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Structure and optical properties of $TeO_2 \cdot PbCl_2 \cdot PbF_2$ glasses doped with Pr and Er, prepared in Au or Pt crucibles

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Influence of crucibles (Au or Pt) on the structure and optical properties of $60TeO_2 \cdot 40PbCl_2$ and $60TeO_2 \cdot 20PbCl_2 \cdot 20PbF_2$ glasses, "pure" and doped with 1000 wt-ppm Pr^{3+} or Er^{3+}, which are added as metals, chlorides, or oxides, is reported. In glasses prepared in Au crucibles, the absorption edge is shifted to shorter wavelengths and the color of the glass is changed from red or orange to yellowish or dirty white, respectively. In the range of 640-700 nm, five Pr or six Er photoluminescence (PL) peaks are observed. In the range of 200 – 1200 cm^{-1}, Raman scattering (RS) spectrums show 6 (for Pr doping) or 7 (for Er doping) bands. Spectrums are deconvoluted using symmetrical Gaussian functions. Relative intensities of PL and RS peaks depend on the chemical form of dopants and on the material of the crucible. Positions of these bands are almost independent of these conditions. On basis of RS spectrums, short-distance ordering of glasses is discussed. Results are compared with those which we have obtained for $70TeO_2 \cdot 30PbCl_2$ glasses.

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Keywords: Tellurite/lead chloride/lead fluoride glasses, Pr^{3+} or Er^{3+} doping, Au or Pt crucibles, Raman scattering, Optical absorption, Photoluminescence

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1. Introduction

Tellurite glasses are of a great scientific and technological interest due to their promising optical properties [1]. They are characterized by a wide transmission range (≈400 nm to 6 μm), lack of toxicity, good glass stability and mechanical strength, good corrosion and 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 [2-7]. These properties are connected with the local order in neighborhood of Te atoms. Good thermal and mechanical properties enable a fiber production [3]. Heavy ions influence the glass forming and optical absorption ability; they shift the IR cut-off towards longer wavelengths [4-13]. Tellurite glasses are interesting also as non-linear optical elements [14-16]. The glasses are used as optical components (windows, prisms, laser glasses), and in fiber optics (optical fibers, fibrous optical amplifiers, and fibrous lasers) [17-20]. The glasses are used also in fiber optics communications [3].

The aim of this work is 1/ to present the Raman scattering, optical absorption, and photoluminescence data of $60TeO_2 \cdot 40PbCl_2$ (6T4P) and $60TeO_2 \cdot 20PbCl_2 \cdot 20PbF_2$ (6T2P2P) glasses, prepared in Pt or Au crucibles, "pure" and doped with 1000 wt-ppm Pr^{3+} or Er^{3+} ions in various chemical forms, 2/ to discuss the influence of the material of crucibles on the microstructure and optical properties of the glasses, 3/ to discuss the relationship between the microstructure and physical properties of the glasses, and 4/ to compare results with those obtained for $70TeO_2 \cdot 30PbCl_2$ (7T3P) glasses [7, 21, 22].

2. Experimental details

Before a synthesis, all starting components of 6T4P and 6T2P2P glasses, are dried under vacuum (230 °C, 5 h), 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 a form from stainless steel 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 [5-7, 21-23]. Upon preparation in Pt crucibles, glasses are red/orange; upon preparation in Au crucibles, glasses are yellowish/dirty white.

The absorption, photoluminescence (PL) and Raman scattering (RS) spectra are measured at RT. For absorption measurements, Specord UV-VIS and Specord 61 NIR spectrometers, Carl Zeiss, Jena, (200-3000 nm), and deuterium discharge tube as a source are used. PL (450-

700 nm) and RS (150-3000 cm^{-1}) spectrums are measured by Raman spectrometer Dilor-Jobin Yvon-Spex, type LabRam, with He-Ne laser (632.8 nm). Both PL and RS spectrums are deconvoluted using symmetrical Gaussian functions [5, 6]. Energies, amplitudes, and half-widths of band maximums are free parameters for each maximum.

3. Results

In Fig. 1, short-wavelength absorption edges of "pure" 6T4P glasses prepared in gold and platinum crucibles are compared. In both "pure" and doped 6T4P glasses prepared in Pt crucibles, an absorption band on the absorption edge is observed [5, 7, 22]. Upon doping, the edge is steeper and the absorption band is weaker but it appears at the same wavelength. The sharpest edge and almost negligible absorption band are observed upon doping with metallic Pr (Fig. 2). In glasses prepared in Au crucibles, the edge is shifted to a shorter wavelength (Fig. 1) and the color of glasses is changed from red to yellowish or dirty white. In glasses prepared in Au crucibles, only a negligible difference of absorption edges between "pure" and doped glasses is observed; absorption bands of Pr^{3+} or Er^{3+} are distinct in all doped glasses (Fig. 3) [5-7, 21, 22].

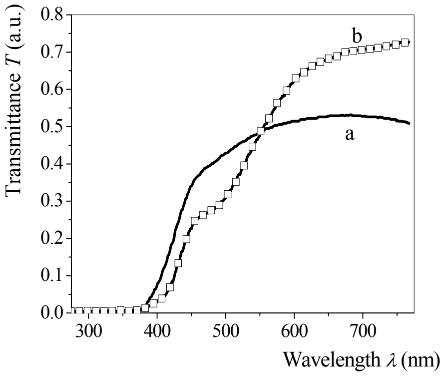


Fig.1. Absorption edges of "pure"6T4P glasses, prepared in a/ Au and b/ Pt crucibles.

In 6T2P2P glasses, prepared in Pt crucibles, two absorption bands in the region of the absorption edge are observed. Upon doping, in these glasses, the absorption edge is steeper and shifted to longer wavelengths (Fig. 3).

In the range of 640-690 nm, five PL bands, at 645.3(3), 652.4(3), 659.3(9), 659(1), and 663.3(1) nm, are observed both in "pure" and Pr-doped 6T4P glasses prepared in both crucibles (Figs. 4, 5). Six PL peaks, at 648(2), 652.9(7), 659(1), 660(1), 663.2(4), and 669(1), are observed in "pure" and Er-doped 6T2P2P glasses and in Er-doped 6T4P glasses (Fig. 6). Relative intensities of PL bands depend on the chemical form of dopants and on the material of the crucible. Positions of these bands are almost independent of the concentration [5, 7] and chemical form of dopants, and of the material of the crucible. The glass composition does not influence the photoluminescence of Er^{3+} significantly.

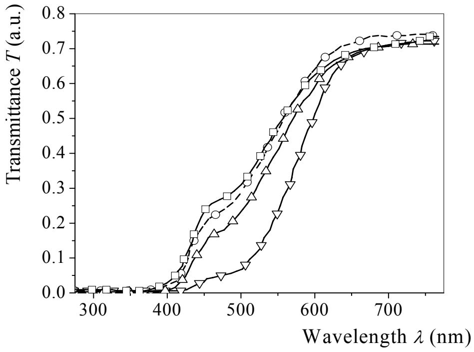


Fig. 2. Absorption edges of "pure" and doped (1000 wt-ppm Pr in various chemical forms) 6T4P glasses, prepared in Pt crucibles, measured at RT ("pure"- □□□, Pr_2O_3 - ooo, $PrCl_3$ - ΔΔΔ, metallic Pr - ∇∇∇).

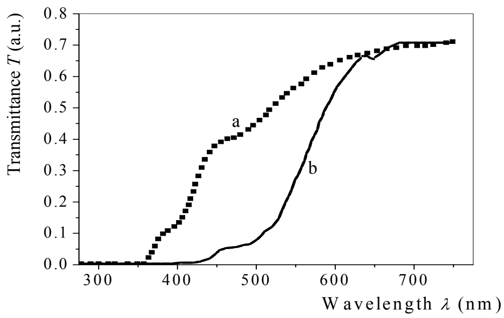
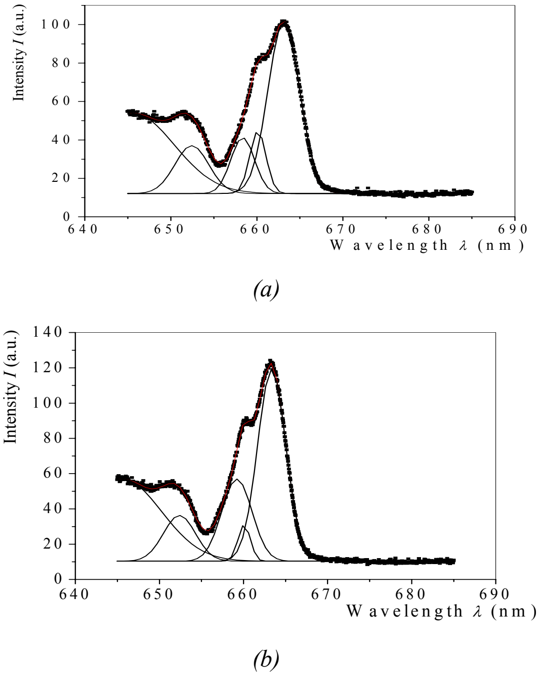


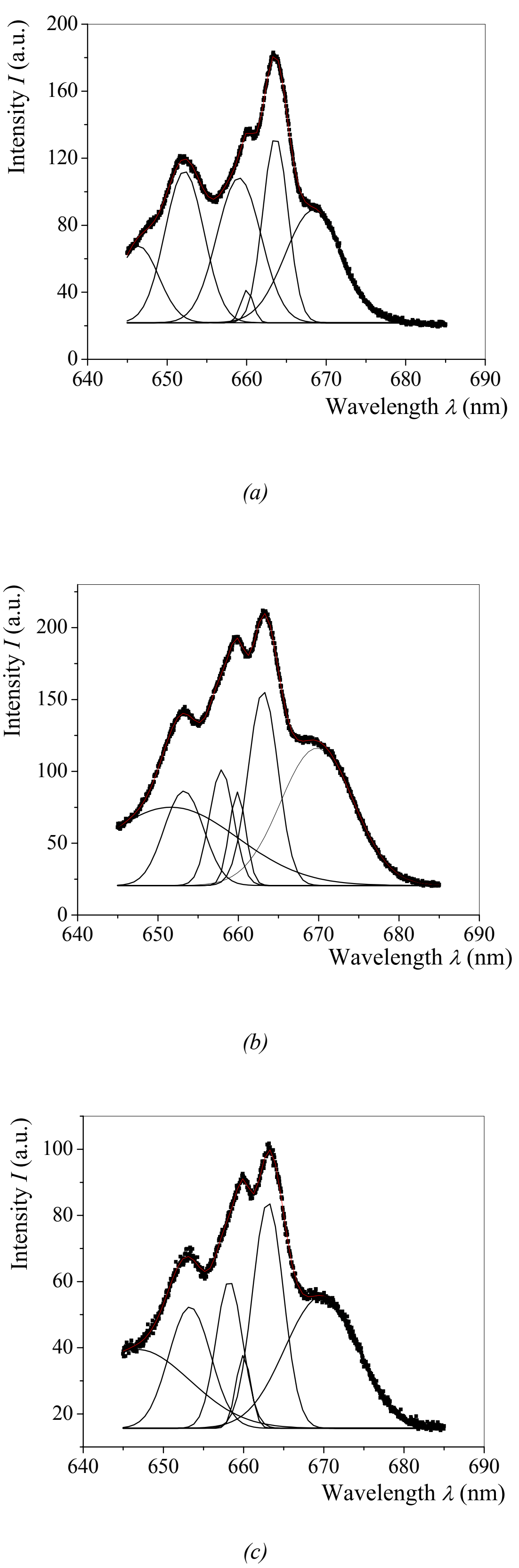
Fig. 3. Absorption edge of 6T2P2P glasses prepared in a Pt crucible: (a) "pure" glass; (b) glass doped with 1000 wt-ppm of Er_2O_3.



(a)

(b)

Fig. 4. PL spectra of 6T4P glasses prepared in a/ Au and b/ Pt crucibles.

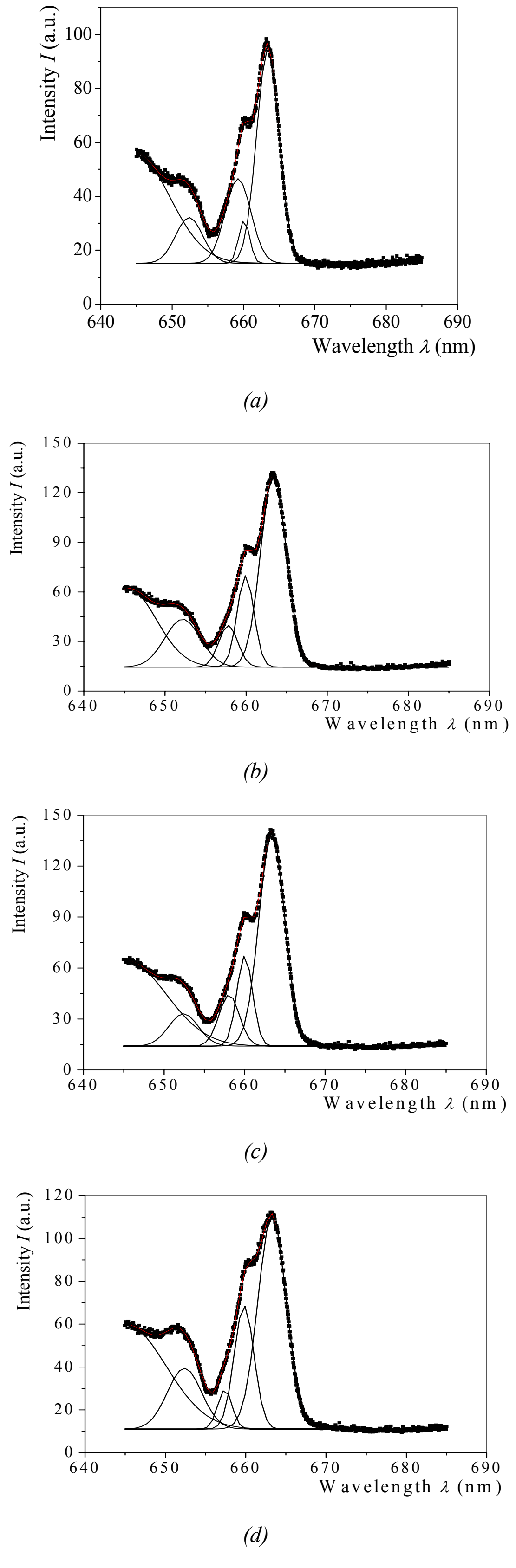


(a)

(b)

(c)

Fig. 6. Deconvoluted PL spectra of 6T2P2P glasses, prepared in Pt crucibles: a/ "pure", b/ doped with Er_2O_3, and c/ of 6T4P glasses, prepared in Pt crucibles, doped with Er_2O_3.



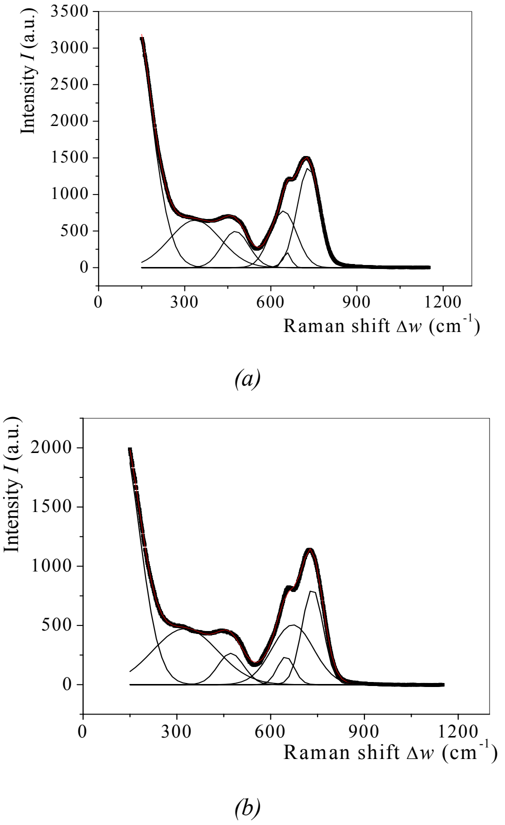
(a)

(b)

(c)

(d)

Fig. 5. Deconvoluted PL spectra of T6P4 glasses a/ doped with Pr_2O_3, prepared in Pt crucible, b/ doped with $PrCl_3$, prepared in Pt crucible, c/ doped with metallic Pr, prepared in Pt crucible, and d/ doped with Pr, prepared in Au crucible.



(a)

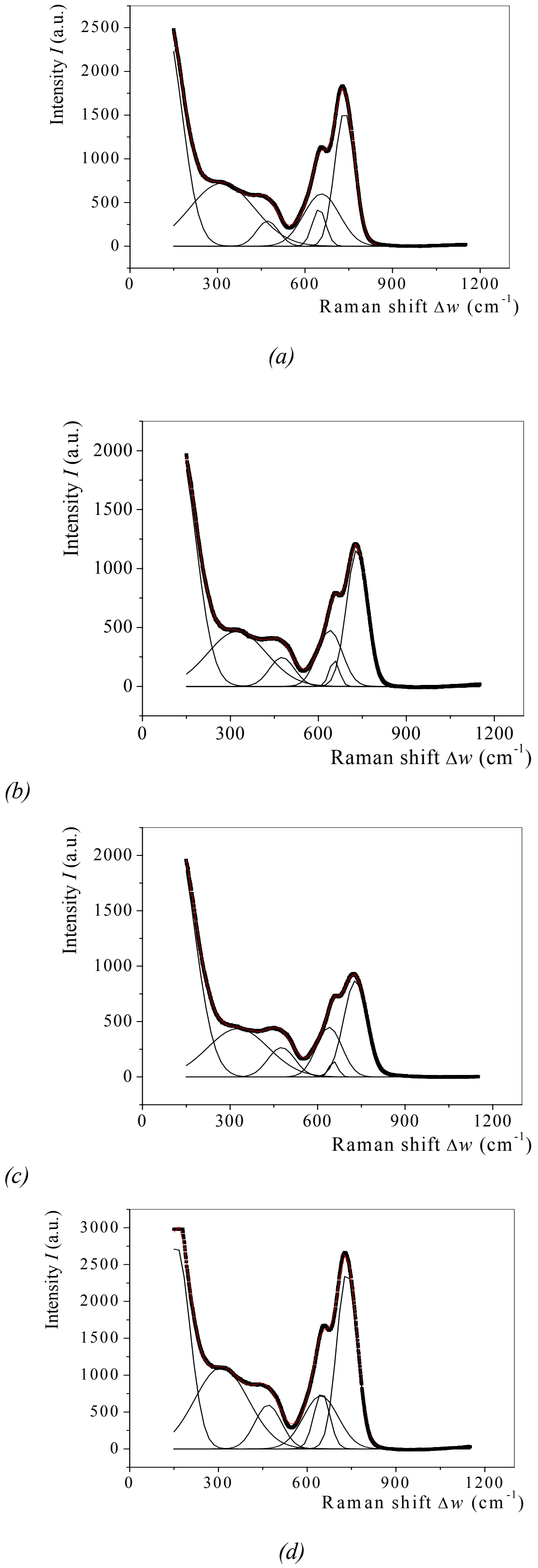
(b)

Fig. 7. Deconvolution of RS spectra in 6T4P glasses, prepared in a/ Au crucibles, and b/ Pt crucibles.

In the range of 200 – 1200 cm^{-1}, in 6T4P glasses, both "pure" and doped with Pr and prepared in both Au and Pt crucibles, six RS peaks, at 122(10), 323(9), 474(2), 643(7), 656(4), and 732(3) cm^{-1}, are observed (Figs. 7, 8). In 6T4P glasses doped with Er and in 6T2P2P glasses, both "pure" and doped with Er, prepared in Pt crucibles, seven RS peaks, at 95(14), 323(25), 494(10), 598(15), 647(4), 727(5), and 862(10) cm^{-1}, are observed (Figs. 9, 10). Relative intensities of RS peaks depend on the chemical form of dopants and on the material of the crucible. Positions of these bands are independent of the dopant concentration [5, 7] and its chemical form, and on the material of the crucible. There is a pronounced difference between RS spectrums of Pr-doped and Er-doped glasses.

4. Discussion

Since the form, slope, and position of the absorption edge depend on the material of the crucible and chemical form of dopants, colors of glasses prepared under different conditions are different. The absorption band (near 480 nm) in the region of the absorption edge is assigned to Pt colloids [24], in both "pure" and doped T6P4 and T6P2P2 glasses prepared in Pt crucibles. In T6P2P2 glasses prepared in Pt crucibles, we observe another band which results, probably, from an interaction of these colloids with fluorine. In both glasses prepared in Pt crucibles, these absorption bands contribute to the shift of the absorption edge towards a longer wavelength. In glasses prepared in



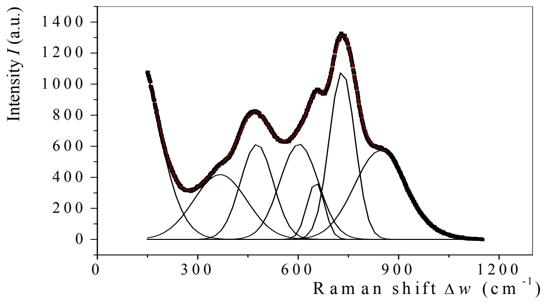
(a)

(b)

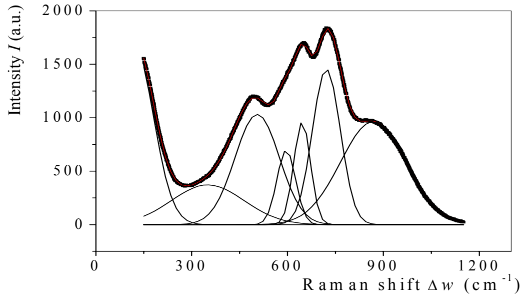
(c)

(d)

Fig. 8. Deconvoluted RS spectra of 6T4P glasses doped with Pr in various chemical forms and prepared in different crucibles: a/ metallic Pr; Pt crucible, b/ Pr_2O_3; Pt crucible, c/ metallic Pr, Au crucible, and d/ $PrCl_3$, Pt crucible.

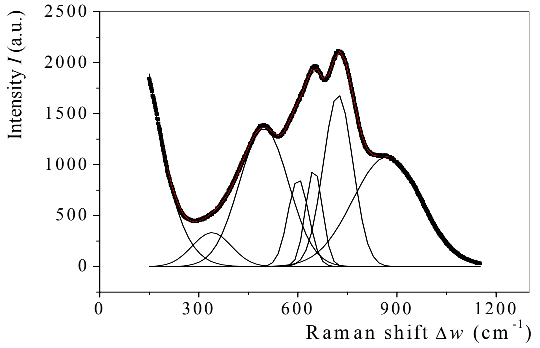


(a)

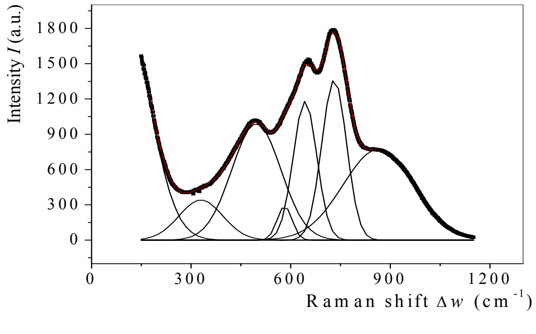


(b)

Fig. 9. Deconvoluted RS spectrums of T6P2P2 glasses, prepared in Pt crucibles, a/ "pure" and b/ doped with Er_2O_3.



(a)



(b)

Fig. 10. Deconvoluted RS spectrums of T6P4 glasses, prepared in Pt crucibles, and doped with a/ Er_2O_3, and b/ $ErCl_3$.

Au crucibles, we do not see any absorption band Au nanoparticles have no absorption band in the region of the absorption edge [25].

In the range of 640-690 nm, five PL bands (645.3(3), 652.4(3), 659.3(9), 659(1), and 663.3(1) nm) are observed both in "pure" and Pr-doped 6T4P glasses which are prepared in both Pt and Au crucibles. They are attributed to $^3P_0 \rightarrow {}^3F_2$, $^3P_1 \rightarrow {}^3F_2$, $^3P_0 \rightarrow {}^3F_3$, $^3P_1 \rightarrow {}^3F_3$, and $^3P_1 \rightarrow {}^3F_4$ transitions in Pr^{3+} ions [7, 8]. Traces of Pr^{3+} ions must be present also in "pure" 6T4P glasses. In the range of 640-690 nm, in glasses containing Er^{3+} and in "pure" 6T2P2P glasses, we can see six PL bands (648(2), 652.9(7), 659(1), 660(1), 663.2(4), and 669(1)) which describe the structure of the "red" band attributed to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions. "Pure" 6T2P2P glasses must also contain traces of Er^{3+} ions. In the range of 640-700 nm, six PL peaks, at 641.5(1), 647.1(4), 652.4(1), 660.8(2), 662.7(4), and 664.5(2) nm, are also observed both in "pure" and Pr-doped 7T3P glasses prepared in both crucibles [5, 7]. It means that the composition and structure of glasses does not influence seriously positions of PL bands and type of optical transitions.

In the range of 200 - 900 cm^{-1}, in 6T4P glasses, both "pure" and doped with Pr, prepared in Au or Pt crucibles, six RS peaks, at 122(10), 323(9), 474(2), 643(7), 656(4), and 732(3) cm^{-1}, are observed (Figs. 7, 8). In 6T4P glasses doped with Er and in 6T2P2P glasses, both "pure" and doped with Er, prepared in Pt crucibles, seven RS peaks, at 95(14), 323(25), 494(10), 598(15), 647(4), 727(5), and 862(10) cm^{-1}, are observed. These RS spectrums are similar to those of pure and binary TeO_2 glasses [10]. An asymmetrical $[TeO_4]$ trigonal bipyramid (tbp), in which one of the equatorial sites is occupied by lone pair electrons, represents the structural unit forming "pure" TeO_2 glass. Upon inclusion of modifiers or intermediates, the coordination state of Te changes, from TeO_4 tbp through an intermediary $[TeO_{3+1}]$ polyhedron to a $[TeO_3]$ trigonal pyramid (tp), and the concentration of non-bridging oxygen increases [11]. Peaks at 730±3 cm^{-1} and 651±5 cm^{-1} are attributed to stretching vibrations of tp and tbp structural units, respectively. The small peak (in Pr-doped glasses), at 645 cm^{-1}, comes, probably, from intermediate TeO_{3+1} polyhedrons. These three structural units (tp, tbp, TeO_{3+1}) are joined with their vertexes into linear or ring chains. The peak near 484 cm^{-1} corresponds to bending or symmetrical stretching vibrations of Te-O-Te linkages of vertex-sharing tbp units [8-10, 26-37]. Its intensity can be considered a measure of the connectivity of the network [12]. Pb^{2+} enters the glass as an intermediate, increases the number of non-bridging oxygens and decreases the coordination number of Te [13]. Peak at 862 cm^{-1} comes probably from Pb-O-Pb or Pb-O stretching vibrations or from stretching vibrations of a tp with non-bridging oxygen [14-16]. At this Raman shift, a vibration from a structural unit similar to the γ-TeO_2 structural unit is also expected [14-17]. It is not yet clear why this structural unit is invoked by a presence of Er. The low frequency peaks in 6T4P and 6T2P2P glasses prepared in both crucibles are assigned to rotational and torsional modes of Te-O-Te linkages [10]. In glasses prepared in gold crucibles, the peak at 468 cm^{-1} is more pronounced than that in glasses doped with Er. It indicates a better connectivity of the glass network in these glasses. Also the intensity ratio of tbp (654 cm^{-1}) and tp (735 cm^{-1}) peaks is significantly larger, in these glasses. The intensity ratio of both peaks determines the ratio of tbp and tp structural units [6]. It seems that the presence of Er increases the number of TeO_3 structural units and decreases the number of Te-O-Te linkages [14]. Raman spectra of the 7T3P glasses, "pure" and doped with Pr, were fitted by six Gaussian bands centered at 184(2), 217(7), 321(2), 468(2), 654(9), 735(5) cm^{-1}, and one small peak at 650 cm^{-1}. Positions of four high frequency peaks and of the small peak are close to those of Pr-doped T6P4 glasses. It means that the composition of glasses does not influence seriously positions of RS bands in halotellurite glasses.

In glasses prepared in gold crucibles, the peak at 468 cm^{-1} is more pronounced than that in glasses doped with Er. It indicates a better connectivity of the glass network in these glasses. Also the intensity ratio of tbp (654 cm^{-1}) and tp (735 cm^{-1}) peaks is significantly larger, in these glasses. The intensity ratio of both peaks determines the ratio of tbp and tp structural units [6]. It seems that the presence of Er increases the number of TeO_3 structural units and decreases the number of Te-O-Te linkages [14].

A strong influence of crucible and chemical form of dopants is observed also in electrical and dielectric properties of halotellurite glasses. Electrical conductivities of 'pure' glasses prepared in different crucibles are significantly different. Upon doping, conductivities of glasses prepared in both crucibles are closer to each other. It is probable that incorporated Au or Pt colloids change the conductivity of glasses [38] due to interaction of colloids with charge carriers.

4. Conclusions

Glasses prepared in gold or Pt crucibles have different positions and slopes of the absorption edge. Therefore, they have different colors. In the range of 640-700 nm, PL bands of glasses containing Pr can be attributed to $^3P_0\rightarrow{}^3F_2$, $^3P_1\rightarrow{}^3F_2$, $^3P_0\rightarrow{}^3F_3$, and $^3P_1\rightarrow{}^3F_3$ transitions in Pr^{3+} ions [7, 8]. In PL spectrum of glasses containing Er^{3+} dopants, we can see the structure of the band $^4F_{9/2}\rightarrow{}^4I_{15/2}$. In the range of 200 – 1200 cm^{-1}, in 6T4P and 6T2P2Pglasses prepared in Pt crucibles, six RS peaks are observed. Relative intensities of PL and RS bands depend on the chemical form of dopants and on the material of the crucible. Positions of these bands are almost independent of chemical forms of dopants and of the material of a crucible.

Acknowledgements

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