INFLUENCE OF THE RARE EARTH ON ELECTRIC, DIELECTRIC AND OPTICAL PROPERTIES OF TeO_2 - $PbCl_2$ - PbF_2 GLASSES

VPLYV VZÁCNEJ ZEMINY NA ELEKTRICKÉ, DIELEKTRICKÉ A OPTICKÉ VLASTNOSTI TeO_2 - $PbCl_2$ - PbF_2 SKIEL

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Abstract

The affect of erbium (1 000 mass ppm) added to 60 TeO_2 - 40 $PbCl_2$ and 60 TeO_2 - 20 $PbCl_2$ - 20 PbF_2 glasses, respectively, on electric, dielectric and optical properties is the content of the paper. The substitution of the part of $PbCl_2$ by fluorine induces the decrease of OH groups but the glass "structure" is changing at the same time. The added rare earth Er^{3+} similarly as the presence of PbF_2 affected the glass structure, too. The chemical form of the added rare earth dominantly determines its chemical activity during its building in the glass net. It is markedly registered on the values of electrical and dielectrical parameters.

Príspevok sa zaoberá vplyvom erbia (1 000 hmot. ppm) na elektrické, dielektrické a optické vlastnosti skiel 60 TeO_2 - 40 $PbCl_2$ a 60 TeO_2 - 20 $PbCl_2$ - 20 PbF_2. Čiastočná substitúcia $PbCl_2$ fluoridom zmení vnútorné usporiadanie skiel, pričom znižuje koncentráciu OH skupín. Pridávané erbium výrazne ovplyvňuje štruktúru skiel. Forma v akej je vzácna zemina pridávaná určuje jej aktivitu v objeme skiel, čo je dobre pozorovateľné na hodnotách elektrických a dielektrických vlastností.

Key words

lead halogeno - tellurite glasses, transmittance, direct electrical conductivity, modulus spectroscopy

olovnatoteluričité sklá, transmitancia, jednosmerné elektrická vodivosť, modulárna spektroskopia

Introduction

With respect to the spreading of the applications utilizing IR radiation research is fixated to look for new materials suitable for using as passive elements and active ones, as well, at present. But they are especially used for preparation optical fibers. The aim of our research was to prepare glass materials (performs) with the high as well as physical purities and with the required optical reproducible properties. We concentrate to search the affect of rare earth (Erbium) added to the glass raw material in various chemical forms in the concentration of 1000 m. ppm. in this contribution. The chosen concentration corresponds to the maximal value of the solution of the rare earth in telluride glasses. The admixtures start to fall out to clusters at the higher concentration [1].

Electrical and dielectrical measurements make possible quickly to survey the properties of new developed glasses. Further it is possible to find the optimal composition of glasses, to determine the temperature stability and the influence of admixtures and to find out the presence of point (physical) as well as the volume defects and micro-crystalline, respectively. We consider as point (physical) defects non-occupant bindings of some atoms in glass.

Experimental

Measured glasses 60 TeO_2 - 40 $PbCl_2$ and 60 TeO_2 - 20 $PbCl_2$ - 20 PbF_2 without the admixture and with erbium as the admixture of 1 000 m. ppm. added in various chemical form were prepared by very pure raw materials dried 5 hours in vacuum at temperature of 230 °C. In this way the dried mixture was put in the stream of oxygen and jet-propelled chlorine atmosphere obtained by the decomposition of CCl_4 at temperature of 800 °C. The melting of the mixture takes 30 min at temperature of 720 °C in Pt crucible. The hot-melt after churning was pour into the brass forms and cooled to the temperature of the laboratory [2,3].

Glasses of the group TeO_2 belong among less stable ones because they have more tendency to create the crystal nuclei. The preparation is very severe also in consequence of the mentioned reason. It takes the technological requirements maintenance precisely. The large measured data dispersion occurs in the opposite case [3]. These glasses are sensitive to the humidity and thus to the presence of OH groups. These affect negatively to the optical properties of glasses, especially. The amount of the effort is devoted to their removal already in the raw material. The substitution of the part of $PbCl_2$ by PbF_2 is predominantly performed in order to decrease the content of OH groups in glass [4].

The samples of the shape of pills, prepared to measure electrical and dielectrical properties (∅ ~ 8 mm and the height of 1 mm) were coated at the contact surface by the conductive layers. Temperature dependencies of the direct electrical conductivity at the heating rate of 5 °C/min were measured by means of piko-ampermeter Keithley 6485 [5]. The measurements of the temperature and frequency dependencies of electrical modulus M^* [6] were measured by the bridge method in the frequency interval of (0.2,100) kHz [5,7]. The measurements of the optical properties were performed by the spectrometer Matson Galaxy 3020.

Studying electrical and dielectrical properties of these special glasses it is possible to utilize the correlation (between the inside ordering and the properties) which is based on the affect of the transport of free electrical charge carriers (direct electrical conductivity) as well as bound electrical charge carriers (complex electrical modulus) [8]. It means that electrical conductivity is affected by temperature while the measured results of direct electrical conductivity σ_{dc} is possible to describe quite well by the relation of Arhénius

$$\sigma_{dc} = \sigma_0 \exp\left\{-\frac{U}{kT}\right\} , \qquad (1)$$

where U is total activation energy needed to the creation an the motion of the electrical charge carrier, k is Boltzman constant, T is thermodynamic temperature and σ_o is pre-exponential factor. Generally we can exploit physical methods and considerations to the non-ordering systems (glasses, ceramics, etc.) as for the crystal materials [9]. It means that one can utilize the modified relations and the imaginations about the electrical charge carriers' migration in the regular grid for the non-ordering net.

One can gain the more complex information on the inside ordering by searching of the bind electrical charge carriers (dipoles) when we determine the values of complex electric modulus. This method is called modular spectroscopy. Macedo [6] defines electric modulus $M^* = 1/\varepsilon^*$, where ε^* is complex permitivity given by the relation

$$\varepsilon^* = \varepsilon^{/} - \mathrm{i}\,\varepsilon^{//} , \qquad (2)$$

where $\varepsilon^{/}$ is real compound which is identical with the relative permitivity of material. $\varepsilon^{//}$ is imaginary compound which characterizes the electrical loses and i is the imaginary unit. One can divide these loses to two groups. The loses caused by the polarization processes belong to the first group and the second one is created by the loses caused by the motion of the free charge carriers. Thus one can write

$$\varepsilon^{//} = \varepsilon^{//}_{pol} + \frac{\sigma_{dc}}{\omega\varepsilon_0} = \varepsilon^{//}_{pol} + \varepsilon^{//}_{cond} , \qquad (3)$$

where ω angular frequency.

Results

Erbium added in chemical forms of Er_2O_3 and $ErCl_3$ to the glasses of the composition 60 TeO_2 – 40 $PbCl_2$ affected only slightly the values of temperature dependency of σ_{dc} and the values of the activation energy at the same time were not changed. In the case when erbium in the form of metal was added to this glass the activation energy was not changed but the values of σ_{dc} were changed (Fig. 1). Similarly the presence of erbium was also registered by temperature and frequency dependencies of ε^* and M^* (Fig. 2a, 2b). When erbium was added in the form of metal, the dependencies of M'' vs. M' were different, too, similarly as in the case of σ_{dc} measurements. This different influence of erbium is probably due to its different chemical activity because the type of the binding among the atom of rare earth and the atoms in surroundings is dominant for the influence of the chemical form of the rare earth. It can not be neglected the fact that together with the chemical form of the rare earth admixture (especially in the case of metal erbium) is also brought the certain amount of OH groups into glass and it should affect its properties [1].

The influence of Er^{3+} added as Er_2O_3 was registered in glasses $60TeO_2$ -$20PbCl_2$ -$20PbF_2$, too. Conductivity of glasses with the admixture of Er_2O_3 was higher as had been measured for glasses without the admixture. The values of activation energy were also changed from the values U_3 = 1.24 eV and U_4 = 1.35 eV to the values U_1 = 0.87 eV and U_2 = 0.81 eV (Fig. 3). The lower values of activation energy confirm that the added admixture affected the more soft glass ordering although the concentration of charge carriers increased.

One can deduce from the measurements of M^* that the measured samples contained not only the large concentration of the point defects (the center of the half-circle is under the axis M') but the glasses contained either micro-crystalline or the defects created by the rare earth fallen out to the clusters. It confirms the appearance of "tails" at the dependencies of M'' vs. M' (Fig. 4. - the part highlighted by the shade lining at the half-circle).

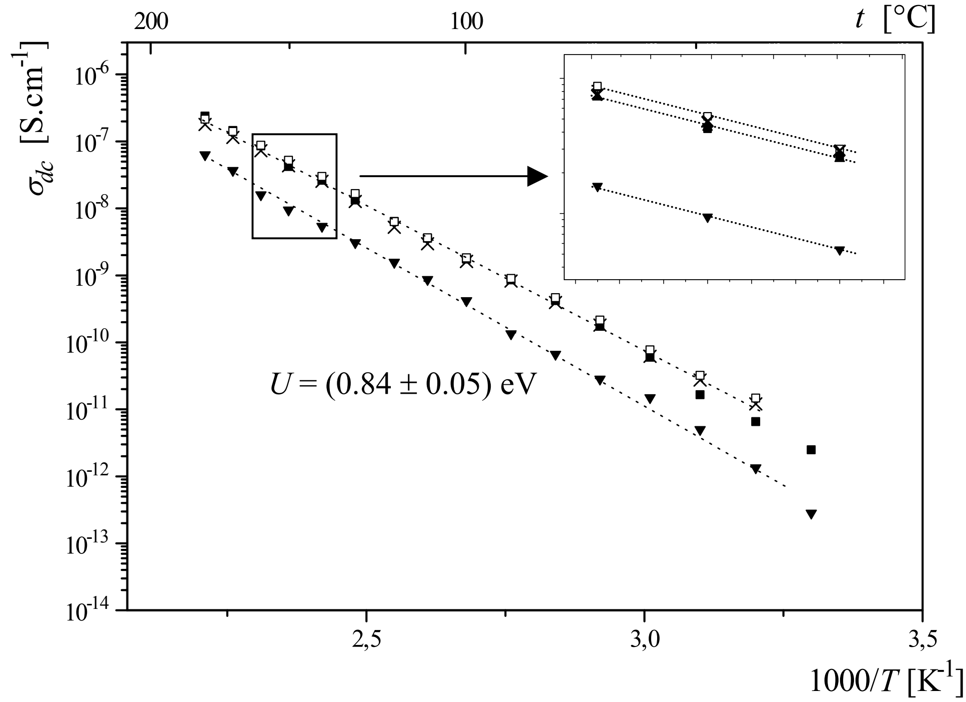
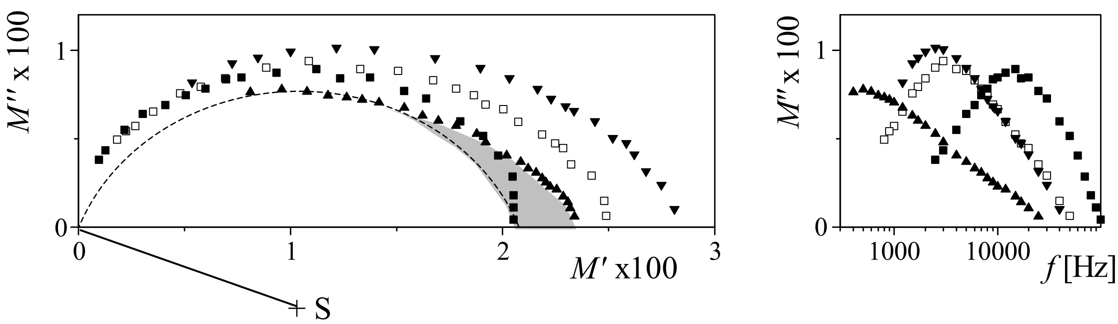


Fig. 1. *Temperature dependencies of σ_{dc} of glasses 60 TeO_2 – 40 $PbCl_2$.* □ *without of the admixtures. Admixtures of Er^{3+} of 1000 m. ppm. added as:* ■ *$ErCl_3$,* ▼ *Er metal and X Er_2O_3*



a) b)

Fig. 2. Dependencies of glasses 60 TeO_2 – 40 PbF_2 measured at temperature of 170 °C. □ *without of the admixtures. Admixtures of Er^{3+} of 1000 m. ppm. added as:* ■ *$ErCl_3$,* ▼ *Er metal and* ▲ *Er_2O_3.*

a) Complex electrical moduly (M '' vs. M ').

b) Frequency dependencies of imaginary compound of complex electrical modulus (M'' vs. f)

The dependencies of transmittance measured for the individual glasses were rectified to the same sample thickness – 1 mm. We compared the relative values of transmittance to the maximal one what was reached for the sake of the better comparison. The gained results for the glass of the basic composition (60 TeO_2 – 40 $PbCl_2$) without the admixture as well as with added erbium showed that the rare earth did not significantly affected transmittance. The exception, similarly as at electrical and dielectrical measurements, was found out in the case of added erbium in the metal form. It is clear in this case too, that erbium in the metal form inserts to the glass the increased content of OH groups. It is confirmed by the substantional decrease of transmittance at the wavelength of 3.25 μm and the lowest transmittance of glass, as well (Fig. 5). The glass (60 TeO_2 – 20 $PbCl_2$ – 20 PbF_2) is optimal substituting 20 PbCl by 20 PbF_2 what the minimum of the concentration of OH groups and the improvement of transmittance confirmed (Fig. 5).

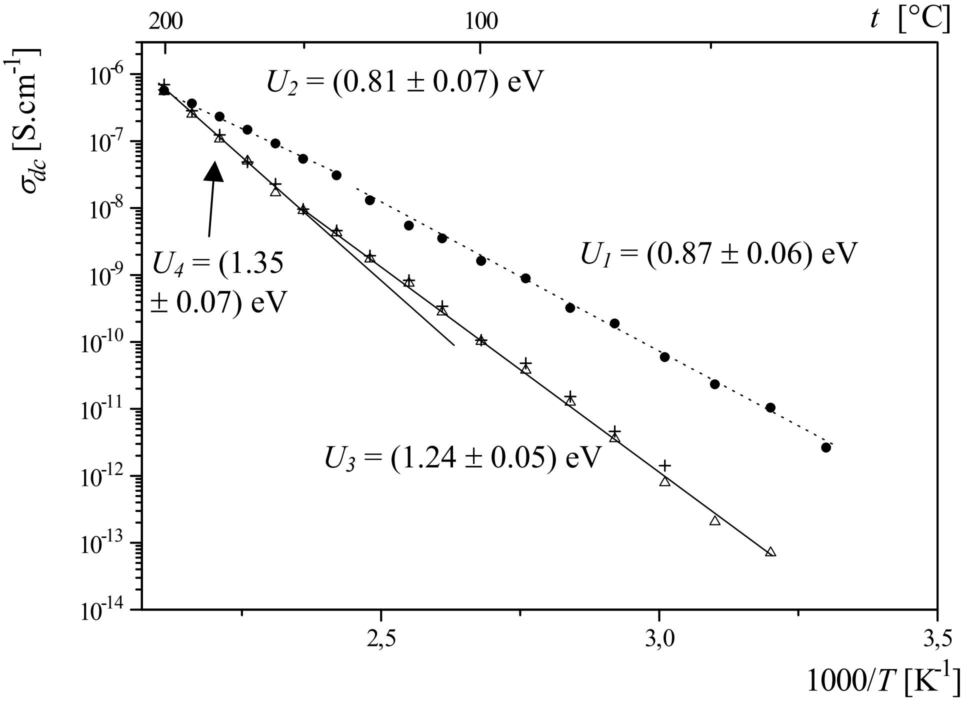


Fig. 3. *Temperature dependencies of σ_{dc} of glasses 60 TeO_2 – 20 $PbCl_2$ – 20 PbF_2. + ,Δ without the admixtures, ● with the admixture of Er^{3+} of 1000 m. ppm. added as Er_2O_3*

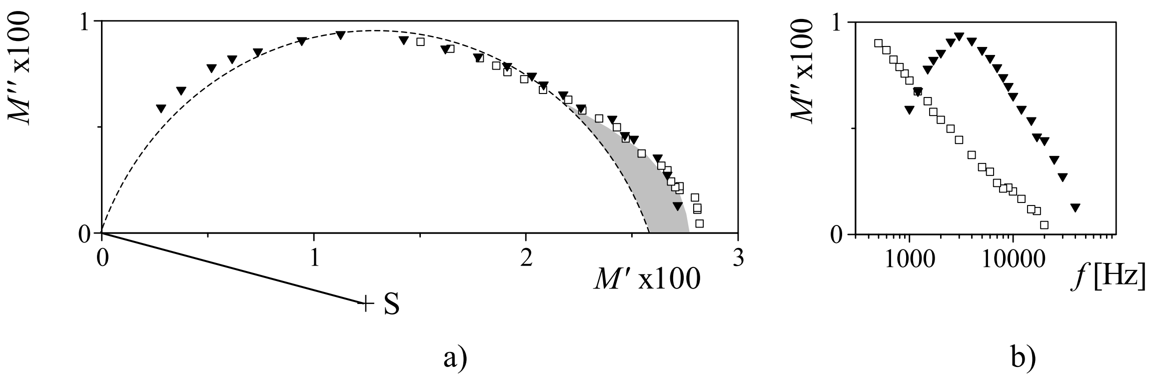


Fig. 4. *Dependencies of glasses 60 TeO_2 – 20 $PbCl_2$ – 20 PbF_2 measured at temperature of 170 °C. □ without of the admixtures, ▼ the admixture of Er^{3+} of 1000 m. ppm. added as Er_2O_3.*

a) Complex electrical moduly (M '' vs. M ').

b) Frequency dependencies of imaginary compound of complex electrical modulus (M'' vs. f).

The results correlate quite well with the electrical and dielectrical properties and also confirmed that the rare earth insert into glasses impurities (mostly OH groups), which are eliminated only hardly. The measured values of transmittance clearly outline that when one can want to utilize the rare earth in order to increase transmittance the admixture added in the forms of $ErCl_3$ or Er_2O_3 was gained as most suitable (Fig. 6).

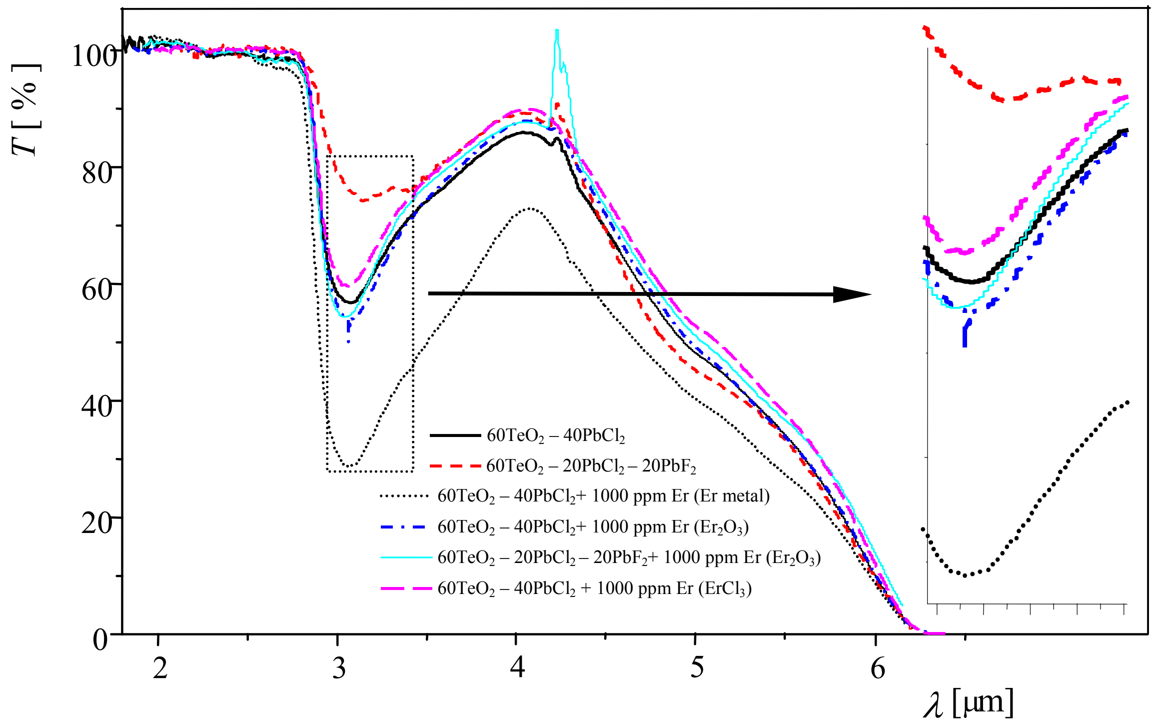


Fig. 5. *The rectified relative values of transmittance of glasses TeO_2 - $PbCl_2$ - PbF_2 with the added rare earth*

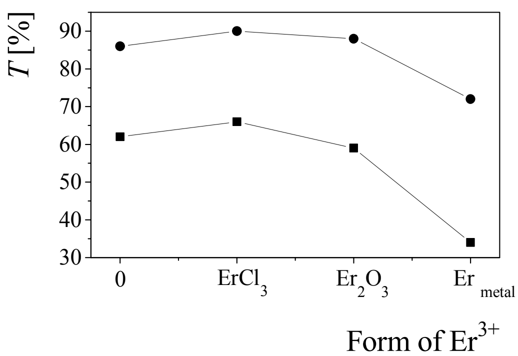


Fig. 6. *The rectified relative values of transmittance of glasses 60 $Te0_2$ – 40 $PbCl_2$ with the rare earth added in the various forms at wavelength of ■ 3.2 μm and ● 4.0 μm*

Discussion and conclusion

The measurements of the temperature dependencies of direct electrical conductivity σ_{dc} as well as the measurements of the temperature and the frequency dependencies of complex electrical modulus confirmed the clear correlation not only among them but also with the results of the transmittance measurements.

One can state that the preparation of the $TeO_2 - PbCl_2$ glasses is very difficult. It is necessary to keep technological course because it significantly affects the final properties of the produced glass. It was shown that the substitution of 20 % $PbCl_2$ by PbF_2 decreased indeed the content of OH groups but it significantly affected the inside ordering the glass. It appeared by the change of activation energy to the value of 1.24 eV. Activation energy deceased by adding the rare earth to the value 0.87 eV what one can take as the evidence of the freer ordering of the glass. Erbium added in the maximal possible concentration (1000 m. ppm.) inserts to the glass the impurities of the type of OH groups, which decrease markedly its transmittance. Erbium added in the form of the metal inserts the most OH groups. In the case of necessity to increase transmittance of glass it is more convenient to add erbium in the forms $ErCl_3$ or Er_2O_3 because these forms affect only slightly transmittance of glass.

The preparation of telluride glasses from the point of view of technology is very severe what the evidence is that the measured samples contained the quite high concentration of the point (physical) defects disturbing their structure. Some of the samples showed the presence of micro-crystalline or the presence of the fallen out ions of the rare earth to the clusters.

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