

Electrical methods for optimization of structural changes and defects in sulphide glasses

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Sulphide glasses $\text{Ge}_{25}\text{Ga}_{10}\text{S}_{65}$ doped by ions of rare earths (Pr^{3+}) are suitable for preparing of active optical fibres because they own low phonon energy needed for activation and rather both high value of refractive index and transparency in IR of spectrum. Suitable electrical and dielectric parameters reflect structural changes in tested glasses and aid to determine the influence of various technological parameters and admixtures. The complex electrical modulus can be used for the investigation of the structural changes of $\text{Ge}_{25}\text{Ga}_{10}\text{S}_{65}$ glasses due to adding of Pr^{3+} ions. By this method the rise of clusters into glasses can be detected. The admixture begins to segregate to cluster at higher concentration (≥ 3000 wt. ppm). Obtained results of the rise of the clusters agree with the observation by means of electron microscopy. The results of electrical measurements of various samples with low and higher Pr^{3+} concentration correspond with results obtained by luminescence (influence of rare earth segregation). The measured results unambiguously confirmed that the prepared sulphide glasses are very homogeneous, mono-phase, long-term stable to the high temperature, up to 300 °C at least. The temperature stability at ≤ 1000 wt. ppm Pr^{3+} up to high temperature remained non-changed. It changed only in the case of the sulphide form of the added admixture ≥ 3000 wt. ppm, when the segregation begun already at temperature of 350 °C.

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1. Introduction

At present there are appeared many applications especially in medicine, chemistry and ecology which utilize optical fibres transmitting radiation of the middle and the far range of IR spectrum. Sulphide glasses with admixture of rare earths (Pr^{3+}) belong among the most perspective materials for their production. They have many advantages to the classical fibres prepared from SiO_2 glass systems and fluorozirconic systems [1-5], respectively. $\text{Ge}_{25}\text{Ga}_{10-x}\text{RE}_x\text{S}_{65}$ glass systems are characterized by the strong chemical stability and the own very firm both fluorescent and luminescent properties [6,7,8,5]. They are dependent on the high purity of glass especially on the low OH^- group concentration. They reduce solubility of rare earths considerably and enhance the probability their come out to clusters. Thus their optical properties become worse, too. The cluster creation depends not only on the concentration of RE^{3+} and OH^- ions, respectively, but on the chemical form, too, as are added to glass (sulphide, chloride, oxide, or metal) [9-14].

We want to show in this paper the usefulness of the exploitation of both electrical and dielectric measurement methods to determine the maximal solubility of rare earth,

temperature stability etc. of $\text{Ge}_{25}\text{Ga}_{10-x}\text{Pr}_x\text{S}_{65}$, ($x = 0 - 6000$ wt. ppm) system.

2. Experimental

The solubility of rare earths ions is dependent not only on the purity of the starting raw but on OH^- group concentration. Therefore it is needed to prepared these systems with the high both physical and chemical purities ($< 5 \times 10^{-4}$ mol %). The impurities affect the cluster creation and it is the reason to the decreasing of luminescence output and the increasing of the optical decrement as the result of the scattering. The important fact from the point of the electrical properties is their P type conductivity performed by the conduction electron mobility.

It is necessary to perform the final purification of the initial elements to eliminate OH impurities which the main sources are the initial raw and the laboratory surroundings. To prepare chalcogenide glasses the method of the divided ampoule was used. There were used two separate and each other connected quartz ampoule where one of them has thin barrier. The preparatory technological steps as heating

of chalcogenide to eliminate the resting water and surface oxides were performed in the first ampoule. The barrier is broken after the vacuum sealing and chalcogenides sublimate to the second ampoule with the purified metals. This ampoule is vacuum sealed, too. Then the glass system synthesis is carried out at pressure of 10^{-3} Pa and temperature of 950°C during 12 hours. Then the hot-melt is short time cooled by emerging the ampoule to water and the slow cooling follows from temperature of 400°C to the room temperature. Praseodymium was added in the form of Pr_2S_3 [15].

The measurements of electrical and dielectrical properties of the glass samples (ϕ 9mm, thickness 2mm) were performed in the temperature interval (20 - 360) $^{\circ}\text{C}$. The surface of sample was coated by the conductive layer of colloidal graphite (Dag 580). Direct conductivity was measured by volt-ampere method by means of the current measurement at the constant voltage of 10 V. The measurements of both temperature and frequency dependencies of complex permittivity were carried on by Schering bridge at the frequency interval (0.05 - 100) kHz [16].

Photoluminescence (PL) spectra were measured at various temperatures and the levels of excitation power. The experimental set-up consists of the optical cryostat based on Helium Refrigerator System (Balzers, USA) and automatic temperature controller that enables to measure at temperatures in the range (4 – 300) K. PL spectra were analysed by 1m focal length monochromator (Yobin-Yvon, THR 1000) coupled with N_2 -cooled Ge detector and/or N_2 -cooled S1 photomultiplier, using lock-in technique and computer controlled data collection. He-Ne and Ar ion lasers were used for excitation. The excitation power densities were varied in the range (0.1 - 100) mW/cm^2 using suitable neutral density filters [17].

Temperature dependencies of direct conductivity in the searched temperature interval is possible to describe for these glass systems by Arrhenius relation

$$\sigma_{\text{dc}} = \sigma_0 \cdot \exp(-E/kT), \quad (1)$$

where σ_0 is pre-exponential factor, E is activation energy, k is Boltzmann constant and T is temperature. To analyze dielectric response of searched systems it is possible to exploit the analyze of the complex electrical modulus measurements introduced by Macedo [18], where the complex electrical modulus M^* is the reciprocal value of complex permittivity ε^* . It is possible to write

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

The plotting of M^* in the complex plane can be expressed by the curve only a little different from half circle with the centre near under M' axis for the system with one relaxation time and the systems with the small interval of relaxation time (the most often case of sulphide glasses). It is possible to sight on the frequency

dependency $M''(f)$ the course a little different from Debye distribution where the maximum is for the frequency value which responds the reciprocal value of the relaxation time ($1/\tau$) [19].

3. Results

It is evident analysing electrical and dielectrical properties of sulphide glass systems $\text{Ge}_{25}\text{Ga}_{10-x}\text{Pr}_x\text{S}_{65}$ that the change of the Pr content in the range (0 - 6000) wt. ppm affected the values of the temperature dependencies of direct conductivity and also the temperature and frequency dependencies of complex electrical modulus, respectively. Analysing the measurements of temperature dependencies of direct conductivity one can state that there exists only one mechanism of conductivity with one type of charge carrier in the measured temperature interval (20 - 370) $^{\circ}\text{C}$ (Fig.1). The measured curves do not show any breakage.

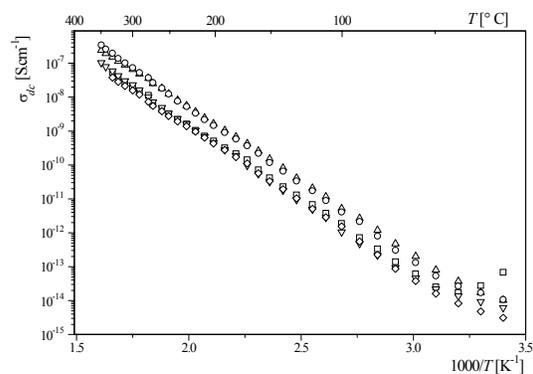


Fig. 1. Temperature dependencies of direct conductivity of glass systems $\text{Ge}_{25}\text{Ga}_{10-x}\text{Pr}_x\text{S}_{65}$ for x [wt. ppm]: \square 0, \circ 500, \triangle 1000, ∇ 3000, \diamond 6000.

The influence of Pr admixture was found out especially at the concentration interval (500 – 1000) wt. ppm where the values of direct conductivity were increasing more markedly. The admixture Pr (0 - 6000) wt. ppm did not affect significantly the values of found out activation energy. The activation energy, representing the intermediate value of the potential barriers is quite low $E = (0.88 \pm 0.02)$ eV.

The measured values of direct electrical conductivity are markedly affected by the admixture of rare earth (Fig.2). One can see the significant increase of these values especially for the admixture values 500 a 1000 wt. ppm. It is possible to detect the influence of Pr concentration in system $\text{Ge}_{25}\text{Ga}_{10-x}\text{Pr}_x\text{S}_{65}$ also in the case of the complex electrical modulus measurements (Fig. 3a). The measurements M'' vs f show that the curves are only little different from the ideal Debye distribution. The maximum position (Fig. 3b) shows the similar increase of frequency maximum (the decrease of relaxation time) as in the case of direct conductivity.

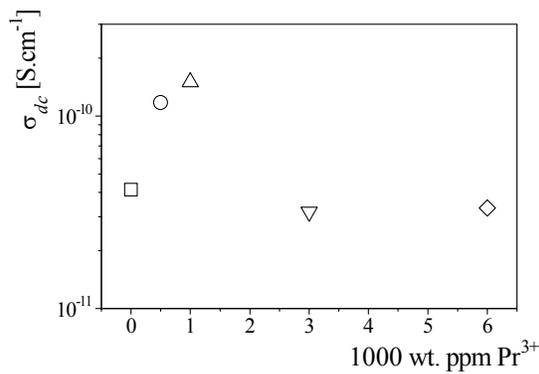


Fig. 2. The influence of Pr concentration on the values of direct conductivity for glass $Ge_{25}Ga_{10-x}Pr_xS_{65}$ at temperature of $150\text{ }^{\circ}C$.

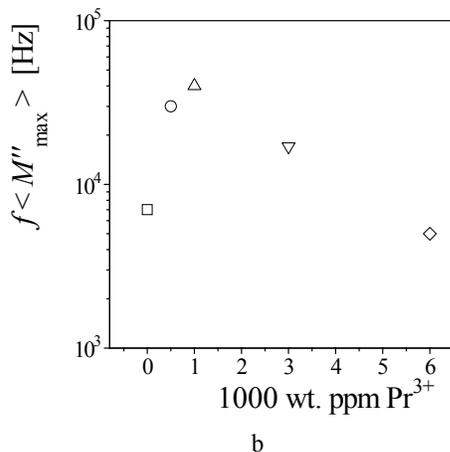
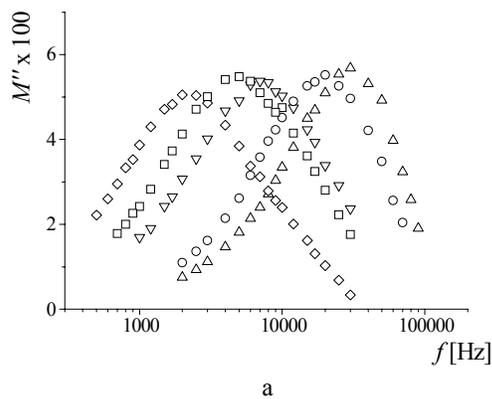


Fig. 3. a) Frequency dependencies of imaginary part of complex electrical modulus M'' vs f glass system $Ge_{25}Ga_{10-x}Pr_xS_{65}$ pri $300\text{ }^{\circ}C$ for x [wt. ppm]: \square 0, \circ 500, \triangle 1000, ∇ 3000, \diamond 6000. b) Plotting of the frequency dependency on Pr concentration when the behaviour M'' vs f show maximum for glass systems $Ge_{25}Ga_{10-x}Pr_xS_{65}$.

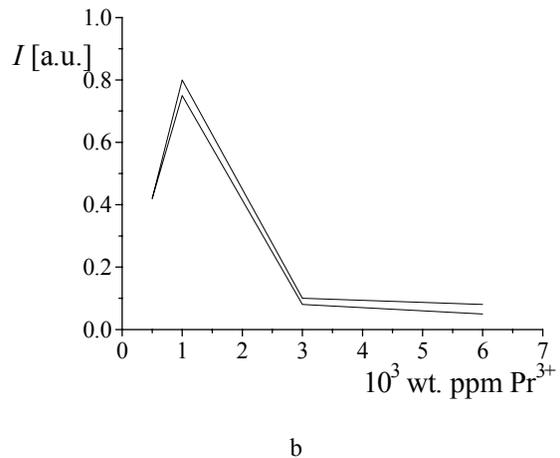
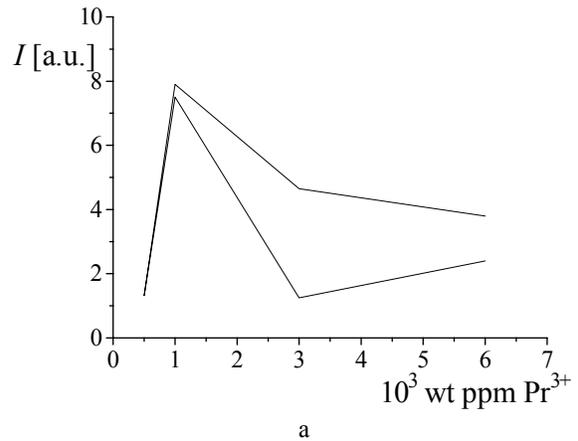


Fig. 4. The influence of Pr concentration of glass systems $Ge_{25}Ga_{10-x}Pr_xS_{65}$ ($x = 0 - 6000$ wt. ppm) on the measured values of intensity of luminiscency for wave length: a) $\lambda = (1.339-1.349)\ \mu m$, b) $\lambda = (1.534-1611)\ \mu m$.

The measurements of luminiscency to evaluate the influence of Pr concentration in searched glass systems in the range of Pr characteristic wave length were performed (Fig. 4), too. The measurements show the similar course as ones for electrical and dielectrical properties (Fig. 2, Fig. 3b). One can assume from the analyse from the shown measurements of luminiscency that the Pr admixture is released from the vitreous phase at the concentration of 1000 wt.ppm. This assumption was confirmed analysing micrographs done by means of the scanning electron microscope (Fig. 5).

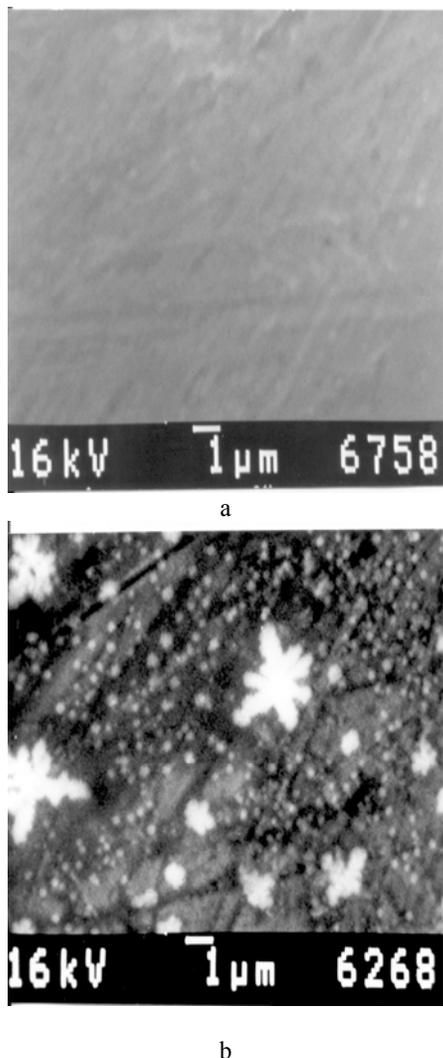


Fig. 5 The SEM micrographs of $\text{Ge}_{25}\text{Ga}_{10-x}\text{Pr}_x\text{S}_{65}$ samples for the following OH group and Pr^{3+} concentrations, (a) 10^{-5} mol %, 1000 wt.ppm; (b) 10^{-5} mol %, 3000 wt.ppm.

The repeated measurements of electrical and dielectric properties of glass systems $\text{Ge}_{25}\text{Ga}_{10-x}\text{Pr}_x\text{S}_{65}$ heated to the higher temperature confirmed the temperature stability of glasses in the dependence to Pr concentration up to 1000 wt. ppm. We found out the non-stability the searched glass at Pr concentration of 3 000 wt. ppm as the change of measured values in glass was heated at temperature of 350 °C.

4. Discussion

Both electrical and dielectric properties of semi conductive glass systems $\text{Ge}_{25}\text{Ga}_{10-x}\text{Pr}_x\text{S}_{65}$ for $x = (0-6000)$ wt. ppm are affected predominantly by Pr concentration. Praseodymium dissolved in the solution of vitreous phase creates the additional energy level in the

forbidden band. Thus the glass conductivity increases by the jumps in the valence band as a consequence of the increase of the number of the electrical charge carriers. The similar effect should be seen in the case of dielectric properties, too, where one can find out the shortening of relaxation time of measured glasses.

It is clearly to see from the shift of the peak of the dependencies M''_{max} vs. f measured at temperature of 300 °C where Pr concentration is a parameter that the solubility maximum is about 1000 wt. ppm of Pr (Fig. 3b). The frequency of maximum begins to decrease and it is lower as for the sample without the admixture when the concentration is 6000 wt. ppm. The similar results are learned by means of the temperature dependency of direct electrical conductivity (Fig. 2). Ions Pr^{3+} segregation in sulphide glasses begins at Pr concentration 3000 wt. ppm and there exists almost the whole disposition of Pr ions from the solid solvent of sulphide glass (the saturate solvent) when Pr concentration is 6 000 wt. ppm. It denotes that the admixture does not segregate if Pr concentration ≤ 1000 wt. ppm and the glass are still in the balanced state. The nuclei of the new phase begin to create when the saturation is bigger ((3000 – 6000) wt. ppm of Pr). It means that the admixture begins to segregate and it merges to the new created phase at the value 6 000 wt.ppm of Pr.

To determine the maximal solubility of the rare earths in these glass systems there is usually employed measurement methods of luminescence and SEM, respectively. Both methods are from the point of view of the sample preparation usually more laborious and require the more financial expenses, too. The measurements performed confirmed information gained by electrical and dielectric ones. Plotted values of luminescence in Fig. 4 were measured at two intervals of wavelength. They supported the idea that there is the maximal solubility of Pr^{3+} at the concentration about 1 000 wt. ppm. The admixture begins to come out to clusters at the higher admixture concentration. In consequence of this the product of luminescence is lower and the transfer losses are larger, too.

The admixtures concentration affects also on the temperature stability of glass systems. If there occurs the segregation of the admixture of rare earths there exist further irreversible changes in the searched glasses already at temperature of 350 °C. The temperature stability of glass system is minimally up to 380 °C if Pr concentration is up to 1 000 wt. ppm.

5. Conclusion

Glasses are in-ordered systems occurred more or less in the stabilized non-balance state. Therefore the important parameters are their time and temperature stability which are depended not only with the production process but with their longtime exploitation, too. The rare earth (RE^{3+}) are added to these glass systems to increase the luminescence output. There was found by means of the

measurements of electrical and dielectrical properties, especially utilizing modulatory spectroscopy that the maximal solubility Pr^{3+} ions in glass systems $\text{Ge}_{25}\text{Ga}_{10-x}\text{Pr}_x\text{S}_{65}$ is about 1 000 wt. ppm. The glass system owning this concentration is the saturate solvent occurring in the stable state without the drop out of the admixture. The admixture is built in the glass structure.

The admixture begins to segregate to clusters at higher Pr concentration (≥ 3000 wt. ppm) and the large scattering of the measured dependencies is the evidence of that. It was confirmed not only by SEM micrographs but by decreasing of luminiscence output, too.

The temperature stability was not changed at Pr concentration of the values ≤ 1000 wt. ppm up to high temperature. It was changed only in the case of concentration ≥ 3000 wt.ppm when the segregation began at temperature of 350°C .

The found out results clearly confirmed that prepared sulphide glass systems are homogeneous monophase and are characterized by longtime stability. The segregation of the admixture starts at the higher temperature and predominately when the Pr concentration is higher than 3000 wt. ppm. In consequence of the optical properties are worse and the luminiscence output is less.

Acknowledgments

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