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Electrical and dielectric properties of doped $TeO_2{\cdot}PbCl_2{\cdot}PbF_2$ glasses, prepared in Au or Pt crucibles

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Influence of crucibles (Au or Pt) on electrical and dielectric properties of $60TeO_2.40PbCl_2$, and $60TeO_2.20PbCl_2.20PbF_2$ glasses, “pure” and doped with 1000 wt-ppm Pr^{3+} or Er^{3+}, added as metals, chlorides, or oxides, is reported. Among “pure” glasses, the highest conductivity is found in $60TeO_2.40PbCl_2$ glasses prepared in Pt crucibles. The lowest conductivity is found in “pure” $60TeO_2.20PbCl_2.20PbF_2$ glasses. Upon doping, the dc conductivity of $60TeO_2.40PbCl_2$ glasses prepared in Pt and Au crucibles decreases or increases, respectively. The dc conductivity of $60TeO_2.20PbCl_2.20PbF_2$ glasses increases upon doping. Static relative permittivity of glasses ranges from 27 up to 34. The activation energy of electrical modulus spectrum is the same as the conduction activation energy (0.68-0.97 eV). The TSDC measurements show 3 types of peaks; one of them correlates with the dc conductivity.

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1. Introduction

Tellurite glasses are of a great scientific and technological interest due to their promising optical properties [1-6]. They are characterized by a wide transmission range (≈400 nm to 6 μm), lack of toxicity, good glass stability and mechanical strength, good corrosion or moisture resistance, low phonon energy (≤ 800 cm^{-1}), high density (≈5.5 g/cm^3), high refractive index (≈2), good solubility of rare earth ions, low melting temperature, and good chemical stability. These properties are connected with the local order in neighbourhood of Te atoms. Good thermal and mechanical properties enable a fiber production [4]. Heavy ions influence the glass forming ability, and absorption ability and shift the IR cut-off towards longer wavelengths [2,3,7,8].

Tellurite glasses are interesting also as non-linear optical elements [5]. The glasses are used as optical components (windows, prisms, laser glasses), and in fiber optics (optical fibers, fibrous optical amplifiers, fibrous lasers).

The aim of this work is to present dc and ac electrical conductivities, thermally stimulated depolarization currents (TSDC), and dielectric response of tellurite/lead chloride/lead fluoride glasses “pure” and doped with 1000 wt-ppm Pr^{3+} or Er^{3+} ions in various chemical forms, prepared in Pt or Au crucibles.

2. Experimental details

Before the synthesis, all starting components of $60TeO_2.40PbCl_2$ (6T4P) and $60TeO_2.20PbCl_2.20PbF_2$ (6T2P2P) glasses, are dried under vacuum (230 °C, 5 h) and then in a flow of oxygen and reactive atomic chlorine atmosphere, obtained by decomposition of CCl_4 at 800 °C. Mixtures are melted in Pt or Au crucibles at 720 °C, for 30 min. The melt is poured into forms and cooled to the room temperature (RT). 1000 wt.-ppm of Er or Pr, in the form of metal, oxide or chloride, are added into the batch [1-3]. Upon preparation in Pt or Au crucibles, glasses are red/orange or yellowish/dirty white, respectively.

For determination of dc conductivity, electric current is measured at a constant voltage of 10 V using Novocontrol Concept 90, in the temperature range from -50 °C up to 180 °C, in N_2. The temperature is measured using a Pt/PtRh thermocouple, with an accuracy of ±1 °C. Temperature dependences of the dc conductivity are measured at increasing temperature, with a heating rate 5 °C/min.

Electrical ac conductivity and relative static permittivity are measured in the temperature range of 20-180 °C, in air, at 0.1-10^5 Hz, with LCR Hitester Hioki 3522-20. Graphite painted electrodes are used. Frequency dependences of the capacity and tg δ are measured in temperature intervals of 10 °C, upon 20 min’s equilibration of the chosen temperature. Other dielectric parameters are calculated. The bulk conductivity (by impedance analysis) and static relative permittivity (by modular analysis) were determined with an accuracy of 5 %. These methods are usable for characterization other materials, too (rubbers, plastics, etc.) [9].

Thermally stimulated depolarization currents are measured using Novocontrol Concept 90. Samples are polarized at 50 °C for 30 min., the intensity of the polarizing field being 100 V/mm. Upon polarization, samples are cooled, with a cooling rate 5 °C/min, to the temperature of -100 °C. They are kept at this temperature for 5 min. Then, the polarizing field is switched off and the sample is kept at this temperature for 2 min. Subsequently, depolarizing currents are measured, with heating rates 2 °C/min, 5 °C/min, and 10 °C/min, in the temperature range from -100 °C up to 180 °C.

Glasses are homogeneous; samples cut from different parts of the glass ingot have identical physical properties.

3. Results

Temperature dependences of the dc conductivity of 6T4P glasses, “pure” and doped with Pr in various chemical forms are presented (Fig. 1). The dc conductivity of “pure” glasses prepared in Au crucibles is significantly lower than that of glasses prepared in Pt crucibles. In glasses prepared in Au crucibles, Pr^{3+} doping increases the dc conductivity and slightly decreases average conduction activation energy (Table 1). At contrary, in glasses prepared in Pt crucibles, doping with various forms of Pr decreases the dc conductivity and increases the average conduction activation energy (Fig. 1, Table 1). The most significant decrease of the conductivity is observed upon doping with metallic Pr. It can be influenced by an enhanced content of OH^- ions in these glasses [2,3].

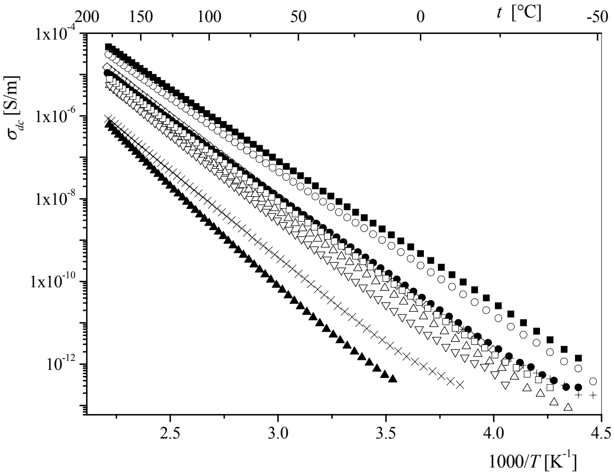


Fig. 1. Temperature dependences of dc conductivity, σ_{dc}, of 6T4P glasses, doped with 1000 wt-ppm Pr or Er added in different chemical forms, prepared in Au crucibles (••• “pure”, ooo metallic Pr), Pt crucibles (■ ■ ■ “pure“, □□□ Pr_2O_3, ∇∇∇ $PrCl_3$, ××× metallic Pr, ◊◊◊ $ErCl_3$, +++ Er_2O_3) and of 6T2P2P glasses doped with 1000 wt-ppm Er, prepared in Pt crucibles (▲▲▲“pure“, ΔΔΔ Er_2O_3).

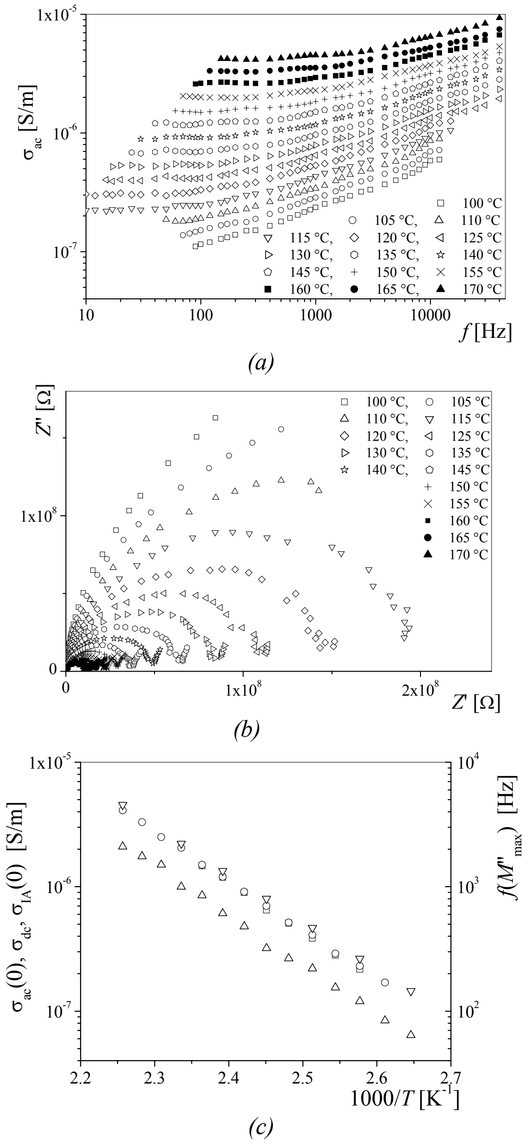
Table 1. Conduction activation energy, E_σ, dc conductivity at 333 K, σ_{333}, static permittivity, ε_s, pre-exponential factor, σ_o, high temperature activation energy, E_σ^*, for various tellurite glasses doped with 1000 wt-% of dopants in different chemical forms.

glass	crucible	dopant	E_σ [eV]	σ_{333} [S/m]	ε_s	σ_o [S/m]	E_σ^* [eV]
6T4P	Pt	pure	0.684	$7.4\cdot10^{-8}$	34.2	$3.5\cdot10^{3}$	0.706
6T4P	Pt	Pr_2O_3	0.742	$8.5\cdot10^{-9}$	27.2	$2.0\cdot10^{3}$	0.752
6T4P	Pt	$PrCl_3$	0.816	$2.7\cdot10^{-9}$	---	$1.2\cdot10^{3}$	0.833
6T4P	Pt	Pr metal	0.837	$4.0\cdot10^{-10}$	30.7	$6.2\cdot10^{3}$	0.881
6T4P	Pt	Er_2O_3	0.734	$1.0\cdot10^{-8}$	34.2	$1.9\cdot10^{3}$	0.743
6T4P	Pt	$ErCl_3$	0.769	$1.0\cdot10^{-8}$	---	$1.7\cdot10^{4}$	0.806
6T4P	Au	pure	0.734	$1.1\cdot10^{-8}$	32.4	$3.7\cdot10^{3}$	0.762
6T4P	Au	Pr metal	0.696	$4.3\cdot10^{-8}$	34.2	$4.2\cdot10^{3}$	0.727
6T2P2P	Pt	pure	0.966	$3.3\cdot10^{-11}$	32.4	$4.9\cdot10^{5}$	1.07
6T2P2P	Pt	Pr_2O_3	0.756	$5.4\cdot10^{-9}$	34.2	$1.8\cdot10^{3}$	0.763

In Fig. 1, temperature dependences of the dc conductivity of 6T4P glasses, “pure” and doped with Er, in various chemical forms, which are prepared in Pt crucibles, are shown. Upon doping, dc conductivity decreases and conduction activation energy increases (Table 1), almost identically for both $ErCl_3$ and Er_2O_3. Then, the temperature dependence of the dc conductivity is close to that of “pure” 6T4P prepared in an Au crucible. Doping with metallic Er decreases the conductivity and increases the conduction activation energy of 6T4P glass prepared in a Pt crucible most effectively (Table 1) [10].

In Fig. 1, temperature dependences of the dc conductivity of 6T2P2P glasses, “pure” and doped with 1000 wt-ppm Er_2O_3, prepared in Pt crucibles, are presented. The conductivity of “pure” 6T2P2P glasses is much lower than that of “pure” 6T4P glasses prepared in both crucibles. Upon doping, the conductivity of 6T2P2P glasses increases and conduction activation energy decreases (Table 1).

In Fig. 2a, frequency dependences of the ac conductivity, σ_{ac}, at various temperatures are presented for the 6T4P glass doped with 1000 wt-ppm Er_2O_3, prepared in a Pt crucible. From extrapolations of dependences to a zero frequency, $\sigma_{ac}(0)$ values are obtained. The temperature dependence of $\sigma_{ac}(0)$ is shown in Fig. 2c; it is identical with the temperature dependence of σ_{dc}. In the temperature region from 100 up to 170 °C, the activation energy is equal to 0.811 eV; the pre-exponential factor, $\sigma_o(0)$ is equal to $7.7 \cdot 10^3$ S/m. In Fig. 2b, impedance diagrams for this glass, in the same temperature interval are shown. Obtained values of $\sigma_{IA}(0)$ are the same as those obtained from the frequency dependence of σ_{ac}. These values of $\sigma_{IA}(0)$ are calculated from intercepts of circular arcs $Z''(Z')$ with Z' axis.



(a)

(b)

(c)

Fig. 2. 6T4P glasses doped with 1000 wt-ppm Er_2O_3, prepared in Pt crucibles,: a/ frequency dependences of the ac conductivity, σ_{ac}, at various temperatures; b/ impedance diagrams at various temperatures, c/ temperature dependences of the frequency of a modular spectrum maximum, $f(M''_{max})$ (ΔΔΔ), of $\sigma_{ac}(0)$ (ooo), of $\sigma_{IA}(0)$ (□□□), and of σ_{dc} (∇∇∇).

In Fig. 3, modular spectrums, $M''(f)$, of different glasses at 120 °C are shown. With increasing conductivity of the glass, the maximum of $M''(f)$ shifts to a higher frequency. Peaks are asymmetric and broadened compared to Debye-like spectrum. In Fig. 4a, the shift of modular peaks with increasing temperature is presented for 6T4P glasses, doped with 1000 wt-ppm Er_2O_3, prepared in Pt crucibles. This shift is temperature activated and its activation energy equals to 0.817 eV (Fig. 2c).

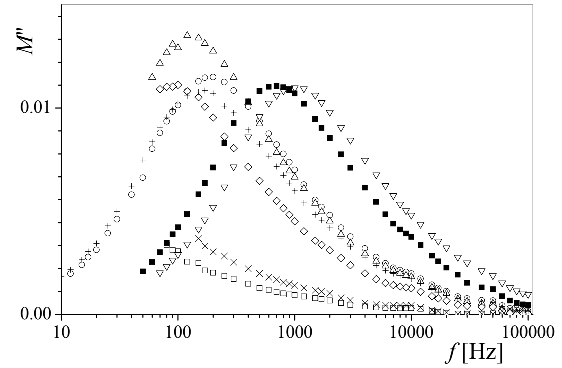
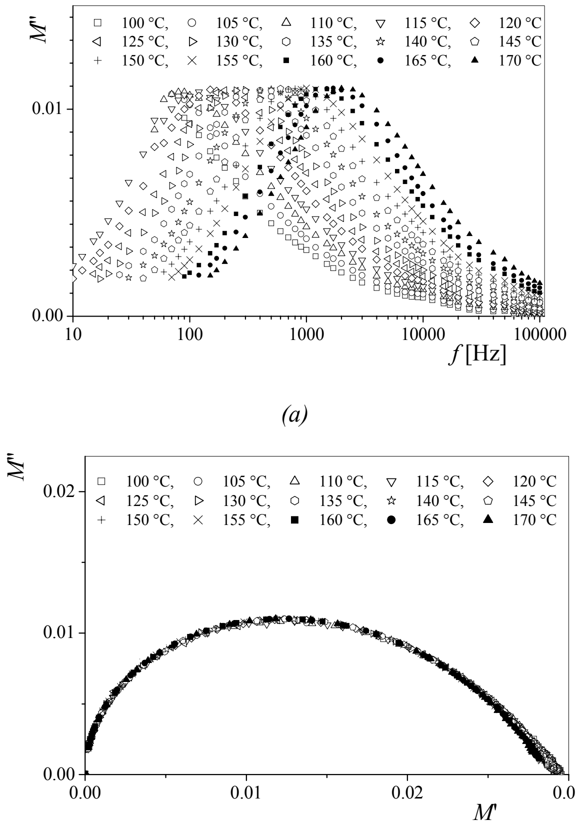


Fig. 3. Modular spectrums of 6T4P glasses, doped with 1000 wt-ppm Pr or Er added in different chemical forms, prepared in Au crucibles (ooo "pure", ■ ■ ■ metallic Pr), Pt crucibles (∇∇∇ "pure", ΔΔΔ Pr_2O_3, ××× metallic Pr, +++ Er_2O_3) and of 6T2P2P glasses doped with 1000 wt-ppm Er, prepared in Pt crucibles (□□□ "pure", ◊◊◊Er_2O_3) at 120 °C.



(a)

(b)

Fig. 4. Temperature dependence a/ of the shift of modular peaks b/ of the modular diagram for 6T4P glasses doped with 1000 wt-ppm Er_2O_3, prepared in Pt crucibles.

In Fig. 4b, modular diagrams, M'' against M', in the complex plane are shown for 6T4P glasses doped with

1000 wt-ppm Er_2O_3 at various temperatures. Reciprocal values of their intercepts with M' axis determine the static relative permittivity, ε_s, of the glass, at the corresponding temperature [11]. The same values of ε_s are obtained from frequency dependences of the complex permittivity by Kramers-Kronig relations. For the most part of glasses, values of ε_s are close to one another, ranging from 32.4 up to 34.2. The lowest permittivity is received for the 6T4P glass melted in Pt crucible upon doping with Pr_2O_3 (ε_s=27.2) or with metallic Pr (ε_s=30.7). The permittivity slightly increases with increasing temperature. Modular plots in the complex plane are formed by a circular arc (with a center below the M' axis), at the low-frequency part of the plot, and by a linear tail, at the high-frequency part of the plot.

In the TSDC measurements, three different types of depolarization peaks are observed. Temperatures of peaks of the first type range from -37 °C up to 69 °C. Their positions depend on the conductivity of corresponding glass; the higher the conductivity of the glass, the lower the temperature of the peak (Fig. 5). However, their activation energies, determined from a shift of the peak with increasing heating rate, are much smaller (0.5-0.7 eV) than conduction activation energies (0.68-0.97 eV). Peaks of the second type range from 100 up to 153 °C. Their positions do not correlate with the conductivity of glasses. Peaks of the third type take place at temperatures higher than 133 °C.

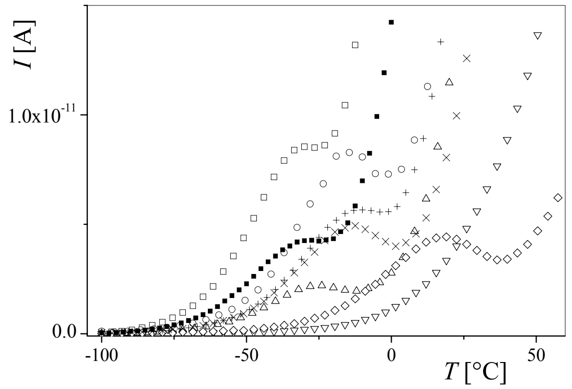


Fig. 5. TSDC plots of 6T4P glasses, doped with 1000 wt-ppm Pr or Er added in different chemical forms, prepared in Au crucibles (ΔΔΔ“pure”, ■ ■ ■ metallic Pr), Pt crucibles (□□□ “pure“, ooo Pr_2O_3, ◊◊◊ metallic Pr, +++ Er_2O_3) and of 6T2P2P glasses doped with 1000 wt-ppm Er, prepared in Pt crucibles (∇∇∇ “pure“, ××× Er_2O_3) for the first type of peaks at heating rate 5 °C.min^{-1}.

4. Discussion

In our glasses, temperature dependences of the dc conductivity (σ_{dc}) are Arrhenius-like,

$$\sigma_{dc} = \sigma_o \exp(-E_\sigma/kT) \qquad (1)$$

where σ_o is the pre-exponential factor, E_σ is the conduction activation energy, T is thermodynamic temperature, and k is Boltzmann constant. In semiconducting glasses, for a band mechanism of conduction, usually σ_o=10^5–10^6 S/m and $2E_\sigma \le E_o$, where E_o is the optical gap. In our glasses, values of σ_o are lower ($2\cdot10^3$-$5\cdot10^5$ S/m) than expected, and the value of E_σ (0.68-0.97 eV) has a reasonable value in comparison with E_o (≈2.5 eV) [3]. It indicates a significant shift of the Fermi level from the centre of the gap supported by a narrowing of the mobility gap compared to optical gap. Values of σ_o, E_σ, and σ_{333} (dc conductivity at 333 K) for different composition of glasses are given in Table 1. The conduction activation energy slightly decreases with decreasing temperature; its value, E_σ^*, at high temperatures is given in Table 1. Glasses prepared in gold or Pt crucibles have different colours as reactions with crucibles result in serious changes in tellurite polyhedrons [7,8]. Due to these changes, electrical conductivities of “pure” glasses prepared in different crucibles are significantly different. Because conduction activation energies of 6T4P glasses prepared in different crucibles are close to each other, probably, only concentration of charge carriers is different. Probably, incorporated Au^+ ions or Au nanoinclusions create traps for charge carriers. Pt nanoinclusions can create excessive charge carriers. However, with increasing concentration of dopants, conductivities of glasses prepared in different crucibles get closer to each other. Upon doping, the conductivity of more conducting 6T4P glass prepared in Pt crucibles decreases and gets closer to that of 6T4P glass prepared in Au crucible. In contrary, upon doping, the conductivity of low conducting 6T4P glass prepared in Au crucible increases and gets closer to that of 6T4P glass prepared in Pt crucible. Doping with metallic Pr is most effective for changing the conductivity of glasses prepared in both types of crucibles. Doping with this chemical form of Pr introduces the highest concentration of OH^- into the glass. Doping with Er, in the form of oxide or chloride, reduces the conductivity of glasses prepared in Pt crucibles and shifts the conductivity closer to the conductivity of “pure” glass prepared in Au crucible. Doping also heavily influences the electrical conductivity of glasses prepared in the Au crucible. It is probable that incorporated Au inclusions act as traps for charge carriers. Upon doping, this decrease of charge carriers is partly compensated by an incorporation of metallic Pr ions and OH^- ions, which act as sources for excessive charge-carriers. In contrary, in glasses prepared in Pt crucibles, Pt inclusions are sources of excessive charge carriers, which are then caught upon doping.

The ac conductivity of semiconducting glasses increases with increasing frequency and its low frequency limit is equal to the dc conductivity. The frequency dependence of the ac conductivity can be described by the equation

$$\sigma_{ac} = \sigma_{dc} + A f^n \qquad (2)$$

where A depends on the temperature and electrodes, $n = 0.8$-1.0. In our glasses, value of n (0.3-0.4) is smaller than expected. It could be connected with inhomogeneities of glasses, with nanoinclusions or with a start of crystallization.

Imaginary part of the complex electrical modulus, M'', is given by the relation

$$M'' = \varepsilon'' / (\varepsilon'^2 + \varepsilon''^2) \tag{3}$$

where ε' and ε'' are the real and imaginary parts of the permittivity. Peaks $M''(f)$ are Debye-like, but asymmetric and broadened what is typical for disordered materials. The activation energy of this relaxation is equal to the conduction activation energy (Fig. 2c). A height of the maximum depends on the composition of the glass (Fig. 3) but it is independent of the temperature (Fig. 4b). This relaxation has the same mechanism and the same activation energy as the dc conductivity.

Plots of thermally stimulated depolarization currents are characterized by asymmetric bell shaped peaks, which appear at temperatures when conductivity of the glass is, under normal conditions, between 10^{-12} S/m and 10^{-10} S/m [12]. This is fulfilled for the first group of peaks. The origin of second group of peaks is not clear. They can result from some dipolar, quadruple or ionic species.

5. Conclusions

Glasses prepared in gold or Pt crucibles have different colours as reactions with crucibles result in serious changes in tellurite polyhedrons [7,8]. Due to these changes, electrical conductivities of "pure" glasses prepared in different crucibles are significantly different. Because conduction activation energies of 6T4P glasses prepared in different crucibles are close to each other, probably, only concentration of charge carriers is changed. Incorporated Au^+ ions or inclusions create traps for charge carriers. Pt inclusions can create excessive charge carriers. With increasing concentration of dopant, conductivities of glasses prepared in different crucibles get closer to each other. A low frequency limit of the ac conductivity is equal to the dc conductivity. The relaxation detected by modular spectroscopy has the same mechanism as the dc conductivity. The low temperature TSDC peaks are connected with the dc conductivity of glasses.

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