of the electrical conductivity show Arrhenius behaviour (Fig. 4), while activation energy tellurium content generally decrease, and, with adding the rare earth, the decrease can be more intensive. If we investigate the influence of the form by which the rare earth impurity is added to the glass, such influence cannot be clearly determined, as the results can be affected by other factors.

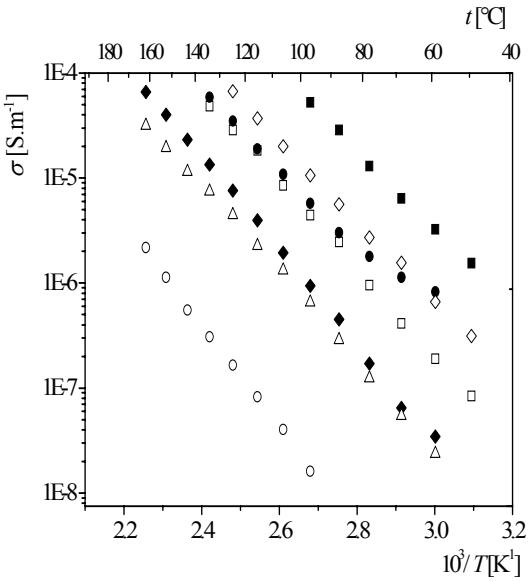

Fig. 4 *The temperature dependence of conductivity for selected glass samples containing praseodymium, holmium and erbium in the form of metal (K) or oxide (O) and without rare earth impurities*
LEGEND:
■ *$Ge_{20}Se_{65}Te_{15}$+1000 wt. ppm Er (K),*
□ *$Ge_{20}Se_{65}Te_{15}$+1000 wt. ppm Ho (O),*
♦ *$Ge_{20}Se_{75}Te_{05}$,*
◇ *$Ge_{20}Se_{65}Te_{15}$,*
○ *$Ge_{20}Se_{70}Te_{10}$+1000 wt. ppm Pr (K),*
● *$Ge_{20}Se_{70}Te_{10}$+2000 wt. ppm Ho (K),*
△ *$Ge_{20}Se_{80}$+1000 wt. ppm Pr (K).*

Presented electrical and dielectric methods appear to be highly promising for the investigation of structural changes and defects also for other systems of special glasses [6, 7 and 8].

Acknowledgements

This paper was supported by the OP Research and Development for the project of Centre of development and application of diagnostic methods in processing of metallic and nonmetallic materials, ITMS: 26220120014, co-financed by the European Regional Development Fund. The authors express gratitude for the contribution of support.

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