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Electrical and dielectrical properties of As – Se – Te glasses

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There were measured temperature dependencies of the direct electrical conductivity as well as temperature and frequency dependencies of the complex electrical modulus for the pure As – Se - Te glasses and those doped by the rare earth (RE^{3+}), too. It is clear analyzing the measured dependencies that the mentioned glasses own only one mechanism of the electrical conductivity (type P), with the activation energy U = (0.80 ± 0.05) eV. The gained results of the complex modulus and its compounds make possible to state that the searched glasses are mono-phase but they contain the certain amount of the physical defects. The glasses are the temperature stable up to 160 °C.

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1. Introduction

At present chalcogenide glasses come to the centre of the observation for their quite good radiation transparency (about 70 %) in the range 0.6 μm up to 16.0 μm. The long-wave edge increases with Te content [1]. The tendency to the crystallization and the phase separation is growing as the concentration of Te is enlarged. Adding As to selenido-teluride glasses their temperature properties are improving but transparency is worsening at the comparison with glasses containing Ge (Fig. 1) [1,2].

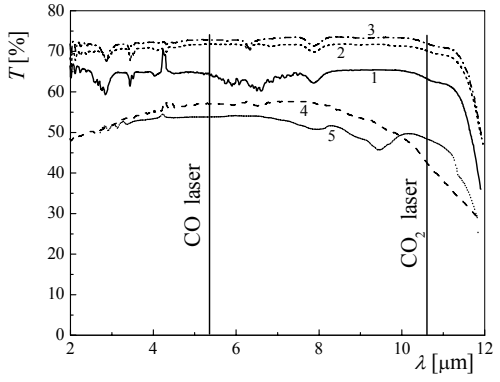

Fig. 1. Transmittance T of As - Se – Te glasses, Ge - Se – Te glasses (pure and doped by 1000 wt. ppm RE^{3+}): 1) $Ge_{0.2}Se_{0.794}Te_{0.006}$ + Er^{3+} (Er_2O_3), 2) $Ge_{0.2}Se_{0.793}Te_{0.007}$ + Er^{3+}(Er_2O_3), 3) $Ge_{0.2}Se_{0.792}Te_{0.008}$ + Er^{3+} (Er_2O_3), 4) $As_{0.35}Se_{0.58}Te_{0.07}$, 5) $As_{0.35}Se_{0.55}Te_{0.10}$.

As – Se - Te glasses are very perspective for the possibility of the opto-electronic applications, because they have relatively high absolute refractive index (n = 3.01), the low optical losses and the good transparency in the middle and far range of infrared part of spectrum (about 60 %) [1-3]. The produced optical fibres are suitable as the transport radiation medium of the CO and CO_2 lasers to the distance up to 10 m, i.e. the laser scalpel used in the surgery. Besides their exploitation in medicine the radiation transport can be employ in the welding and cutting operation but as detectors of temperature in the inaccessible places, too. The optical transparency of these glasses is decreased by the presence of oxide and hydroxide impurities [4], thus it is necessary to ensure their chemical and optical purity for their optical application, as recently achieved [5].

Each glass is characterized its own specific physical properties which determine but also restrict its utilization in various applications. The temperature as well as the structural stability is the important parameter for transport of the high power of IR radiation. Therefore it is necessary to know not only their temperature stability but also the maximal temperature to which the fibres can be permanent heated during the transport of high power radiation in order not to become the changes in their structure.

2. Experimental details

The glasses were prepared by melting of the purified starting elements in the sealed quartz ampoule evacuated to the pressure up to 10^{-3} Pa during the period of 15 – 20 hours. Then the melting was cooled in the air or by emerging the ampoule to water (under the glass composition) and consequently slowly cooled to the room temperature. Prepared ingots had diameter of 10 mm and the length 50 – 80 mm [6].

The samples for the measurements of electrical and dielectrical properties (∅ ~ 10 mm and the thickness about 1 mm) were coated by the conductive layers at the contact surfaces. The temperature dependencies of direct electrical conductivity $\sigma_{dc}(T)$ at the heating rate 5 °C.min^{-1} were measured by piko-ampere-meter Keithley 6485. The measurements of the temperature and the frequency dependencies of complex electrical modulus ($M^*=1/\varepsilon^*$) [7] were measured by bridge in frequency interval (0.2, 100) kHz [8,9]. The measurements of the optical properties were performed by spectrometer Matson Galaxy 3020.

Direct electrical conductivity presents the competence of the charge particles to move by ordered motion in the large distance comparing the nuclei dimensions. It is affected by temperature and the measured results could be relatively suitable described by Arhénius relation [10]

$$\sigma = \sigma_0 \mathrm{e}^{-\frac{U}{kT}}$$

where σ is direct electrical conductivity, U is the total activation energy needed to the creation and the motion of the free charge career, k is Boltzmann constant, T is thermo-dynamical temperature a σ_0 is pre-exponential factor. In general we can exploit for in-ordered systems (glasses, ceramics, etc.) the same physical methods as for crystallised materials. It means to use modified relations and conceptions about the charge careers migration in the in-ordered net [10].

Thus we find out information about the inside ordering of chalcogenide glasses affecting free charge careers transport by temperature. We gain more complex information about the inside ordering also searching the motion of the bound charge careers (dipoles) by means of the measurements of complex electrical modulus and complex permitivity, respectively. These quantities record especially the changes in the volume of material caused by temperature and frequency, too.

Macedo define complex electrical modulus M^* as the reciprocal value of complex permitivity ($M^* = \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - \mathrm{i}\varepsilon''}$) where ε' is real compound of complex permitivity which is identical with the relative permitivity of material, ε'' is the imaginary compound of the complex permitivity which characterizes electrical losses and i is the imaginary unit. We can consider these losses as the losses occurring as consequence of the polarization processes and the conducted losses caused by the motion of the free charge careers. Then ε'' should be written as $\varepsilon'' = \varepsilon_{pol}'' + \frac{\sigma}{\omega\varepsilon_o} = \varepsilon_{pol}'' + \varepsilon_{cond}''$ where ω is the circular frequency of the alternate current.

3. Results

a) Temperature stability

We performed the measurements of $\sigma_{dc}(T)$ as well as temperature and frequency dependencies of $M^* = 1/\varepsilon^*$ for the pure glasses As – Se – Te and those doped by the rare earth (RE^{3+}). To determine temperature when the irreversible changes in structure did not yet come in being we exploited (apart from the direct conductivity measurements) also the complex electrical modulus measurements, which are more sensible because they record the bound charge motion.

The measurement of M^* showed that the structural reversible changes already occur at temperature up 100 °C in consequence of releasing of the weak bindings but the maximal values of M'' at dependencies $M''(f)$ were not changed. It is the evidence that the original glass structure remains without changes (Fig. 2a, 2b). It was confirmed by the dependencies of M^*, too, which were not changed at the repeated measurements at temperature of 100 °C after heating to the temperature of 160 °C (Fig. 3). The changes of dependencies $M''(M')$, $M''(f)$, $M'(f)$ are registered already by the measurements at temperature of 170 °C and higher. The maximal values M'' of the dependencies $M''(f)$ decrease at the same time (Fig.3c,3d). Therefore we can consider temperature of 170 °C as the starting point of the origin the permanent structural changes. It was confirmed by the measurements of $\sigma_{dc}(T)$ (Fig. 4).

We determined as the limit temperature of the permanent As – Se – Te glasses heating temperature of 160 °C for the further measurements of their electrical and dielectrical properties considering the presented results.

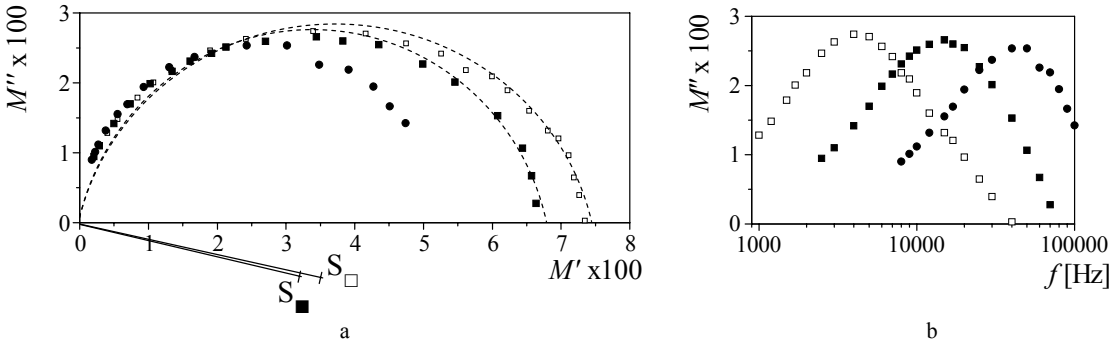

Fig. 2. Dependencies of $As_{0.35}Se_{0.55}Te_{0.10}$ glasses measured at temperature: □ 100° C, ■ 120°C a ● 140°C. a) Complex electrical moduly M'' (M'). b) Frequency dependence of the imaginary compound M''(f) of the complex electrical modulus.

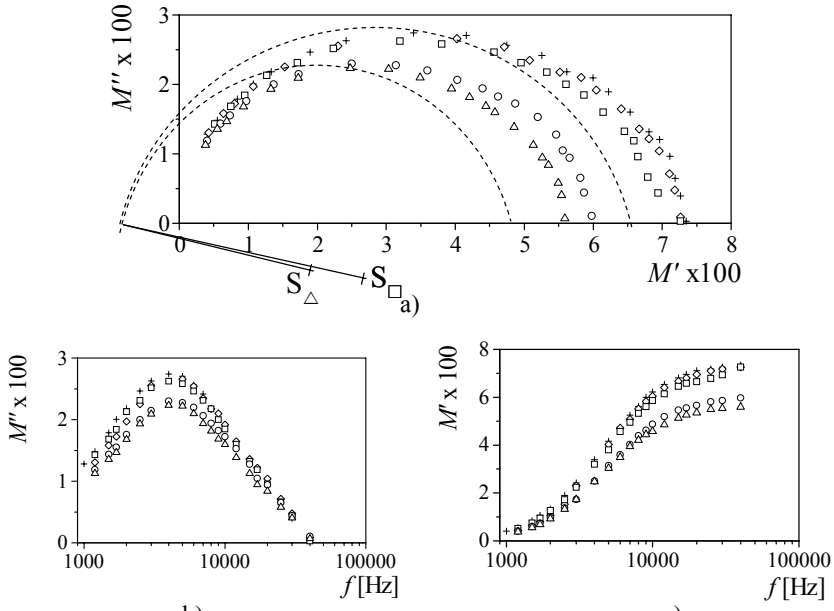

Fig. 3. Dependencies of $As_{0.35}Se_{0..55}Te_{0.10}$ glasses measured at temperature of 100 °C after heating to the higher temperature (20 min.): + without the foregoing heating (virginal sample), ◊ 160° C, □ 170 °C, ○ 180 °C, △ 190 °C. a) M'' (M'), b) M''(f), c) M'(f).

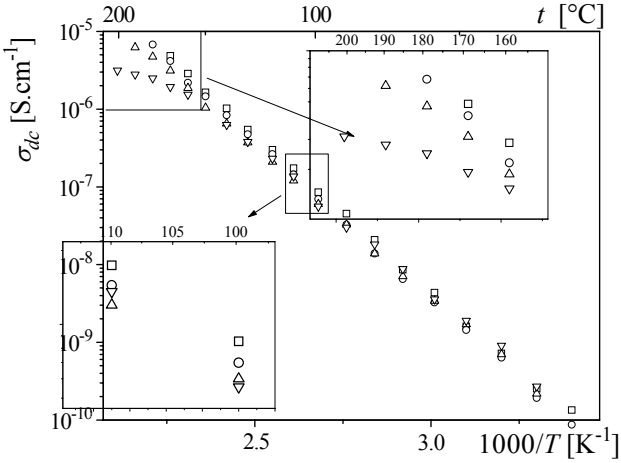

Fig. 4. Dependencies $\sigma_{dc}(T)$ of $As_{0.35}Se_{0.55}Te_{0.10}$ glasses – repeated measurements up to temperature: □ 170 °C, ○ 180 °C, △ 190 °C, ▽ 200 °C.

b) The influence of glass composition on their electrical and dielectrical properties

The measurements of $\sigma_{dc}(T)$ confirmed that the *p* type of the electrical conductivity (without respect the change of the chemical composition) remains with the same activation energy ($U = 0.80 \pm 0.05$ eV). The glasses conductivity of the same composition without the admixtures as well as with the admixtures of the rare earth (Pr) of the concentration 1 000 wt. ppm does not affect to the electrical conductivity of ($As_{0.35}Se_{0.6}Te_{0.05} + Pr_2O_3$ and $As_{0.35}Se_{0.55}Te_{0.10} + Pr_2S_3$, respectively) (Fig. 5). It was shown (Fig. 6) by means of the frequency dependencies of M* that the influence of the rare earth (Er, Pr) added in the various chemical form can be recorded (the changes of results are larger as the measurements correctness).

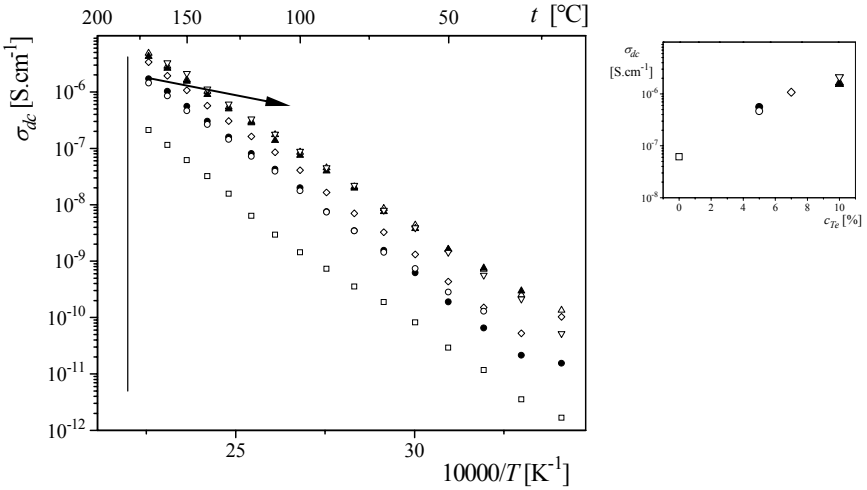

Fig. 5. Dependencies $\sigma_{dc}(T)$ As - Se - Te glasses (pure and doped by RE^{3+} of the concentration of 1000 wt. ppm in various forms): □ As_2Se_3, ○ $As_{0.35}Se_{0.60}Te_{0.05}$, ●$As_{0.35}Se_{0.60}Te_{0.05}$ + (Pr_2O_3), ◊ $As_{0.35}Se_{0.58}Te_{0.07}$, Δ $As_{0.35}Se_{0.55}Te_{0.10}$, ∇ $As_{0.35}Se_{0.55}Te_{0.10}$, ▲$As_{0.35}Se_{0.55}Te_{0.10}$ +(Pr_2S_3). The detail shows the dependence of σ_{dc} at temperature 150 °C on the concentration of Te.

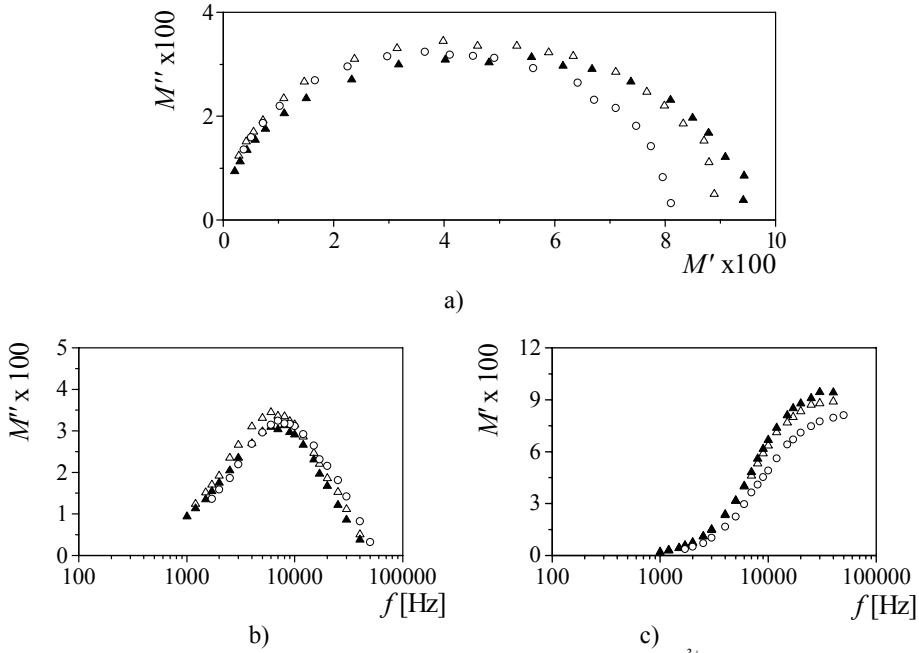

Fig. 6. Dependencies of As – Se – Te glasses (pure and doped by the rare earth RE^{3+} of the concentration 1000 wt. ppm added in the various chemical forms) measured at temperature of 100 °C: ○ $As_{0.35}Se_{0.55}Te_{0.10}$ + (Er_2O_3), Δ $As_{0.35}Se_{0..55}Te_{0.10}$, ▲ $As_{0.35}Se_{0.55}Te_{0.10}$ + (Pr_2S_3). a) M '' vs. M '. b) M'' vs. f. c) M ' vs. f.

This also confirms that the measurement sensibility of the complex modulus and thus the possibility to gain more information about the changes of the glass ordering affected not only by temperature but the chemical form of admixtures, too. In opposite, the small changes of Te concentration were clearly occurred at the measurements of electrical and dielectrical properties, as well. It confirms the significant influence of tellurium on the glass structure and its final properties (Fig. 5).

The preparation technology of As – Se – Te is quite good mastered. The evidence is the fact that the glasses prepared in the various time period had the same electrical properties. Though these glasses are relatively homogeneous, what confirms their equal values of the activation energy, they contain rather big amount of defects – the centre of the half circle is deep-set under the axis M' (Fig. 3a, 3b). It is interesting that the changes in the glass ordering caused by higher temperature had no influence to the concentration of the point defects (the shift of the centre S under the axis M' is just the same). Because there were not measured "tails" at the dependencies $M''(M')$ the volume defects (micro-crystals, fallen-out rare earth to the clusters, bubbles, etc.) did not occur in these glasses.

As – Se – Te pure glasses as well as those doped by ions of the rare earth own the similar properties as glasses Ge – Se – Te [11]. However the values of the direct conductivity As glasses are higher, activation energy (Fig. 7) and transmittance (Fig. 1) are lower. Presented As glasses do not contain the defects of the larger dimensions.

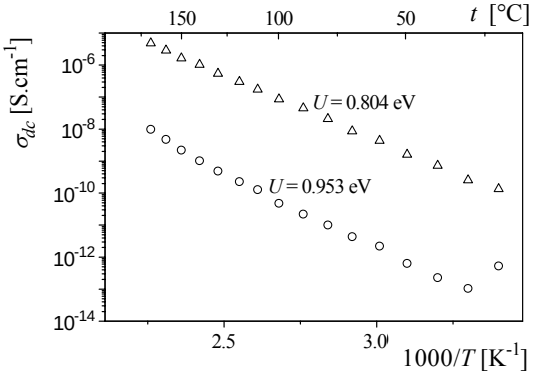

Fig. 7. Dependencies $\sigma_{dc}(T)$ for glasses: ○ $Ge_{0.2}Se_{0.795}Te_{0.005}$, Δ $As_{0.35}Se_{0.55}Te_{0.10}$.

4. Discussion and conclusions

We can state with respect of the measured results of the electrical and dielectrical properties of the pure As – Se – Te glasses and those with the admixtures of the rare earth RE^{3+} that these glasses are not homogeneous but they contain the amount of the physical defects as the point defects (unsaturated bindings). However they do not contain defects of the larger dimensions as micro-crystals, clusters and bubbles. That is confirmed by the found out results of the measurements of complex electrical modulus. In general the next rule is valid. The more the centre of the half circle is under the axis M' at the dependencies $M''(M')$ all the more the measured glass is different comparing the "ideal" glass and contains more mentioned physical defects. In the case that the glasses were heated over the temperature of 160 °C, the glasses changed their inside structure and the irreversible changes were performed what the results of the electrical and dielectrical properties confirmed (Fig. 3, 4). It is interesting that the glass ordering was changed but the concentration of the point defects remained unchanged (Fig. 3a).

The presence of As in chalcogenide glasses As – Se – Te is expressed in the different ordering comparing with Ge – Se – Te glasses. As – Se – Te glasses own the higher values of the conductivity and the lower values of the activation energy. It is caused by the more vacancies in the glass structure similarly as in the case of sulphide glasses [12]. It is caused by the fact that the ordering of As-X glasses (where X is chalcogenide element, for example Se) is created by the deformed original structure framed by the units $AsSe_{2/3}$ that should be connected by circles (over plus of Se) or by the chains mainly in the case of glasses containing Te. Moreover the presence of As caused the decrease of the probability of the volume defects creation (micro-crystals, clusters, etc.)

The influence of the ion addition of the rare earth RE^{3+} causes the enlargement of the gain of luminescence but it is practically negligible and it does not affect electrical and dielectrical glass properties (Fig. 5, 6).

The advantages of the measurements of the electrical and dielectrical properties in the wide range of temperature and frequency are as follows. The measurements not only make possible the short orientation on the properties of glasses but they give the possibility to search the glass ordering changes, too. Utilizing also optical properties (i.e. transmittance) we can exploit their at the optimisation of processing technology. It is necessary to remember the mentioned methods are relative and there is requirement to use further (control) method and/or the found out results to compare with the results of the sample of the desired properties.

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