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OPTICAL PROPERTIES OF TEO2 PBCL2 PBF2 GLASSES DOPED WITH PR AND ER

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Abstract: *Influence of crucibles (Au or Pt) on the structure and optical 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+}, 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 to yellowish, 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. On basis of RS spectrums, short-distance ordering of glasses is discussed.*

Key words: *glass, photoluminescence, raman scattering*

1. INTRODUCTION

Tellurite glasses are characterized by a wide transmission range (≈400 nm-6 μm), low phonon energy (≤ 800 cm^{-1}), high density (≈5.5 g/cm^3), and high refractive index (≈2).Good thermal and mechanical properties enable fiber production. This paper presents 1/ Raman scattering, optical absorption, and photo-luminescence of $60TeO_2.40PbCl_2$ (6T4P) and $60TeO_2.20PbCl_2.20PbF_2$ (6T2P2P) glasses, prepared in Pt or Au crucible sand doped with 1000 wt-ppm Pr^{3+} or Er^{3+}in various chemical forms, and 2/ influence of crucibles on the microstructure and optical properties of the glasses. Electrical properties and structure are interesting too (Bošák 2007, Kubliha 2009).

2. EXPERIMENTAL DETAILS

Glasses are melted in Pt or Au crucibles at 720 °C, for 30 min. 1000 wt-ppm of Er or Pr in the form of metal, oxide or chloride are added (O'Donnell 2003, Popescu 2007, Trnovcová 2007). Upon preparation in Pt and Au crucibles, glasses are red or yellowish, respectively. Absorption, photoluminescence (PL) and Raman scattering (RS) spectra are measured at RT. For absorption measurements, (200-3000 nm), deuterium discharge tube as a source is used. For PL (450-700 nm) and RS (150-3000 cm^{-1}) measurements, He-Ne laser (632.8 nm) is used.

3. RESULTS AND DISCUSSION

In 6T4P glasses prepared in Pt crucibles, an absorption band on the absorption edge is observed (Fig. 1A). It is assigned to Pt colloids. In T6P2P2 glasses prepared in Pt crucibles, we observe another band resulting from their interaction with fluorine. Upon doping, the edge gets steeper. In glasses prepared in Au crucibles, 1/ the edge is shifted to a shorter wavelength, 2/ the color of glasses is changed, 3/doping has a negligible influence on the absorption edge, and 4/ no absorption band on the absorption edge is observed.

In the range of 640-690 nm, five PL bands, at 645.3, 652.4, 659.3, 659, and 663.3nm, are observed both in "pure" and Pr-doped 6T4P glasses (Fig.1B). They are attributed to $^3P_1 \rightarrow ^3F_2$, $^3P_0 \rightarrow ^3F_2$, $^3P_1 \rightarrow ^3F_3$, $^3P_0 \rightarrow ^3F_4$, and $^3P_1 \rightarrow ^3F_4$ transitions in Pr^{3+} ions.

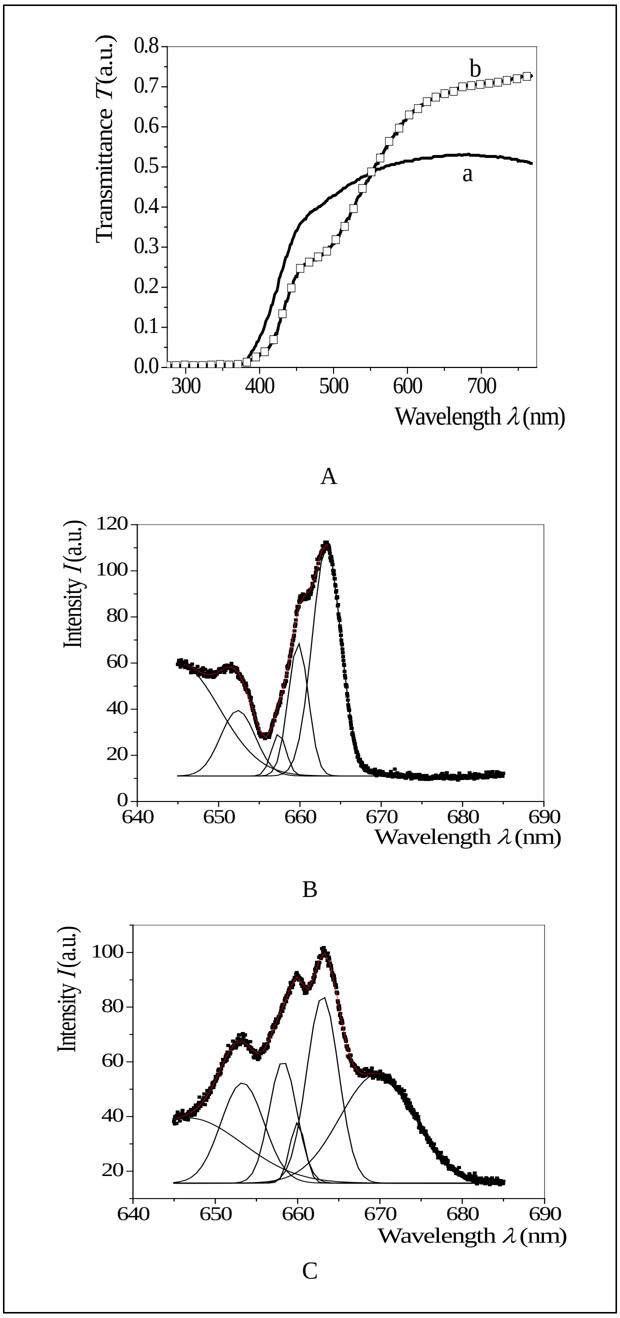

Fig.1. A/ Absorption edges of "pure"6T4P glasses prepared in a/ Au and b/ Pt crucibles; B/ deconvoluted PL spectrum of 6T4P glass prepared in Au crucible, doped with 1000 wt-ppm Pr; C/ deconvoluted PL spectrum of 6T4P glass, prepared in Pt crucibles, doped with 1000 wt-ppm Er_2O_3

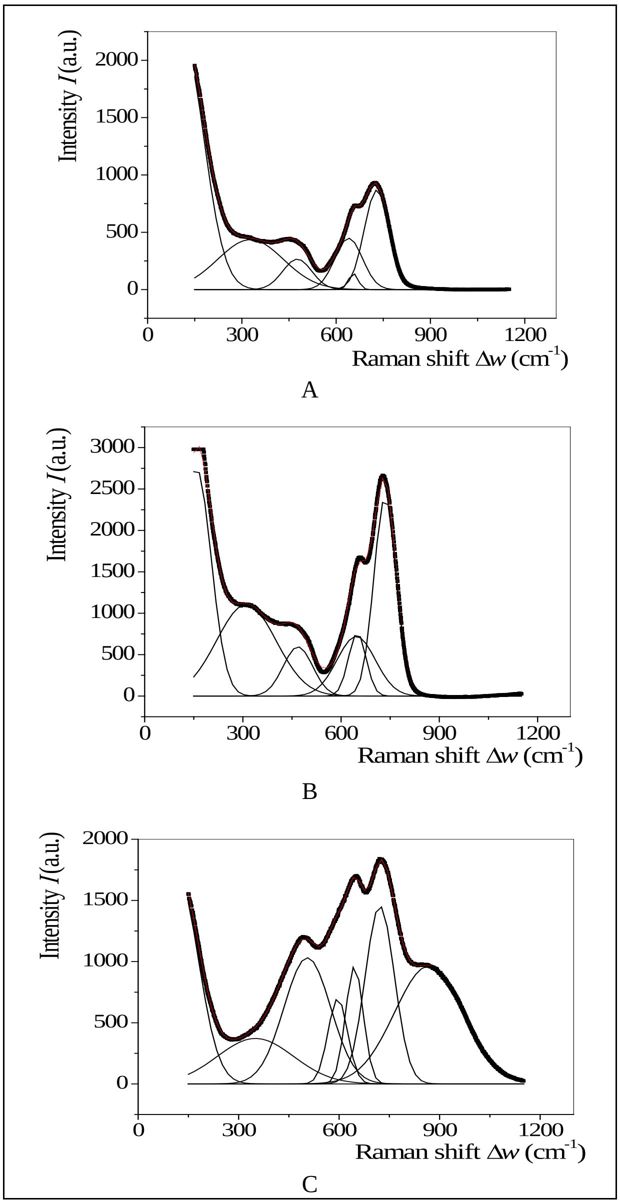

Fig. 2. Deconvoluted RS spectra of 6T4P glasses A/ doped with metallic Pr; prepared in Au crucible, B/ doped with $PrCl_3$, prepared in Pt crucible, and C/ of 6T2P2P glass, prepared in Pt crucible, doped with Er_2O_3 (Kubliha, M., Trnovcová, V., 2009)

Traces of Pr^{3+} ions are present also in "pure" 6T4P glasses. Six PL peaks, at 648, 652.9, 659, 660, 663.2, and 669 nm, are observed in "pure" and Er-doped 6T2P2P glasses and in Er-doped 6T4P glasses (Fig. 1C). They are attributed to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions. "Pure" 6T2P2P glasses contain traces of Er^{3+} ions.

Relative intensities of PL bands depend on the chemical form of dopants and on the crucible. Positions of these bands are almost independent of the concentration and chemical form of dopants, material of the crucible, and glass composition.

In the range of 200–1200 cm^{-1}, in 6T4P glasses, both "pure" and doped with Pr, prepared in Au or Pt crucibles, six RS peaks, at 122, 323, 474, 643, 656, and 732cm^{-1}, are observed (Figs. 2A,B). 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, 323, 494, 598, 647,727, and 862cm^{-1}, are observed (Fig. 2C).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 concentration and chemical form of dopants, and of the material of the crucible. There is a pronounced difference between RS spectrums of Pr-doped and Er-doped glasses.

Basic structural units in tellurite glasses are asymmetrical $[TeO_4]$ trigonalbipyramids (tbp) with lone pair electrons. Adding modifiers, 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. Peaks at 732±5 cm^{-1} and 652±5cm^{-1} are attributed to stretching vibrations of tp and tbp, respectively. The peak at 645 cm^{-1} comes from TeO_{3+1} polyhedrons. The peak near 480 cm^{-1} corresponds to bending or stretching vibrations of Te-O-Te linkages of vertex-sharing tbp units. Its intensity can be considered a measure of the network connectivity. Pb^{2+} enters the glass as an intermediate, increases the number of non-bridging oxygens and decreases the coordination number of Te.

Peak at 862 cm^{-1} comes probably from Pb-O, Cl-Pb-Cl or F-Pb-F stretching vibrations. However, it is not clear why these vibrations are supported by Er. Low frequency peaks are assigned to rotational and torsional modes of Te-O-Te linkages.

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. It seems that the presence of Er increases the number of TeO_3 structural units and decreases the number of Te-O-Te linkages (O'Donnell 2003).

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