Effect of OH^- on upconversion lminescence of Yb^{3+}/Tm^{3+}-codoped oxyhalide tellurite glasses

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Recently, considerable attention has been devoted to the conversion of near infrared radiation to visible light in rare-earth doped glass materials, for a wide range of applications, including upconversion lasers, color displays, optical data storage, biomedical diagnostics, sensors, and undersea optical communications [1–4]. Many trivalent rare-earth ions such as Er^{3+}, Tm^{3+}, Ho^{3+}, Pr^{3+}, and Nd^{3+} were introduced as absorption and emission centers in glass hosts [5]. Among the rare-earth ions, Tm^{3+} is one of the most studied rare-earth ions for blue laser operation based on upconversion [6, 7]. One approach to improving the luminescence efficiency of Tm^{3+} is to codope it with other rare-earth ions [8]. The host materials for Tm^{3+}-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 mutiphonon relaxation and thus achieves strong upconversion luminescence. So far, much effort has been spent on fluoride glasses owing to their lower phonon energy than oxide glasses. In order to increase luminescence efficiency of Tm^{3+}, the general method is search of upconversion materials with lower phonon energy. However, that the phonon energy was lowered can lead to poorer thermal stability. 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 stability 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 effect of OH^- on fluorescence of rare-earth doped glasses [11–13], but little attention has been paid to the study of effect of OH^- on upconversion lminescence of Tm^{3+}. In this letter, effect of OH^- on upconversion lminescence of Yb^{3+}/Tm^{3+}-codoped oxyhalide tellurite glasses was investigated. The investigated results were conducing to increase upconversion luminescence efficiency of Tm^{3+}.

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, Tm_2O_3, and Yb_2O_3. The composition (mol%) of the prepared glasses is $75TeO_2$–$20ZnO$–$5La_2O_3$-$0.1Tm_2O_3$–$3Yb_2O_3$ (TZL), $60TeO_2$–$40PbF_2$–$0.1Tm_2O_3$–$3Yb_2O_3$ (TPF), and $60TeO_2$–$40PbCl_2$–$0.1Tm_2O_3$–$3Yb_2O_3$ (TPC). 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 with an N_2 atmosphere. 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 to the preparation of ZLT glass with 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 upconversion luminescence spectra were obtained with a TRIAX550 spectrofluorimeter upon excitation of 980 nm LD with a maximum power of 2 W. The Raman spectrum was recorded on a FT Raman spectrophotometer Nicolet MODULE within the range of 100–1200 cm^{-1}. Nd: YAG operating at 1064 nm is 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)

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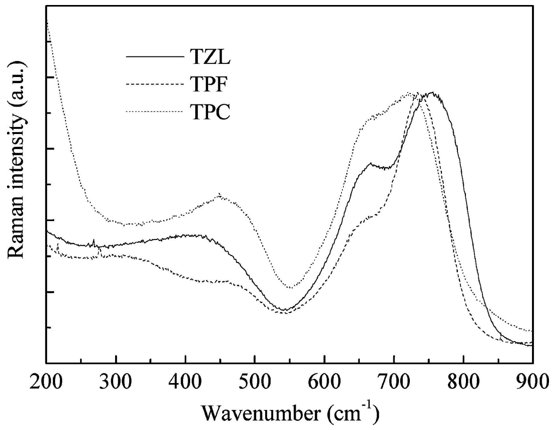

Figure 1 The Raman spectra of undoped TZL, TPF, and TPC glasses.

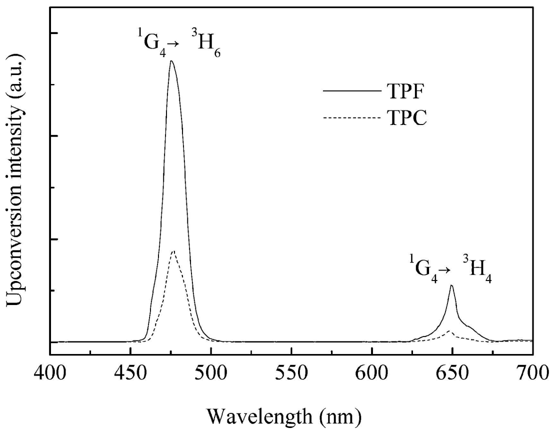

Figure 2 Upconversion luminescence spectra of Yb^{3+}/Tm^{3+}-codoped TPF and TPC glasses under 980 nm excitation.

within the wavenumbers 1000–4000 cm^{-1}. All the measurements were made taken at room temperature.

Fig. 1 presents the Raman spectra of undoped TZL, TPF, and TPC glasses. For TZL glass, the dominated 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 [14, 15]. For TPF and TPC glasses, important changes are observed in the spectra compared to the TZL glasses. The maximum phonon energy in TZL glass is 758 cm^{-1} while those in TPF and TPC glasses are 734 and 720 cm^{-1}, respectively, which is that the addition of fluoride and chlorine ions into glass network increases the mass of the ligands, leading to reduction of phonon vibraional energies. Since glasses host with low phonon energy can reduce the non-radiative due to the multiphonon relaxation and realize strong upconversion luminescence. Therefore, it can be deduced that the upconversion luminescence intensity of Yb^{3+}/Tm^{3+}-codoped TPF glass is lower than that of Yb^{3+}/Tm^{3+}-codoped TPC glass.

The room temperature upconversion luminescence spectra in the range of 400–700 nm for Yb^{3+}/Tm^{3+}-codoped TPF and TPC glasses under 980 nm excitation are shown in Fig. 2. Two emission bands centered at 476 and 649 nm corresponding to the transitions$^1G_4 \rightarrow {}^3H_6$ and$^1G_4 \rightarrow {}^3H_4$ of Tm^{3+}, respectively, were simultaneously observed. From Fig. 2, it is observed that the upconversion luminescence intensity of Yb^{3+}/Tm^{3+}-codoped TPF glass is stronger than that of Yb^{3+}/Tm^{3+}-codoped TPC glass, which is contradiction with rule of upconversion luminescence determined by phonon energy due to the phonon energy of TPF glass higher than that of TPC glass. The results can be related with OH^- in glass host, because both Yb^{3+}/Tm^{3+}-codoped TPF glass and TPC glass were not removing water in the preparation process.

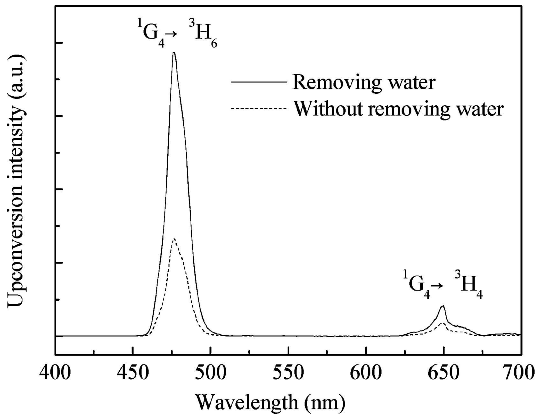

Figure 3 Upconversion luminescence spectra of Yb^{3+}/Tm^{3+}-codoped TZL glasses with and without removing water under 980 nm excitation.

The room temperature upconversion luminescence spectra in the range of 400–700 nm for Yb^{3+}/Tm^{3+}-codoped TZL glasses with and without removing water under 980 nm excitation are shown in Fig. 3. Obviously, upconversion luminescence of Yb^{3+}/Tm^{3+}-codoped TZL glasses with removing water is stronger than that of Yb^{3+}/Tm^{3+}-codoped TZL glasses without removing water. The relative integral intensities of blue (476 nm) and red (649 nm) emissions in Yb^{3+}/Tm^{3+}-codoped TZL glasses with removing water increase by a factor about 2.9 and 2.2, respectively, when compared with those in Yb^{3+}/Tm^{3+}-codoped TZL glasses without removing water. The lifetime of$^1G_4$ level of Tm^{3+} in TZL glass with removing water is 0.18 ms, whereas the lifetime of$^1G_4$ level of Tm^{3+} in TZL glasses without removing water is 0.14 ms. Although glass hosts are the same, the lifetime of$^1G_4$ level of Tm^{3+} in TZL glass with removing water are enhanced compared with Tm^{3+} in TZL glass without removing water, leading to upconversion luminescence of Tm^{3+} increases. Therefore, that upconversion luminescence intensity of Yb^{3+}/Tm^{3+}-codoped TPF glass is stronger than that of Yb^{3+}/Tm^{3+}-codoped TPC glass is related with OH^-.

Infrared spectra of Yb^{3+}/Tm^{3+}-codoped TPF and TPC glasses from 1000 to 4000 cm^{-1} are shown in Fig. 4. The absorption bands in the figure are ascribed to the stretching of hydroxyl groups vibration. The absorption coefficient of OH^- at absorption peak in the glass can

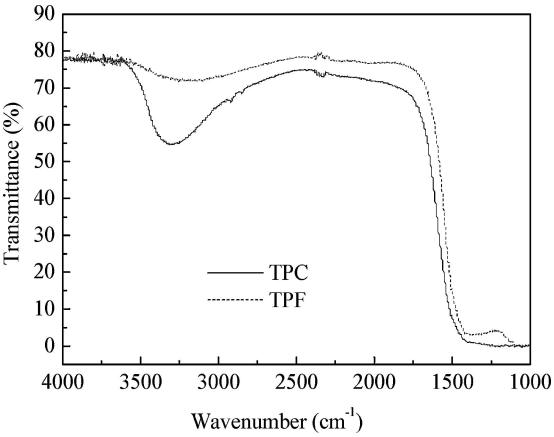

Figure 4 Infrared spectra of Yb^{3+}/Tm^{3+}-codoped TPF and TPC glasses.

be determined by $\alpha = \log(T_0/T)/L$ [16], where L is the glass thickness, T_0 is the maximum transmittance, and T is the transmittance at absorption peak. For Yb^{3+}/Tm^{3+}-codoped TPF and TPC glasses, the absorption coefficient of OH^- is 0.157 and 0.865, respectively. The obtained results suggest that the OH^- absorption coefficient of Tm^{3+} in TPC glass is bigger than that in TPF glass, which results in the large nonradiative decay rate of Tm^{3+} in TPC glass. From phonon energy, the nonradiative decay rate Tm^{3+} in TPF glass is larger than that in TPC glass, but the effect of OH^- on the nonradiative decay rate Er^{3+} can be more than that of phonon energy in our experiments, and thus the upconversion luminescence intensity of Yb^{3+}/Tm^{3+}-codoped TPF glass is stronger than that of Yb^{3+}/Tm^{3+}-codoped TPC glass.

In conclusion, effect of OH^- on upconversion lminescence of Yb^{3+}/Tm^{3+}-codoped tellurite gasses under 980 nm excitation was investigated. The results found that phonon energy of TPF glass is higher than that of TPC glass, but upconversion luminescence intensity of Yb^{3+}/Tm^{3+}-codoped TPF glass is stronger than that of Yb^{3+}/Tm^{3+}-codoped TPC glass. The analysis found that OH^- in glass host has a large effect on upconversion luminescence of Tm^{3+} by investigation on upconversion luminescence of Yb^{3+}/Tm^{3+}-codoped TZL glasses with and without removing water. The OH^- absorption coefficient of Tm^{3+} in TPC glass is bigger than that in TPF glass by investigation on infrared spectra of Yb^{3+}/Tm^{3+}-codoped TPF and TPC glasses, which results in the large nonradiative decay rate of Tm^{3+} in TPC glass. Effect of OH^- on the nonradiative decay rate of Tm^{3+} can be more than that of phonon energy in our experiments, and thus the upconversion luminescence intensity of Yb^{3+}/Tm^{3+}-codoped TPF glass is stronger than that of Yb^{3+}/Tm^{3+}-codoped TPC glass.

Acknowledgments

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