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TRANSPORT PROPERTIES OF Ge – Se – Te GLASSES

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The temperature dependencies of direct electrical conductivity, temperature and frequency dependencies of complex permitivity and complex electrical modulus ($M^* = 1/\ \varepsilon^*$), have been measured in $Ge_{0.2}$-$Se_{0.8-x}$-Te_x glasses pure and doped by $Pr^{3+}$and Er $^{3+}$ (1 000 wt. ppm). On the basis of measured results it was found that these glasses exhibit only one mechanism of electrical conductivity with activation energy $U = (0.95 \pm 0.10)$ eV. The results of complex electrical modulus showed, that the measured glasses are single-phase but not homogeneous, with high concentration of the point defects due to the presence of Te and they are stable up to the temperature of 180 °C. The influence of chemical composition, non-stoichiometry and admixtures is usually low, because the formed compounds are in-built to the glass skeleton as configurations with saturated bonds.

1. Introduction

The new opto-electronic applications require new materials with specific properties. They must exhibit luminescence, low phonon energy, high refractive index and, also, transparency in the middle and far IR spectra. It is quite well handled the production of glasses with transparency up to 8 μm wavelength, which are used for the preparation of optical fibers for radiation transport from CO lasers (5.3 μm), and to produce also passive and active elements [1]. It is advantageous to utilize for many applications the 10.6 μm radiation of CO_2 laser, too. Therefore, one looks for materials fulfilling this requirement. Ge-Se-Te glasses are very prospective from this point of view. Their utilization is thought namely for the applications where the fibers are used as a transport medium for high power laser radiation [2].

Selenide glasses on the basis of As and Ge show very good transparency in the IR range. Difficulties during the preparation of Se/Te glasses are caused by the presence of tellurium because for higher content of Te in this system the tendency to crystallization becomes higher [1,2].

We shall focus in this paper to the study of the electrical as well as dielectrical properties of Ge-Se-Te pure glasses and with the admixture of rare-earth RE^{3+} (Pr, Er). They reach quite good transparency (68-78%) up to 12 μm wavelength [3,4] (Fig. 1).

One of the requirements for the application of these glasses in the case of high power laser radiation transport is their temperature stability. The maximum temperature up to which the fiber can be heated restricts the transmitted power of the laser radiation. The optical transparency at the wavelength of CO_2 laser is limited namely by the presence of oxide and various physical impurities. Therefore, it is necessary not only to pay attention to the chemical and optical purity of the essential materials but, also, to look for the removing of the impurities during the glass preparation [3].

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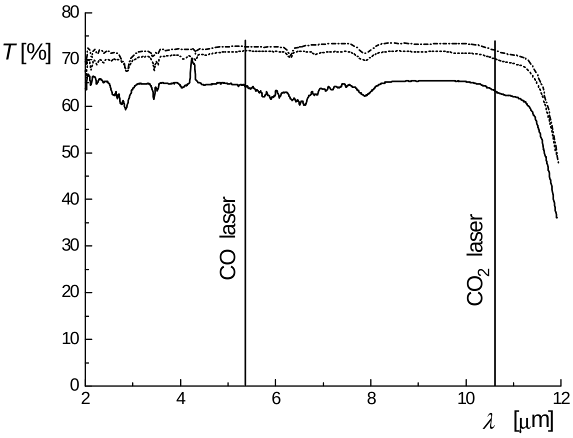


Fig. 1. Dependence of transmittance of glasses GeSeTe + 1000 mass ppm ER^{3+} (added as Er$_2$O$_3$) on wavelength: —— Ge$_{0.2}$Se$_{0.792}$Te$_{0.008}$ h = 2.0 mm, ····· Ge$_{0.2}$Se$_{0.793}$Te$_{0.007}$ h = 2.0 mm, —·— Ge$_{0.2}$Se$_{0.794}$Te$_{0.006}$ h = 1.2 mm (h is sample thickness).

Electrical and dielectrical measurements make possible to get information on the properties of the measured glasses quickly thus giving the possibility to choose the most suitable composition of the raw glass. In conjunction with the optical properties, i.e. transmission, scattering, we can use the data in the optimization of the preparation technology and to find if a given ingot has the required properties for the next stage of processing or must be excluded.

It is necessary to remark that these methods are not absolute; it means that the obtained results must be compared with those on the glasses exhibiting the required properties.

2. Experimental

Glasses were prepared by melting the starting elements (sealed in quartz ampoules and evacuated to pressure 10^{-3} Pa) in the temperature range (850 – 950) °C during 15 – 20 hours. The glass melts are cooled to the room temperature in air or by immersing the ampoules into water (it depends on the composition). Ingots of diameter 10 mm and lengths in the range (50 – 80) mm [3] have been obtained.

The samples for the measurements of electric and dielectric materials (ϕ 10 mm and thickness ≈ 1 mm) were coated by conductive layers. The temperature dependence of direct conductivity of the samples heated with temperature gradient 5 °C/min was measured by an vibrational electrometer. The measurements of temperature and frequency dependencies of complex electrical modulus ($M^* = 1/\varepsilon^*$) [5] were carried out by the bridge method within the frequency range (0.2 – 100) kHz [6,7]. The measurements of the optical properties were performed with the spectrometer Matson Galaxy 3020 [3].

3. Results

3.1. Temperature stability

Before performing the detailed measurements it was necessary to determine the temperature corresponding to the limit of appearance of the irreversible changes. The temperature T_g that makes possible to estimate the temperature range of the glass utilization is not exactly known because the data in literature are spread [1]. Therefore, we used the measurements of the temperature dependencies of direct conductivity and temperature and frequency dependencies of complex permitivity and complex electrical modulus ($M^*=1/\varepsilon^*$), respectively, for the determination of maximal temperature to which glass should be heated. These measurements are more sensitive than the other ones because they can “sense” the movement of the free and the bound carriers of the electrical charge.

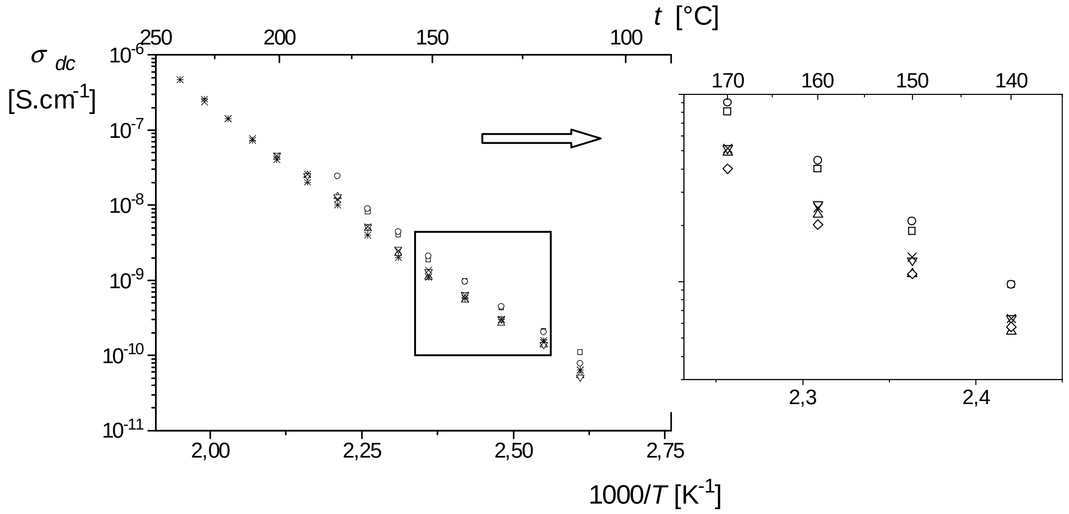


Fig. 2. Temperature dependencies of direct conductivity of glass $Ge_{0.2}Se_{0.794}Te_{0.006}$ + 1 000 mass ppm Er^{3+} (Er_2O_3): □ new sample measured up to 170 °C and its repeated measurements up to ○ 180 °C, △ 190 °C, ▽ 200 °C, × 230 °C, ◇ 240 °C.

We performed the measurements of the temperature dependence of direct conductivity (σ_{dc} vs $1/T$) of the chosen glass, while the temperature during the repeated measurements was increased in steps of 10 °C (Fig. 2). The glass that shows irreversible changes in the ordering caused by temperature, changes permanently its electrical properties and this is shown by the deviation from the initial behaviour. It was found out only low but permanent decrease of dc conductivity when the sample was heated above the temperature of 180 °C (Fig. 2b). The similar measurements of temperature and frequency dependencies of complex electrical modulus M^* show visible changes with the temperature (Fig. 3). The results confirm clearly that the permanent changes in the atomic ordering of the samples occur at temperatures about 180 °C as presented in Fig. 4. Obviously, no permanent changes occur in the structure of Ge-Se-Te up to the temperature of 180 °C. Taking into account this result we did not overrun the temperature of 170 °C which we considered as the limit where glass conserves unchanged its properties. The knowledge of this temperature is very important for the technology and is related to the restriction for the transport of laser radiation power through optical fibers.

3.2. The influence of chemical composition of glasses on electrical and dielectrical properties

The temperature dependencies of direct electrical conductivity, *dc*, of glasses based on Ge-Se-Te + RE^{3+} ($Ge_{0.2}Se_{0.8-x}Te_x$ for x = 0 - 0.8) and Pr_2S_3 or Er_2O_3, concentration of RE^{3+} is 1000 wt. ppm) are plotted in Fig. 5. The conductivities of the glasses both with: admixtures and without admixtures did not change with the changes of the composition. The activation energy of the good glasses was the same and had the value $U = (0.95 \pm 0.10)$ eV. It follows from the measurements that the influence of the chemical composition as well as that of the rare-earths are small. The measured values of *dc* are within the interval of the errors of measurements. It confirms that the influence of the admixtures and stoichiometry, on the direct electrical conductivity is usually small because the individual compounds are built in the glass skeleton as atoms with the saturated bonds [1] (Fig. 5a).

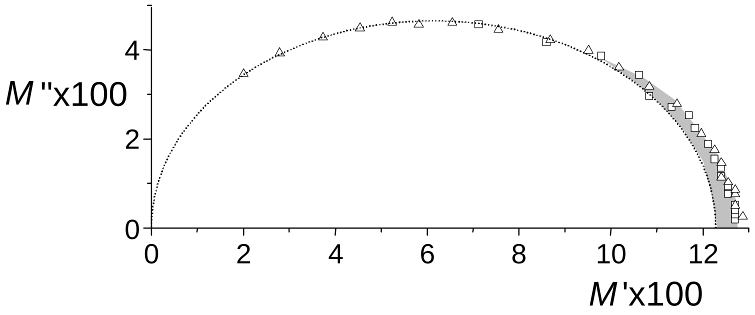


Fig. 3. Complex electric modulus (*M''* vs. *M'*) measured in the glass $Ge_{0.2}Se_{0.795}Te_{0.005}$ at the temperatures: □ 160 °C, Δ 180 °C.

Similar results were found out from the measurements of electric modulus M^*, too. These can be seen clearly in the dependence *M'* vs. *f* (Fig. 5b).

The measurement of complex electric modulus is more sensible to the changes of the atomic ordering, which are connected with the glass composition as observed in the measurements of the temperature dependencies of *dc*. This is confirmed by the results obtained for M^* and plotted in Fig. 6, where the small differences in concentration of Te in Ge-Se-Te glasses are markedly displayed. Similarly, the influence of Te was observed in the behaviour of the transmittance. The transmittance decreases when the Te concentration increases (Fig. 1).

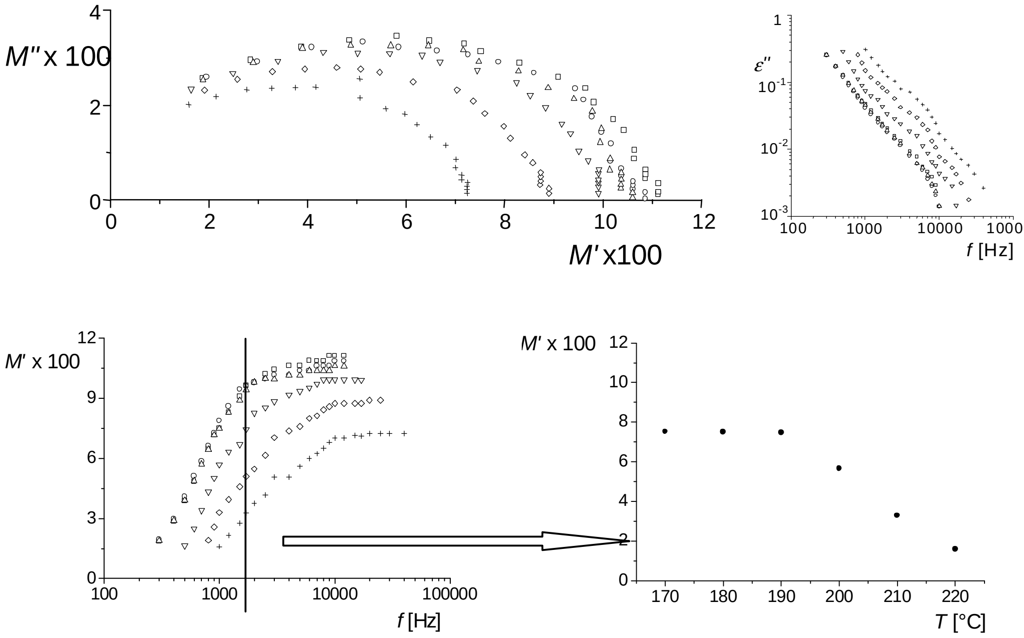
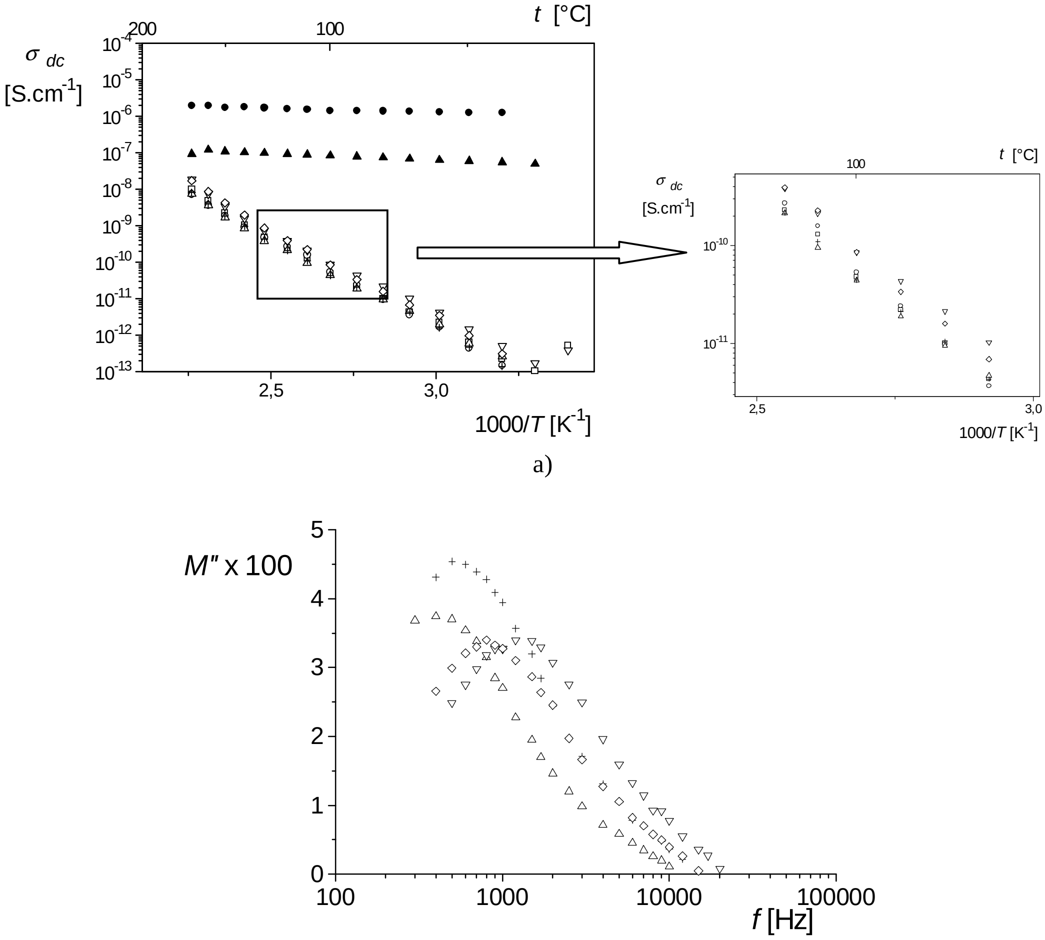


Fig. 4. Dependencies measured for glass $Ge_{0.2}Se_{0.793}Te_{0.007}$ + 1000 mass ppm Er^{3+} (Er_2O_3) at temperature of 170 °C after heating (20 min.): □ 170 °C, O 180 °C, Δ 190 °C, ▽ 200 °C, ◇ 210 °C, + 220 °C. a) *M''* vs. *M'*. b) Frequency dependencies of the imaginary component of the complex permitivity (*ε''* vs. *f*). c) Frequency dependencies of the real component of the complex electric modulus (*M'* vs. *f*). d) Dependence of the values of the real component of the complex electric modulus measured at the frequency of 1000 Hz *vs.* temperature of the heated glass (*M'* vs. *T*).

All the samples of Ge-Se-Te studied in our laboratory contain a relatively large amount of point distortions what is confirmed by the shift of the centers of half-circles at the dependencies of *M''* vs. *M'* below *x* axis (Fig. 6a). Because the "tails" were measured on the dependence *M''* vs. *M'* at the high-frequency part, these glasses contain besides the point distortions, inhomogeneities of larger size. The appearance of the distortions should be caused by the presence of crystallite in Te glasses because glasses containing Te exhibit higher tendency to the crystallization [1].

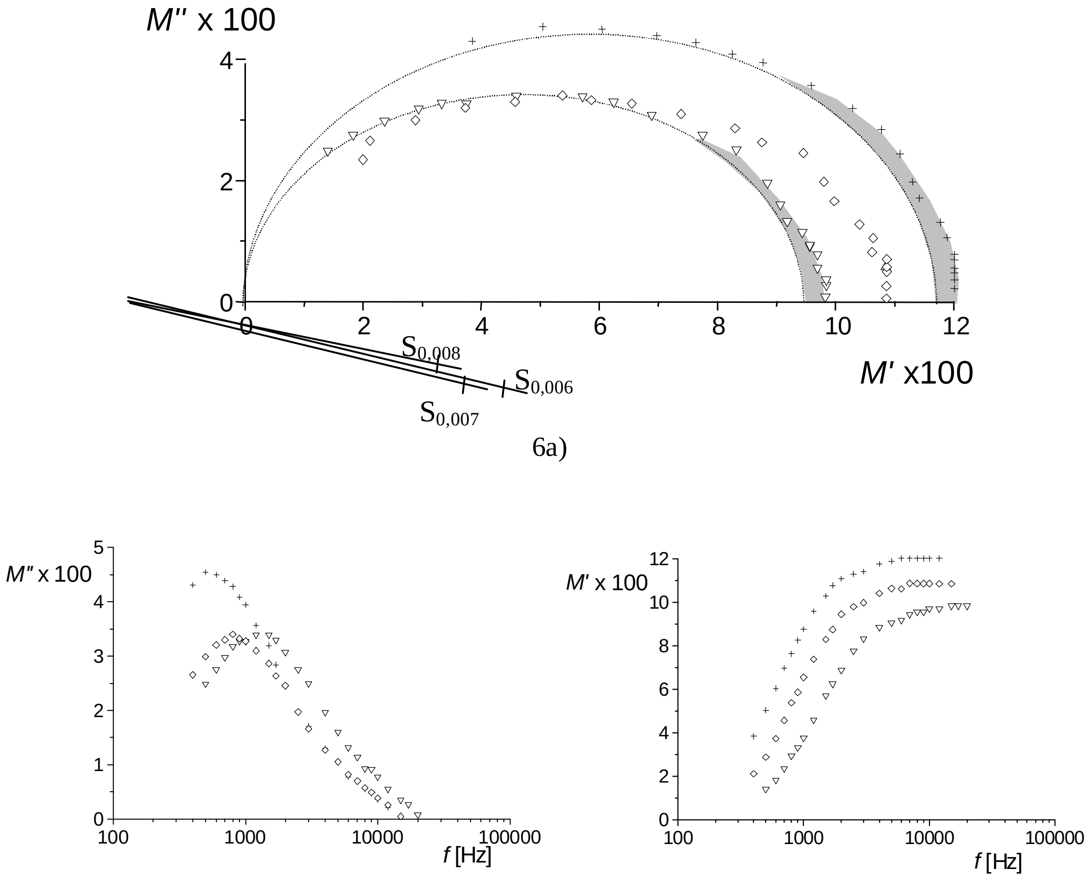


a)

b)

Fig. 5. Temperature dependencies of direct electric conductivity of glasses Ge-Se-Te with admixtures of rare-earths of concentration 1000 wt. ppm added in various forms: □ - $Ge_{0.2}Se_{0.795}Te_{0.005}$, ○ - $Ge_{0.2}Se_{0.795}Te_{0.005}$, Δ - $Ge_{0.2}Se_{0.794}Te_{0.006}$ + Pr_2S_3, + - $Ge_{0.2}Se_{0.794}Te_{0.006}$ + Er_2O_3, ∇ - $Ge_{0.2}Se_{0.792}Te_{0,008}$ + Er_2O_3, ▲ - $Ge_{0.2}Se_{0.792}Te_{0.008}$ + Pr_2S_3, ◇ - $Ge_{0.2}Se_{0.793}Te_{0.007}$ + Er_2O_3, ● - $Ge_{0.2}Se_{0.793}Te_{0.007}$. a) Temperature dependencies of direct electric conductivity. b) Frequency dependencies of the imaginary component of the complex electric modulus (M'' vs. f).

From the measured results (Fig. 5) one can state that in some samples, no glass phase was formed (probably because the technology was not correct). When the crystal phase is created in some part of the sample, the sample conductivity becomes very large and during heating changes significantly (Fig. 5). It is interesting to remark that Sharma et al. [8] has shown in Se-Te rich films that electrical conductivity increases by several orders of magnitude on crystallization. The new samples prepared by the same technology had not changed the activation energy but their conductivity was different.



6a)

6b) 6c)

Fig. 6. The dependencies measured at the temperature of 170 °C for glasses Ge-Se-Te with admixtures of Er^{3+}, 1000 mass ppm (Er_2O_3): + $Ge_{0.2}Se_{0.794}Te_{0.006}$, ∇ $Ge_{0.2}Se_{0.792}Te_{0.008}$, ◇ $Ge_{0.2}Se_{0.793}Te_{0.007}$. a) *M''* vs. *M'*. b) Frequency dependencies of the imaginary component of the complex electric modulus (*M''* vs. *f*). c) Frequency dependencies of the real component of the complex electric modulus (*M'* vs. *f*).

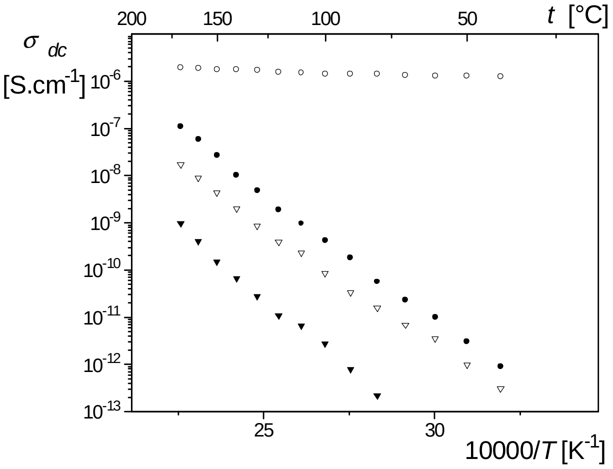


Fig. 7. The temperature dependencies of direct electric conductivity of the glasses Ge-Se-Te with admixtures of Er^{3+} of concentration 1000 mass ppm ($Ge_{0.2}Se_{0.793}Te_{0.007}$) ● 07.04.2003 and ○ 13.12.2001, $Ge_{0.2}Se_{0.793}Te_{0.007}$ + Er_2O_3 ▼ 18.02.2003 and ∇ 06.12.2001.

4. Discussion and conclusions

The measurements of the temperature dependence of direct conductivity and both temperature and frequency dependencies of complex permitivity and complex electrical modulus, as well, are very effective methods to find out the glass temperature stability. It is also possible to determine macroscopic values, as e.g. chemical and optical purity, the presence of inhomogeneities, the influence of admixtures, etc., that characterize the glass besides the above mentioned possibilities. These measurements allow to estimate quickly the quality of the produced ingot and make possible to eliminate from the processing those ingots not having the required properties.

The results show that these glasses are not homogeneous. They contain not only point inhomogeneities but, also, inhomogeneities of larger dimension. The results of the complex electrical modulus measurements confirm the inhomogeneity. In general the following rule is valid: more the center of the half-circle *M”* vs *M’* is under the axes *M’* more the measured glass deviates from “ideal glass” and contains more point defects. The distance of the centers of the half-circles are different for the individual glasses in the range of 5 – 15 % of the assumed radius. The fact that $M''_{max} \neq 1/2\, M'_{max}$ confirms the presence of point defects of various concentration in the individual glasses.

The results of the measurements confirm that glasses Ge-Se-Te are stable up to 180 °C. No permanent changes occur in the atomic–scale ordering in glass up to this temperature. The rare-earth RE^{3+} with the concentration of 1000 mass ppm, added to improve the luminescence, have not significant influence on the direct electrical conductivity. The observed differences are only caused by the technological processing during the fabrication.

Acknowledgement

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