Journal of Alloys and Compounds 541 (2012) 505–509

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Red, green, blue and bright white upconversion luminescence of $CaTiO_3$: $Er^{3+}/Tm^{3+}/Yb^{3+}$ nanocrystals

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ARTICLE INFO

Article history:
Received 29 November 2011
Received in revised form 18 April 2012
Accepted 3 July 2012
Available online 11 July 2012

Keywords:
Rare-earth
$CaTiO_3$
Upconversion
White light

ABSTRACT

Under laser excitation of 976 nm, the green and red UC emissions of $CaTiO_3$: Er^{3+} nanocrystals were consistent with $^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}, respectively. The green and red UC luminescence of $CaTiO_3$: Er^{3+}/Yb^{3+} nanocrystals were significantly stronger than the counterpart of $CaTiO_3$: Er^{3+} nanocrystals, which was resulted from energy transfer between Yb^{3+} and Er^{3+}. The blue and red UC emissions of $CaTiO_3$: Tm^{3+}/Yb^{3+} nanocrystals near 480 and 650 nm were observed due to the $^1G_4 \rightarrow {}^3H_6$ and $^1G_4 \rightarrow {}^3F_4$ transition of Tm^{3+}, respectively. The overall and relative UC luminescence intensities of $Er^{3+}/Tm^{3+}/Yb^{3+}$ tridoped $CaTiO_3$ nanocrystals were found to be depended highly on the concentration of Yb^{3+} and Tm^{3+}, for which the involved mechanisms were demonstrated. By adjusting the concentration of Yb^{3+} and Tm^{3+}, $CaTiO_3$: $Er^{3+}/Tm^{3+}/Yb^{3+}$ nanocrystals with the CIE coordinates close to (0.33, 0.33) were obtained.

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1. Introduction

The investigation of rare earth doped upconversion (UC) materials has been increasingly interesting these years due to a large number of potential applications such as detectors for infrared radiation, fluorescent labels for sensitive detection of biomolecules, UC lasing, volumetric three-dimensional displays and temperature sensors, etc. [1–4]. More attention has been paid to UC white light in recent years, as the excitation source is an infrared laser, which is compact, power-rich, inexpensive, and also can be commercially available [5–7]. Due to the abundant energy levels and narrow emission spectral lines, the Er^{3+} ion, which is the first and the most popular ion showing green and red UC emissions, and the Tm^{3+} ion showing blue UC emission have been regarded as the most efficient UC activators [8,9]. Yb^{3+} ion is a well-known sensitizer that will conspicuously increase the optical pump efficiency due to the high absorption cross-section of Yb^{3+} ion around 980 nm and the efficient energy transfer from Yb^{3+} ion to Er^{3+} and Tm^{3+} ions [10–12]. High chemical stability and low phonon energy, efficient absorption and controllable emissions of the three primary colors (red, green, and blue) are essential conditions for a good white light source. However, it is worthwhile to point out that UC white light can only be achieved in suitable host lattices when RE^{3+} ions are appropriately incorporated.

Up to now, there have been many reports on various host matrix for UC luminescence, such as oxides, fluorides, and phosphates [13–17]. The host materials with low phonon energy can result in a reduction of the multiphonon relaxation and thus help efficient UC occur [18]. Among these materials, the phonon energy (about 470 cm^{-1}) of $CaTiO_3$ is quite low, which makes it suitable for host matrix as UC phosphors [19]. In this perovskite, the substitution of the A site (Ca^{2+} ion) by trivalent ions (Er^{3+}) results in the formation of Ca^{2+} vacancies, which consequently affect the UC properties of the materials [20–22]. It was reported that strong green anti-Stokes emission was observed in $CaTiO_3$: 5%Er^{3+} prepared by sol–gel method, which illustrated higher concentration of RE^{3+} ions doped into $CaTiO_3$ [22]. The sol–gel process is an efficient method for the synthesis of nanocrystals owing to the good mixing of starting materials and relatively low reaction temperature, resulting in more homogeneous products and accurate concentration proportion [6,23,24]. However, there is no investigation on the white luminescence of RE doped $CaTiO_3$ nanocrystals. In this paper, we first report on generating of white UC fluorescence in $Er^{3+}/Tm^{3+}/Yb^{3+}$-codoped $CaTiO_3$ nanocrystals prepared by the sol–gel method under diode laser excitation of 976 nm, according to our knowledge.

2. Experimental materials and methods

In a typical experiment, $CaTiO_3$ doped with 0.5% mol of Er^{3+}, 0.7% mol of Tm^{3+} and 7% mol of Yb^{3+} was prepared using calcium acetate monohydrate [$Ca(CH_3COO)_2$], tetrabutyl titanate [$Ti(OC_4H_9)_4$], erbium nitrate [$Er(NO_3)_3$], thulium

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http://dx.doi.org/10.1016/j.jallcom.2012.07.008

nitrate [$Tm(NO_3)_3$] and ytterbium nitrate [$Yb(NO_3)_3$] as starting reagents. A certain amount of $Ca(CH_3COO)_2$, $Er(NO_3)_3$, $Tm(NO_3)_3$ and Yb $(NO_3)_3$ were dissolved into 10 mL distilled water and then 5 mL nitric acid and 20 mL ethanol were added to the above solution under vigorous stirring, which marked as solution-A. Seven milliliters of $Ti(OC_4H_9)_4$ and 30 mL ethanol were uniformly mixed, which marked as solution-B. Solution-A was added to solution-B under stirring and then the pH of the mixed solution was adjusted to about 3 by the addition of an appropriate amount of nitric acid. After stirring for half an hour transparent sol was obtained. Subsequently, the sol was dried at 90 °C for 2 h until it was transformed into xerogel. $CaTiO_3$ doped with 0.5% mol of Er^{3+}, 0.7% mol of Tm^{3+} and 7% mol of Yb^{3+} nanocrystals were obtained by further sintering at 800 °C for 2 h.

X-ray diffraction pattern was obtained for the powder specimen on a D/max-γB X-ray diffractometer using a graphite monochromator Cu Kα radiation (40 kV, $\lambda = 0.1546$ nm). The scanning rate was $0.02°\ min^{-1}$ over a range of $2\theta = 10–80°$. The powder morphology was characterized by a HITACHI H-8100 transmission electron microscope (TEM). The samples for the TEM study were prepared by drop casting of ethanol solutions of nanocrystals onto carbon-coated copper grid. The UC emission spectra at room temperature were measured under a 976 nm diode laser (Hi-Tech Optoelectronics Co. Ltd., Beijing) excitation and detected from 400 to 700 nm by a lens-coupled monochromator with an attached photomultiplier. The powders were pressed to form smooth and flat pellets to be utilized for UC spectral studies.

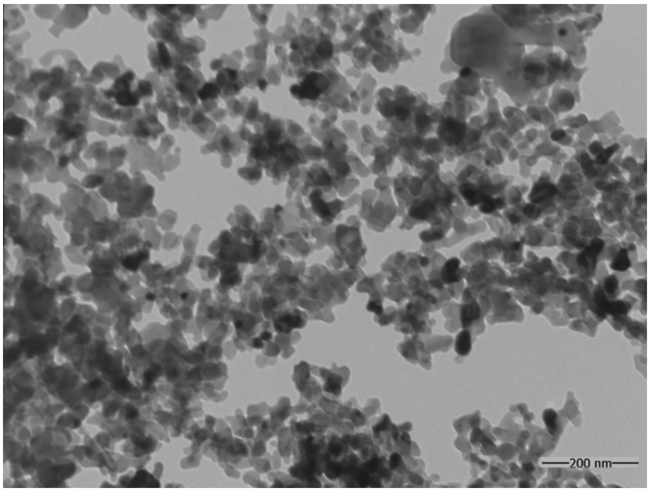

Fig. 2. TEM characterization of $CaTiO_3$: $0.5\%Er^{3+}/0.7\%Tm^{3+}/7\%Yb^{3+}$ nanocrystals.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the X-ray diffraction patterns of the rare-earth doped $CaTiO_3$ nanocrystals. All samples are of cubic structure, corresponding well to the standard pattern of $CaTiO_3$ (JCPDS file number 08–0091). And no extra peaks can be assigned to Er^{3+}, Tm^{3+} or Yb^{3+} in the X-ray diffraction patterns, which indicated that Er^{3+}, Tm^{3+} and Yb^{3+} ions were effectively incorporated into the matrix lattice. Fig. 2 displays the TEM image of the $CaTiO_3$: $0.5\%Er^{3+}/0.7\%Tm^{3+}/7\%Yb^{3+}$ sample. As shown in the Fig. 2, the nanocrystals are uniformly distributed particles with an average particle size of 30–40 nm.

3.2. Optical properties

3.2.1. UC luminescence

UC fluorescence emission spectra of the $CaTiO_3$ nanocrystals doped with $0.5\%Er^{3+}$, $0.5\%Er^{3+}/5\%Yb^{3+}$ and $0.5\%Tm^{3+}/5\%Yb^{3+}$ under the diode laser excitation of 976 nm at same condition (power density = $20\ W\ cm^{-2}$) are shown in Fig. 3. The strong green emission (528 nm, 550 nm) and the weak red emission (665 nm) are observed in of $CaTiO_3$: $0.5\%Er^{3+}$ nanocrystals. The green emission peaks can be attributed to $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} ions, and the red one corresponds to $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} ions, respectively. The green and red UC emissions of $CaTiO_3$: $0.5\%Er^{3+}$ nanocrystals can be adjusted by adding Yb^{3+} ions into the sample. The emission intensity of $CaTiO_3$: $0.5\%Er^{3+}/5\%Yb^{3+}$ nanocrystals changes greatly in comparison with $CaTiO_3$: $0.5\%Er^{3+}$ nanocrystals. The $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (Er^{3+}) red emission of $CaTiO_3$: $0.5\%Er^{3+}/5\%Yb^{3+}$ nanocrystals is significantly stronger than the counterpart of $CaTiO_3$: $0.5\%Er^{3+}$ nanocrystals as shown in Fig. 3(a) and (b). The $CaTiO_3$: $0.5\%Tm^{3+}/5\%Yb^{3+}$ nanocrystals exhibit a bright blue emission at 480 nm ascribed to $^1G_4 \rightarrow {}^3H_6$ transition of Tm^{3+} ions coupled with a relatively weak red emission near 650 nm assigned to $^1G_4 \rightarrow {}^3F_4$ transition of Tm^{3+} ions. The blue fluorescence dominates comparing with the red one observed in the emission spectrum.

3.2.2. UC mechanisms

The upconverted luminescence intensity (I) of the green, red and blue emission in $CaTiO_3$: $0.5\%Er^{3+}/5\%Yb^{3+}$ and $CaTiO_3$:

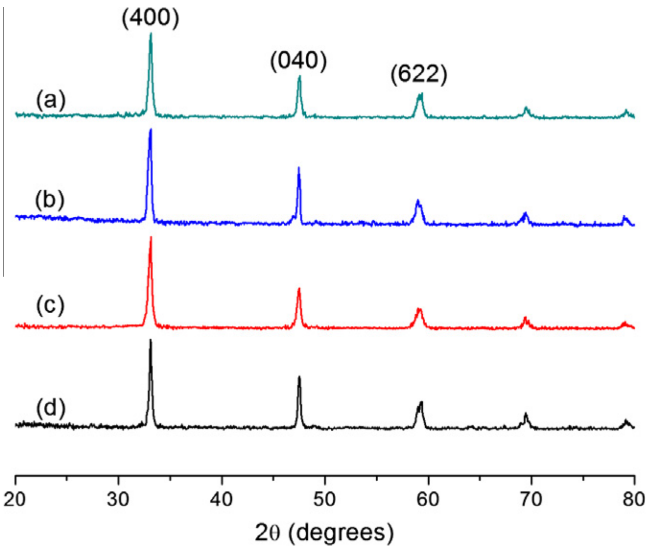

Fig. 1. X-ray powder diffraction patterns of the $CaTiO_3$: ER^{3+} nanocrystals (a) $CaTiO_3$: $0.5Er^{3+}$, (b) $CaTiO_3$: $0.5\%Er^{3+}/5\%Yb^{3+}$, (c) $CaTiO_3$: $0.5\%Tm^{3+}/5\%Yb^{3+}$, (d) $CaTiO_3$: $0.5\%Er^{3+}/0.7\%Tm^{3+}/7\%Yb^{3+}$, respectively.

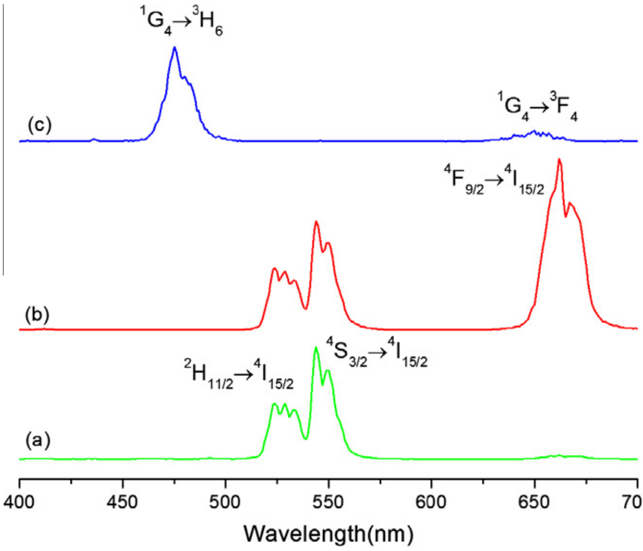

Fig. 3. Upconversion fluorescence emission spectra of (a) $CaTiO_3$: $0.5\%Er^{3+}$, (b) $CaTiO_3$: $0.5\%Er^{3+}/5\%Yb^{3+}$, (c) $CaTiO_3$: $0.5\%Tm^{3+}/5\%Yb^{3+}$ under 976 nm laser excitation at room temperature.

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