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Upconversion luminescence of Tm^{3+}/Yb^{3+} codoped oxyfluoride glasses*

Duan Zhong-Chao(段忠超)[a)b)†], Zhang Jun-Jie(张军杰)[a)], He Dong-Bing(何冬兵)[a)b)], Dai Shi-Xun(戴世勋)[a)], and Hu Li-Li(胡丽丽)[a)]

[a)] *Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai* 201800, *China*

[b)] *Graduate School of the Chinese Academy of Sciences, Beijing* 100039, *China*

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Novel oxyfluoride glasses are developed with the composition of $30SiO_2-15Al_2O_3-28PbF_2-22CdF_2-0.1TmF_3-xYbF_3-(4.9-x)\ AlF_3$($x$=0, 0.5, 1.0, 1.5, 2.0) in mol fraction. Furthermore, the upconversion luminescence characteristics under a 970nm excitation are investigated. Intense blue, red and near infrared luminescences peaked at 453nm, 476nm, 647nm and 789nm, which correspond to the transitions of Tm^{3+}: $^1D_2 \rightarrow {}^3F_4$, $^1G_4 \rightarrow {}^3H_6$, $^1G_4 \rightarrow {}^3F_4$, and $^3H_4 \rightarrow {}^3H_6$, respectively, are observed. Due to the sensitization of Yb^{3+} ions, all the upconversion luminescence intensities are enhanced considerably with Yb^{3+} concentration increasing. The upconversion mechanisms are discussed based on the energy matching rule and quadratic dependence on excitation power. The results indicate that the dominant mechanism is the excited state absorption for those upconversion emissions.

Keywords: upconversion luminescence, Tm^{3+}/Yb^{3+} codoped, oxyfluoride glass
PACC: 7820, 8160E, 8160D

1. Introduction

In recent years, the upconversion of infrared to visible light has been extensively investigated in rare-earth ions doped glasses and crystals, due to the possibility of infrared-pumped visible lasers and the potential applications in areas such as optical data storage, sensors, lasers, and optical displays.[1−4] Glass materials are attractive as hosts because of their easier fabrication and machining. Most of the oxide glasses have large phonon energies (>1000cm^{-1}) due to the lattice vibration of network-forming oxides. Fluoride glasses have the advantage of high quantum efficiencies of various active transitions of rare-earth ions due to their lower phonon energies (300–500cm^{-1}). But their chemical and thermal durabilities precluded their practical applications. In order to seek for a novel material with excellent stability and optical properties, a variety of glasses have been investigated. Among those materials available, the oxyfluoride glasses have aroused the interest of many investigators most. Particularly, the $SiO_2-Al_2O_3-PbF_2-CdF_2$ glasses[5] emerge as a potential candidate for photonic device applications. These glasses have some advantages, for example, their mechanical strength, chemical durability, and thermal stability are better than those of fluoride-based glasses and their maximum phonon energy is mediate between energies of silicate and fluoride based glasses.

For the majority of rare-earth singly doped systems the upconversion process has been proven inefficient for pumping in the wavelength region around 1,000nm, particularly for those ions capable of generating blue upconversion emission. However, when rare-earth doped materials are sensitized by trivalent ytterbium,[6−10] both the high absorption cross-section of the ytterbium sensitizer and the efficient energy-transfer mechanism between Yb^{3+} ions and the rare-earth acceptor ions, lead to a considerable enhancement in the upconversion efficiency as demonstrated previously.[6−11]

In the present paper, we report on the fabrication and upconversion luminescence characteristics of a new kind of Tm^{3+}/Yb^{3+} codoped

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†Corresponding author. E-mail: dzc80@163.com

$SiO_2-Al_2O_3-PbF_2-CdF_2$ (SAPC) oxyfluoride glass. Furthermore, the upconversion mechanism is discussed.

2. Experiment

The glass used in this work was synthesized by means of conventional melting and quenching. The starting materials were reagent-grade SiO_2, Al_2O_3, PbF_2, CdF_2 and AlF_3. Tm^{3+} and Yb^{3+} were introduced through TmF_3 and YbF_3 with high purity (>99.99%). The glass samples with the composition of $30SiO_2-15Al_2O_3-28PbF_2-22CdF_2-0.1TmF_3-xYbF_3-(4.9-x)AlF_3$ in mol fraction were prepared. About 20g of the well-mixed raw material a batch was melted at 1050°C for 10–15 minutes in aluminium oxide crucibles in an electronic furnace in air atmosphere. After the material was completely melted into a liquid state, it was cast into preheated plumbaginaceous mould. The obtained glass was annealed at its corresponding glass transition temperature (T_g), and then was cut and polished carefully in order to meet the requirements for optical measurements.

The thermoanalytical temperatures were obtained by differential scanning calorimetry (DSC) at a heating rate of 10°C/min, using an aluminium oxide ceramic pan. The UV–Vis/NIR absorption spectrum was recorded between 400nm and 1800nm by a Perkin-Elmer Lambda 900 spectrophotometer. The upconversion luminescence spectrum was obtained with a TRIAX550 spectrofluorimeter upon excitation of 970nm LD with a maximum power of 2W. All the measurements were performed at ambient temperature.

3. Results and discussion

Figure 1 gives the absorption spectra of SAPC glasses with $0.1Tm^{3+}$ and $1.0Yb^{3+}/0.1Tm^{3+}$ contents in mol%. For only Tm^{3+} doped SAPC glasses, there are three absorption bands peaked at 683nm, 789nm and 1200nm, which correspond to $^3F_2$, $^3H_4$ and $^3H_5$ level of Tm^{3+}, respectively. When Yb^{3+} is added in, there appears a strong absorption around at 970nm, due to the ground state absorption (GSA) of the Yb^{3+} $^2F_{5/2}$ level, which is much stronger than other absorption bands. Therefore, a 970nm pump source is very suitable for Tm^{3+}/Yb^{3+} codoped SAPC glass upconversion luminescence.

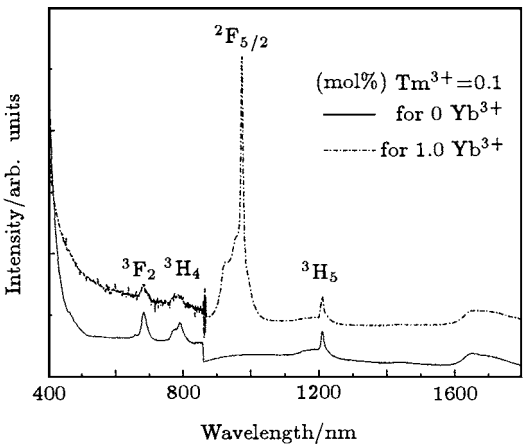


Fig.1. Absorption spectra of Tm^{3+}/Yb^{3+} codoped oxyfluoride glass samples.

Figure 2 shows the upconversion spectra of Tm^{3+}/Yb^{3+} codoped SAPC glasses as a function of the Yb^{3+} content at room temperature. We can see four emission bands peaked at 453, 476, 647, and 789nm that correspond to transitions of Tm^{3+} ions from excited states to the ground state. Intense blue, NIR and red emission bands at around 453, 476, 789, and 647nm wavelength are attributed to the transitions from ($^1D_2 \rightarrow ^3F_4$) ($^1G_4 \rightarrow ^3H_6$) ($^3H_4 \rightarrow ^3H_6$) and ($^1G_4 \rightarrow ^3F_4$), respectively. All the upconversion luminescences are enhanced strongly with Yb^{3+} contents increasing. It is because of the contribution of Yb^{3+} in energy transfer process, which will be discussed later.

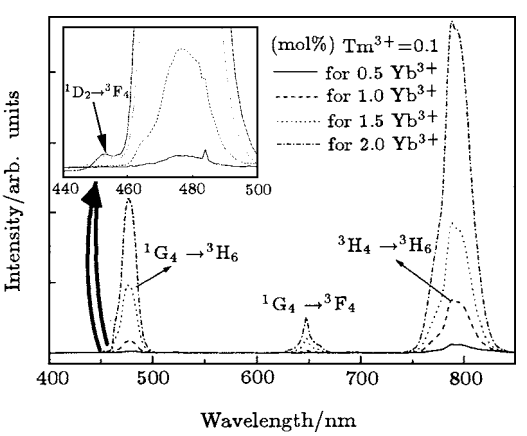


Fig.2. The upconversion luminescence spectra of SAPC glass samples.

The following three possible mechanisms have been proposed to explain the frequency upconversion phenomena of rare earth ions: excited state absorption (ESA), energy transfer upconversion (ETU), and photon avalanche upconversion processes.[12] According to the level diagrams of Tm^{3+}/Yb^{3+}, the upconversion process of Tm^{3+} in SAPC glasses is proposed,

as shown in Fig.3. It is suggested that the dominant mechanism is the ESA for Tm^{3+} upconversion luminescence; however it also involves an ETU process for a 453nm blue upconversion emission. When the glass is excited by a 970nm laser, the $^2F_{5/2}$ level of Yb^{3+} is populated by the ground state absorption (GSA) first. And then the energy is transferred from Yb^{3+} to Tm^{3+} which is in $^3H_5$ state. Consequently, the $^3H_5$ level is populated via the energy transfer (ET) step ($Yb:^2F_{5/2}+Tm:^3H_6 \rightarrow Yb:^2F_{7/2}+Tm:^3H_5$). It is important to point out that this ET process is necessary for $Tm^{3+}:^3H_5$ level population. As we can see in the absorption spectra of Tm^{3+}, the absorption band of ($^3H_6 \rightarrow ^3H_5$) transition is not matchable with a 970nm pump light, while Yb^{3+} can absorb the 970nm laser beam and produce a ($^2F_{7/2} \rightarrow ^2H_{5/2}$) transition. Therefore, increasing the Yb^{3+} content will enhance the absorption of pump light and improve its upconversion quantum efficiency. On the other hand, with Yb^{3+} concentration rising, the spacings among Yb^{3+} ions decrease. So, the energy transfer probability (W_{ET}) between Yb^{3+} and Tm^{3+} increases. In terms of Dexter's calculation[13] the dependence of W_{ET} on interionic spacing is described as

$$W_{ET} = \frac{\text{const}}{v^2 n^4 R^k} f_D f_A \int g_D(\nu) g_A(\nu) d\nu, \qquad (1)$$

where R is the spacing between donor and acceptor centres; n is the polarization-averaged index of refraction at an energy $\nu(cm^{-1})$; f is oscillator strengths of both energy transfer centres; and g is the integrated overlap of the normalized donor emission and acceptor absorption spectral features; The superscripts k are 6, 8, and 10 for electric dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole contributions, respectively. For each transition the contribution of R to the energy transfer probability is great, consequently, the upconversion emission intensity increases rapidly with Yb^{3+} concentration increasing.

When $Tm^{3+}:^3H_5$ level is populated, it relaxes to $^3F_4$ level easily by a nonradiative transition ($^3H_5 \rightarrow ^3F_4$), and then the $^3F_2$ level is populated via an ESA process. The energy gap among $^3F_2$, $^3F_3$ and $^3H_4$ is so small that Tm^{3+} in $^3F_2$ level relaxes to $^3H_4$ level finally. In Miyakawa–Dexter theory,[14] the nonradiative decay rate due to a multiphonon relaxation process is expressed as

$$W_{mp} = W_0 \exp(-\alpha \Delta E / h\omega), \qquad (2)$$

where W_{mp} is the multiphonon decay rate, ΔE is the energy gap relative to the next lower level and $h\omega$ is the phonon energy. It is easy to know that in the same host materials, the less the energy gap, the larger the nonradiative decay rate. That is to say, a level with small energy gap relative to the next lower level is easy to relax to a lower level.

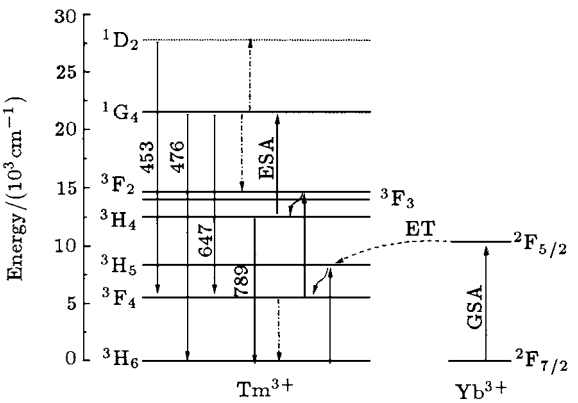


Fig.3. Simplified energy diagram and proposed upconversion mechanism of Tm^{3+}/Yb^{3+}.

The $^1G_4$ level may be populated by a further ESA ($^3H_4 \rightarrow ^1G_4$) as shown in Fig.3. While the $^1D_2$ level should be populated by a ETU process ($^1G_4$,$^1G_4$) $\rightarrow$ ($^3F_2$,$^1D_2$) or ($^1G_4$,$^3F_4$) $\rightarrow$ ($^1D_2$,$^3H_6$), according to Eq.(1), at low dopant concentration levels ($\leq$0.1%) in homogeneously-doped materials, W_{ET} will approach zero. Therefore, the ETU probability is very small, compared with ESA. The 453nm blue emission ($^1D_2 \rightarrow ^3F_4$) is much weaker than other upconversion luminescence. As indicated in Fig.2, the 453nm blue luminescence can hardly occur if Yb^{3+} concentration is less than 1%. This confirms the assumed upconversion mechanism for the 453nm blue emission, which is due to the ETU. The dominant ETU process is ($^1G_4$,$^3F_4$) $\rightarrow$ ($^1D_2$,$^3H_6$), which is of a three-photon upconversion process.

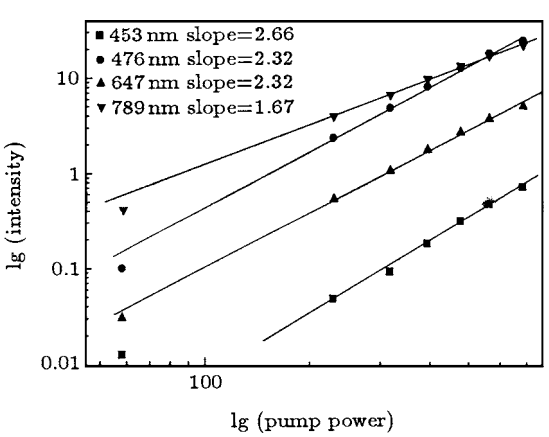


Fig.4. Upconversion intensities as a function of the excitation power at 970nm. Solid lines correspond to the linear fitting.

In a frequency upconversion process, the increase in upconversion emission intensity I_{UC} is proportional to the nth power of infrared excitation intensity I_{IR}, that is

$$I_{UC} \propto I_{IR}^{n}, \tag{3}$$

where n is the number of the absorbed infrared photons per emitted visible photon.[15] A plot of $\lg(I_{UC})$ vs $\lg(I_{IR})$ yields a straight line with a slope n. Figure 4 shows such plots for the 453nm, 476nm, 647nm and 789nm emissions in SAPC glass under a 970 nm excitation. Values of 2.66, 2.32, 2.32, and 1.67 are obtained for n corresponding to the 453nm, 476nm, 647nm and 789nm emission bands, respectively. The results indicate that 476nm blue and 647nm red emissions originate from the three-photon upconversion process, while the NIR luminescence comes from a two-photon upconversion process. This is in agreement with the proposed upconversion mechanism above. It is interesting to point out that the 453nm blue upconversion is of a four-photon process, though the slope 2.66 is much less than 4. This is because Tm^{3+} in $^1D_2$ state is very prone to take a cross relax nonradiative transition.

4. Conclusions

In the Tm^{3+}/Yb^{3+} codoped SAPC glass, frequency upconversion of Tm^{3+} has been investigated. Under a 970nm excitation, efficient 453nm, 476nm blue and 647nm red and 789nm NIR upconversion fluorescence emissions are observed. Further research indicates that 476nm ($^1G_4 \rightarrow ^3H_6$) and 647nm ($^1G_4 \rightarrow ^3F_4$) luminescences are due to a three-photon upconversion process, however, the 789nm ($^3H_4 \rightarrow ^3H_6$) emission comes from a two-photon process. As an increasing Yb^{3+} content can improve the absorption of pump light and energy transfer probability, all upconversion emission intensities depend strongly on the Yb^{3+} concentration. Owing to the efficient upconversion fluorescence, Tm^{3+}/Yb^{3+} codoped SAPC glasses can be used as a potential host material for upconversion luminescence.

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