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Changes of sulphide glasses caused by the presence of As

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The contribution presented summarizes knowledge about the influence of As added to sulphide glasses on the measured values of electrical and dielectrical properties. To decrease the tendency to crystallize and to separate phases of Ge – Ga – S glasses, as well, the part of Ga is substituted by As. The original net "ordering" is significantly changed already by the addition a little amount of As (5 mol %) because there is formed partial glass netting by creating covalent bonds among the molecular strings. The mentioned effects are marked at the measurements of electrical and dielectrical parameters.

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1. Introduction

Chalcogenide glasses are characterized by appropriate optical properties in the region of wave length (0.6 – 16) μm although optical transparency reaches 60 to 80 percent in the middle and the far infrared region. It is possible to dope hem by the rare earth elements (RE^{3+}) in many cases. Their maximal solubility does not overreach 1 000 wt. ppm. usually. The gain of luminescence increases when (RE^{3+}) are added to glasses [1-8]. The limit of maximal solubility is possible to determine by means of the sensitive measurements of electrical and dielectrical properties, as well [9.10]. These measurements are less demanding experimentally and they are comparable by their sensitivity, accuracy and rate with classical method as for example method utilizing the optical properties measurements, electron microscopy, X diffraction, ect. [11]. The value of the long wave edge (the maximal value of wave length effective to transport radiation) is affected by the vibrations in the glass net especially. It means that it depends on atomic mass of the used chalcogenide element. It can be anticipated that this limit in chalcogenide glasses will increase by the enlarging the proportion of S to Te [1]. The role of As is to increase homogeneity and so to suppress the phase separation and to decrease the tendency to create crystalline phase in glass volume, too. In general the presence of As supports in-ordering of the base net because there is created the more complicated volume ordering of the previous motive of net considering the conditions of covalent bonds. The change of this stage to crystalline it means regular is connected with the larger requirements on the value of the needed energy. Three dimension net rises in sulphide glasses with As nodes which connect Ge-S strings where As bonds are markedly space oriented.

The contribution content is the presentation of the influence of As admixture in sulphide glasses on the measured values of electrical and dielectrical properties.

2. Experimental details

Technology of the preparation of chalcogenide glasses is oriented especially to reach the lowest concentration of OH groups and hydride impurities SH, which cause the increase of optical absorption and decrease of temperature stability of glasses. Thus they support the formation of crystalline phase created by rare earth elements dropped out to clusters [11]. Apart of this the limit of the solubility is deceasing by their influence. Chalcogenide glasses are prepared by means of the original compounds of high purity in vacuum, usually [1].

Sulphur re-sublimated in the reactive atmosphere was used to eliminate impurities during the preparation of sulphide glasses Ge-Ga-S and Ge-As-Ga-S pure and with admixtures Pr^{3+}, too. Germanium, gallium and arsenic, respectively, are melted together in the ceramic crucible from BN in high vacuum at temperature of 950°C. Next glasses are prepare by melting re-purified materials and Pr_2S_3 in sealed special ampoule evacuated to 10^{-3} Pa and to keep at the temperature 950°C during 20 hours. Then melting was cooled merging to water and followed out the slow cooling from temperature of 400°C to the room temperature [12].

The prepared ingots were cylinders with the diameter of 10 mm and the length of (50 – 80) mm. The measured sample were the thickness of ~ 1 mm. The bottom and the top of the sample were coated by the conductive layer from colloid graphite (DAG 580). The measurements of the temperature conductivity of the direct conductivity were performed by direct (Volt – Ampere) method by means of electrometer Keithley 6514in the temperature interval (20 - 400) °C [13]. The rate of heating was 5° C.min^{-1}. The temperature increase of the direct conductivity values of chalcogenide glasses σ_{dc} can be expressed e.g. by Arhénius relation [14]

$$\sigma_{dc} = \sigma_0 \mathrm{e}^{-\frac{U}{kT}} , \quad (1)$$

were U is activation energy determined by energy which is necessary to create an electrical charge and its transport, k is Boltzman constant, T is temperature and σ_0 is pre-exponential factor. Following the influence of temperature to the ordering of glasses by means of the direct electrical conductivity measurements we detect the affection of the creation and the mobility of free electrical charge careers in the volume.

We can obtain more complex information about the changes of inside ordering utilizing the observation of the bind electrical charge careers mobility in the glass volume by means of complex electrical modulus M^* which was introduced by Macedo et al. [15] as a reciprocal value of complex permittivity ε^*

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

where ε^* is determined by the relation $\varepsilon^* = \varepsilon' - \mathrm{i}\varepsilon''$. The real compound ε' is identical with the relative permittivity of material, ε'' is imaginary compound characterizing electrical losses [15]. Measurements of temperature and frequency dependency of M^*, as well, were performed by the device GOODWILL LCR 819 in the temperature interval (20 - 200) °C and the frequency interval of (0.2-100) kHz [16].

3. Results and discussion

Investigated sulphide glasses $Ge_{25}Ga_{10-x}S_{65}$ a $Ge_{25}As_5Ga_{5-x}S_{65}$ pure and with admixtures Pr^{3+}(x = (0 - 1000) wt. ppm) are affected by Ge. It stronger bond with the chalcogenide element originates the increase of the temperature stability but it supports the creation of crystalline phase at the higher temperature, too. The reason is that at the original net of glass the space parts (-S-Ge-S-)$_n$ are oriented linearly, slightly different from the regular ordering. Gallium discriminates the region where the glass is created, it means that it supports the glass creation, because its adding affects to the increase of non-ordering of the original glass net. Thus it is decreasing glass tendency to the phase separation. The interval of transparency of these glasses is 0.6 – 7 µm [2], therefore these glasses are perspective to transport the radiation of YAG and CO lasers.

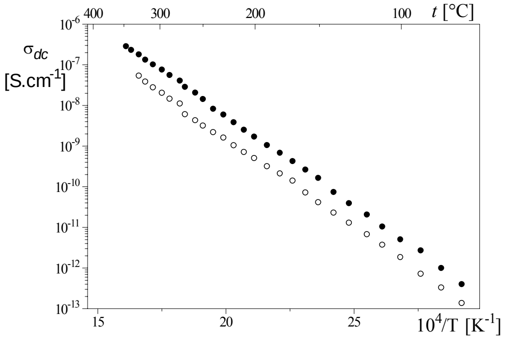
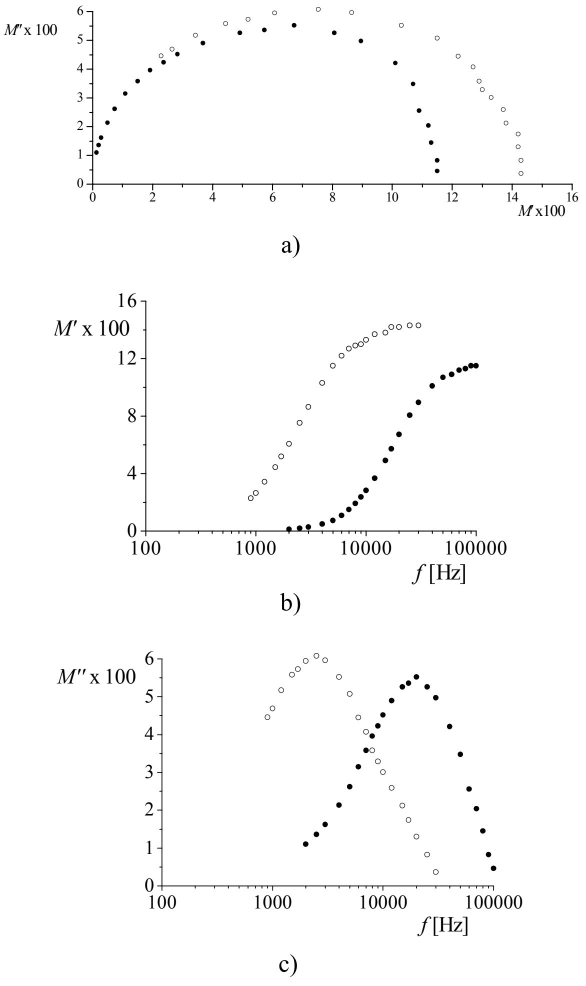


Fig. 1.Temperature dependencies of direct electrical onductivity of glasses ● $Ge_{25}Ga_{10-x}S_{65}Pr_x$ and glasses ○ $Ge_{25}As_5Ga_{5-x}S_{65}Pr_x$ (x = 500 wt. ppm Pr).



a)

b)

c)

Fig. 2. Dependencies measured at temperature of 300°C for glasses ● $Ge_{25}Ga_{10-x}S_{65}Pr_x$ and ○ $Ge_{25}As_5Ga_{5-x}S_{65}Pr_x$ (x = 500 wt. ppm). a) Complex electrical moduly (M'' vs M'). b) Frequency dependencies of real compound of complex electrical modulus (M' vs f). c) Frequency dependencies of imaginary compounds of complex electrical modulus (M'' vs. f).

The strong change in the ordering of Ge-Ga-S glass net is met when As is added. It is affected by the formation of the new more complicated space ordering of the net. Glass with higher resistance to create the crystalline phase at the higher temperature rises by partial netting which is affected by solid covalent bonds among the strings with the space bifurcated structure. The change in the glass ordering adding As is shown also by the change of the other properties. The change is detectable on the measured values of direct electrical conductivity (Fig. 1) and on the values of dielectrical properties expressed by means of complex electrical modulus (Fig. 2). The activation energy of the direct electrical conductivity with the admixture As does not change and can be expressed by interval $U = (0.85 \pm 0.02)$ eV. Dielectrical properties are affected mainly at the higher frequency of electrical voltage when the strong decrease (10 times) of the relaxation time of polarization is occurred.

4. Conclusions

In general admixtures of rare earth (RE^{3+}) in chalcogenide glasses significantly do not affect the electrical properties. It suggests that individual compounds of this glass are built in to the glass skeleton as atoms with saturated bonds [1]. In the case of the presence of 5 mol % As in sulphide glasses (Ge-Ga-S we get the expressive changes which are caused by the formation of the new space ordering of the glass net crating the solid covalent bonds. Thus the temperature stability is increased and the electrical and dielectrical properties were change, too [12].

This new space ordering reduces significantly the transport of the free electrical charge and also the bounded one. The original mechanism of the charge transport is not changed. It means that the qualitative change in inside ordering of sulphide glasses $Ge_{25}Ga_{10-x}S_{65}Pr_x$ by the exchange of the part of Ga by arsenic brings only quantitative change of the measured values of the electrical and dielectrical properties.

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