



Pure red upconversion emission from $\text{CaF}_2:\text{Yb}^{3+}/\text{Eu}^{3+}$

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ARTICLE INFO

Article history:

Received 21 October 2016

Received in revised form

16 January 2017

Accepted 17 January 2017

Available online 18 January 2017

Keywords:

Upconversion luminescence

Cooperation sensitization

Inorganic material

CIE

ABSTRACT

Single phase cubic CaF_2 microcrystals co-doped with Eu^{3+} and Yb^{3+} ions were synthesized through a coprecipitation process followed by annealing at 1200 °C. Under the excitation of 980 nm laser, the intensive emission at ~ 614 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) in the red region was observed at room temperature. The color coordinate of $\text{CaF}_2:0.1\%\text{Yb}^{3+}/0.1\%\text{Eu}^{3+}$ was calculated with the Commission Internationale de l'Eclairage (CIE) chromaticity coordinate of ($x=0.572$, $y=0.265$). The excitation of Eu^{3+} ions came from the energy transfer of Yb^{3+} -dimers through a cooperation sensitization process. Furthermore, not only the emissions from the $^5\text{D}_i$ ($i=0, 1, 2, 3$) $\rightarrow$ $^7\text{F}_j$ ($j=0, 1, 2, 3$) transitions but also the rarely reported emission (~ 398 nm) from the $^5\text{L}_6 \rightarrow ^7\text{F}_0$ transition was recorded. The cooperation sensitization process was so effective in the $\text{Yb}^{3+}/\text{Eu}^{3+}$ co-doped system that all the cooperative luminescence (CL) from Yb^{3+} -clusters were quenched and only the red upconversion luminescence of Eu^{3+} ions could be seen.

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1. Introduction

Upconversion luminescence (UCL) phosphors can absorb more than one low energy photon and convert them to a high energy photon through metastable energy levels of doped lanthanide ions. This process is relatively effective in lanthanide-doped (Ln) inorganic materials, and therefore most of UCL phosphors are solid compounds and have gained great attention in the fields of 3D displays, light-emitting devices, biomarkers, bioassays, solid laser, light-emitting diodes (LEDs) [1–8]. Through the investigations of decades, researchers have found that the most efficient UCL systems are Yb^{3+} and $\text{Er}^{3+}/\text{Tm}^{3+}$ co-doped fluorides, in which energy transfer upconversion mechanism (ETU) plays a dominant role [9–11]. In general, UC emissions of red, green, and blue, (three primary colors) can be obtained from the Ho^{3+} , Er^{3+} , and Tm^{3+} -doped materials, respectively. Other colors can be realized through changing concentration of these ions. Among lanthanide elements the Europium (Eu) is usually used to be a red emitting lanthanide ion, and for this reason Eu^{3+} doped materials are widely used as red phosphors in television screens and fluorescent lamps etc via downconversion [12]. However, Eu^{3+} has been rarely considered as an UCL ion in the regime of NIR excitation until 2009 due to Eu^{3+} cannot be excited directly by NIR or sensitized by an excited Yb^{3+} ion. In that year, our group reported the red UC emission of Eu^{3+} ions under NIR excitation by introducing Tm^{3+} as “bridging”

ions [13]. Only bluish white light has been obtained although intense red UCL from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} ions was recorded because Tm^{3+} ions served as sensitizers as well as good blue emitters. Other researchers also reported that the UC transition of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ was obtained through cooperation energy transfer in $\text{Yb}^{3+}/\text{Eu}^{3+}$ co-doped systems [14–19]. However, the intensity of this transition was still relatively weak and the influence of “bridging” ions cannot be neglected. In recent years, UC red emission was also obtained by introducing Mn^{2+} and Mg^{2+} ions into fluoride nanocrystals as matrix ions [20,21]. Fluorides are known as efficient UC hosts because of their low phonon energies [22,23]. Here, we demonstrated the intense red light emission from $\text{CaF}_2:0.1\%\text{Yb}^{3+}/0.1\%\text{Eu}^{3+}$ pumped by 980 nm laser and based on a cooperation sensitization process from Yb^{3+} -dimers to Eu^{3+} ions. The first observations of cooperative absorption and cooperative luminescence of Yb^{3+} -dimers were reported in 1961 and 1970, respectively [24,25]. Since then, cooperative transitions of Yb^{3+} -dimers have been investigated in many Yb^{3+} , Eu^{3+} co-doped materials [26–39]. Eu^{3+} ions doped CaF_2 luminophores have been studied since 1954 [40–43]. Calcium fluoride consists of a simple cubic lattice of fluorine ions in which every other body center position is occupied by a Ca^{2+} ion. When a lanthanide ion with trivalence oxidation state is doped in an alkaline-earth fluoride, non-equilibrium of charge arises in the lattice due to the lanthanide ion usually occupy the position of an alkaline-earth ion with divalent oxidation state. The non-equilibrium of charge produces crystal defects such as the interstitials of F^- ions and cation vacancies in order to compensate excess plus charges, which gives

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non-uniform distribution of lanthanide ions. Yb^{3+} ions with a large absorption cross-section at near infrared (NIR) [44–47] act as sensitizers and increase the UC emission intensity [48]. Eu^{3+} ions are attractive as efficient emitters because of the sharp single-band UC emissions in the red region ($^5\text{D}_0 \rightarrow ^7\text{F}_2$). Yb^{3+} -dimers are excited by NIR radiation and transfer their energies to Eu^{3+} ions, providing them necessary energy for their excitation.

In this letter, we present a study on UC emissions of Eu^{3+} ions in CaF_2 . By using Yb^{3+} as sensitizer and a 980 NIR diode laser as pump power, all the cooperative luminescence (CL) from Yb^{3+} -clusters were quenched and all the excited Yb^{3+} -dimers transferred their energy to Eu^{3+} ions through a cooperation sensitization process. Furthermore, we discussed the mechanism of co-operation sensitization involving a two-photon population in detail.

2. Experimental section

In a typical synthesis process, 2 mmol $\text{Ca}(\text{NO}_3)_2$, $\text{Yb}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$, and 50 mL ethanol were added into a 100 mL beaker. After stirring for 30 min, 20 mmol NH_4F was added into the solution. The precursor was vigorously stirred for 24 hours under room temperature. Subsequently, the precipitate was separated by centrifugation and washed with deionized water and ethanol several times. Finally, the particles were dried in a vacuum oven at 80°C , and then annealed at 1200°C in an argon atmosphere for 2 hours to grow the crystallites. All the raw materials were analytical reagents without further purification.

3. Characterization

UC spectra were recorded by a Hitachi F-4500 spectrograph equipped with a Hamamatsu R928 photomultiplier (PMT) using a 2 W 980-nm continuous wave diode laser as the excitation source. All spectral measurements were carried out with the same instrument parameters (2.5 nm slit width and 700 V PMT voltage) at room temperature. A Rigaku RU-200b X-ray powder diffractometer (XRD) was used to analyze the crystal structures using a nickel-filtered Cu-K α radiation ($\lambda = 0.15405$ nm) in the range of $20^\circ \leq 2\theta \leq 70^\circ$. The accelerating voltage was 40 kV, and the emission current was 200 mA. A digital oscilloscope (DPO4104B, bandwidth 1 GHz, sampling rate 5 GSs $^{-1}$; Tektronix, Shanghai, China), a power-adjustable continuous wave laser diode (CW978 nm, 10 W), and a chopper (pulse width 4 KHz) were used to record decay curves.

4. Results and discussion

The composition and phase purity of the products were first examined by XRD. It is well known that CaF_2 has a cubic crystal lattice of fluorine ions and its lattice parameter values are $a=5.463$ nm, $b=5.463$ nm, $c=5.463$ nm in which every other body center position is occupied by a Ca^{2+} ion. As shown in the Fig. 1, all the patterns can be indexed to the pure cubic phase of CaF_2 (JCPDS 4-864) and no impurity peaks have been observed. According to the XRD patterns, neither the impurity peaks nor a second phase can be detected at the current doping level. It is clearly implied that the doping of Yb^{3+} and Eu^{3+} ions does not cause any significant change in the host structure.

The UC spectrum of $\text{CaF}_2:0.1\%\text{Yb}^{3+}/0.1\%\text{Eu}^{3+}$ under 980 nm laser excitation was recorded, as shown in Fig. 2. Characteristic peaks of Eu^{3+} ions can be found clearly, the f-f transition bands cover the spectral region between 370 nm and 670 nm, which is in

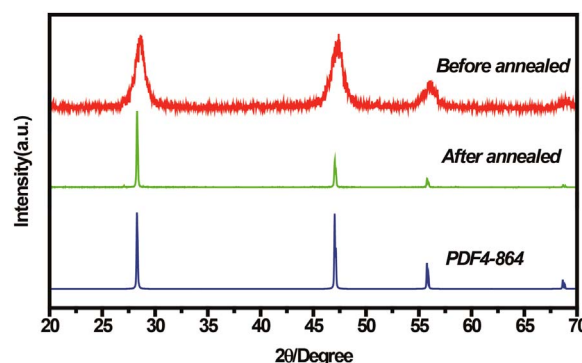


Fig. 1. Powder XRD patterns of $\text{CaF}_2:0.1\%\text{Yb}^{3+}/0.1\%\text{Eu}^{3+}$ sample.

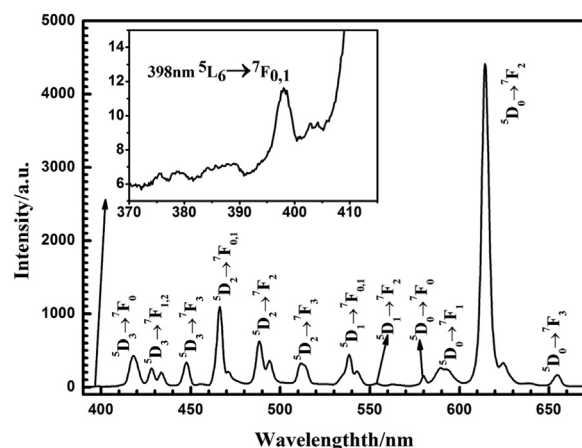


Fig. 2. Emission spectra of $\text{CaF}_2:0.1\%\text{Yb}^{3+}/0.1\%\text{Eu}^{3+}$ phosphor under 980 nm excitation (annealed at 1200°C).

the range of ultraviolet (UV) and visible light. The UCL of Eu^{3+} ions includes not only the emissions of $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j=0,1,2,3,4$), $^5\text{D}_1 \rightarrow ^7\text{F}_j$ ($j=0,1,2$), and $^5\text{D}_2 \rightarrow ^7\text{F}_j$ ($j=0,1,2,3$) but also includes the unusual emissions $^5\text{D}_3 \rightarrow ^7\text{F}_j$ ($j=0,1,2,3$) as well as the rarely reported emission of $^5\text{L}_6 \rightarrow ^7\text{F}_0$ in ultraviolet region (as shown in the insert chart). The intensity of transitions between different J levels depends on the symmetry of the local environment of the Eu^{3+} activators and can be described in terms of the Judd-Ofelt theory [49]. Magnetic dipole transition is permitted and electric dipole transition is forbidden, but for the most cases, the local symmetry of the Eu^{3+} activators do not have an inversion center and the parity forbidden is partially permitted, such as Eu^{3+} ions occupying C_2 sites in $\text{Y}_2\text{O}_3:\text{Eu}$ [50]. It is well known that the relative intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (a typical magnetic dipole transition) or $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (a typical electric dipole transition) depends strongly on the local symmetry of Eu^{3+} ions. Subsequently, when Eu^{3+} ions occupy the inversion center sites, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition should be relatively strong, while the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is parity forbidden and should be very weak. In addition, numerous surface defects exist and these defects may increase the degree of disorder and lower the local symmetry of Eu^{3+} ions located at the surface of the particles. This will increase the transition probability of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and enhance the red emission in visual. The cooperation energy transfer process from excited Yb^{3+} -dimers to Eu^{3+} ions is efficient, which leads to the result that all the cooperative emissions from Yb^{3+} -clusters were quenched and only the red upconversion luminescence of Eu^{3+} ions could be seen.

Fig. 3 describes schematically possible UC processes in energy level diagrams of the cooperation energy transfer from Yb^{3+} -dimers to Eu^{3+} ions. The large energy gap between the ground state

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