Investigation of electrical and dielectric properties of Ge$_{20}$Se$_{80-x}$Te$_x$ glasses doped by Er, Ho, Pr

J. KALUŽNÝ[a*], J. PEDLÍKOVÁ[b], P. KOSTKA[b], V. LABAŠ[a], M. KUBLIHA[a], J. ZAVADIL[c], S. MINÁRIK[a]

[a]Department of Physics, Institute of Materials Science , Faculty of Material Science and Technology of the Slovak University of Technology, Paulínska 16, 917 24 Trnava, Slovakia
[b]Laboratory of Inorganic Materials, Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řeř u Prahy, The Czech Republic,
[c]Department of Diagnostics, Institute of Photonics and Electronics, Academy of Sciences of the Czech Republic, Chaberská 57, 182 51 Prague, The Czech Republic.

There were measured temperature dependencies of direct electrical conductivity, temperature and frequency dependencies of complex permitivity and complex electrical modulus ($M^* = 1/\varepsilon^*$) as well, for glasses Ge$_{20}$Se$_{80-x}$Te$_x$ (where x is 0, 5, 10 and 15) doped by Pr^{3+}, Er^{3+}, Ho^{3+} (1 000 wt. ppm). The admixture of rare earth was added in the form of oxide or the pure metal. The measured results confirm that searched glasses own only one mechanism of electrical conductivity where activation energy is affected by Te concentration. This parameter affects the increase of the values of conductivity, too. Results of measurements of complex electrical modulus showed, that the measured glasses are otherwise characterized as mono-phase but non-homogeneous with the high concentration of the point defects and they are stable up to temperature of 180 °C. The influence of chemical composition, non-stechiometry, as well, is usually only low. The admixtures are inbuilt to the glass skeleton as atoms with the saturated bonds. Considering the reached results it is possible to say that the reached quality of glasses with respect to the amount of defects is probably given mainly by the concentration of the rare earth.

1. Introduction

The present opto-electronic applications demand the preparation of new materials with the goal-directed properties. Chalcogenide glass systems Ge – Se – Te doped by the rare earths Pr, Er, Ho represent glasses suitable for the transfer of power radiation. They own the low phonon energy, the high value of index of refraction and especially the very high wave transparency in the middle IR spectrum range up to wavelength of CO$_2$ laser and also the sufficient luminescence output in some cases [1,2,3,4,5]. Te in the mentioned glasses ensures the higher optical transparency in the range of CO$_2$ laser wavelength. Ge stabilizes the inner ordering of the prepared glass. It means that it prevents from the secondary glass crystallization and increases its temperature and time stability, as well. The rare earth elements (Pr, Er, Ho) are added to these glass systems in the various forms [6,7,8,9].

2. Experimental

Glasses with Ge are melted at (900 – 950) °C. Further increase of the temperature of the synthesis is limited by the softening temperature of the silica ampoule, which is about of (1200 – 1250) °C. The necessary chemical and physical purity of prepared glasses should be about 10^{-5} mol % for the presence of OH, SH, SeH groups and the

concentration of physical defects in the range ($10^2 – 10^3$) cm^{-3}. In glasses prepared only by direct synthesis from pure starting elements the average concentration of hydride impurities is about of 10^{-3} mol % and the concentration of structural defects about 10^4 cm^{-3}. The major sources of hydride and carbon impurities seem to be starting elements (Ge, Se, Te, etc.) and therefore repurification of these elements must be carried out [10,11,12].

The sublimation under vacuum and the reactive atmosphere proved to be very effective for Se, Te and melting under vacuum showed similar effects for Ge. The technological procedures involving the distillation, synthesis of undoped and RE doped glasses and the preparation of preforms for fibre drawing were carried out in one special silica ampoule [13]. This procedure lowers the possibility of contamination during preparation steps. The melting temperature of glasses is about (850 – 950) °C. The melting time was (15 – 20) h and then the ampoule with glass melt was cooled to room temperature. Preforms of 10 mm in a diameter and (50 – 80) mm in length were obtained. The concentration of Pr, Er, Ho was 1000 wt. ppm and oxide or elemental form were used for the dotation [10,11,12,14].

The measurements of electrical and dielectric properties were performed for samples of diameter ϕ ~ 9 mm and the thickness 2mm at the temperature interval (20 - 180) °C. The contact surfaces of the samples were coated

by the conductive coloidal graphite (Dag 580). Direct electrical conductivity was measured by volt-ampere method measuring current by means of Keithley 6485 apparatus at the constant voltage 10 V. The measurements of temperature and frequency dependecies of complex permitivity were carried out by means of Hioki 3522-50 apparatus at the frequency range (0.001 - 100) kHz [7].

The temperature dependencies of direct electrical conductivity of the searched glasses is possible to describe by Arrhénius relationship at the metioned temperature range [15,16,17,18,19]

$$\sigma_{dc} = \sigma_0 \cdot \exp\left(-E/kT\right), \qquad (1)$$

where σ_0 is the pre-exponential factor, E is activation energy, k is Boltzmann constant and T is temperature. To explain the dielectric response of searched systems it is possible to exploit the analyze by means of measurements of the complex electrical modulus M^* introduced by Macedo [20, 21, 22] as the reciprocal value of complex permittivity ε^* under the relation

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

The plotting of complex electrical modulus in the complex plane is prospective to describe by the course only little different from half circle with the centre near the axe M' for systems with one or with the very narrow interval of relaxation time (the most frequent case). One can find out the frequency dependency $M''(f)$ slightly different from Debye distribution with maximum at frequency responding to the reciprocal value of the relaxation time $(1/\tau)$ [23]. The temperature decrease of the value of the relaxation time can be describe by relation

$$\tau = \tau_0 \cdot \exp(E_\tau / kT), \qquad (3)$$

(τ_0 is pre-exponential factor) for these glass systems if they show the dielectric response corresponding to one or the narrow interval of the relaxation time.

3. Results

The difference of the chemical composition of glass systems $Ge_{20}Se_{80-x}Te_x$ where x is 0, 5, 10 and 15 without and with admixtures Pr^{3+}, Er^{3+}, Ho^{3+} (1 000 wt. ppm) is

clearly shown on measurements of both electrical and dielectric properties these materials. The temperature dependencies of direct conductivity in the measured interval of temperature (20 – 180) °C are characterized by one conductivity mechanism of one type of charge carrier (Fig. 1). The values of electrical conductivity are markedly dependent on the chemical composition. They dominantly increase and the values of activation energy decrease as the Te concentration is higher. Table 1 shows the values of activation energy and the pre-exponential factor determined from the temperature dependencies of direct conductivity by means of the method of the least squares.
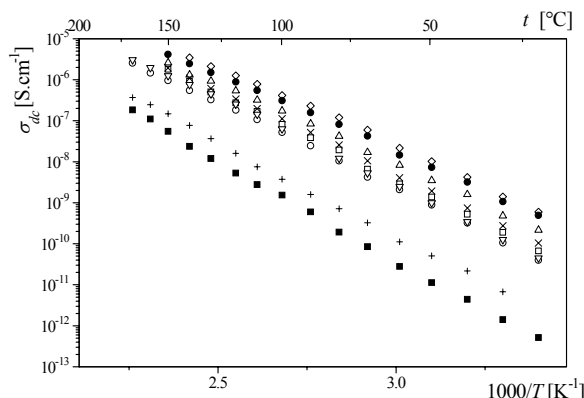

Fig. 1. Temperature dependencies of direct electrical conductivity of glass systems □ $Ge_{20}Se_{70}Te_{10}$, ○ $Ge_{20}Se_{70}Te_{10}$ + 1000 wt. ppm Pr (oxide), △ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Pr (oxide), ▽ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Ho (oxide), ◇ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Er (metal), ✛ $Ge_{20}Se_{75}Te_5$ + 1000 wt. ppm Er (metal), ✘ $Ge_{20}Se_{70}Te_{10}$ + 1000 wt. ppm Ho (oxide), ■ $Ge_{20}Se_{80}$ + 1000 wt. ppm Er (metal), ◆ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Er (oxide).

Similarly dielectric parameters are affected by chemical glass composition. The searched glass systems show behaviour only slight different from materials owning one relaxation time. Measured values of complex electrical modulus plotted in the complex plane are practically identical with the dependencies responding to dielectric response of material owning one relaxation time (Fig. 2). The measured value deformation at higher frequencies is noticeable if the admixture concentration of rare earth in glass systems is increased (■ 2000 wt. ppm Ho, ● 2000 wt. ppm Ho).

Table. 1. The values of activation energy E and pre-exponetial factor σ_0 of direct electrical conductivity and activation energy E_τ of relaxation time and the pre-exponential factor τ_0 (The parameters determined in the temperature interval (20 –180) °C).

Glass	Rare earth 1000 wt.ppm	Form of rare earth	E [eV]	σ_0 [S.m^{-1}] $\times 10^{-3}$	E_τ [eV]	τ_0 [s] $\times 10^{16}$
$Ge_{20}Se_{65}Te_{15}$			0.78	389	0.78	2.08
$Ge_{20}Se_{65}Te_{15}$	Er	metal	0.78	214	0.73	3.22
$Ge_{20}Se_{65}Te_{15}$	Er	oxide	0.73	251	0.71	6.98
$Ge_{20}Se_{65}Te_{15}$	Ho	metal	0.73	123	0.73	6,21
$Ge_{20}Se_{65}Te_{15}$	Ho	oxide	0.73	149	0.77	3.26
$Ge_{20}Se_{65}Te_{15}$	Pr	metal	0.74	267	0.73	4.64
$Ge_{20}Se_{65}Te_{15}$	Pr	oxide	0.75	213	0.76	3.74
$Ge_{20}Se_{65}Te_{15}$	Ho (1500 wt. ppm)	metal	0.74	218	0.75	3.31
$Ge_{20}Se_{70}Te_{10}$			0.81	505	0.81	1.43
$Ge_{20}Se_{70}Te_{10}$	Er	metal	0.82	625	0.82	1.50
$Ge_{20}Se_{70}Te_{10}$	Er	oxide	0.80	208	0.81	4.05
$Ge_{20}Se_{70}Te_{10}$	Ho	metal	0.80	205	0.83	1.91
$Ge_{20}Se_{70}Te_{10}$	Ho	oxide	0.83	770	0.82	2.08
$Ge_{20}Se_{70}Te_{10}$	Pr	oxide	0.80	265	0.80	3.44
$Ge_{20}Se_{70}Te_{10}$	Pr	metal	0.76	22.8	0.76	3.26
$Ge_{20}Se_{70}Te_{10}$	Ho (2000 wt. ppm)	metal	0.73	81.4	0.77	3.45
$Ge_{20}Se_{75}Te_{05}$			0.83	294	0.82	3.93
$Ge_{20}Se_{75}Te_{05}$	Er	metal	0.84	181	0.82	10.40
$Ge_{20}Se_{75}Te_{05}$	Er	oxide	0.78	50	0.81	12.09
$Ge_{20}Se_{75}Te_{05}$	Pr	oxide	0.82	101	0.82	8.62
$Ge_{20}Se_{80}$	Er	oxide	0.88	270		
$Ge_{20}Se_{80}$	Pr	metal	0.92	90.2		
$Ge_{20}Se_{80}$	Pr	oxide	0.94	204	0.91	35.24

One can see differences only lightly different from Debye distribution on the frequency dependencies of the imaginary part of complex electrical modulus (Fig. 3). The glass composition markedly affects the maximum position of the individual dependencies responding to the reciprocal value of relaxation time ($1/\tau$). It is possible to see for the individual glasses the maximum displacement only to higher frequencies it means to the shorter relaxation times with the increased temperature (the example is showed in Fig. 4). The measured values deformation is again observable at the higher frequencies and the growth of the measured maximum, too, with temperature for glass systems owning the rare earth content larger as is the limit of the solubility (Fig. 5 shows an example).
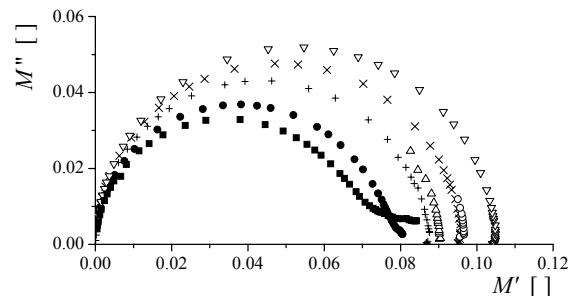

Fig. 2. Values of complex electrical modulus at 50 °C: ○ $Ge_{20}Se_{80}$ + 1000 wt. ppm Pr (oxide), △ $Ge_{20}Se_{75}Te_5$, ▽ $Ge_{20}Se_{70}Te_{10}$, ◇ $Ge_{20}Se_{65}Te_{15}$, ✚ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Er (oxide), ✗ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Pr (metal), ■ $Ge_{20}Se_{70}Te_{10}$ + 2000 wt. ppm Ho (metal), ● $Ge_{20}Se_{65}Te_{15}$ + 1500 wt. ppm Ho (metal).

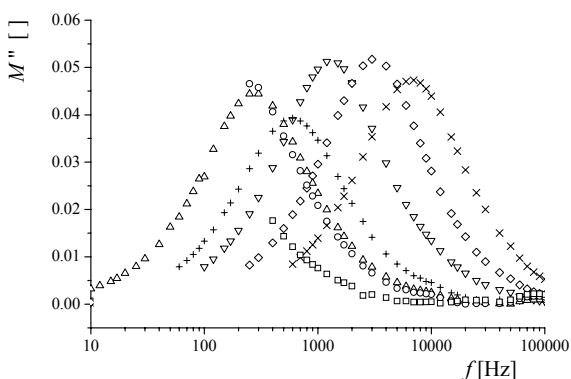*Fig. 3. Frequency dependencies of the imaginary part of complex electrical modulus at 70 °C □ Ge₂₀Se₈₀ + 1000 wt. ppm Er (oxide), ○ Ge₂₀Se₈₀ + 1000 wt. ppm Pr (oxide), △ Ge₂₀Se₇₅Te₅, ▽ Ge₂₀Se₇₀Te₁₀, ◇ Ge₂₀Se₆₅Te₁₅, ✚ Ge₂₀Se₆₅Te₁₅ + 1000 wt. ppm Er (oxide), ✗ Ge₂₀Se₆₅Te₁₅ + 1000 wt. ppm Pr (metal).*
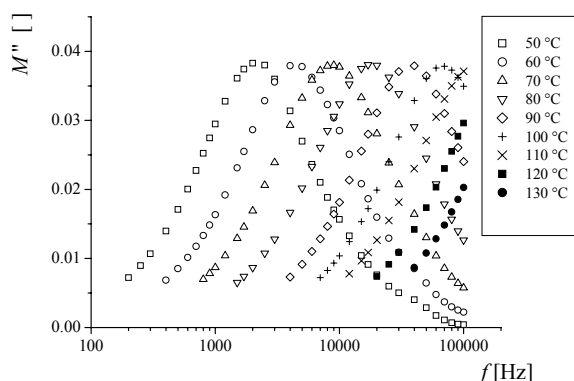
Fig. 4. Frequency dependencies of the imaginary part of complex imaginary part of complex electrical modulus M'' vs f glass sample Ge₂₀Se₆₅Te₁₅ + 1000 wt.ppm Er (metal) at various temperatures.
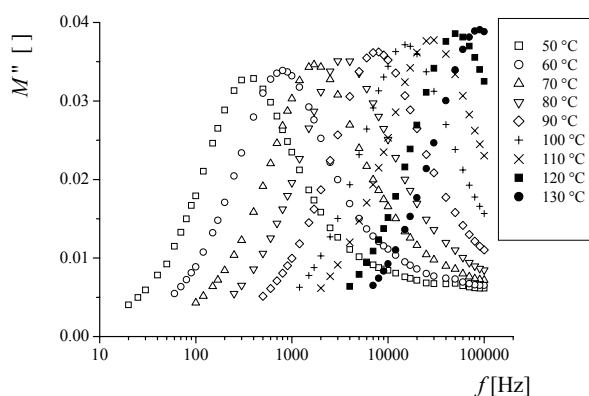
Fig. 5. Frequency dependencies of the imaginary part of complex electrical modulus M'' vs f glass sample Ge₂₀Se₇₀Te₁₀ + 2000 wt. ppm Ho (metal) at various temperatures.

With respect to the fact that the measured values of the frequency dependencies of the imaginary part of

complex electrical modulus are only few different from Debye distribution (Fig. 6 shows the typical example) we can their behaviour describe by relationship [23]

$$M'' = M_S \frac{2\pi f \tau}{1 + \left(2\pi f \tau\right)^2} , \qquad (4)$$

where M_S is constant, f is frequency of the measured electrical voltage and τ is relaxation time.

The determined temperature dependencies of the relaxation time amount correspond quiet well to the relationship (3) and their dependencies are few different only from the straight line in semilogarithmic plotting (the example is shown in Fig. 7). There were determined the values of activation energy E_τ, relaxation time and pre-exponential factor τ_0, as well. The values of both parameters are shown in Table 1. The values of the relaxation time on individual glasses are similarly as in the case of electrical conductivity significantly dependent on the chemical composition (Fig. 8). The values of the relaxation time decrease especially as Te concentration is increased. Concurrently the values of activation energy and the relaxation time slightly decrease as Te content is increasing.
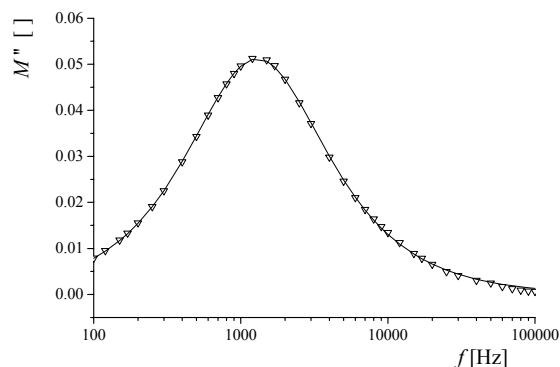

Fig. 6. Frequency dependencies of the imaginary part of complex electrical modulus M'' vs f the glass sample Ge₂₀Se₇₀Te₁₀ at temperature 70 °C with Debye distribution plotted by straight line.
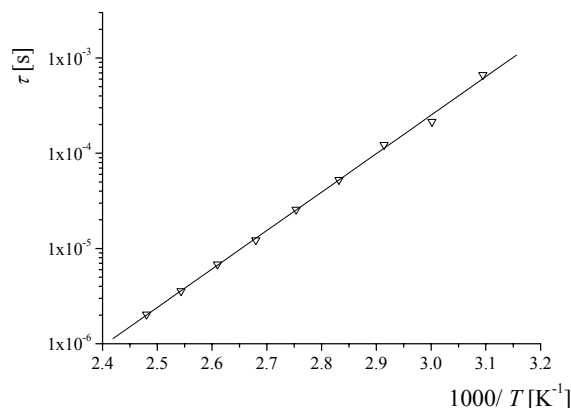
Fig. 7. Temperature dependencies of the relaxation time determined by the approximation of glass Ge₂₀Se₇₀Te₁₀ with plotting of the approximation straight line responding to the relationship (4).
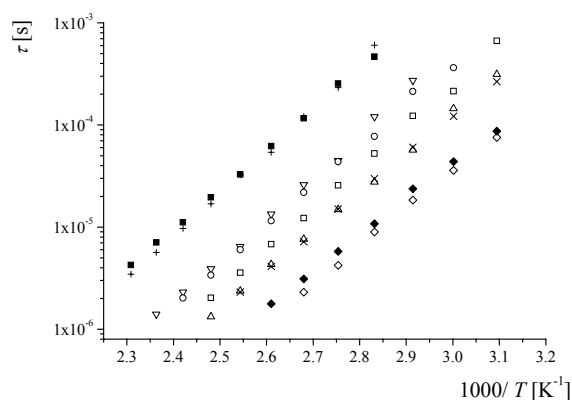
Fig. 8. Temperature dependencies of direct electrical conductivity glasses $\square$ $Ge_{20}Se_{70}Te_{10}$, $\bigcirc$ $Ge_{20}Se_{70}Te_{10}$ + 1000 wt. ppm Pr (oxide), $\triangle$ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Pr (oxide), $\triangledown$ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Ho (oxide), $\diamondsuit$ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Er (metal), $+$ $Ge_{20}Se_{75}Te_5$ + 1000 wt. ppm Er (metal), $\times$ $Ge_{20}Se_{70}Te_{10}$ + 1000 wt. ppm Ho (oxide), $\blacksquare$ $Ge_{20}Se_{80}$ + 1000 wt. ppm Er (metal), $\blacklozenge$ $Ge_{20}Se_{65}Te_{15}$ + 1000 wt. ppm Er (oxide).

4. Discussion

Chalcogenide glass samples of the composition $Ge_{20}Se_{80-x}Te_x$ (x = 0, 5, 10, 15) without and with the admixtures of rare earths Er, Ho, Pr show one mechanism of electrical charge transport in the searched temperature interval and also their dielectric response is fairly described by one value of relaxation time while the rare earth concentration does not overdraw the solubility limit of rarer earth. In term of the measured parameters it is possible these glass systems characterize as homogeneous without the occurrence of volume defects affecting the electrical charge transport. One can find out the creation of the deformation of measured values of complex electrical modulus especially at the higher measuring frequencies for glasses of the higher rare earth concentration (1500 a 2000 wt. ppm). One can assume that the new phase create in glass volume after overdrawing the solubility limit of rare earth over 1 500 and 2 000 wt. ppm. The appearance of the new phase is relatively small and thus it does not affect the measured dielectric parameters. The influence is dominant at the higher frequency values so in the range responding dimensionally to the small particles (microcrystalline, clusters).

There is noticeable influence of Te concentration and the rare earth admixture, too, if the glasses do not overdraw own the rare earth concentration below the solubility limit. In general the values of electrical conductivity are increasing mostly if the Te content is enlarging and the values of relaxation time are decreasing, too. These parameters are affected by the same factors. As evidence one can compare the values of activation energy of the electrical conductivity and relaxation time shown in Table 1. The activation energy of electrical conductivity

and also activation energy of relaxation time is slightly decreasing if Te content is enlarging. The influence of the rare earth admixture to the measured values is not as significant as in the case of Te concentration. In general the rare earth admixture causes the increase of electrical conductivity but the decrease the values of relaxation time and both activation energy, too.

5. Conclusion

It is possible to state as the results of the measurements of electrical and dielectric parameters, as well, that searched glass systems $Ge_{20}Se_{80-x}Te_x$ (x = 0, 5, 10, 15) also with rare earth admixtures Er, Ho, Pr in concentration up to 1 000 wt. ppm added in metal or oxide form are mostly homogeneous without volume defects. Overdrawing the solubility limit there is created new phase affected especially dielectric parameters.

If the content of the rare earth of glasses does not overdraw the value 1 000 wt. ppm one can describe the transport of the free charge carriers by one mechanism. In this case the values of electrical conductivity are dominantly enlarged by the increased Te content and lesser by the rare earth one. Activation energy of direct electrical conductivity decreases together with Te content and rare earth one, too. Dielectric behaviour of glass sample is affected by the same parameters as in the case of direct conductivity. It demonstrates particularly the similarity the values of activation energy of relaxation time and electrical conductivity, as well.

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[*]Corresponding author: jan.kaluzny@stuba.sk,