Structural and up-conversion luminescence properties in
Tm$^{3+}$/Yb$^{3+}$-codoped heavy metal oxide–halide glasses

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Abstract

Tm$^{3+}$/Yb$^{3+}$-codoped heavy metal oxide–halide glasses have been synthesized by conventional melting and quenching method. Structural properties were obtained based on the Raman spectra, indicating that halide ion has an important influence on the phonon density and 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. The possible up-conversion mechanisms are discussed and estimated. With increasing halide content, the up-conversion luminescence intensity and blue luminescence lifetimes of Tm$^{3+}$ ion increase notably. Our results show that with the substitution of halide ion for oxygen ion, the decrease of phonon density and maximum phonon energy of host glasses both contribute to the enhanced up-conversion emissions.

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1. Introduction

Recently, with the commercialization of high-power solid-state laser diodes (LD) emitting in the 800–1000 nm infrared range, the development of LD pumped up-conversion lasers is a promising concept towards all solid-state visible wavelength lasers [1]. Optical properties of trivalent lanthanide ions such as Er$^{3+}$, Ho$^{3+}$ and Nd$^{3+}$ in glasses have been extensively studied to develop highly efficient up-conversion 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 up-conversion fluorescence. Recently, it was reported that a blue up-conversion of Tm$^{3+}$ was discovered in fluorozirconate glass by co-pumping at both 676.4 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 up-conversion in Tm$^{3+}$-doped glasses [9]. Host material for Tm$^{3+}$ ions plays an important role in obtaining highly efficient up-conversion signal, since glass host with low phonon energy can reduce the multiphonon relaxation (MPR), and thus, achieves strong up-conversion luminescence [10,11]. Among oxide glasses, lead germanium glasses combine high mechanical strength, high chemical durability and temperature stability with good transmission in the infrared region up to 4.5 μm, which make them promising materials for technological applications such as new lasing materials, up-conversion phosphors and optical waveguides [12].

As is known, heavy metal oxide–halide glasses are suitable glass systems for all-solid-state up-conversion lasers because they combine the good optical properties of halide glasses (low maximum phonon energy) with the better chemical and thermal stability of oxide glasses [12]. Recently, many investigations have focused on oxide–halide tellurite glasses, and attributed the enhanced up-conversion emissions to the decreasing maximum phonon energy of glass matrix [13]. Raman scattering, which studies the interaction between
photons and high frequency optical phonons caused by vibration of molecules and atoms in matter, is a nondestructive and convenient diagnostic tool for material characterization and analysis. Compared with phonon side-band spectroscopy, Raman spectroscopy extracts more information including both phonon energy and phonon density [14]. In this paper, up-conversion luminescence and structural properties in Tm\(^{3+}\)/Yb\(^{3+}\)-codoped heavy metal oxide–halide glasses have been systematically investigated. Structural properties were obtained based on the Raman spectra. Our results show that with the substitution of halide ion for oxygen ion, the decrease of phonon density and maximum phonon energy of host glasses both contribute to the enhanced up-conversion emissions.

2. Experiments

The starting materials are reagent-grade PbO, PbCl\(_2\), BaCl\(_2\), Bi\(_2\)O\(_3\) and high-purity GeO\(_2\), Yb\(_2\)O\(_3\) and Tm\(_2\)O\(_3\) (>99.999%). The studied glasses were prepared in the compositions: (mol\%) 30GeO\(_2\) –30Bi\(_2\)O\(_3\) –5BaCl\(_2\) –(35 – x) PbO –xPbCl\(_2\) –0.05Tm\(_2\)O\(_3\) –1Yb\(_2\)O\(_3\) (x = 0, 10, 20, 30, 35), which titled GBBC0, GBBC10, GBBC20, GBBC30 and GBBC35, respectively. Undoped GBBC0, GBBC10, GBBC20, GBBC30 and GBBC35 glasses were also prepared for measuring the Raman spectra. About 20 g batches of the well-mixed raw materials were melted at 1200–1300 °C for 30–60 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. The annealed samples were cut using a low-speed diamond saw and polished with 5-μm diamond paste. The polished samples have plate shapes with 20 mm × 10 mm × 1 mm for optical measurements. The Raman spectrum was recorded on a FT-Raman spectrophotometer (Nicolet MODULE) within the range of 50–900 cm\(^{-1}\). The visible up-conversion luminescence measurements were performed with a TRIAX550 spectrophotometer upon excitation of 975 nm LD with the maximum power of 2 W. Blue luminescence (477 nm) decays were measured using a modulated 975 nm laser and a computer-controlled digitizing oscilloscope. The lifetime was calculated by fitting the exponential function to the decay data. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Structural analysis of these oxide–halide glasses

Fig. 1 shows the Raman spectrum of undoped GBBC0 glass. 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 be Gaussian [15]. Then, the Raman spectrum is developed through a deconvolution using Gaussian distribution and five bands appear at around 130, 200, 370, 550 and 750 cm\(^{-1}\). The Raman spectrum of undoped GBBC0 glass shows only one high-frequency band around 750 cm\(^{-1}\) and it has been well understood and is assigned to rather localized Ge–O\(^{-}\) stretching modes of the metagermanate units (interconnected tetrahedra with two nonbridges \([\text{GeO}_4]^{2-}\) ) [16]. The strongest 370 cm\(^{-1}\) band could be attributed to the superposition of Bi–O–Pb and Ge–O–Pb bridging vibrations, while the 550 cm\(^{-1}\) band is from the Bi–O–Bi and/or Ge–O–Ge stretching vibration [15–18]. The bands in low-frequency region could be attributed to vibrations involving Ge and Pb atoms, respectively [19]. As shown in Fig. 2, with the substitution of PbCl\(_2\) for PbO, the maximum phonon energy...
of these halide modified GBBC\(x\) glasses shifts from 750 to 730 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 heavy metal oxide glass results in a lowering of the maximum phonon energy, which is lower than those of phosphate: 1100 cm\(^{-1}\), silicate: 1000 cm\(^{-1}\), tellurite: 800 cm\(^{-1}\) [20,21]. Therefore, it can be concluded that the halide modified GBBC\(x\) glasses are better candidates for up-conversion luminescence of Tm\(^{3+}\) ions.

### 3.2. Up-conversion fluorescence mechanism analysis

The room temperature up-conversion luminescence spectra of GBBC0 and GBBC35 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 \(1 \text{G}_4 \rightarrow 3 \text{H}_6\) and \(1 \text{G}_4 \rightarrow 3 \text{H}_4\) 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 GBBC0 and GBBC35 glass samples. It is also important to point out that the intense blue up-conversion fluorescence is bright enough to be observed by the naked eye at excitation power as low as 80 mW for GBBC0 and GBBC35 glasses.

In frequency up-conversion process, the up-conversion emission intensity \(I_{\text{up}}\) increases in proportion to the \(n\)th power of infrared (IR) excitation intensity \(I_{\text{IR}}\), that is,

\[
I_{\text{up}} \propto I_{\text{IR}}^n,
\]

where \(n\) is the number of IR photons absorbed per visible photon emitted. A plot of \(\log I_{\text{up}}\) versus \(\log I_{\text{IR}}\) yields a straight line with slope \(n\). Fig. 4 shows such a plot for the 477 and 650 nm emissions in GBBC35 glass under 975 nm excitation. Values of 2.50 and 2.28 for GBBC35 glass were obtained for \(n\) corresponding to the 477 and 650 nm emission bands, respectively. The results indicate that a three-photon up-conversion process is responsible for the blue (477 nm) and red (650 nm) emissions from the \(1 \text{G}_4 \rightarrow 3 \text{H}_6\) and \(1 \text{G}_4 \rightarrow 3 \text{H}_4\) transitions, respectively. The reason that the slopes for the blue and red emissions are smaller than three is mainly due to the saturation effect because the pump beam was focused into the sample. According to the energy matching conditions, the possible up-conversion mechanisms for the blue and red emissions are discussed based on the energy level of Tm\(^{3+}\) and Yb\(^{3+}\), as presented in Fig. 5. The excitation process for the \(1 \text{G}_4 \rightarrow 3 \text{H}_6\) and \(1 \text{G}_4 \rightarrow 3 \text{H}_4\) transitions can be explained as follows. In the first step, a 975 nm photon is absorbed by Yb\(^{3+}\) by ground state absorption (GSA), which provokes the \(2 \text{F}_{7/2} \rightarrow 2 \text{F}_{5/2}\) transition, and then the excitation of Tm\(^{3+}\) in \(3 \text{H}_5\) is involved by non-resonantly energy transfer (ET) of excited Yb\(^{3+}\) to Tm\(^{3+}\):

\[
2 \text{F}_{5/2} (\text{Yb}^{3+}) + 3 \text{H}_6 (\text{Tm}^{3+}) \rightarrow 2 \text{F}_{7/2} (\text{Yb}^{3+}) + 3 \text{H}_5 (\text{Tm}^{3+}).
\]

This transition requires the lattice phonon to absorb about 1940 cm\(^{-1}\). In the second step, Tm\(^{3+}\) in \(3 \text{H}_5\)
excited state relaxes nonradiatively to the metastate level $\text{^3}H_4$. Then, the $\text{^3}H_4$ level is excited to $\text{^3}F_{2,3}$ level by ET from the second excited $\text{^2}F_{7/2}$ and a photon absorption. Thus, the population of $\text{^3}F_{2,3}$ level is based on the processes as follows: ET from $\text{^2}F_{7/2}(\text{Yb}^{3+})+\text{^3}H_4(\text{Tm}^{3+})\rightarrow\text{^2}F_{7/2}(\text{Yb}^{3+})+\text{^3}F_{2,3}(\text{Tm}^{3+})$ and excited state absorption (ESA): $\text{^3}H_4(\text{Tm}^{3+})+\text{a photon} \rightarrow \text{^3}F_{2,3}(\text{Tm}^{3+})$. Then, the $\text{^3}F_{2,3}$ states also relaxes by a multiphonon assisted process to the $\text{^3}H_4$ level. This ET in the second step loses energy of about 1000 cm$^{-1}$. Finally, $\text{^3}H_4$ in the $\text{^3}F_{2,3}$ level is excited to $\text{^1}G_4$ level by nonresonant ET from $\text{Yb}^{3+}$ and a photon absorption. Therefore, the population of $\text{^1}G_4$ is based on the processes as follows: ET from $\text{^2}F_{7/2}(\text{Yb}^{3+})+\text{^3}F_{2,3}(\text{Tm}^{3+})\rightarrow\text{^2}F_{7/2}(\text{Yb}^{3+})+\text{^1}G_4(\text{Tm}^{3+})$ and ESA: $\text{^2}F_{7/2}(\text{Tm}^{3+})+\text{a photon} \rightarrow \text{^1}G_4(\text{Tm}^{3+})$. From the $\text{^1}G_4$ level, the $\text{Tm}^{3+}$ ions decay radiatively to the $\text{^3}H_6$ ground state, generating the intense blue emission around 477 nm. The major contribution to the red (650 nm) emission is attributed to the $\text{^1}G_4 \rightarrow \text{^3}H_6$ 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 up-conversion process is responsible for blue (477 nm) and red (650 nm) emission.

3.3. The origin of notably enhanced up-conversion emissions

The efficiency of up-conversion emissions depends on the lifetime of the intermediate excited state, $\tau$, whose magnitude is governed by the radiative and nonradiative decay processes as

$$\frac{1}{\tau} = W_{\text{RD}} + W_{\text{MP}} + W_{E},$$

where $W_{\text{RD}}$ is the radiative decay rate, $W_{\text{MP}}$ the multiphonon relaxation rate and $W_{E}$ is the energy transfer rate due to the cross-relaxation process between rare-earth ions [22]. In the weak-coupling case of rare-earth luminescence centers, $W_{\text{MP}}$ follows an exponential gap law given by

$$W_{\text{MP}} = C \left( \frac{\exp(h\omega_p/kT)}{\exp(h\alpha P/kT) - 1} \right) \epsilon^{-\alpha/D\Delta E}.$$

In Eq. (3), $P = \Delta E/\hbar\omega_p$ is the phonon order, $\alpha = -\ln(e) / \hbar\omega_p$ where $\epsilon$ accounts for the exact nature of the ion–phonon coupling and is insensitive as the log dependence in the formula and $C$ is a constant dependent on the host [23,24]. This multiphonon decay of rare-earth ions in glass, in general, depends on the maximum phonon energy of the host glass as we observe its exponential dependence in Eq (3). As a result, the lifetime of the intermediate excited state and the intensity of the luminescence, increase with decreasing maximum phonon energy. Fig. 6 shows the dependence of total up-conversion luminescence intensity and blue luminescence lifetimes of $\text{Tm}^{3+}$ on halide content. With increasing halide content, the up-conversion total up-conversion luminescence intensity and blue luminescence lifetimes of $\text{Tm}^{3+}$ increase notabily, which confirms the expectation based on the results of Raman spectra. However, in view of notably enhanced up-conversion emission with the replacement of oxide by halide, we believe that there must be other important factors that determine the up-conversion efficiency. In Eq (3), the constant $C$, if we look at it in more detail, depends on the phonon density of the matrix. Based on the Debye approximation,

$$C \propto \rho(\omega)^{1/2}$$

where $\rho(\omega)$ is the phonon density of state of the matrix [25]. Therefore, a smaller phonon density will result in a smaller $C$, implying a smaller $W_{\text{MP}}$ and a stronger up-conversion luminescence. With the introduction of halide content, the intensities of Raman peaks for these oxide–halide glasses become weaker, as shown in Fig. 2, indicating that the phonon density of these oxide–halide glasses becomes smaller. Considering the large difference of up-conversion luminescence in these oxide–halide glasses, we could deduce that this phonon density effect also contributes to the enhanced up-conversion emissions. This interpretation (effect of phonon density on up-conversion luminescence in oxide–halide glasses) has not been used in previous studies. Analysis of vibrational energy as well as the phonon density through Raman spectroscopy, as a result, is of great significance in understanding up-conversion luminescence.

4. Conclusions

In conclusion, we have studied the structure of heavy metal oxide–halide glasses by Raman spectra. The Raman spectra investigation indicates that halide ion plays an important role in the formation of glass network, and has an important influence on the maximum phonon energy and phonon density of host glasses. Intense blue and weak red emissions centered at 477 and 650 nm, corresponding to the transitions...
$^1G_4 \rightarrow ^3H_4$ and $^1G_4 \rightarrow ^3H_6$, respectively, were observed at room temperature, which are due to three-photon absorption processes. With increasing halide content, the up-conversion luminescence intensity and blue luminescence lifetimes of Tm$^{3+}$ ion increase notably. Our results show that with the replacement of oxygen ion by halide ion, the decrease of phonon density and maximum phonon energy of host glasses both contribute to the enhanced up-conversion emissions.

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