Rapid communication

Effect of OH⁻ on upconversion luminescence of Er³⁺-doped oxyhalide tellurite glasses

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Abstract

The Raman spectra, infrared spectra and upconversion luminescence spectra were studied, and the effect mechanism of OH⁻ groups on the upconversion luminescence of Er³⁺-doped oxyhalide tellurite glasses was analyzed. The results show that the phonon energy of lead chloride tellurite (PCT) glass was lower than that of lead fluoride tellurite (PFT) glass, but upconversion luminescence intensity of Er³⁺-doped PFT glass was higher than that of Er³⁺-doped PCT glass. The analysis considers that it was attributed mainly to the effect of OH⁻ groups. The lower the absorption coefficient of the OH⁻ groups, the higher the fluorescence lifetime of Er³⁺, and as a result the higher upconversion luminescence intensity of Er³⁺. In this work, the effect of OH⁻ groups on the upconversion luminescence of Er³⁺ was bigger than that of the phonon energy.
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1. Introduction

Solid-state blue and green light sources are desirable for high-density optical storage, color displays, optoelectronics, and medical diagnostics [1–5]. Upconversion lasers have realized various transitions in erbium, thulium, neodymium and praseodymium. One of the most promising candidates for a green upconversion laser is the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition in trivalent erbium [6–8]. The host materials for Er³⁺-doping are very important for obtaining highly efficient upconversion because host materials with low phonon energy can reduce the non-radiative loss due to the multiphonon relaxation thus achieving strong upconversion luminescence. So far, much effort has been made on fluoride glasses owing to their lower phonon energy when compared to oxide glasses. In order to increase luminescence efficiency of Er³⁺, the general method is to search upconversion materials with lower phonon energy. As is known, glasses based on mixed oxide–halide systems combine the good optical properties of fluoride glasses (a broad range of optical transmittance and low optical losses) with the better chemical and thermal stabilities of oxide glasses [9,10]. So it is expected that the mixed glasses including tellurite and halide should bring together the interesting properties of the two systems. Many studies have focused on the effect of OH⁻ groups on fluorescence of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er³⁺-doped glasses [11–14], but little attention has been paid to the study of the effect of OH⁻ groups on the upconversion luminescence of Er³⁺. In this letter, the effect of OH⁻ groups on the upconversion luminescence of Er³⁺-doped oxyhalide tellurite glasses was investigated. The investigated results were conducive to increase the upconversion luminescence efficiency of Er³⁺.

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2. Experimental

The glasses used in this work were synthesized by a conventional melting and quenching method. The starting materials are reagent-grade TeO_2, ZnO, La_2O_3, $PbCl_2$, PbF_2, and Er_2O_3. The composition (mol%) of the prepared glasses is $20ZnO$–$5La_2O_3$–$75TeO_2$–$0.5Er_2O_3$ (ZLT), $40PbF_2$–$60TeO_2$–$0.5Er_2O_3$ (lead fluoride tellurite (PFT)), and $40PbCl_2$–$60TeO_2$–$0.5Er_2O_3$ (lead chloride tellurite (PCT)). About 50 g batches of starting materials were fully mixed and then melted between 700 and 800 °C in covered platinum crucibles in a SiC Globar furnace. When the melting was completed, the glass liquids were cast into stainless-steel plates. Glass liquid was bubbled with high-purity oxygen gas through a quartz tube for 30 min for the preparation of ZLT glass by removing water. The obtained glass sample was cooled to room temperature at a rate of 10 °C/h, and then was cut and polished carefully in order to meet the requirements for optical measurements. The undoped ZLT, PFT and PCT glasses were also prepared for measuring the vibrational spectra.

The glass transition temperature (T_g), and crystallization onset temperature (T_x) were determined by differential thermal analysis (DTA) at a heating rate of 10 °C/min, using an aluminum oxide ceramic pan. The upconversion luminescence spectra were obtained with a TRIAX550 spectrofluorimeter upon excitation of 980 nm LD with a maximum power of 2 W. In order to compare the luminescence intensity of Er^{3+} in different samples as accurately as we can, the position and power (100 mW) of the pumping beam and the width (1 mm) of the slit to collect the luminescence signal were fixed under the same condition, and the samples were set at the same place in the experimental setup. In addition, the integrated intensities for the green and red emissions were also calculated to illustrate the variations in the luminescence intensity. The Raman spectra were recorded on an FT Raman spectrophotometer Nicolet MODULE within the range of 100–1200 cm^{-1}. Nd: YAG operating at 1064 nm was used as the excitation source, and the laser power level was 500 mW. Infrared (IR) transmittance was measured by a Bio-Rad Fourier transform infrared spectrometer (FTIR) within the wavenumbers 1000–4000 cm^{-1}. All the measurements were taken at room temperature.

3. Results and discussion

The difference between T_x and T_g, $\Delta T = T_x - T_g$ has been frequently used as a rough estimate of the glass formation ability or glass stability. Since fiber drawing is a reheating process and any crystallization during the process will increase the scattering loss of the fiber followed by a degradation of the optical properties [15].

To achieve a large working range of temperature during our sample fiber drawing, it is desirable for a glass host to have ΔT as large as possible [15]. Fig. 1 shows T_x, T_g, and $\Delta T = T_x - T_g$ of Er^{3+}-PFT and PCT glasses. From Fig. 1, it can be seen that the T_x and T_g values of Er^{3+}-PFT glass are bigger than those of Er^{3+}-PCT glass, respectively, but the ΔT value of Er^{3+}-PCT glass is bigger than that of Er^{3+}-PFT glass, which indicates that the thermal stability of Er^{3+}-PCT glass ($\Delta T = 122$ °C) is better than those of tellurite ($\Delta T = 118$ °C) and fluoride (105 °C) glasses [16,17].

Fig. 2 presents the Raman spectra for undoped ZLT, PFT, and PCT glasses. All the spectra have been normalized to the maximum intensity around 750 cm^{-1}. For ZLT glass, the dominant features are the broad modes at about 450 cm^{-1} assigned to bending vibrations of Te–O–Te linkages, 670 cm^{-1} due to the stretching vibrations of TeO_4, and 758 cm^{-1} due to the stretching vibrations of TeO_3 and/or TeO_{3+1} trigonal pyramids [18,19]. For PFT and PCT glasses, important changes are observed in the spectra compared with the ZLT glass. The maximum phonon energy in ZLT glass is 758 cm^{-1} while those in PFT and PCT glasses are 734
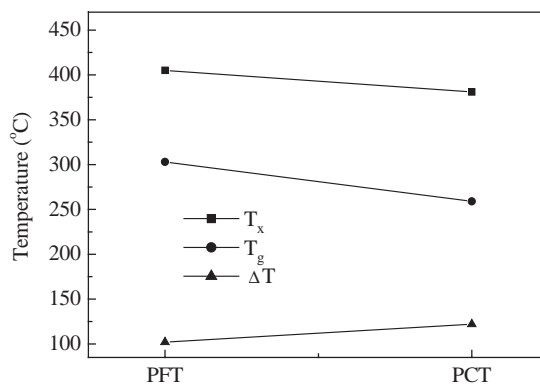

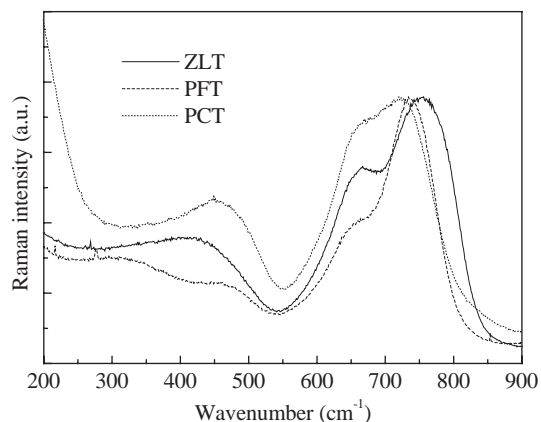Fig. 1. T_x, T_g, and $\Delta T = T_x - T_g$ of Er^{3+}-PFT and PCT glasses.

Fig. 2. The Raman spectra for undoped ZLT, PFT, and CTP glasses.

and $720 \, \text{cm}^{-1}$, respectively, which is why the addition of fluoride and chlorine ions into glass network increases the mass of the ligands, leading to the reduction in the phonon vibration energies. Since the glasses host with low phonon energy this reduces the non-radiative loss due to the multiphonon relaxation and realizes strong upconversion luminescence. Therefore, it can be deduced that the upconversion luminescence intensity of PFT glass is lower than that of PCT glass.

The room temperature upconversion luminescence spectra in the range of 500–700 nm for Er^{3+}-doped PFT and PCT glasses under 980 nm excitation are shown in Fig. 3. The upconversion emission bands centered at 525, 543, and 655 nm are attributed to the transitions from excited states $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ to the ground state $^4I_{15/2}$ of Er^{3+}, respectively. From Fig. 3, it is observed that the upconversion luminescence intensity of Er^{3+}-doped PFT glass is higher than that of Er^{3+}-doped PCT glass, which is contradictory to the rule of upconversion luminescence intensity determined by the phonon energy. The result can be related with OH^- groups in the glass host because there is no removal of water in the TPF and TPC glasses. This is because both Er^{3+}-doped PFT glass and Er^{3+}-doped PCT glass did not remove water in the preparation process.

The room temperature upconversion luminescence spectra in the range of 500–700 nm for Er^{3+}-doped ZLT glasses with and without removing water under 980 nm excitation are shown in Fig. 4. Obviously, upconversion luminescence intensity of Er^{3+}-doped ZLT glass with the removal of water is higher than that of Er^{3+}-doped ZLT glass without the removal of water. The relative integral intensities of the green (531 and 545 nm) and red (656 nm) emissions in Er^{3+}-doped ZLT glass with the removal of water increases by a factor of about 1.85, 1.7 and 5.6, respectively, when compared with those in
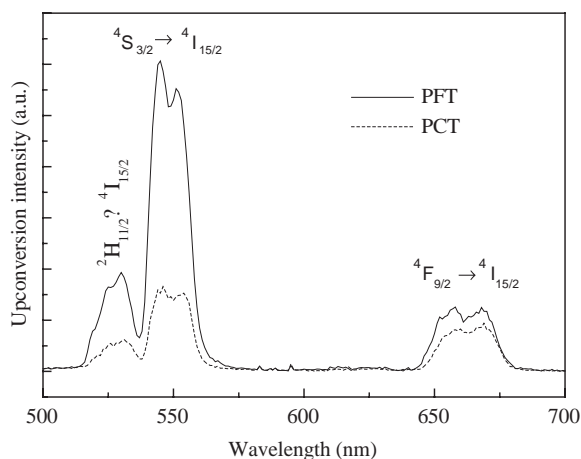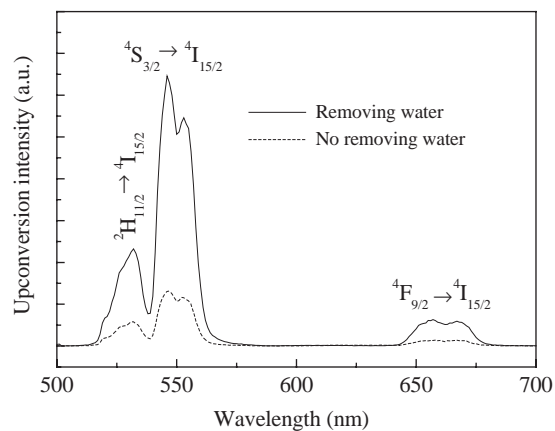

Fig. 4. Upconversion luminescence spectra of Er^{3+}-doped ZLT glasses with and without the removal of water under 980 nm excitation.
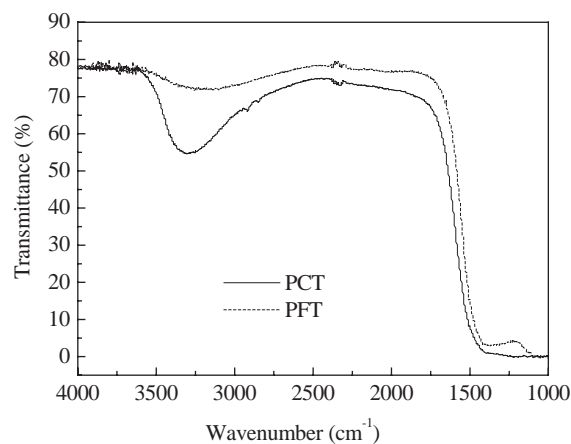

Fig. 5. Infrared spectra of Er^{3+}-doped TPF and TPC glasses.

Fig. 3. Upconversion luminescence spectra of Er^{3+}-doped PFT and PCT glasses under 980 nm excitation.

Er^{3+}-doped ZLT glass without the removal of water. The lifetimes of $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er^{3+} in ZLT glass with the removal of water are 0.41 and 0.56 ms, respectively, while the lifetimes of $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er^{3+} in ZLT glass without the removal of water are 0.27 and 0.32 ms, respectively. Although the phonon energy of ZLT glasses is the same, the lifetimes of $^4S_{3/2}$ and $^4F_{9/2}$ levels of Er^{3+} in ZLT glass with the removal of water are enhanced compared with Er^{3+} in ZLT glass without the removal of water, leading to an increase in the upconversion luminescence. Therefore, this upconversion luminescence intensity of Er^{3+}-doped TPF glass is higher than that of Er^{3+}-doped TPC glass in relation to the OH^- groups.

Infrared spectra of Er^{3+}-doped PFT and PCT glasses from 1000 to $4000 \, \text{cm}^{-1}$ are shown in Fig. 5. The absorption bands in the figure are ascribed to the stretching of hydroxyl groups vibration. The absorption coefficient of OH^- groups at the absorption peak in the

glass can be determined by $\alpha = \log(T_0/T)/L$ [20], where L is the glass thickness, T_0 is the maximum transmittance, and T is the transmittance at absorption peak. For Er^{3+}-doped PFT and PCT glasses, the absorption coefficient of OH^- groups is 0.157 and 0.865, respectively, which results in the large non-radiative decay rate of Er^{3+} in PCT glass due to the OH^- groups. From the phonon energy, the non-radiative decay rate of Er^{3+} in PFT glass is larger than that in PCT glass, but the effect of OH^- groups on the non-radiative decay rate Er^{3+} can be bigger than that of phonon energy in our work, and thus the upconversion luminescence intensity of Er^{3+} in PFT glass is higher than that of Er^{3+} in TPC glass.

4. Conclusions

The Raman spectra, infrared spectra and upconversion luminescence spectra were studied. From the results it was found that the phonon energy of PFT glass is larger than that of PCT glass, but upconversion luminescence intensity of Er^{3+}-doped PFT glass is also higher than that of PCT glass. By investigating the upconversion luminescence of the analyzed Er^{3+}-doped ZLT glasses with and without the removal of water, it was found that OH^- groups in the glass host have a large effect on the upconversion luminescence of Er^{3+}. An investigation on the infrared spectra of Er^{3+}-doped PFT and PCT glasses reveals that the OH^- groups absorption coefficient of Er^{3+} in PCT glass is higher than that in PFT glass, which results in the large non-radiative decay rate of Er^{3+} in PCT glass which is due to the OH^- groups. Effect of the OH^- groups on the non-radiative decay rate Er^{3+} can be bigger than that of the phonon energy in our work, and thus the upconversion luminescence intensity of TPF glass is higher than that of TPC glass.

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