TRANSPORT PROPERTIES OF Ge-Ga-S GLASS DOPED BY PRASEODYMIUM

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The temperature dependencies of direct electrical conductivity and temperature and frequency dependencies of permittivity of prepared sulphide glasses doped by praseodymium ions (Ge_{25} Ga_{10-x} Pr_x S_{65}, x = 1000 wt. ppm) were measured. The results indicate the existence of one conductivity mechanism with activation energy 0.91 eV up to the temperature 360 °C. The dependencies of electrical modulus M'' versus M' as well as the frequency dependencies M'' versus f show that the glass has monophase structure and is very homogeneous with the presence of only one relax time. The glass exhibits new relax time distribution indicating the formation of new structure when it was tempered up to 380 °C, that means just below T_g ~ 400 °C.

INTRODUCTION

Advantageous optical properties of $Ge_{25}Ga_{10-x}Pr_xS_{65}$ glasses for photonic applications have attracted attention of research workers [1, 2]. Basis material Ge-Ga-S should be doped by the rare earth ions (in our case by Pr^{3+}) to utilize it for the production of active glass fibres in the infrared region for increasing luminiscence. The investigation was mainly focused on the elucidation of the influence of glass preparation on the optical properties and structure. The relaxation mechanism of the glass structure is not fully classified, although the data of both electrical and dielectric properties are known. No universal model explaining this mechanism in a general way was achieved until present. The presence of structural disorder, inhomogenities as well as the glass temporal and temperature stabilities and successive origin of new phases can be found from the temperature dependency of direct conductivity (*dc*) as well as from both temperature and frequency dependencies of complex permittivity. The results are sensitive to the temperature procedures of the glass preparation involving the glass-cooling regime and to the chemical homogeneity of the glass melt. Therefore it can be said that the chemical and physical quality of prepared glass can be characterized from above given measurements.

EXPERIMENTAL PART

Glass preparation and the methods of measurements

As the presence of OH groups substantially influences the solution of praseodymium ions Pr^{3+}, it is necessary to prepare the glass with the low concentration of water dissolved. The main sources of impurities are the starting elements and the laboratory environment. With respect to this reason it is important to perform supplementary purification of starting materials; sulphur is resublimed in the reactive atmosphere, germanium and gallium are melted together in the ceramic boat from nitride boride in a high vacuum at the temperature about 950 °C. Glasses are prepared by melting of re-purified mixture of elements with the compound Pr_2S_3. Melting is carried out for 20 hours in evacuated (~ 10^{-3} Pa) sealed ampoule at 950 °C. The glass melt is cooled by immersing the ampoule in the water and consequently slowly quenched from 400 °C to the room temperature [3, 4].

The samples for the measurements of both electrical and dielectric properties having diameter 9 mm and the thickness 2 mm were coated by colloidal graphite (Dag 580). Direct conductivity was measured by the standard method of a vibration electrometer in the temperature range 20 – 400 °C. The measurements of temperature and frequency dependencies of alternating conductivity were made in the temperature range 20 – 360 °C using a TR – 970 fy ORION bridge in the frequency range 0.5 – 100 kHz [5].

RESULTS

Arrhenius relationship [6]

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E}{kT}\right) [S\ m^{-1}]$$

where E is an activation energy (eV), σ_0 is preexponential factor (S m^{-1}), k is Boltzmann constant (J K^{-1}) and

T is temperature (K)) is valid for the direct conductivity within the measured temperature range.

It was found out from the direct conductivity measurements (figure 1) that there exists only one mechanism of conductivity with the activation energy ~ 0.91 eV. The conductivity was increased and the activation energy was also changed (~ 0.81 eV) after repeated measurements when the sample was heated in the first measurement to 380 °C it means closely below the point T_g (~ 400° C). It confirms the changes in the glass structure arrangement.

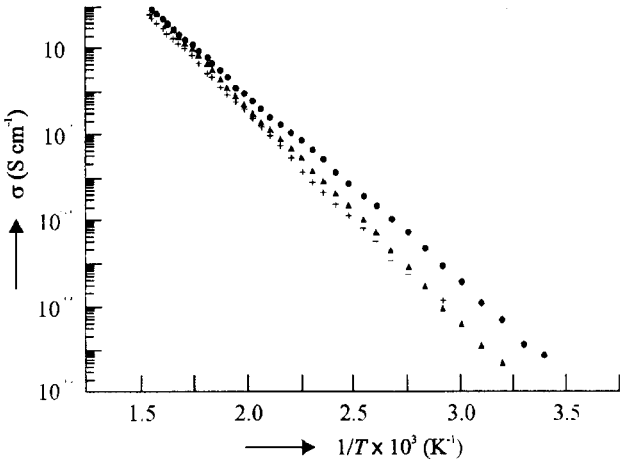

Figure 1. Repeated measurement of the temperature dependency of the direct conductivity up to 380 °C.
▲ - the first measurement, ● - the second measurement, + - the third measurement

The complex permittivity is important quantity characterizing glass. It is advantageous to analyze the measured temperature and frequency dependencies by means of complex electrical modulus [7]. In that case the results are not influenced by direct conductivity.

Complex electrical modulus is defined as follows:

$$M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - i\varepsilon''} = M' + iM'' \,, \quad \varepsilon^* = \varepsilon_s - i\varepsilon''$$

where $\varepsilon_s = \frac{1}{M_s}$ is determined by means of the point of intersection of modular diagrams M'' versus M' respectively. $\varepsilon'' = \frac{\sigma}{\omega\varepsilon_0}$ is proportional to the dielectric losses, σ is specific electrical conductivity, ε_0 is permittivity of vacuum and $\omega = 2\pi f$, where f is frequency. If we consider a frequency independent ε' then $\varepsilon' = \varepsilon_s$.

The processes connected with relaxation and migration phenomena as well as structural changes of the arrangement are reflected in modular diagrams marked out in the complex plane M'' versus M'. The values M'' versus M' for the sample measured for the first time are plotted in figure 2. Temperature did not exceed the value 360 °C during the repeated measurements. The measured dependencies are slightly different from ideal half-circles, their centers are shifted below the axe (S_1). It means that we can describe the relaxation arising due to the alternate electrical field and caused by migrating charge carriers in the volume of glass by only one relaxation time. The measured dependencies M'' versus f (figure 3) differing unsubstantially from Debye dependencies due to the existence of only one relaxation time confirm this fact. The shape of dependencies do not change during repeated measurements as well as when keeping the sample at the temperature below 360 °C for several hours.

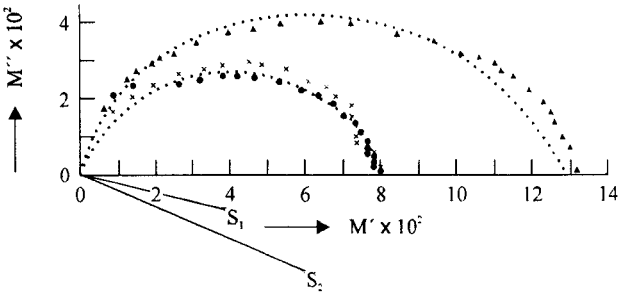

Figure 2. The dependence of electrical complex modulus M'' versus M'.
× – the sample measured at 270 °C, ● - the same sample measured at 270 °C after heating to 360 °C, ▲ - the same sample measured at 270 °C after heating to 380 °C.

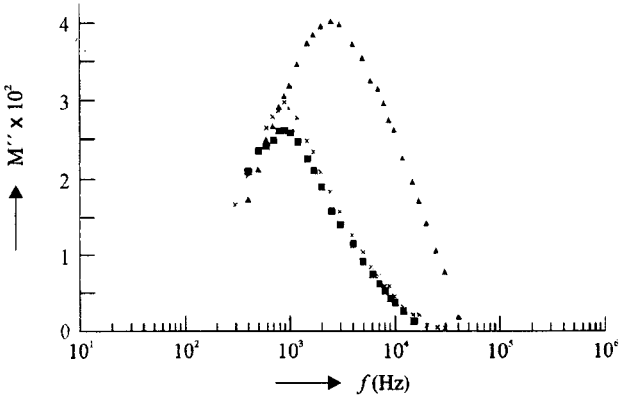

Figure 3. The frequency dependence of M'' versus f for the first measurement of the sample heated to 270 °C for various periods of time.
× – 1.5 hours, ■ - 6 hours, ▲ - the sample heated to 380 °C and then measured at 270 °C.

The dependencies M'' versus M' measured for the sample heated during the measurements to the tempe-

rature of 380 °C slightly below T_g (~ 400 °C) are of a substantially different character (figures 2 and 4). It can be seen from the measured dependencies that the glass structure was changed during this heat treatment. The dependencies measured are different from "ideal" half-circles, their centres are shifted below the axe (S_2). The rise of a new relaxation spectrum can also be seen in dependencies M'' versus f (figure 3).

DISCUSSION

The purity of glass covering the structural disturbances, crystalline particles and phase separation is closely connected with the technology of the preparation and especially with melting and cooling procedures.

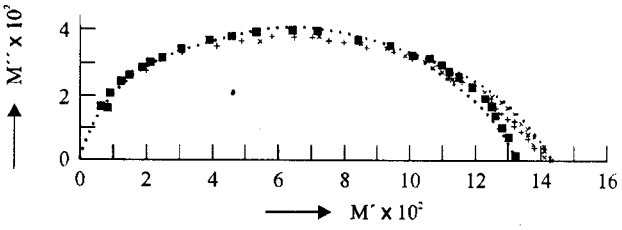

Figure 4. Dependencies of complex electrical modulus (M'' versus M', respectively) of the sample heated to 380 °C and then measured at different temperatures.
× - 215 °C, + - 243 °C, ■ - 270 °C.

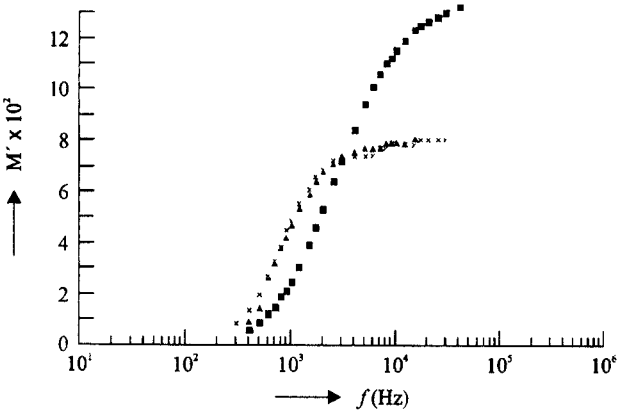

Figure 5. The frequency dependence of M' versus f for the first measurement of the sample hold at 270 °C for various periods of time.
× – 1.5 hours, ▲ - 6 hours, ■ - the sample heated to 380 °C and then measured at 270 °C.

It can be stated on the basis of the measured values analysis of both direct conductivity temperature dependencies and temperature and frequency dependencies of complex permittivity that the measured glass exhibits up to 360 °C one phase with only one mechanism of conductivity realized by one charge carries. Slight difference was found out for the measured dependencies between the first and the second measurement at the temperature 270 °C (figures 2, 3) what can ascribed to the elimination of the stresses in the samples caused by processing (cutting, grinding, polishing, etc.).

The asymmetric tail prolongation at the dependencies was not discovered in the high frequency part of the spectrum of glass, which was not heated to more than 360 °C. This fact indicates that the larger groups of various microcrystals which, would not manage to follow the changes of electrical field, were not present.

The structure of the glass heated to the temperature 360 °C was changed (figures 2, 5). The tail appears in the dependencies M'' versus M' in the high frequency part (figure 4). This is probably caused by the presence of microcrystals, bubbles and dust particles. The glass structural ordering with new properties is still very stable. The changes during other measurements were not found neither in dependencies M'' versus M' nor M'' versus f.

The complex permittivity is strongly influenced by the new phases and inhomogeneities. The changes in the measured dependencies M'' versus M' (figure 2), M' versus f (figure 3), but mainly in M' versus f are the evidence of the origin of a brand-new glass structure.

CONCLUSION

The activation energy representing the mean value of the potential wells distribution which the migrating ion must overcome is quite low (0.91 eV). The glass is characterized by small differences between the particular potential hole which also confirms these results:

- Relaxation maximum of M'' versus f is closed to Debye's dependency.
- The temperature independent distribution of the relaxation time is confirmed by the fact, that the shape and the maximum of the dependence M'' versus f do not change with temperature when the sample is not heated above 360 °C.
- The new relaxation time distribution connected with the permittivity changes is observed when heating the sample above 360 °C. This result confirms the formation of new glass structure arrangement. The existence of two structures with different relaxation times can be considered from dependencies M'' versus M', M'' versus f, and M' versus f.

The stability of the glass up to the temperature 360 °C is very important for the production of elements used in technical practice.

Acknowledgement

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TRANSPORTNÉ VLASTNOSTI Ge-Ga-S SKLA DOPOVANÉHO PRASEODYMOM

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V článku sú popísané merania teplotných závislostí jednosmernej elektrickej vodivosti a teplotnej a frekvenčnej závislosti permitivity sulfitových skiel dopovaných praseodymom (Ge_{25} Ga_{10-x} Pr_x S_{65}, x = 1000 wt. ppm). Z meraní je zrejmé, že po teplotu 360 °C pri týchto sklách existuje jediný vodivostný mechanizmus s aktivačnou energiou 0,91 eV. Zo závislostí elektrických modulov M'' versus M' a z frekvenčných závislostí M'' versus f je vidieť, že sklo je veľmi homogenná štruktúra s jediným relaxačným časom. V blízkosti teploty 380 °C, teda pod teplotou T_g ~ 400 °C zistilo sa nové rozdelenie relaxačného času. Z nameraných závislostí je zrejmé, že sklo je veľmi stabilné do teploty 360 °C. Tento poznatok má podstatný význam pri výrobe elementov využívaných v technickej praxi.