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Influence of preparation technique and Pr^{3+} doping on the absorption edge, photoluminescence, and Raman spectra of $70TeO_2 \cdot 30PbCl_2$ glasses

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Tellurite glasses, $70TeO_2.30PbCl_2$, were prepared in Au and Pt crucibles. Pr^{3+} ions were added in different chemical forms (metals, chlorides, oxides), in concentrations of 500 – 1500 wt-ppm. In the range of 640-700 nm, six photoluminescence (PL) peaks were observed, at 641.5, 647.1, 652.4, 660.8, 662.9, and 664,5 nm, both in "pure" and doped glasses. In the range of 200 – 1200 cm^{-1}, seven Raman scattering (RS) peaks were observed, at 184, 217, 321, 468, 654, 735 cm^{-1}, and a small peak at 650 cm^{-1}. Both spectra were deconvoluted using symmetrical Gaussian functions. Energies, amplitudes and half-widths of band maximums were free parameters. Doping with Pr^{3+} and reactions with crucibles result in structural changes of tellurite polyhedrons. The influence of Pr^{3+} on the local structure is similar to that of incorporated Au^+ from the crucible. Relative intensities of PL bands and RS ones depend on the concentration of Pr^{3+} and on the material of the crucible. Positions of these bands are independent of Pr^{3+} concentration and of the material of the crucible. The form, slope, and position of the absorption edge depend on the material of the crucible, and on the concentration and chemical form of Pr. Absorption edge of glasses prepared in Au crucibles is much sharper and shifted to shorter wave-length in comparison to that of glasses prepared in Pt crucibles.

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Keywords: Tellurite/lead chloride glasses, Pr^{3+} doping, Absorption, Photoluminescence, Raman scattering, Au, Pt crucibles

1. Introduction

Tellurite glasses are of a great scientific and technological interest due to their promising optical properties [1]. Their most important advantages are: wide transmission range (≈400 nm to 6 μm), lack of toxicity, good glass stability and 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. The glasses can be used in optical components (windows, prisms, laser glasses) or in fiber optics communications [2]. In binary and ternary systems, heavy ions influence the glass forming ability, absorption ability and shift the IR cut-off towards longer wavelengths.

The aim of this work is to present the absorption, photoluminescence and Raman spectra of tellurite/chloride glasses, $70TeO_2 \cdot 30PbCl_2$, doped with Pr^{3+} ions in various concentrations and chemical forms, which are prepared in Pt or Au crucibles. Experimental results are discussed from the point of view of the microstructure and optical properties of glasses.

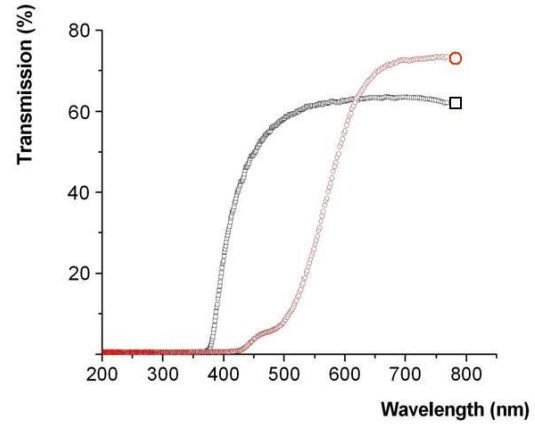
2. Experimental details

Studied tellurite/chloride glasses, $70TeO_2 \cdot 30PbCl_2$ (7T3P), were prepared using the method of a „divided ampoule" [3, 4]. They were doped with praseodymium (0 - 1500 wt-ppm), which was added as metal (Pr), chloride ($PrCl_3$) or oxide (Pr_2O_3). Glasses were prepared in Pt or Au crucibles. Samples prepared in Pt and Au crucibles were orange or yellowish, respectively. Absorption, photoluminescence and Raman spectra were measured at room temperature. For absorption measurements, Specord UV-VIS and Specord 61 NIR spectrometers, Carl Zeiss, Jena, (200-3000 nm), and deuterium discharge tube as a source were used. Photoluminescence (450-700 nm) and Raman (150-3000 cm^{-1}) spectra were measured using Raman spectrometer Dilor-Jobin Yvon-Spex, type LabRam. He-Ne laser (632.8 nm) was used as the excitation source.

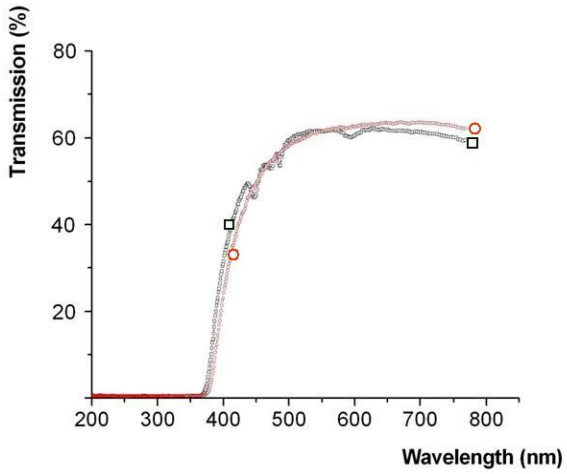
3. Results and discussion

In Fig. 1a, absorption edges of "pure" 7T3P glasses prepared in gold and platinum crucibles are compared. In „pure" glasses, prepared in Pt crucibles, the extrapolated short-wave absorption cut off (E_{g1}) is located at 509 nm. In both "pure" and doped glasses prepared in Pt crucibles, a step on the short-wave absorption edge is observed, near 490 nm. Due to this step, the effective short-wave cutoff (E_{g2}) is shifted to 412 nm. In glasses prepared in Au crucibles, no step at the absorption edge is observed; the edge is shifted to a shorter (370 nm) wavelength. Only a

slight difference of the absorption edge between "pure" and doped 7T3P glasses, prepared in Au crucibles, is observed. In doped glasses, absorption bands of Pr^{3+} are distinct (Fig. 1b). For glasses prepared in Pt crucibles, the influence of various concentrations of metallic Pr (0-1500 wt-ppm) on the position and slope of the absorption edge is presented in Fig. 2a. Upon doping, the absorption edge is flatter and shifted to shorter wavelengths. The influence of the chemical form of Pr on the absorption edge is presented in Fig. 2b. Doping with Pr_2O_3 brings about the most significant shift of the absorption edge to a shorter wavelength. As the form, slope, and position of the absorption edge depend on the material of the crucible and on the concentration or chemical form of Pr, colors of glasses prepared under different conditions are different.

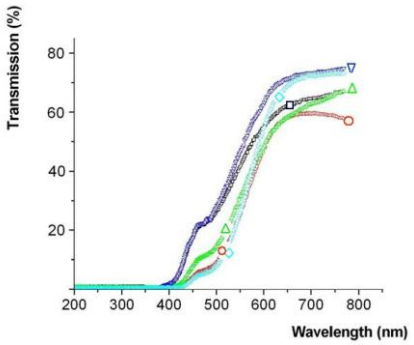


a



b

Fig. 1. Absorption edges of a/ "pure" 7T3P glasses, prepared in Pt (○, red) and Au (□□□, black) crucibles, b/ „pure" and doped 7T3P glasses prepared in Au crucibles ("pure" (ooo, red), and doped (□□□, black) with 1000 wt-ppm $PrCl_3$).



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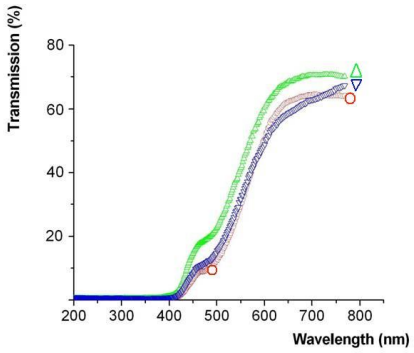
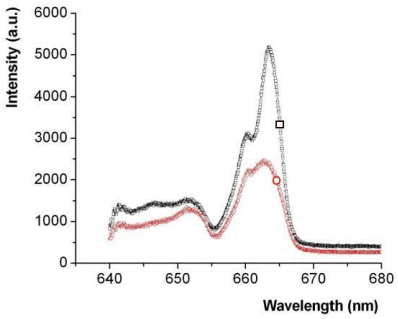


b

Fig. 2. Absorption edges of 7T3P glasses, prepared in Pt crucibles, a/ doped with metallic Pr ("pure", ◊◊◊ (turquoise), 500 wt-ppm, □□□ (black), 800 wt-ppm, ooo *(red), 1000 wt-ppm, ΔΔΔ (green), 1500 wt-ppm, ∇∇∇ (blue)), and b/ doped with 1000 wt-ppm Pr^{3+} (metallic Pr, ∇∇∇ (blue), Pr_2O_3, ΔΔΔ (green), $PrCl_3$,* ooo *(red)).*



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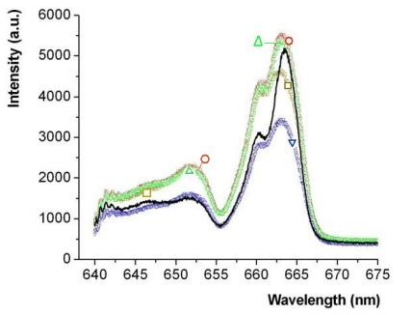
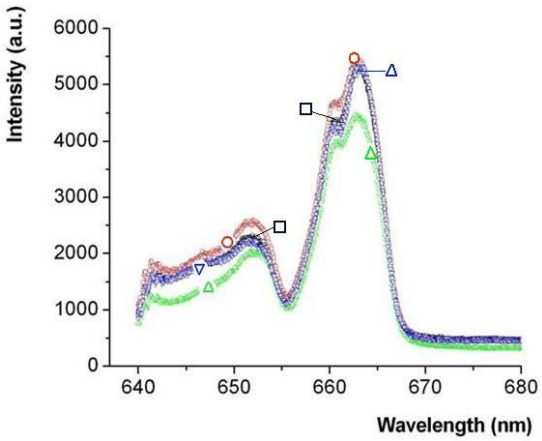


b

Fig. 3. Photoluminescence spectra of 7T3P glasses a)"pure" glasses, prepared in Pt (□□□, black) or Au (○○○, red) crucibles; b) prepared in Pt crucibles, doped with Pr in a metallic form (500 wt-ppm, □□□ (brown), 800 wt-ppm, ○○○ (red), 1000 wt-ppm, ΔΔΔ (green), 1500 wt-ppm, ∇∇∇ (blue), "pure" - full line).

Influences of the crucible (Pt or Au) and Pr^{3+} concentration (in a metallic form) on the photoluminescence (PL) spectrum of 7T3P glasses are shown in Fig. 3a or 3b, respectively. The influence of a chemical form of Pr^{3+} on the PL spectra is shown in Fig. 4. The experimental dependences were fitted by a sum of symmetrical Gaussian distributions (Figs. 5, 6). Energies of band maximums, amplitudes and half-widths were free parameters. In the range of 640-700 nm, six PL peaks, centered at 641.5(1), 647.1(4), 652.4(1), 660.8(2), 662.7(4), 664.5(2) nm, were observed, both in pure and doped glasses. The same positions of these bands were found in glasses prepared in both gold and platinum crucibles. However, relative intensities of these bands depended on the chemical form and concentration of Pr^{3+}, and on the material of the crucible. Supposing that also "pure" glasses contain traces of Pr^{3+} these bands 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 [5-8]. $PbCl_2$ component can enhance the up-conversion intensity [9].



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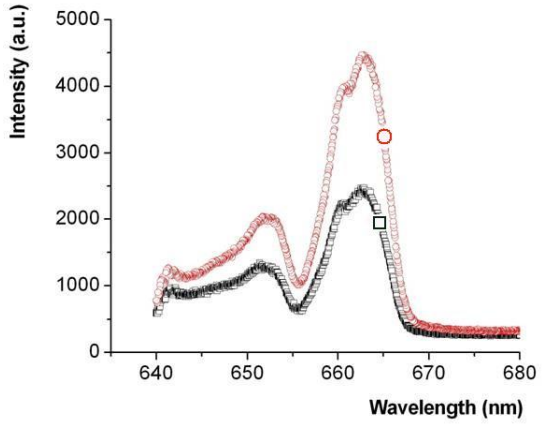
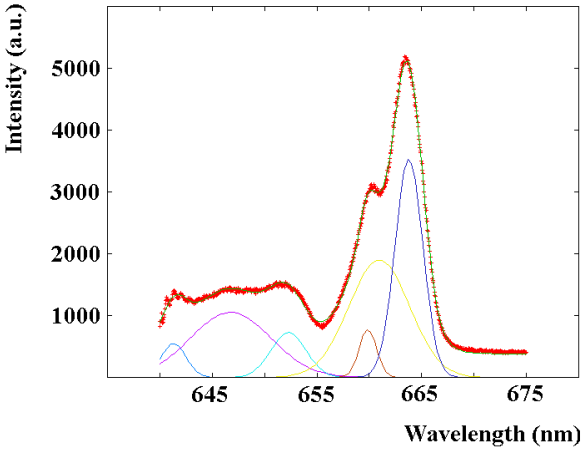


b

Fig. 4. Influence of the chemical form of Pr on the PL spectra of 7T3P glasses prepared in a/ Pt crucibles (1000 wt-ppm Pr_2O_3, □□□ (black), 1000 wt-ppm $PrCl_3$, ○○○ (red), 1000 wt-ppm Pr, ∇∇∇ (blue), and in an Au crucible (1000 wt-ppm $PrCl_3$, ΔΔΔ (green),) b/ Au crucibles ("pure", □□□ (black), 1000 wt-ppm $PrCl_3$, ○○○ (red)).



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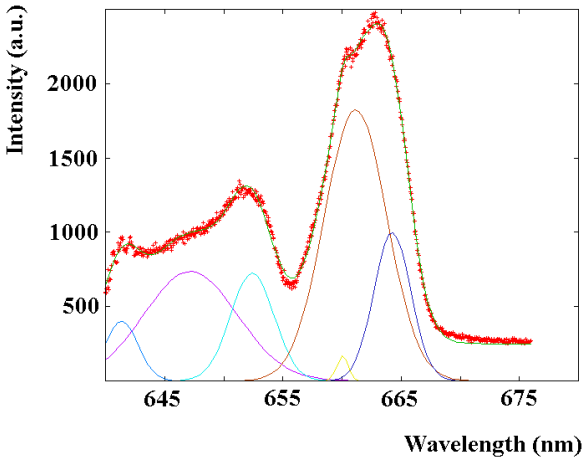

b

Fig. 5. Deconvolution of PL spectra in undoped 7T3P glasses prepared in a/ Pt, b/ Au crucibles.

In Figs. 7, 8, Raman spectra of the T7P3 glasses are presented. No systematic influence of the crucible or Pr^{3+} doping in any chemical form on the positions of RS bands was observed. (Only peaks of "pure" T7P3 glass prepared in a Pt crucible are slightly shifted to smaller wave numbers). Experimental dependences were fitted by a sum of Gaussian distributions. 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}, were determined (Figs. 9,10). In the range of 350 - 900 cm^{-1}, the spectra are similar to those of pure and binary TeO_2 glasses [10-12]. The structural unit making up TeO_2 glass is an asymmetrical [TeO_4] trigonal bipyramid (tbp) in which one of the equatorial sites is occupied by a lone pair of electrons. Upon inclusion of modifiers or intermediates, the coordination state of Te changes from TeO_4 trigonal bipyramids (tbp) by means of an intermediary [TeO_{3+1}] polyhedron to [TeO_3] trigonal pyramids (tp), and concentration of non-bridging oxygen increases [13]. Peaks at 735 and 654 cm^{-1} are attributed to stretching vibrations of TeO_3 trigonal pyramids (tp) or those of TeO_4 trigonal bipyramids (tbp), respectively. The small peak at 650 cm^{-1} probably comes from intermediate TeO_{3+1} polyheders. (This peak seems to be significant for the

spectrum around 650 cm^{-1}. Its intensity increases significantly in 'pure' glasses prepared in Pt crucibles.) These three structural units are connected each other with their corners into linear or ring chains. The peak at 468 cm^{-1} is assigned to bending vibrations of Te-O-Te linkages of vertex-sharing tbp units [9-16]. Its intensity can be considered as a measure of the connectivity of the network [17]. Pb^{2+} enters the glass as an intermediate (between the network former and network modifier) and increases the number of non-bridging oxygens [17,18]. The peak at 322 cm^{-1} can be probably assigned to Pb-Cl vibrations. Relative intensities of the peaks depend on doping and on the material of the crucible. In glasses prepared in gold crucibles, the peak at 468 cm^{-1} is more pronounced than that in glasses prepared in Pt crucibles. It indicates a better connectivity of the glass network. Also the tbp (654 cm^{-1}) peak is more pronounced, in comparison to the tp (735 cm^{-1}) peak, in glasses prepared in gold crucibles. The intensity ratio of both peaks determines the ratio of tbp and tp structural units [16]. It seems that presence of $PbCl_2$, in "pure" glasses prepared from Pt crucibles, increases the number of TeO_3 structural units and decreases the number of Te-O-Te linkages [20]. Doping of glasses prepared in gold crucibles does not change substantially their Raman spectrum.

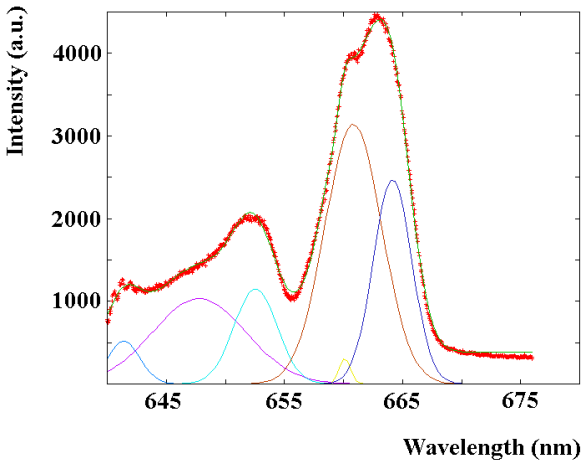

Fig. 6. Deconvolution of PL spectra in 7T3P glasses doped with 1000 wt-ppm $PrCl_3$, prepared in a/ Au, and b/ Pt crucibles.

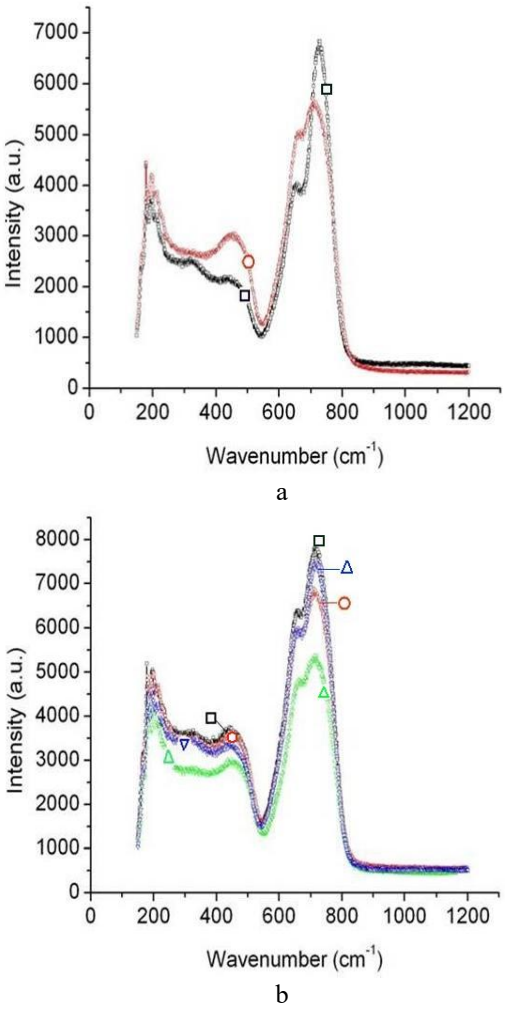

Fig. 7. Raman spectrum of 7T3P glasses, a) "pure" glasses, prepared in a Pt (□□□, black) or Au (○○○, red) crucible, b) doped with 1000 ppm Pr_2O_3 (□□□, black), 1000 ppm $PrCl_3$ (○○○, red), 1000 ppm Pr (∇∇∇, blue), prepared in Pt crucibles, and 1000 ppm $PrCl_3$ (ΔΔΔ, green), prepared in Au crucibles.

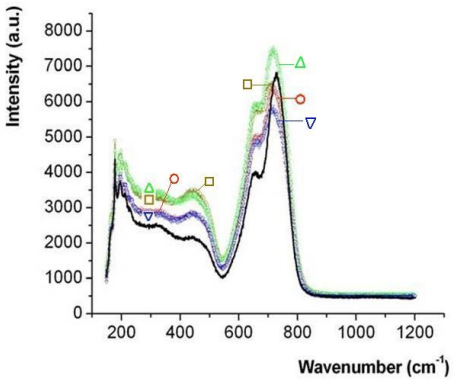

Fig. 8. Raman spectra of 7T3P glasses, prepared in Pt crucibles, doped with metallic Pr (500 wt-ppm (□□□, brown), 800 wt-ppm (○○○, red), 1000 wt-ppm, (ΔΔΔ, green), 1500 wt-ppm, (∇∇∇, blue), "pure" glass (full black line)).

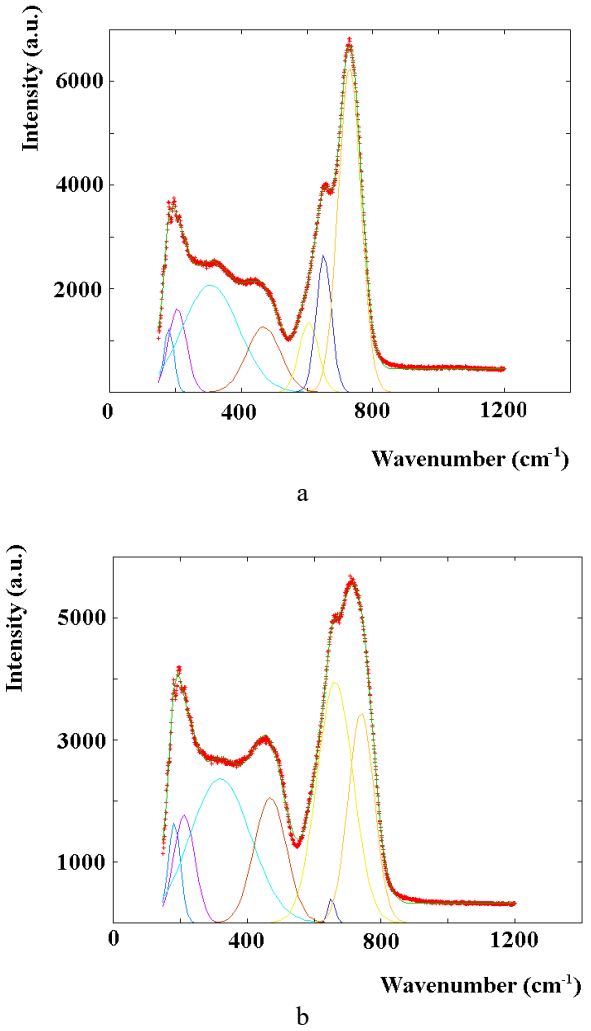

Fig. 9. Deconvolution of Raman spectra in undoped tellurite glasses (70 TeO_2·30$PbCl_2$) prepared in a/ Pt, b/ Au crucibles.

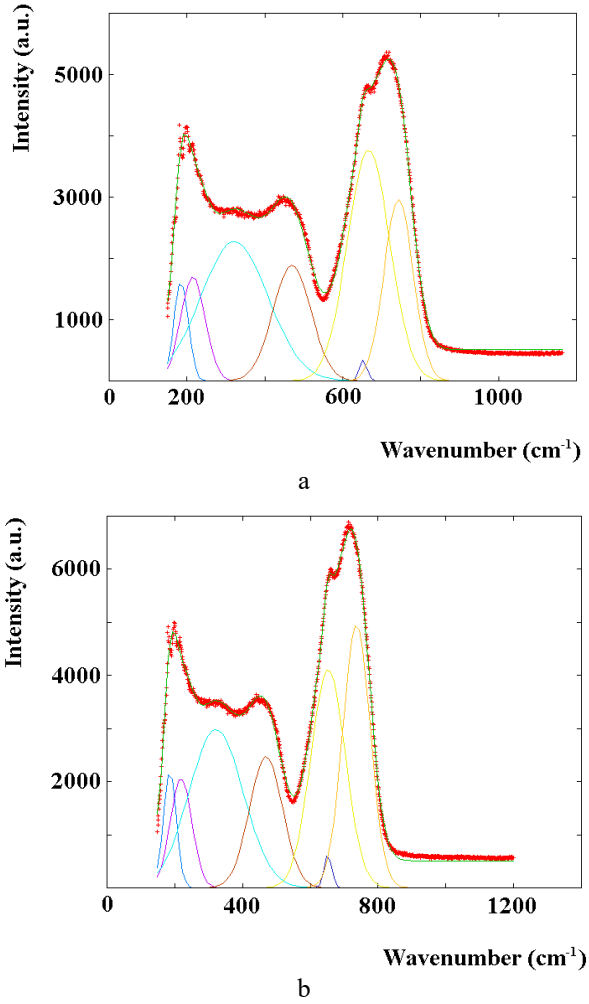

Fig. 10. Deconvolution of Raman spectra of T7P3 glasses doped with 1000 wt-ppm $PrCl_3$ prepared in a/ Pt, b/ Au crucibles.

Doping of glasses prepared in Pt crucibles increases intensities of both the peak at 468 cm^{-1} and that one at 654 cm^{-1}. Spectra of doped glasses prepared in different crucibles are more similar than spectra of "pure" glasses. It seems that reactions with crucibles and a fast diffusion of Au into the glass result in serious structural changes in tellurite polyhedrons. The influence of Pr^{3+} and Au^{+} on the structure of glasses is similar [16]. Upon doping, a partial conversion of the TeO_4 trigonal bipyramidal units into TeO_3 trigonal pyramidal units, with non-bridging oxygen, is possible [14-23]. Ab-initio calculations indicate [24] that the observed bands at around 640 cm^{-1} are attributed to the vibrations localized within the TeO_4 trigonal bipyramids, while the vibrations in the ranges 400-500 cm^{-1} and 720-780 cm^{-1} are due to the vibrations localized within the Te-$_{eq}O_{ax}$-Te linkages.

4. Conclusions

The T7P3 glasses prepared in gold or Pt crucibles have different positions and slopes of the absorption edge. Therefore, they have different colors. Glasses prepared in Pt crucibles have a step on the absorption edge. Doping with rare earth elements and reactions with crucibles result in serious changes in tellurite polyhedrons. Influence of Pr^{3+} and Au^{+} admixtures on the glass structure is similar. In the range of 600-700 nm, six PL peaks, centered at 641.5(1), 647.1(4), 652.4(1), 660.8(2), 662.7(4), 664.5(2) nm, were observed, both in pure and doped glasses. Relative intensities of these peaks depend on the concentration of Pr and on the material of the crucible. In the range of 200 – 1200 cm^{-1}, six Raman 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}, were determined. Three peaks at higher frequencies are assigned to vibrations of TeO_4 or TeO_3 polyhedrons, and Te-$_{eq}O_{ax}$-Te linkages. The peak at 322 cm^{-1} can be probably assigned to Pb-Cl vibrations. Influences of Pr^{3+} and Au^{+} on the glass structure are

similar. Relative intensities of both PL and RS peaks depend on the concentration of Pr and on the material of the crucible. Their ratios indicate the ratios of concentrations of various structural units in glasses. Three RS peaks are assigned to vibrations of TeO_n polyhedrons. One RS peak is attributed to symmetric stretching of Te-O-Te links. The peak at 322 cm^{-1} can be probably assigned to Pb-Cl vibrations.

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