Spectroscopic Properties of Pr^{3+} Ion in Various Tellurite Glasses

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The goal of this work was to investigate the spectroscopic properties of Pr^{3+} ions (of a comparable concentration of the order of 0.2 mol/dm^3) embedded in the tellurite glass matrix, i.e. TeO_2-WO_3-PbO modified with lanthanum and lutetium oxides. The difference is that the last components of both glasses provide ions which are optically inactive within the $4f$ shell, since this shell is completely empty for La^{3+} ion and completely filled for Lu^{3+} ion. The absorption and fluorescence spectra of Pr^{3+} doped in tellurite glass has been recorded and analyzed in terms of the Judd–Ofelt theory. The studies of the glasses comprised ellipsometric, spectrophotometric and photoluminescence measurements. The ellipsometric studies yield the refraction index dispersion which appears to be quite similar for all the studied glasses. From the spectrophotometric measurements, the absorption spectra have been obtained which, for Pr^{3+}-doped samples, have been analyzed in terms of the Judd–Ofelt theory. Finally, the photoluminescence studies demonstrate a clear visible emission from $^3P_0$ level to lower-lying states of Pr^{3+} ion.

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1. Introduction

Triply ionized Pr^{3+} doped tellurite glasses are extensively studied because of its emission at 1.3 lm, so-called second telecom window [1], and its wide applications in many optical devices. The energy level diagram of Pr^{3+} contains several metastable states that provide the possibility of simultaneous emissions in the blue, green, orange, red and infrared (IR) regions [2]. Pr^{3+} ions have the ability to show four-level laser action associated with transitions from $^3P_0$ state in certain host systems as the potentially active ions for a visible laser generation [3]. The weak $^3P_2 \rightarrow ^3H_4$ transition in Pr^{3+} ions is observed only when a glass host has low phonon energy [4]. Hence, recently heavy metal oxide glass (HMO) have been found to be more promising glassy materials for photonic applications with reasonably low phonon energies [5]. The tellurite glasses are more attractive systems with advantages such as low melting point, good thermal stability, low phonon energy, wide transmission region (0.36–6.3 μm), high refractive index ($n_{633} = 2.3$) and high rare earth solubility [6–8].

Lanthanum (La) has no electrons in its $4f$ subshell, while lutetium (Lu) has it completely populated. In the case of lanthanum (La) to the $4f$ subshell is not at all electrons, while lutetium (Lu) has it completely populated. Electronic transitions in these two cases are therefore impossible. Thus the aim of our studies was to compare two different glass matrix from the TeO_2–WO_3–PbO_x glass system, where x was substituted by the same amount of La_2O_3 and Lu_2O_3. Particularly we would like to determine the influence of non optically active ions onto refractive index of glass and transmittance.

2. Experimental

Host glass compositions were selected as TeO_2–WO_3–PbO–La_2O_3 (TWPLa) and TeO_2–WO_3–PbO–Lu_2O_3 (TWPLu). Both of host glasses show relevant high rare earth stability and resistance against crystallization during reheating. In order to introduce the Pr^{3+} ions into the TWPLa and TWPLu glass matrix, the respective oxides of an amount of 0.1 g of Pr^{3+} has been added to the batches. The resulting molar concentrations of Pr^{3+} ions are equal to 0.151 mol/dm^3 for TWPLa and 0.23 mol/dm^3 for TWPLu. The following raw materials were used to prepare the batches: tellurium oxide (TeO_2), tungsten trioxide (WO_3), lead oxide (PbO), lanthanum oxide (La_2O_3), lutetium oxide (Lu_2O_3), and praseodymium oxide (Pr_6O_{11}). All the chemicals were mixed properly to ensure the homogeneity. Tellurite glass was obtained by melting 25 g batch in gold crucible in an electric furnace at the temperature 850 °C in air atmosphere. The crucible was covered with a platinum plate

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to avoid vaporization losses. The melt was poured onto a steel plate which was preheated to 340 °C, forming a layer thickness of 2 to 5 mm, then annealed in the temperature range 310–350 °C.

For spectroscopic measurements, the annealed glass samples were sliced and polished to dimensions of about $10 \times 10 \times 3$ mm^3. The luminescence spectra and luminescence decay curves were measured following a short pulse excitation provided by an optical parametric oscillator (OPO) pumped by a third harmonic of a I Nd:YAG laser. The resulting luminescence signal was filtered using a monochromator GDM-1000, detected by a Hamamatsu R928 photomultiplier or InSb detector and recorded with a oscilloscope Tektronix TDS3052. The emission spectra, measured at 300 K, have been corrected for the equipment answer and the relative error in measurements of the fluorescence lifetime is estimated to be ±2%.

The ellipsometric data were collected with a M-2000 Woollam ellipsometer in the spectral range 190–1700 nm. Knowledge of Ψ and Δ allows one to determine not only the dispersion of the optical constants but also roughness σ of a glass [9]. The samples have been measured for three angles of incidence, namely 65°, 70° and 75°. To analyze the data, we have combined all the angular spectra and we have fitted all the data simultaneously. The data have been analyzed using CompleteEASE 4.1 software.

3. Results

The amorphous nature of the Pr^{3+}-doped TWPLa and TWPLu glasses has been verified by the X-ray diffraction analysis.

The spectroscopic ellipsometry measurements have been performed to get the dispersion relation for the refractive index n (Fig. 1).

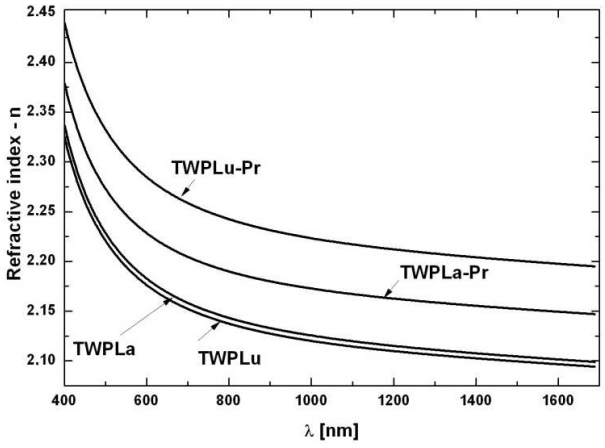

Fig. 1. Dispersion of the refraction coefficient obtained for the investigated glasses from elipsometric measurements.

The refractive index of tellurite glasses exhibit very high values, over 2.1, within the 400–1700 nm spectral range which are considerably higher than those obtained for standard optical glasses. The ellipsometric studies have proved that presence of Pr^{3+} ions change the refractive index of the tellurite glass matrix. The value of refractive index for sample TWPLu-Pr is higher about 0.1 compared with sample TWPLu in the range 400–1700 nm.

The optical absorption spectra of Pr^{3+} in TWPLa and TWPLu glasses in the range of 0.5–3 eV are presented in Fig. 2a,b. The glasses has revealed seven bands four each in UV–Vis and NIR regions from ground state ($^3H_4$) to various higher energy states of Pr^{3+} ions. They are assigned to the transitions of $^3H_4 \rightarrow {}^3F_2$, $^3F_3$, $^3F_4$, $^1G_4$, $^1D_2$, $^3P_0$, ($^3P_1$, $^1I_6$).

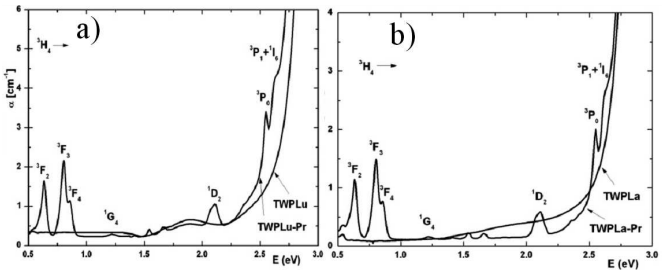

Fig. 2. Absorption spectra of un-doped and Pr^{3+}-doped TeO_2–WO_3–PbO–La_2O_3 glasses (a), TeO_2–WO_3–PbO–Lu_2O_3 glasses (b).

In the near infrared the absorption spectrum of Pr^{3+} ion is characterized by two intense bands corresponding to transitions of the basic multiplet $^3H_4$ to excited levels $^3F_{2,3,4}$ and relatively weak band with a maximum at 1.22 eV, which was identified as a spin-forbidden electron transition $^3H_4 \rightarrow {}^1G_4$. In the visible spectral range spectra of Pr^{3+} in TWPLa and TWPLu glasses are characterized by a band at 2.1 eV corresponding to the transition $^3H_4 \rightarrow {}^1D_2$ and a group of bands assigned to the above-lying transitions $^3P_{0,1}$ multiplets, and $^1I_6$ level.

The radiative transition probabilities for excited levels of Pr^{3+} ion in TWPLa and TWPLu glasses have been calculated using the standard Judd-Ofelt (J–O) theory; the experimental oscillator strengths for transitions from the ground $^3H_4$ level of Pr^{3+} ion, to excited levels were determined by numerical integration of the corresponding absorption bands appearing in the 0,5–3 eV range (Fig. 2a,b).

The absorption spectra registered at the $T = 300$ K as well as the calculated oscillator strengths for Pr^{3+} ion in TWPLa and TWPLu glasses are shown in Fig. 2a,b and in Table. The phenomenological J–O parameters for Pr^{3+} ions are found to be: for sample TWPLa $\Omega_2 = 21.22 \times 10^{-20}$ cm^2, $\Omega_4 = 6.94 \times 10^{-20}$ cm^2 and $\Omega_6 = 12.7 \times 10^{-20}$ cm^2 and for sample TWPLu $\Omega_2 = 18.75 \times 10^{-20}$ cm^2, $\Omega_4 = 4.99 \times 10^{-20}$ cm^2, $\Omega_6 = 11.78 \times 10^{-20}$ cm^2.

The fluorescence emission spectrum registered at 300 K (13000–20000 cm^{-1}) of Pr^{3+}: TWPLa glass excited by wavelength $\lambda_{exc} = 467$ nm and TWPLu glass excited by wavelength $\lambda_{exc} = 478$ nm are shown in Figs. 3, 4.

TABLE

Measured and calculated oscillator strengths of Pr^{3+} in glass

Transition from $^3H_4$	Energy ν [cm^{-1}]	Oscillator strength P [10^{-6}]			
		TWPLa: Pr		TWPLu: Pr	
		P_{exp}	P_{cal}	P_{exp}	P_{cal}
$^3F_2$	4850	22.60	22.59	17.30	17.29
$^3F_3$ + $^3F_4$	6622	38.60	38.77	29.70	29.93
$^1G_4$	9833	1.20	1.15	8.82	9.58
$^1D_2$	16474	13.00	13.85	7.10	6.33
$^3P_0$	20491	6.51	7.52	5.10	4.64
$^3P_1$, $^1I_6$	21097	5.61	5.92	4.33	4.72

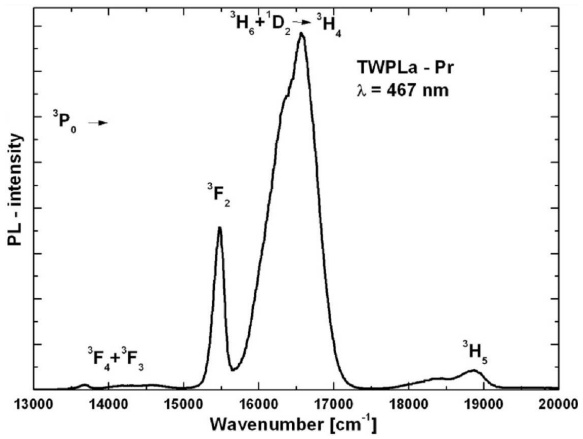

Fig. 3. Emission spectra of Pr^{3+} ions in the TeO_2–WO_3–PbO–La_2O_3 glass at 300 K corresponding to transitions from the $^3P_0$ level to lower-lying states.

The recorded spectral band correspond to electron transition from the excited $^3P_0$ state. Emission spectra are dominated by luminescence, which corresponds to transitions $^3P_0 \rightarrow ^3H_4$ (16567 cm^{-1}) and $^3P_0 \rightarrow ^3F_2$ (15471 cm^{-1}) for tellurite glasses of the system: 60TeO_2–27WO_3–10PbO–3La_2O_3 doped with praseodymium ions

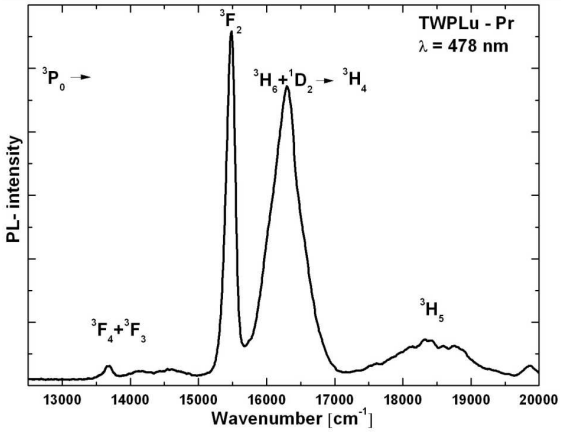

Fig. 4. Emission spectra of Pr^{3+} ions in the TeO_2–WO_3–PbO–Lu_2O_3 glass at 300 K corresponding to transitions from the $^3P_0$ level to lower-lying states.

(0.1 g) and for glasses of 60TeO_2–27WO_3–10PbO–3Lu_2O_3 doped also ions Pr^{3+} (0.1 g), $^3P_0 \rightarrow ^3H_4$ (16300 cm^{-1}) and $^3P_0 \rightarrow ^3F_2$ (15486 cm^{-1}).

4. Conclusion

The results of the presented work may be summarized as follows:

(i) The refractive index is high ($n > 2.1$) and its dispersion is quite similar for all studied samples, however a slight increasee of n with Pr^{3+} ion doping is observed.

(ii) The absorption bands of Pr^{3+}-doped tellurite glassses are very similar, resulting in similar Judd–Ofelt parameters (see Table), but the TWPLu matrix appears to be less transparent that the TWPLa one (cf. Fig. 2a,b).

(iii) The emission spectra of Pr^{3+}-doped tellurite glassses are also quite similar, but the order of two highest maxima for TWPLu: Pr^{3+} glass is reversed with respect to TWPLa: Pr^{3+} one (cf. Figs. 3 and 4), probably due to a higher Pr^{3+} concentration in the former glass (0.23 against 0.151 mol/dm^3).

Acknowledgments

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