

Enhancement of the upconversion luminescence in $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ powders by codoping with La^{3+} ions

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Infrared-to-visible upconverted luminescent spectra of Er^{3+} and La^{3+} codoped Y_2O_3 powders are investigated. By introducing La^{3+} ions, the upconversion green radiation is found to be greatly enhanced when compared with the powders with La^{3+} absent. Such enhancement can be attributed to the modification of the local symmetry surrounding the Er^{3+} ion, which benefits the intra-4*f* transitions of Er^{3+} ion, and the decreasing interaction between Er^{3+} ions, which suppresses the energy transfer process $^4\text{F}_{7/2} + ^4\text{I}_{11/2} \rightarrow ^4\text{F}_{9/2} + ^4\text{F}_{9/2}$.

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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^[1-3], 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-4*f* electronic transitions of RE^{3+} are parity forbidden, and become partially allowed when intermixing the 4*f* state with higher electronic configurations is enabled by the local crystal field of host lattice^[4,5]. Therefore, a promising route to enhance the RE^{3+} ions' luminescence is to tailor their local environment in the host lattice. As La^{3+} has the largest cationic radius among the RE^{3+} ions, it may be an ideal cation for tailoring the local crystal field of RE^{3+} ions in some hosts, such as RE sesquioxides Y_2O_3 , Sc_2O_3 and Lu_2O_3 , etc. In this Letter, we primarily report on an innovative route to increase the UC green emission in $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ powders via codoping with La^{3+} ions.

Er^{3+} has been chosen here because it is one of the most popular and most efficient ions among the RE^{3+} ions^[6]. Moreover, Y_2O_3 , which has intriguing chemical and optical properties, is a promising host material for RE ions^[7]. Furthermore, UC photoluminescence (PL) in $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ powders has been reported^[8,9], while the enhancement of the UC-PL intensity in La^{3+} and Er^{3+} codoped Y_2O_3 powders has not been investigated.

Y_2O_3 powders doped with 5 mol.% Er^{3+} and 0, 5, 10, 12 mol.% La^{3+} were prepared by gel combustion method, which has been used to produce fine and homogeneous powders^[10]. 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 PHASER Diffractometer with Cu-K_α radiation ($\lambda = 1.5406 \text{ \AA}$). 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 Y_2O_3 powders doped with 5 mol.% Er^{3+} ions and various La^{3+} ions are shown in Fig. 1(a). All of the diffraction peaks of the samples are only from cubic Y_2O_3 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 La^{3+} ion concentration. From Fig. 1(b), it can be seen that the main diffraction peak of $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ powders moves toward lower angles with an increase in La^{3+} 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^[11], are found to increase gradually with the increasing La^{3+} concentration [Fig. 1(c)]. This is because the substitution of Y^{3+} ions with the larger La^{3+} ions can cause the host lattice to expand^[12]. Moreover, the average crystallite sizes of $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ powders codoped with 0, 5, 10, and 12 mol.% La^{3+} ions, accounting to the Scherrer's equation^[7,11], were calculated to be about 33, 31, 30, and 30 nm, respectively.

Figure 2(a) shows the UC spectra of Er^{3+} ions in Er^{3+} and La^{3+} codoped Y_2O_3 powders with different La^{3+} concentration under a 980 nm excitation. The green emission ranging from 516 to 570 nm is associated with transitions $^2\text{H}_{11/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$, and the red emission from 644 to 685 nm is attributed to transition $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$. The specimen only doped with Er^{3+} emits relative weak intensity in the green regions, while the green radiation changes dramatically upon adding La^{3+} ions. Figure 2(b) illustrates the integral intensity of green emission as a function of La^{3+} ions. The fluorescence dramatically increases with La^{3+} ions of 0–10 mol.%, and decreases at higher

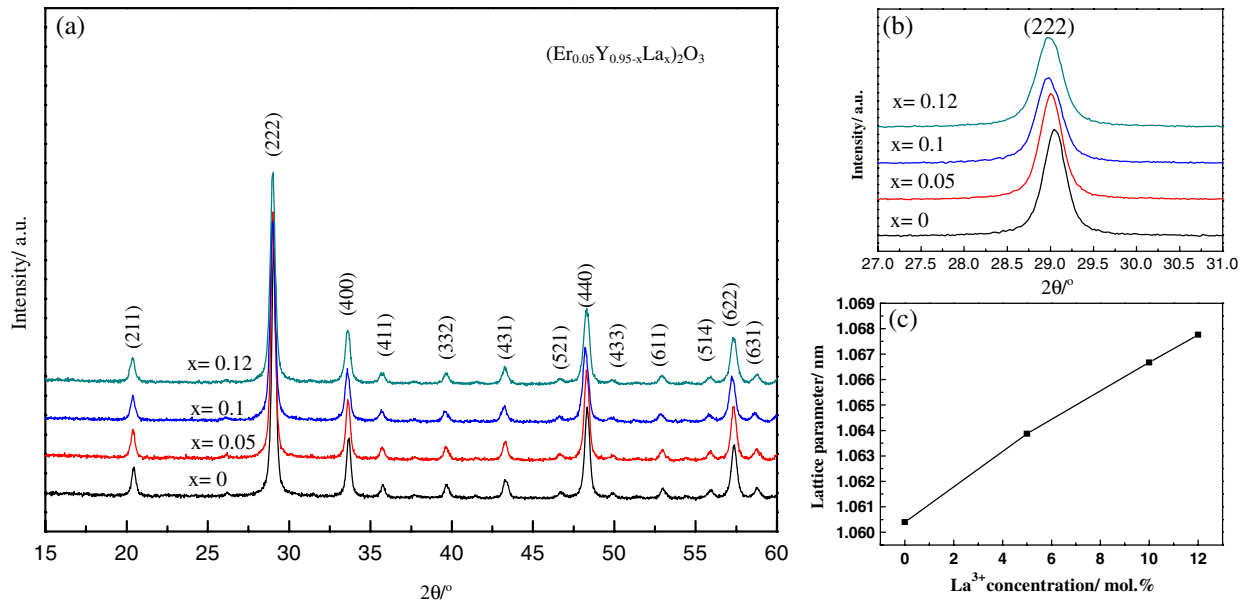


Fig. 1. (a) XRD patterns of $(\text{Er}_{0.05}\text{Y}_{0.95-x}\text{La}_x)_2\text{O}_3$ powders ($x = 0, 0.05, 0.1, \text{ and } 0.12$). (b) The enlarged pattern of (222) diffraction peaks. (c) The variation of lattice parameter with the increase in La^{3+} concentration in the lattice.

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 $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ powders can significantly favor the green UC emission.

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

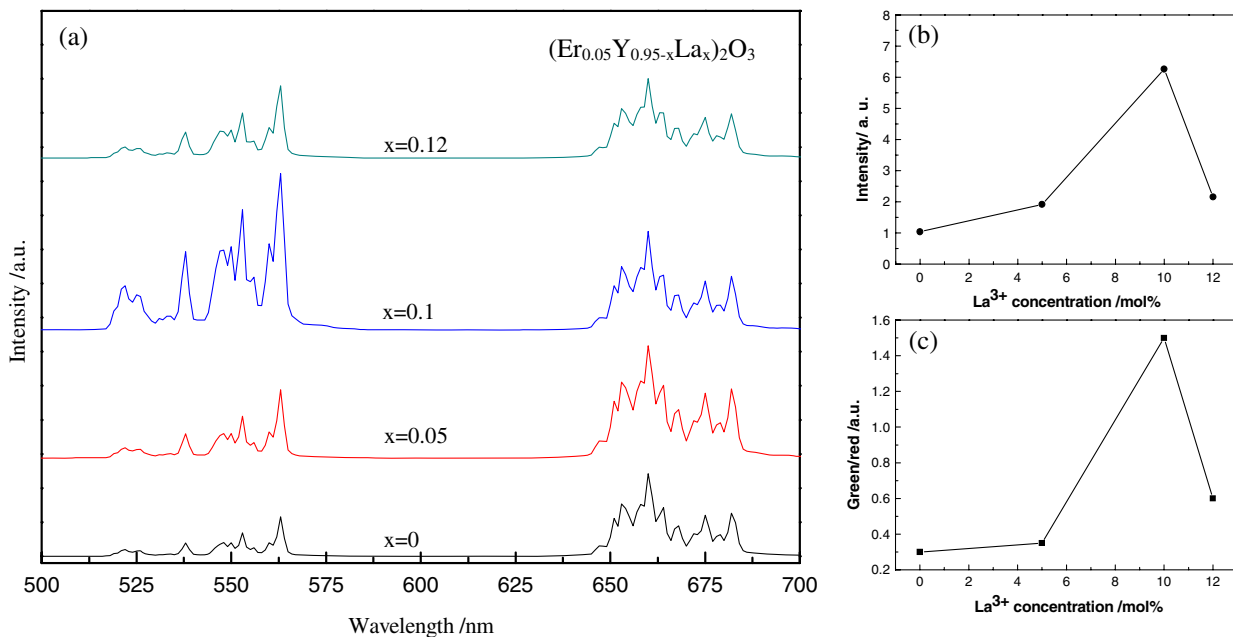


Fig. 2. (a) Measured UC spectra in Y_2O_3 powders doped with 5 mol.% Er^{3+} ions and several La^{3+} ions under a 980 nm excitation. (b) The integral intensity of green emission as a function of La^{3+} ions. (c) The intensity ratio of the green to red as a function of La^{3+} ions.

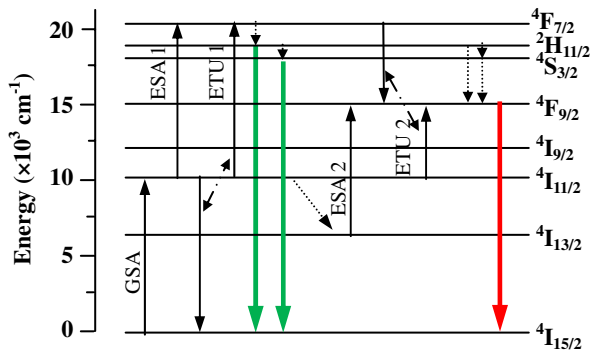


Fig. 3. Energy levels diagram of Er^{3+} ion and UC-PL processes under 980 nm excitation.

excited to the ${}^4\text{F}_{9/2}$ state by ESA2 process. The ${}^4\text{F}_{9/2}$ state can also be populated by the multiphonon-assisted relaxations from the upper ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2}$ state to ${}^4\text{F}_{9/2}$ state, as well as the ETU2 process of ${}^4\text{F}_{7/2} + {}^4\text{I}_{11/2} \rightarrow {}^4\text{F}_{9/2} + {}^4\text{F}_{9/2}$. The ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transition gives rise to the red emission.

It is reported that the infrared-to-visible UC processes described above are strongly dependent on the local symmetry of Er^{3+} ions' local environment^[5,14]. As confirmed by XRD results, the lattice parameter of Y_2O_3 increases after La^{3+} ions substitute the sites of Y^{3+} , which indicates the doped La^{3+} ions can slightly adjust the structure of Y_2O_3 lattice. Consequently, the Er-O bond distortion is expected, which reduces the local symmetry of the crystal field around Er^{3+} . That means some banned electric-dipole transitions of Er^{3+} may become allowed due to the intermixing of the intra-4f states with higher electronic configurations, resulting in an increase of the optical transition probability^[5,14]. Thus, it can be suggested that the enhancement of UC-PL intensity by doping La^{3+} in the $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ powders arises from the increasing asymmetry of crystal field around Er^{3+} .

Moreover, after La^{3+} ions diffuse into the Y_2O_3 lattice, the distance between Er^{3+} and Er^{3+} ions increases due to the expansion of the host lattice. Then the interaction between the neighboring Er^{3+} ions is reduced, which leads to the decrease of the ETU2 process ${}^4\text{F}_{7/2} + {}^4\text{I}_{11/2} \rightarrow {}^4\text{F}_{9/2} + {}^4\text{F}_{9/2}$ and benefits a larger population in the ${}^4\text{F}_{7/2}$ state^[15]. As the ${}^4\text{F}_{7/2}$ state is responsible for populating Er^{3+} ions in state ${}^2\text{H}_{11/2}/{}^4\text{S}_{3/2}$, the increases in the green emission and also the green to red ratio can be expected.

The key mechanism for the green UC enhancement arises from the fact that the codoping of La^{3+} can tailor the local environment around the Er^{3+} ions, and

eventually alter their radiation properties. However, both green and red emissions become weak, when La^{3+} concentration increases from 10 to 12 mol.%. This may come from the fact that as excess La^{3+} ions are present, the local crystal field around Er^{3+} might become symmetric again. As mentioned above, symmetric crystal field is unfavorable for the UC-PL emission.

In conclusion, the enhancement of the green UC emission under the 980 nm laser excitation in La^{3+} and Er^{3+} codoped Y_2O_3 powders is reported. Such enhancement is mainly attributed to the modification of the local crystal field around the Er^{3+} ions and the decrease of the interaction between Er^{3+} ions by the presence of La^{3+} ions. Although the enhancement induced by the La^{3+} ions is demonstrated here in $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ powders, we believe the route can be further developed to apply to other RE^{3+} ions doped materials to improve the UC emission.

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