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Enhancement of the upconversion luminescence in Y₂O₃:Er³⁺ powders by codoping with La³⁺ ions

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Infrared-to-visible upconverted luminescent spectra of Er³⁺ and La³⁺ codoped Y₂O₃ powders are investigated. By introducing La³⁺ ions, the upconversion green radiation is found to be greatly enhanced when compared with the powders with La³⁺ absent. Such enhancement can be attributed to the modification of the local symmetry surrounding the Er³⁺ ion, which benefits the intra-4f transitions of Er³⁺ ion, and the decreasing interaction between Er³⁺ ions, which suppresses the energy transfer process 4F_7/2 → 4I_{15/2} → 4F_9/2 + 4F_5/2.

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Rare-earth (RE) ions doped upconversion (UC) materials have potential applications in the field of color display, UC lasers and temperature sensors, etc. However, insufficient intensity still constitutes the main limitation for their practical applications. Therefore, new routes are needed to be developed to greatly increase the UC emissions in order to meet their application requirements.

It is well known that intra-4f electronic transitions of RE³⁺ are parity forbidden, and become partially allowed when intermixing the 4f state with higher electronic configurations is enabled by the local crystal field of host lattice. Therefore, a promising route to enhance the RE³⁺ ions’ luminescence is to tailor their local environment in the host lattice. As La³⁺ has the largest cationic radius among the RE³⁺ ions, it may be an ideal cation for tailoring the local crystal field of RE³⁺ ions in some hosts, such as RE sesquioxides Y₂O₃, Sc₂O₃ and Lu₂O₃, etc. In this Letter, we primarily report on an innovative route to increase the UC green emission in Y₂O₃:Er³⁺ powders via codoping with La³⁺ ions.

Er³⁺ has been chosen here because it is one of the most popular and most efficient ions among the RE³⁺ ions. Moreover, Y₂O₃, which has intriguing chemical and optical properties, is a promising host material for RE ions. Furthermore, UC photoluminescence (PL) in Y₂O₃:Er³⁺ powders has been reported, while the enhancement of the UC-PL intensity in La³⁺ and Er³⁺ codoped Y₂O₃ powders has not been investigated.

Y₂O₃ powders doped with 5 mol.% Er³⁺ and 0, 5, 10, 12 mol.% La³⁺ were prepared by gel combustion method, which has been used to produce fine and homogeneous powders. Stoichiometric amounts of solid oxides of yttrium, erbium and lanthanum were dissolved in dilute nitric acid to make nitrate solution. Required amount of glycine was added by keeping nitrate to glycine ratio 1:1.66. The mixed solution was heated at 100°C to form a clear glassy gel. This gel on further heating at 300°C was converted to a white fluffy powder and then was calcined at 1200°C for 2 h.

X-ray diffraction (XRD) measurements were carried on the synthesized powders using a Bruker D2 PHASE Diffractometer with Cu-Kα radiation (λ = 1.5406 Å). The UC spectra of the samples were measured at room temperature by a FLUOROLOG3/Jobin-Yvon spectrofluorometer under the excitation of a 980 nm laser diode.

The XRD patterns of Y₂O₃ powders doped with 5 mol.% Er³⁺ ions and various La³⁺ ions are shown in Fig. 1(a). All of the diffraction peaks of the samples are only from cubic Y₂O₃ phase (JCPDS No. 65-3178), and no other phase can be detected, which confirms the synthesis of phase pure material. However, the position of the diffraction peaks shifts with La³⁺ ion concentration. From Fig. 1(b), it can be seen that the main diffraction peak of Y₂O₃:Er³⁺ powders moves toward lower angles with an increase in La³⁺ concentration, which implies the expansion of the host lattice. Meanwhile, the lattice parameters of the samples, calculated based on the least square fitting of the diffraction peaks, were found to increase gradually with the increasing La³⁺ concentration [Fig. 1(c)]. This is because the substitution of Y³⁺ ions with the larger La³⁺ ions can cause the host lattice to expand. Moreover, the average crystallite sizes of Y₂O₃:Er³⁺ powders codoped with 0, 5, 10, and 12 mol.% La³⁺ ions, accounting to the Scherrer’s equation, were calculated to be about 33, 31, 30, and 30 nm, respectively.

Figure 2(a) shows the UC spectra of Er³⁺ ions in Er³⁺ and La³⁺ codoped Y₂O₃ powders with different La³⁺ concentration under a 980 nm excitation. The green emission ranging from 516 to 570 nm is associated with transitions 3H_11/2 → 4I_{13/2}, 4I_{15/2}, and the red emission from 644 to 685 nm is attributed to transition 4F_5/2 → 4I_{15/2}. The specimen only doped with Er³⁺ emits relative weak intensity in the green regions, while the green radiation changes dramatically upon adding La³⁺ ions. Figure 2(b) illustrates the integral intensity of green emission as a function of La³⁺ ions. The fluorescence dramatically increases with La³⁺ ions of 0–10 mol.%, and decreases at higher...
concentrations. The integrated intensity of the green emission from the specimen doped with 10 mol.% La$^{3+}$ is about 6 times greater than that from the sample without La$^{3+}$. On the other hand, Fig. 2(c) shows that the intensity ratio of the green to red of the sample without La$^{3+}$ is only about 0.3, whereas an increase of the La$^{3+}$ concentration to 10 mol.% leads to about 1.5, which indicates that the increased percentage of the green emission is larger than that of the red emission. The above results illustrate that codoping La$^{3+}$ ions in Y$_2$O$_3$:Er$^{3+}$ powders can significantly favor the green UC emission.

Figure 3 shows the UC mechanisms of the green and red emissions. Under the 980 nm excitation, the Er$^{3+}$ ion can be excited to the \textit{4}I$_{11/2}$ state through ground state absorption (GSA) of laser photons, and further to the \textit{4}F$_{7/2}$ state via the excited state absorption (ESA) 1 or energy transfer UC (ETU) 1 processes. While the emission of Er$^{3+}$ ions from the \textit{4}F$_{7/2}$ state to ground state is restricted, they can nonradiatively relax to the \textit{2}H$_{11/2}$ and \textit{4}S$_{3/2}$ states, from these two states the photons in green wavelengths are emitted. Alternatively, the Er$^{3+}$ ion at the \textit{4}I$_{11/2}$ state can nonradiatively relax to the \textit{4}I$_{13/2}$ state, and is further

![Fig. 1](image1.png)

Fig. 1. (a) XRD patterns of (Er$_{0.05}$Y$_{0.95-x}$La$_x$)$_2$O$_3$ powders ($x = 0, 0.05, 0.1,$ and 0.12). (b) The enlarged pattern of (222) diffraction peaks. (c) The variation of lattice parameter with the increase in La$^{3+}$ concentration in the lattice.

![Fig. 2](image2.png)

Fig. 2. (a) Measured UC spectra in Y$_2$O$_3$ powders doped with 5 mol.% Er$^{3+}$ ions and several La$^{3+}$ ions under a 980 nm excitation. (b) The integral intensity of green emission as a function of La$^{3+}$ ions. (c) The intensity ratio of the green to red as a function of La$^{3+}$ ions.
It is reported that the infrared-to-visible UC processes codoped Y2O3 powders is reported. Such enhancement is mainly attributed to the modification of the local crystal field around the Er3+ ions and the decrease of the interaction between Er3+ ions by the presence of La3+ ions. Although the enhancement induced by the La3+ ions is demonstrated here in Y2O3;Er3+ powders, we believe the route can be further developed to apply to other RE3+ ions doped materials to improve the UC emission.

In conclusion, the enhancement of the green UC emission under the 980 nm laser excitation in La3+ and Er3+ codoped Y2O3 powders is reported. Such enhancement is mainly attributed to the modification of the local crystal field around the Er3+ ions and the decrease of the interaction between Er3+ ions by the presence of La3+ ions. Although the enhancement induced by the La3+ ions is demonstrated here in Y2O3;Er3+ powders, we believe the route can be further developed to apply to other RE3+ ions doped materials to improve the UC emission.

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