ELECTRICAL, DIELECTRIC AND OPTICAL PROPERTIES OF TeO_2-$PbCl_2$-PbF_2 GLASS SYSTEMS

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The paper describes electrical, dielectric and optical properties of glasses selected from the system $(TeO_2)_{60} (PbCl_2)_{40-x} (PbF_2)_x$, where $x \in (0, 32)$. The influence of the replacement of Cl by F on electrical and optical properties has been investigated. The presence of PbF_2 affects markedly the inside glass ordering. When the concentration of fluoride is increasing, the OH group content is decreasing but the glass tendency to crystallization is increasing at the same time. It follows from reported electrical and optical characterisation that the optimum value of $PbCl_2$ concentration corresponds to x=20.

1. Introduction

Glasses prepared on the basis of TeO_2 oxides, such as TeO_2-$PbCl_2$ system, are the subject of the intensive research [1,2], oriented to their utilization in optoelectronic applications. The high chemical purity with the lowest possible OH group content is one of the application requirements of these glasses. The presence of this impurity supports the creation of clusters that contribute to the scattering of the transmitted infrared radiation and thus to the increase of optical losses of corresponding fibres [3].

Elevated temperature causes changes in the glass structure ordering. TeO_2 glasses have the tendency to create the crystallization nuclei near the temperature of T_g and it is the reason why their production is not easy [4]. By partial substitution of chloride $PbCl_2$ by fluoride PbF_2 both the above mentioned difficulties due to OH group content and temperature effects, are simultaneously improved [5-9]. However, the glass "structure" may change abruptly due to the gradual replacement of $PbCl_2$ by PbF_2, what represents the disadvantage of this substitution. Thus the possible increase of PbF_2 concentration is limited due to the tendency to create the crystalline phase, when PbF_2 concentration exceeds certain limit. One of the goals of our study was the determination of this limiting PbF_2 concentration.

We report the preparation of samples in the glass system $(TeO_2)_{60} (PbCl_2)_{40-x} (PbF_2)_x$ with $x \in (0, 32)$ and their characterisation by electrical measurements, optical transmission spectroscopy and X-ray diffraction.

2. Experimental

Glasses $(TeO_2)_{60}$-$(PbCl_2)_{40-x}$-$(PbF_2)_x$ where $x \in (0 - 32)$ mol% had been prepared under the same preparation technology as described earlier [3,7]. All starting compounds, before the synthesis itself started, were dried under vacuum (230 °C, 5 hours) then in a flow of oxygen and reactive atomic

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chlorine atmosphere in order to remove the moisture from their surface. Melting of the mixtures in Pt crucibles was carried out for 30 minutes at the temperature of 720 °C. Subsequently the glass melt was poured into forms having 8 mm in diameter and 35 - 50 mm in length. Prepared glasses were annealed slowly to room temperature from the temperature close to their T_g. After annealing samples were cut and polished to optical quality. The thickness of samples, measured by absorption spectrometer, varied from approximately 0.2 up to 2.5 cm. The decrease of the OH group concentration by means of the partial replacement of $PbCl_2$ by PbF_2 was the major goal in the study of this glass system.

Both electrical and dielectric properties have been measured on cylindrical samples with diameter 10 mm and thickness of about 1 mm. The contact surfaces were coated by the graphite conductive layer. The temperature dependencies of the direct electrical conductivity were measured by means of pikoampere-meter Keithley 6485 with the heating rate 5 °C/min. The measurements of both temperature and frequency dependencies of complex electrical modulus M^* [10] were performed by means of the bridge in the frequency range of 200 Hz – 100 kHz [11]. The Mattson Galaxy 3000 FTIR spectrometer was used to obtain infrared absorption spectra; for measurements in UV/VIS region the Specord M400 Spectrometer, Zeiss Jena, was used. The Philips PW1710 was used for X-ray diffraction measurements.

Consequently we can investigate the changes of inside glass structure ordering by means of observing the creation and the motion of free charge careers by measuring direct electrical conductivity and/or the bound charge careers by determining complex electrical modulus. Thus the creation of a new phase [11, 12] could be registered by means of gained results.

The direct electrical conductivity σ_{dc} can be well described by Arrhenius relation

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

where U is the total activation energy needed for the creation and moving of the charge carrier, k is Boltzman constant, T is the absolute temperature and σ_o is a pre-exponential factor.

More detailed information on inside glass ordering can be found out by observing bound charge careers via determining the values of complex electrical modulus. Macedo [10] introduced modular spectroscopy defining electrical modulus M^* as the reciprocal value of complex permittivity $M^* = \dfrac{1}{\varepsilon^*}$ while complex permittivity is given as

$$\varepsilon^* = \varepsilon' - i\varepsilon'',$$ (2)

where real part ε' of complex permittivity is identical with the relative permittivity of material and imaginary part ε'' of complex permittivity characterizes electrical loses. Two major contributions to losses are due to polarization processes and conductivity mediated by free charge careers. Thus, the imaginary part could be written as:

$$\varepsilon'' = \varepsilon''_{pol} + \frac{\sigma_{dc}}{\omega\varepsilon_0} = \varepsilon''_{pol} + \varepsilon''_{con},$$ (3)

where ω is angular frequency of the alternate current.

3. Results

Since the T_g temperature of studied glasses is not reliably known we first determined the maximum temperature at which the internal structure of the glass does not change. A dc electrical conductivity was repeatedly measured on a chosen set of samples and plotted as a function of 1/T. In these experiments the upper temperature limit has always been increased by 10 °C. The highest temperature at which the internal restructuring still does not take place was determined in this way as equal to 200 °C. These experiments are documented in Fig. 1, where dc electrical conductivity is

plotted for (TeO$_2$)$_{60}$(PbCl$_2$)$_{40}$ and (TeO$_2$)$_{60}$(PbCl$_2$)$_{20}$(PbF$_2$)$_{20}$ glass systems, respectively. Repeated measurements show that no irreversible changes appear for temperatures below 200 °C.

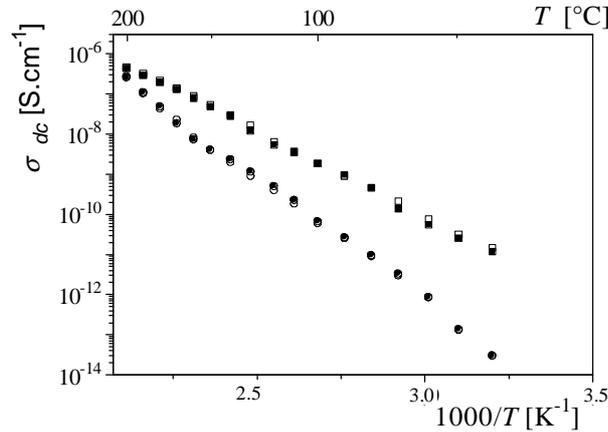Fig. 1. Temperature dependencies of direct electric conductivity σ_{dc} glasses: □ ■ (TeO$_2$)$_{60}$(PbCl$_2$)$_{40}$ and ○ ● (TeO$_2$)$_{60}$(PbCl$_2$)$_{20}$(PbF$_2$)$_{20}$, where the marks ■ ● present the repeated measurements.

The influence of replacement of PbCl$_2$ by PbF$_2$ on dc electrical conductivity is shown in more detail in Fig. 2 for parameter x changing gradually in the range (0, 32). Measured data for glass systems with x = 0, 8, 12 and 16 are shown in Fig. 2a, while the data for systems with parameter x = 0, 20, 28 and 32 are plotted in Fig. 2b. It could be seen that even the substitution of   8 mol % PbF$_2$ in PbCl$_2$ causes a meaningful influence in the inside glass ordering. It is manifested by the changes of both the conductivity and the values of activation energy.
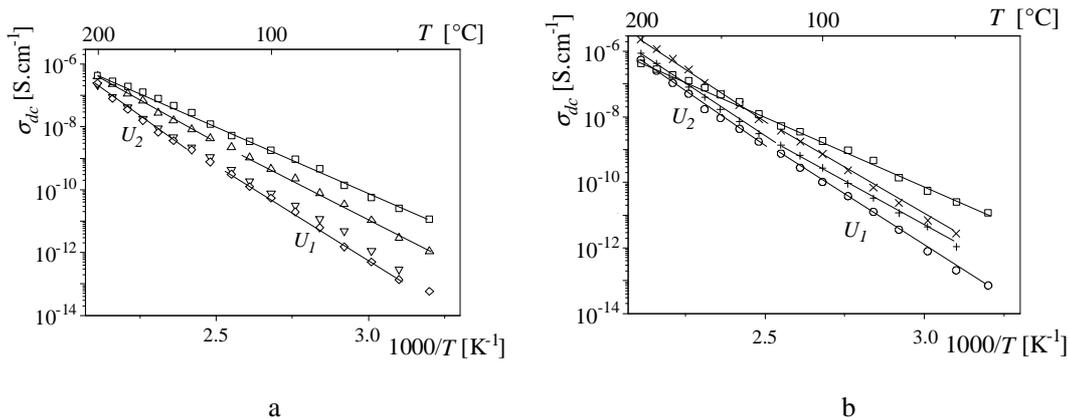

a   b

Fig. 2. Temperature dependencies of direct electric conductivity σ_{dc} the glasses system (TeO$_2$)$_{60}$(PbCl$_2$)$_{40-x}$(PbF$_2$)$_x$ for $x \in$ (0-32)mol %: a) □ 0, △ 8, ∇ 12, ◊ 16, b) □ 0, ○ 20, + 28, x 32.

From inspection of Fig. 2 we can see that systems with the parameter x≥8 are characterised by two activation energies. The activation energies obtained from measured dc electrical conductivity of (TeO$_2$)$_{60}$(PbCl$_2$)$_{40-x}$(PbF$_2$)$_x$ where x∈(0 – 32) mol% glass systems are given in Table 1. It could be seen from the inspection of Fig. 2 and Table 1 that with increasing x from 0 to 20 the absolute value of dc conductivity is steadily decreasing while the activation energy is steadily increasing. This steady behaviour is reversed for x exceeding the value of 20 mol%. This behaviour and the role of PbF$_2$ substitution on the values of dc electrical conductivity and corresponding activation energy are shown

in Fig. 3a and Fig. 3b, respectively. The dependence of dc conductivity σ_{dc} as a function of PbF_2 molar concentration is shown in Fig. 3a for two temperatures 180 and 100 °C by upper and lower curves, respectively. It follows from the plotted experimental data that minimum is reached for the concentration of 20 mol % PbF_2. Corresponding two characteristic activation energies as a function of PbF_2 molar concentration is shown in Fig.3b. In accord with σ_{dc} behaviour we similarly observe the local extreme (maximum) of both activation energies around the concentration of PbF_2 equal to 20 mol %.
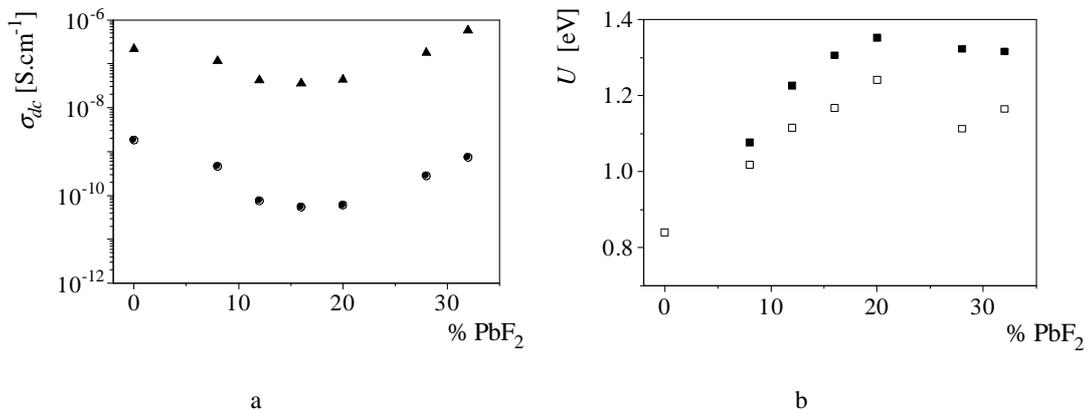

a   b

Fig. 3. Measurements of the glass system $(TeO_2)_{60}(PbCl_2)_{40-x}(PbF_2)_x$ for $x \in (0\text{-}32)$mol %:
a) Dependencies of the direct electrical conductivity σ_{dc} as a function of PbF_2 concentration at temperatures of 180 °C and 100 °C are shown by the upper and lower curve, respectively.
b) Dependencies of the activation energies U_1 (□) and U_2 (■), as a function of PbF_2 concentration are shown by the lower and upper curves, respectively.

Table 1. Activation energies of the glass system $(TeO_2)_{60}(PbCl_2)_{40-x}(PbF_2)_x$, derived from the measurements of *dc* electrical conductivity.

x [mol %]	U_1 (20 - 110°C) [eV]	U_2 (130 - 200°C) [eV]
0	0.84±0.03	
8	1.018±0.021	1.076±0.023
12	1.115±0.035	1.226±0.037
16	1.167±0.032	1.306±0.051
20	1.241±0.024	1.352±0.035
28	1.113±0.017	1.323±0.015
32	1.165±0.024	1.316±0.020

The measured dependencies of complex electrical modulus (M'' vs. M') on samples with various PbF_2 concentrations are shown in Fig. 4. The most pronounced changes of the above mentioned dependencies are seen for the values of concentration 28 mol % and 32 mol %, respectively. The shift of the centre of the half-circles "S" deeply below the M' axis shows the presence of defects in glass volume and the creation of new phase at higher PbF_2 concentration. These glasses contain the crystalline phase (Pb_2OF_2 tetragonal phase) as was confirmed by X - ray analysis of studies samples shown in Fig. 5. X-ray diffraction analysis is shown for four glass systems corresponding to x=0, 8, 28 and 32. The presence of the crystalline phase was not found for glassy samples $(TeO_2)_{60}(PbCl_2)_{40}$ and $(TeO_2)_{60}(PbCl_2)_{32}(PbF_2)_8$ with zero or the lowest PbF_2 concentrations. It is evident that at higher values of PbF_2 concentration, the tendency to the creation of micro-crystals is increasing.
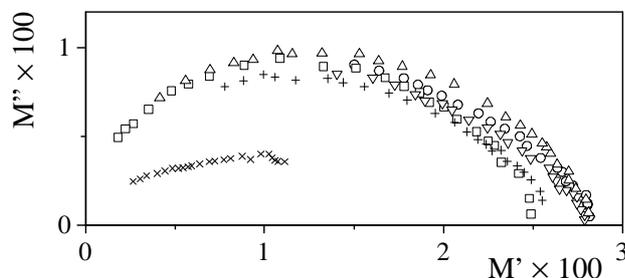
Fig. 4. The imaginary part of complex electric modulus versus the real part is plotted for the glass systems $(TeO_2)_{60}(PbCl_2)_{40-x}(PbF_2)_x$ with $x \in$ (0-32)mol %. The assignment of symbols and parameters x are as follows: □ 0, Δ 8, ∇ 12, ○ 20, + 28, x 32.

The transmission spectroscopy was used for optical characterisation of prepared glasses. The absorption edges are located at the wavelength of about 500 nm in case of short wavelength edge and at about 6.5 μm in case of long wavelength absorption edge. The infrared transmission spectra are shown in Fig. 6 for samples with x=0, 12, 20, 28 and 32. The observed absorption band at 2.93 μm is caused by the presence of OH⁻ groups in the glass matrix; it corresponds to the fundamental vibration of OH⁻ groups. In the inset of Fig, 6 are plotted values of transmission at the wavelength λ=2.93 μm as a function of $PbCl_2$ molar concentration. It can be seen from this inset that maximum transmission appears around x=20 mol % in good agreement with conclusions derived from electrical measurements.
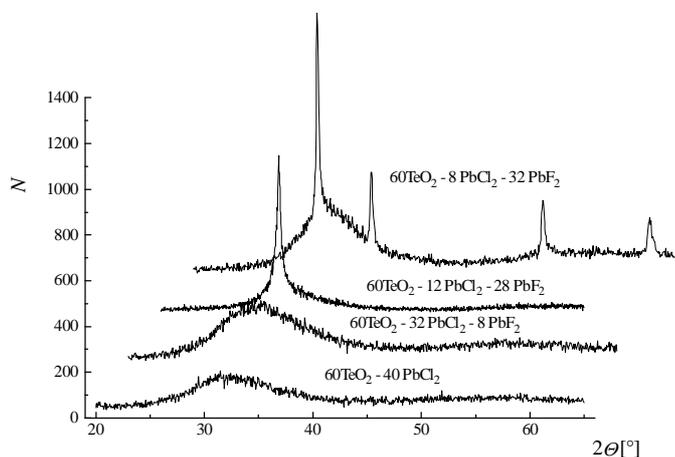

Fig. 5. X - ray difraction records of the glass system $(TeO_2)_{60}(PbCl_2)_{40-x}(PbF_2)_x$ with $x=0$, 8, 28 and 32 mol% are shown. The used wavelength is $\lambda_{Co} = 0.1788965$ nm.

The efficiency of diminishing the OH impurities can even better be estimated from the values of extinction coefficient calculated for this absorption band. The extinction coefficient was calculated according to relation $\alpha = \ln(I_0/I)/d$, where I_0 and I are the intensities of transmitted radiation at the baseline and at the OH⁻ groups peak, respectively, d is the sample thickness and α is the extinction coefficient. The influence of $PbCl_2$/PbF_2 substitution on OH⁻ group concentration is demonstrated in Fig. 7, where calculated extinction coefficients are plotted as a function of PbF_2 mol %. As can be seen from Fig. 6, the increase of PbF_2 concentration causes the decrease of concentration of OH⁻

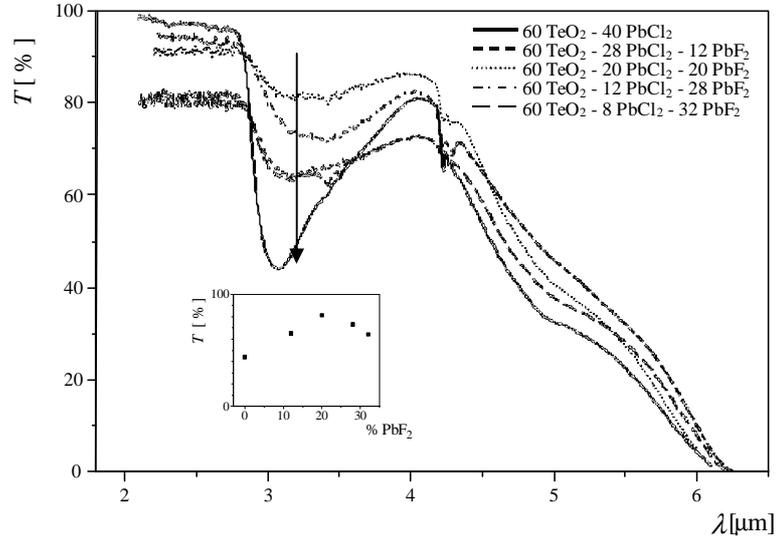groups by almost four times. The minimum of extinction coefficients corresponds approximately to 20 mol % of PbF_2.

Fig. 6. Infra-red transmission spectra of the glasses system $(TeO_2)_{60}(PbCl_2)_{40-x}(PbF_2)_x$ for $x \in (0\text{-}32)$ mol % are shown. The curves are described in the figure. The pronounced absorption band at 2.93 μm corresponds to the presence of OH groups. It is seen from the inset that maximum suppression of the absorption band at 2.93 μm is obtained for x~20 mol %.
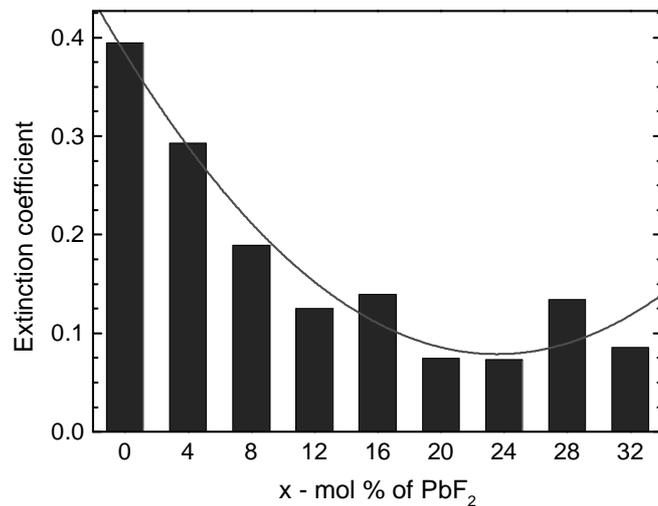

Fig. 7. The influence of $PbCl_2/PbF_2$ substitution on OH⁻ groups concentration in prepared glasses in the $(TeO_2)_{60}(PbCl_2)_{40-x}(PbF_2)_x$ system. Extinction coefficient was calculated for OH⁻ group band at 2.93 μm.

4. Discussion and conclusion

The influence of the replacement of $PbCl_2$ by PbF_2 on OH groups concentration and inner glass ordering has been investigated in glass system $(TeO_2)_{60}(PbCl_2)_{40-x}(PbF_2)_x$ with $x \in (0, 32)$, by measuring *dc* electrical conductivity and complex electrical modulus, together with transmission

spectroscopy and X-ray diffraction. A clear influence of PbF_2 concentration, already at the value of 8 mol % PbF_2, on the values of measured parameters has been proved. A significant qualitative change in the glass inside ordering with the tendency to the creation of crystalline phase, at the case of high concentration the value of 28 mol % PbF_2, has been demonstrated.

One can observe the local extreme of the values of electrical and dielectric parameters at the concentration of ~ 20 mol % PbF_2. Glasses are characterised by the smallest values of conductivity and the biggest values of the activation energy around this optimal value of concentration. This fact clearly confirms the great changes of the glass inside ordering caused by the presence of PbF_2 exceeding certain limit. Optical transmission is also affected by PbF_2 concentration increase because it decreases OH group concentration. The increasing of PbF_2 concentration above the value of 12 % clearly causes the tendency to the crystallization in the volume of the glass. It shows the tendency to inside ordering what is the reason of the degradation of the optical properties of glass. The performed measurements also confirmed that $(TeO_2)_{60}(PbCl_2)_{40}$ glasses can be permanently heated up to temperature 240 °C.

Acknowledgement

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