Intense frequency upconversion luminescence in Yb^{3+}/Tm^{3+}-codoped oxychloride germanate glasses

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Yb^{3+}/Tm^{3+}-codoped oxychloride germanate glasses for developing potential upconversion lasers have been fabricated and characterized. Structural properties were obtained based on the Raman spectra analysis, indicating that $PbCl_2$ plays an important role in the formation of glass network and has an important influence on the maximum phonon energies of host glasses. Intense blue and weak red emissions centered at 477 and 650 nm, corresponding to the transitions $^1G_4 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3H_4$, respectively, were observed at room temperature. With increasing $PbCl_2$ content, the intensity of blue (477 nm) emission increases significantly, while the red (650 nm) emission increases slowly. The results indicate that $PbCl_2$ has more influence on the blue emissions than the red emission in oxychloride germanate glasses. The possible upconversion mechanisms are discussed and estimated. Intense blue upconversion luminescence indicates that these oxychloride germanate glasses can be used as potential host material for upconversion lasers.

1. Introduction

Optical properties of trivalent lanthanide ions such as Er^{3+}, Ho^{3+}, and Nd^{3+} in glasses have been extensively studied to develop upconversion visible or ultraviolet lasers which can be operated at room temperature [1–6]. Among the trivalent lanthanide ions, Tm^{3+} ion has stable excited levels suitable for emitting blue and ultraviolet upconversion fluorescence. It was reported that a blue upconversion of Tm^{3+} was discovered in fluorozirconate glass by co-pumping at both 676.4 nm and 647.1 nm using a krypton ion laser and by single wavelength pumping at 650 nm [7, 8]. In addition, we found both blue and ultraviolet upconversion in Tm^{3+}-doped and Yb^{3+}/Tm^{3+}-codoped glasses [9, 10]. Host material for Tm^{3+} ions plays an important role in obtaining high-efficient upconversion signal, since glass host with low phonon energy can reduce the multiphonon relaxation (MPR) and thus achieves strong upconversion luminescence [11, 12]. Though fluoride glasses have been studied due to low phonon energies, oxide glasses are more appropriate for practical applications due to their high chemical durability and thermal stability. Among oxide glasses, bismuthate and germanate glasses combine high mechanical strength, high chemical durability, and temperature stability with good transmission in the infrared region, which make them promising materials for technological applications such as new lasing materials, upconversion phosphors, and optical waveguides [1, 2, 4, 13, 14]. To develop oxide glasses with extended infrared transmittance, large cations with low field strength, such as lead oxide, can be added.

As is known, glasses based on mixed oxide-halide systems combine the good optical properties of halide glasses (a broad range of optical transmittance and low optical losses) with the better chemical and thermal stability of oxide glasses [14]. So it is expected that oxychloride germanate glass should bring together the interesting properties of the two systems. Recently, many investigations have focused on oxyhalide tellurite glasses [3]. However, to the best of our knowledge, little attention has been paid to the study of Tm^{3+}-doped oxychloride germanate glass. In this paper, the structural and upconversion fluorescence properties of oxychloride germanate glasses were investigated. The results indicate that $PbCl_2$ has more influence on the blue emissions than the red emission in oxychloride germanate glasses. Intense blue upconversion fluorescence has been observed, and the possible upconversion mechanisms are discussed and estimated.

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2. Experimental

The glasses used in this work were synthesized by conventional melting and quenching method. The starting materials are reagent-grade $PbCl_2$, PbO, BaF_2, and high-purity GeO_2, Tm_2O_3, and Yb_2O_3(>99.999%). The samples studied have the following composition: (mol%) $55GeO_2$-$25BaF_2$-(20-x)PbO-$x$$PbCl_2$-$0.05Tm_2O_3$-$1Yb_2O_3$ (GBx) (x = 0, 5, 10, 15, 20). Undoped GBx (x = 0, 5, 10, 15, 20) glasses were also prepared for measuring the Raman spectra. About 20 g batches of the well-mixed raw materials were melted at 1250°C for 30 min in covered aluminium oxide crucibles in an electronic furnace with Cl_2 atmosphere. When the melting was completed, the liquid was cast into stainless steel plate. The obtained glasses were annealed for several hours at the glass transition temperatures before cooling them to room temperature at a rate of 20°C/h, and then were cut and polished carefully in order to meet the requirements for optical measurements.

The Raman spectrum was recorded on a FT-Raman spectrophotometer (Nicolet MODULE) within the range of 100–1000 cm^{-1}. Nd: yttrium-aluminum-garnet operating at 1064 nm was used as the excitation source and the laser power level was 500 mW. The upconversion luminescence spectrum was obtained with a TRIAX550 spectrofluorimeter upon excitation of 975 nm LD with a maximum power of 2 W. In order to compare the luminescence intensity of these Tm^{3+}/Yb^{3+}-codoped oxychloride germanate glasses as accurate as we can, the position and power (90 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 sample was set at the same place in the experimental setup. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the Raman spectrum of undoped GB0 glass, and the spectrum is composed of three spectral regions: (i) low-frequency region (<300 cm^{-1}), attributed to the collective modes of local structures and heavy metal vibrational modes [15, 16]; (ii) intermediate region (300 to 660 cm^{-1}), attributed to the deformation of vibrational modes of a glass network structure with bridged oxygen [17–20], and (iii) high-frequency region (>660 cm^{-1}), attributed to the stretching vibrational modes of the glass network former [19, 20]. A least-squares fit was made for the Raman spectrum, assuming a Gaussian shape for each Raman band. In general, the low frequency Raman band is neither expected to be Gaussian-like, nor even symmetric, but on a first approximation, the low frequency features were also assumed to Gaussian [21]. Then the Raman spectrum is developed through a deconvolution using Gaussian distribution and five bands appear at around 120, 190, 410, 530, and 820 cm^{-1}. The Raman spectrum of undoped GB0 glass shows only one high-frequency band around 820 cm^{-1}, and it has been well understood and is assigned to Ge-O stretching vibration of the fourfold coordinated [GeO_4] [22]. The strong 410 cm^{-1} band could be attributed to the Ge-O-Pb bridging vibrations [23, 24], while the 530 cm^{-1} band is from the Ge-O-Ge stretching vibration [21–25]. The bands in low-frequency region could be attributed to vibrations involving Ge and Pb atoms, respectively [26, 27]. As shown in Fig. 2, with the replacement of PbO by $PbCl_2$, the maximum phonon energy of these oxychloride germanate glasses shifts from 820 to 804 cm^{-1}. Then we can deduce that $PbCl_2$ has an important influence on the formation of the glass network. Addition of $PbCl_2$ into germanium glass results in a lowering of the maximum phonon energy, which is lower than those of phosphate: 1100 cm^{-1}, silicate: 1000 cm^{-1}, germanate: 900 cm^{-1}, pure GeO_2 glass: 865 cm^{-1} [26, 27]. Therefore, it can be expected that these oxychloride germanate glasses are better candidates for upconversion luminescence of Tm^{3+} ions.

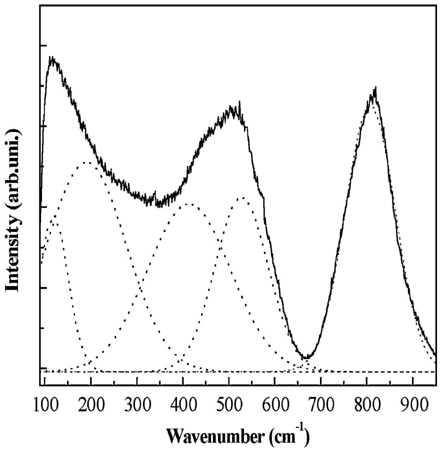

Figure 1 Peak-deconvolution of FT-Raman spectrum of undoped GB0 glass.

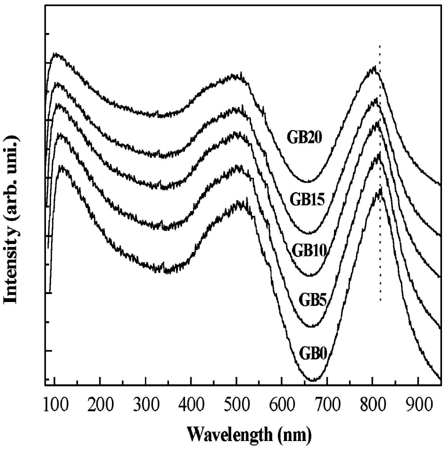

Figure 2 FT-Raman spectra of undoped GB0, GB5, GB10, GB15, and GB20 glasses.

The room temperature upconversion luminescence spectra of GB5, GB10, GB20 glasses in the wavelength region from 400 to 700 nm are shown in Fig. 3. Two emission bands centered at around 477 and 650 nm corresponding to the transitions $^1G_4 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3H_4$ of Tm^{3+}, respectively, were simultaneously observed. Clearly, the red emission at 650 nm is much weaker than the blue emission at 477 nm in Tm^{3+}/Yb^{3+}-codoped GB5, GB10, GB20 glasses. For the GB5, GB10, GB20 glasses, the

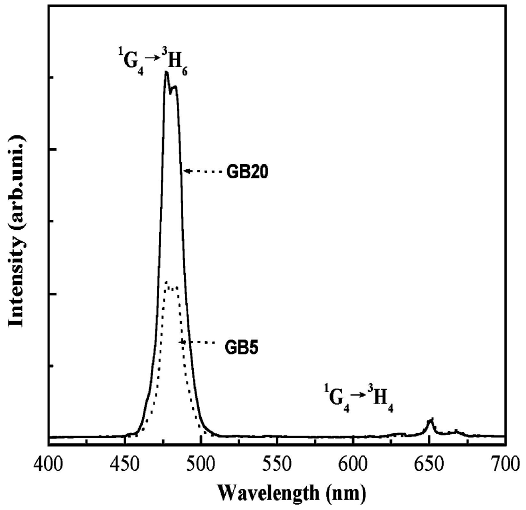

Figure 3 Upconversion fluorescence spectra of Tm^{3+}/Yb^{3+}-codoped GB5 and GB20 glasses under 975 nm LD excitation.

integrated intensities of the blue emission from 450 to 510 nm are 40.2, 59.6, and 94.3, respectively, while those of red emission from 620 to 670 nm are 3.2, 3.4, and 4.1, respectively. The fact confirms the expectation that chloride ions with low phonon energy contribute much to the increase of upconversion luminescence intensity at room temperature. It might be the reason that the addition of chloride ions increases the mass of the ligands, leading to lowering of the phonon vibrational energies, and thus, to a reduction of multiphonon relaxation rates and to enhance upconversion luminescence intensity. The results show that the dominant emission is the blue emission in Tm^{3+}/Yb^{3+}-codoped oxychloride germanate glasses. The blue emission in the region 450–510 nm accounts for more than 90% of the total emitted light in the spectral region studied. It is also important to point out that the intense blue upconversion fluorescence is bright enough to be observed by the naked eye at excitation power as low as 50 mW for these oxychloride germanate glasses. Fig. 4 shows the dependence of upconversion luminescence intensity ratios on $PbCl_2$ content. The integrated intensity ratios of red emission increase slightly with increasing $PbCl_2$ content, while those of blue emission increase notably. The blue emission intensity of GB20 glass is more than three times stronger than that of GB0 glass. Then we can conclude that these chloride modified germanate glasses are more preferable for blue emissions than red emission. In frequency upconversion process, the upconversion emission intensity I_{up} increases in proportion to the nth power of infrared (IR) excitation intensity I_{IR}, that is,

$$I_{\text{up}} \propto I_{\text{IR}}^n \tag{1}$$

where n is the number of IR photons absorbed per visible photon emitted [16]. A plot of log I_{up} vs. log I_{IR} yields a straight line with slope n. Fig. 5 shows such a plot for the 477 and 650 nm emissions in GB20 glass under 975 nm LD excitation. Values of 2.83 and 2.57 were obtained for n corresponding to the 477 and 650 nm emission bands, respectively. The results indicate that a three-photon upconversion process is responsible for the blue (477 nm) and red (650 nm) emissions from the $^1G_4 \to {}^3H_6$ and $^1G_4 \to {}^3H_4$ transitions, respectively.

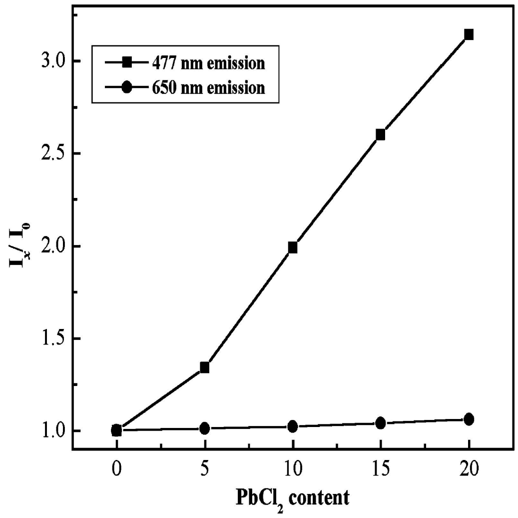

Figure 4 Relative intensity ratios of the blue and red upconversion luminescence as a function of $PbCl_2$ content in GB0, GB5, GB10, GB15, and GB20 glasses. I_x/I_0 is the intensity ratio of the blue and red upconversion emissions, respectively, between glasses with x mol% $PbCl_2$ and 0 mol% $PbCl_2$.

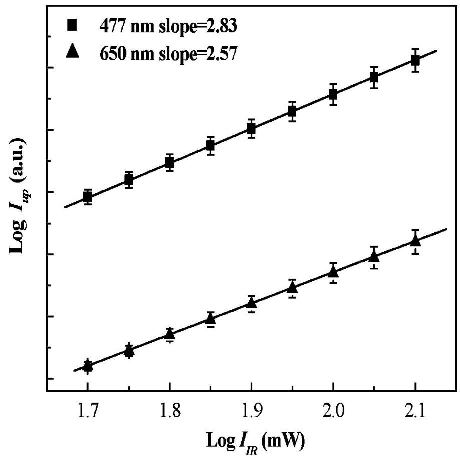

Figure 5 Dependence of upconversion fluorescence intensity on excitation power under 975 nm LD excitation for Tm^{3+}/Yb^{3+}-codoped GB20 glass.

According to the energy matching conditions, the possible upconversion mechanisms for the blue and red emissions are discussed based on the energy level of Tm^{3+} and Yb^{3+} presented in Fig. 6 [28]. The excitation process for the $^1G_4 \to {}^3H_6$ and $^1G_4 \to {}^3H_4$ transitions can be explained as follows. In the first step, a 975 nm photon is absorbed by Yb^{3+}, which provokes the $^2F_{7/2} \to {}^2F_{5/2}$ transition and then the excitation of Tm^{3+} in the $^3H_5$ is involved by energy transfer (ET) mechanism of excited Yb^{3+} to Tm^{3+}: $^2F_{5/2}(Yb^{3+}) + {}^3H_6(Tm^{3+}) \to {}^2F_{7/2}(Yb^{3+}) + {}^3H_5(Tm^{3+})$. In the second step, Tm^{3+} in the $^3H_5$ excited state relaxes nonradiatively to the metastate level $^3H_4$. Tm^{3+} in the $^3H_4$ level is excited to $^3F_{2,3}$ level by ET from Yb^{3+} and absorption a photon. Thus, the population of $^3F_{2,3}$ level is based on the processes as follows: ET from Yb^{3+}: $^2F_{5/2}(Yb^{3+})$

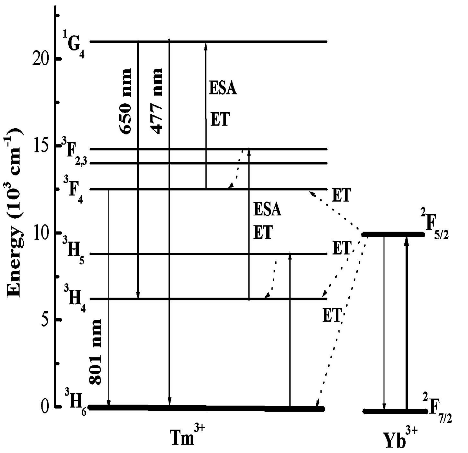

Figure 6 Simplified energy level diagram of Tm^{3+} and Yb^{3+} ions and possible transition pathways in these oxychloride germanate glasses.

+ $^3H_4(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^3F_{2,3}(Tm^{3+})$ and excited state absorption (ESA): $^3H_4(Tm^{3+})$ + a photon → $^3F_{2,3}(Tm^{3+})$. Then the $^3F_{2,3}$ states also relaxes by a multiphonon assisted process to the $^3F_4$ level. Finally, Tm^{3+} in the $^3F_4$ level is excited to $^1G_4$ level by ET from Yb^{3+} and absorption a photon. Therefore, the population of $^1G_4$ is based on the processes as follows: ET from Yb^{3+}: $^2F_{5/2}(Yb^{3+}) + {}^3F_4(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+})$ + $^1G_4$ (Tm^{3+}) and ESA: $^3F_4(Tm^{3+})$ + a photon → $^1G_4$ (Tm^{3+}). From the $^1G_4$ level, the Tm^{3+} ions decay radiatively to the $^3H_6$ ground state, generating the intense blue emission around 477 nm. The major contribution to the red (650 nm) emission is attributed to the $^1G_4 \rightarrow {}^3H_4$ transition, while the transition probability involved in the above process is small, then the red emission observed is weak. From the above results it can be concluded that a three-photon upconversion process is responsible for blue (477 nm) and red (650 nm) emission.

4. Conclusions

In conclusion, we have studied the structure of oxychloride germanate glasses by Raman spectra, which indicates that $PbCl_2$ plays an important role in the formation of glass network, and has an important influence on the maximum phonon energy of host glasses. Intense blue and weak red emissions centered at 477 and 650 nm, corresponding to the transitions $^1G_4 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3H_4$, respectively, were observed at room temperature under 975 nm LD excitation, which are due to three-photon absorption processes. With increasing $PbCl_2$ content, the intensity of blue (477 nm) emission increases significantly, while the red (650 nm) emission increases slowly. The results indicate that $PbCl_2$ has more influence on the blue emissions than the red emission in oxychloride germanate glasses. Intense blue upconversion luminescence indicates that these oxychloride germanate glasses can be used as potential host material for upconversion lasers.

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