



# Enhanced up-conversion luminescence intensity in single-crystal SrTiO<sub>3</sub>: Er<sup>3+</sup> nanocubes by codoping with Yb<sup>3+</sup> ions



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## ABSTRACT

A series of Er<sup>3+</sup> doped and Er<sup>3+</sup>/Yb<sup>3+</sup> codoped SrTiO<sub>3</sub> nanocubes with varying dopant concentrations have been successfully synthesized by a facile hydrothermal method. The doping effects on phase purity, morphology and microstructure of samples were identified by power X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The results showed that SrTiO<sub>3</sub> nanocubes have a typical perovskite structure with the edge length ranging 20–50 nm. The Er<sup>3+</sup> and Yb<sup>3+</sup> ions were successfully doped into the crystal lattice of SrTiO<sub>3</sub>, but did not alter crystal structure of SrTiO<sub>3</sub>. The photon up-conversion (UC) photoluminescence (PL) measurements indicated that the intense green light emission of Er<sup>3+</sup> ions around 525 nm, 550 nm and red light emission centered at 670 nm in UC processes populated by 980 nm laser excitation have been achieved in SrTiO<sub>3</sub> nanocubes. Moreover, the PL intensity of Er<sup>3+</sup>-doped SrTiO<sub>3</sub> nanocubes was greatly enhanced while introducing the Yb<sup>3+</sup> to the crystal structure, especially the red emission. The mechanisms for these emissions probably due to the excited state absorption (ESA) and energy transfer (ET) process. Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped single-crystal perovskite SrTiO<sub>3</sub> nanocubes could be interesting objects for applications in mechanical–electrical luminescence such as electric field modulation luminescence and mechanoluminescence.

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## 1. Introduction

In recent years, photon up-conversion (UC) from the near-infrared (NIR) to visible light in rare-earth (RE) ions doped materials has attracted intense interests because of their outstanding properties and practical applications, such as photovoltaics, solar cells, color displays, and biological imaging [1–5]. The UC performance of a material could be significantly enhanced by the suitable selection of host matrix [6]. Moreover, tremendous researches on the energy transition determined by doping ions were emerged, aimed at optimizing the properties and extending the applications of UC materials.

ABO<sub>3</sub> perovskite oxides (SrTiO<sub>3</sub>, BaTiO<sub>3</sub>, PbTiO<sub>3</sub>, etc.) exhibit many intriguing physical properties, such as piezoelectricity and ferroelectricity, affording wide applications from electro-mechanical systems to data storage devices [7,8]. Owing to large-

range toleration with chemical doping, trivalent lanthanide ions (Ln<sup>3+</sup>) were introduced into the perovskite-related oxides to adjust their luminescence properties. Nowadays, various PL and electro-luminescence (EL) have been achieved in perovskite-type oxides, from crystalline powders, thin films to amorphous particles, offering the opportunity to lighting and flat-plane displaying. Generally, the trivalent rare earth ions, including Er<sup>3+</sup>, Ho<sup>3+</sup>, Tm<sup>3+</sup> and Yb<sup>3+</sup>, have been introduced into host matrix as absorption or emission centers to design the UC PL properties [9–13]. Among them, Er<sup>3+</sup> ions are of particular attraction as a luminescent activator because of its long lifetime, sharp emission bandwidth and tunable emission [14]. For example, Gong et al. synthesized Er<sup>3+</sup> doped preperovskite and perovskite PbTiO<sub>3</sub> nanofibers, respectively. It has been found that the UC PL properties were significantly different in preperovskite and perovskite PbTiO<sub>3</sub> since the substitution sites and chemical environments of Er<sup>3+</sup> ions were different in their structures [15]. However, in singly doped nanocrystals, two major parameters that effect UC processes are the distance between two neighboring activator ions and the absorption cross-section of the ions. Therefore, the concentration of activator ions should be

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kept low and precisely adjusted to avoid the quenching effect. Otherwise, the overall UC efficiency of singly doped nanocrystals would be relatively low [14,16]. To enhance UC luminescence efficiency, a sensitizer with a sufficient absorption cross-section in the NIR region is usually co-doped along with the activator to take advantage of the efficient energy transfer upconversion (ETU) process. For example, Sun et al. reported the infrared-to-visible UC PL properties of BaTiO<sub>3</sub> nanocrystals with dopant of Er<sup>3+</sup> ions, and their intensities have enhanced while Li<sup>+</sup> and Er<sup>3+</sup> were codoped [17]. Furthermore, the sensitization of rare earth Yb<sup>3+</sup> ion, is a well-known one for increasing the optical pump efficiency, as well as its application in optical devices [18,19].

SrTiO<sub>3</sub>, a typical perovskite oxide, has many fascinating properties, such as high dielectric constant, high charge storage capacity, excellent chemical and physical stability, and good transparency in the visible range [20–23]. In particular, the vibrational frequency of SrTiO<sub>3</sub> is quite low. So, it is suitable to be host matrix for UC excitation phosphors. It has been observed that nanoparticles have different properties compared with bulk compounds, such as light emissions, which increases in particles on the nanoscale. For example, the intensity of the emitted radiation in Er<sup>3+</sup>/Yb<sup>3+</sup>: SrO·TiO<sub>2</sub> glass ceramic is much higher than in the glass. Because the glass ceramic has Er<sup>3+</sup>/Yb<sup>3+</sup>-doped nanocrystalline phase in it, which is benefited to the UP PL emissions [24]. In addition, Souza et al. reported that the photoluminescence of SrTiO<sub>3</sub>, which is excited by 350 nm visible-UV, could be significantly affected by the particle size and morphology [25]. It has been demonstrated that the particles with cubic morphology have more intense photoluminescent emissions because of its close to single-crystal feature and small dimension. However, the UC PL of Er<sup>3+</sup>/Yb<sup>3+</sup> doped SrTiO<sub>3</sub> with single-crystalline and uniform dimensions is rarely reported. Herein, in this work, Er<sup>3+</sup> doped and Er<sup>3+</sup>/Yb<sup>3+</sup> codoped SrTiO<sub>3</sub> nanocubes with various dopant concentrations were synthesized by a facile hydrothermal method. The intense green light emission of Er<sup>3+</sup> ions around 525 and 550 nm and red light emission centered at 660 nm in UC processes populated by 980 nm laser excitation have been achieved in SrTiO<sub>3</sub> nanocubes. Interestingly, UC emission intensity of Er<sup>3+</sup>/Yb<sup>3+</sup> codoped SrTiO<sub>3</sub> nanocubes was greatly enhanced compared to that of Er<sup>3+</sup> doped SrTiO<sub>3</sub>.

## 2. Experimental section

### 2.1. Synthesis of Er<sup>3+</sup> doped and Er<sup>3+</sup>/Yb<sup>3+</sup> codoped SrTiO<sub>3</sub> nanocubes

Strontium nitrate (Sr(NO<sub>3</sub>)<sub>2</sub>), erbium nitrate (Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O) and P25 were chemistry grade and used as received without further purification. Potassium hydroxide (KOH) were used as mineralizer. The Er-doped SrTiO<sub>3</sub> samples were synthesized via a hydrothermal method. Er<sup>3+</sup> doping concentration was set as atomic ratio of 0 mol %, 1 mol%, 3 mol%, 5 mol%, respectively. In a typical procedure, 6.25 mmol Sr(NO<sub>3</sub>)<sub>2</sub> and stoichiometric Er(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O with different concentrations were dissolved in 10 mL deionized water with stirring until it transformed to a transparent solution. Meanwhile, 13.466 g KOH was dissolved in 20 mL deionized water under stirring at room temperature. Then, 0.3994 g P25 was slowly added to KOH solution. Subsequently, the above two precursor solutions were mixed together with violently stirring for 1 h. The resulting precursor suspension was transferred into 50 mL stainless-steel Teflon-lined autoclave for the hydrothermal treatment. The autoclave was sealed and held at 180 °C for 12 h. After cooling down to room temperature naturally, the resultant products were filtered and washed with deionized water and ethanol for several times, and subsequently air-dried at 80 °C for the characterization. For the Er<sup>3+</sup>/Yb<sup>3+</sup> codoped SrTiO<sub>3</sub> nanocubes, the synthetic procedure is

similar to that of Er<sup>3+</sup> doped SrTiO<sub>3</sub> sample. However, the concentration of Er<sup>3+</sup> ion was fixed at 3 mol%. Meanwhile, Yb<sup>3+</sup> ion concentration in the co-doped SrTiO<sub>3</sub> were 0, 1 mol%, 2 mol%, 3 mol %, 5 mol%, respectively. The samples were named as SrTiO<sub>3</sub>: Er 3%, SrTiO<sub>3</sub>: Er 3%, Yb 1%, SrTiO<sub>3</sub>: Er 3%, Yb 2%, SrTiO<sub>3</sub>: Er 3%, Yb 3% and SrTiO<sub>3</sub>: Er 3%, Yb 5%.

### 2.2. Characterizations

X-ray diffraction (XRD) patterns were collected at room temperature on a Bruker D8 Advance power diffractometer with Bragg-Brentano geometry by Cu K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). Scanning electron microscopy (SEM) tests, used to observe the morphology of samples, were conducted with a Hitachi SU8010. Transmission electron microscopy (TEM) images, high resolution TEM (HRTEM) images, scanning transmission electron microscopy (STEM) images and energy-dispersive spectroscopy (EDS) results were taken on FEI F20 using an accelerating voltage of 200 kV. The UC spectra were obtained at room temperature by using a PL3-211-P spectrometer (HORIBA JOBIN YVON, America). The emitted UC spectra was collected by a lens-coupled monochromator of a 1 nm spectral resolution. For UC steady-state spectra investigation, a 980 nm continuous diode laser (maximum output power: 2 W) was used to pump the samples.

## 3. Results and discussions

The room temperature UC emission spectra of SrTiO<sub>3</sub> nanocubes doped with different Er<sup>3+</sup> concentrations are shown in Fig. 1. Excited by the 980 nm diode laser with a power of 500 mW, the strong green emissions peaking at the center of 525 nm and 550 nm and the faint red emission around 670 nm were observed, which come from the <sup>4</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> and the <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions of Er<sup>3+</sup> ions, respectively. From the emission spectra, it is clear that the relative intensities of the green and red emission band change with the Er<sup>3+</sup> ions concentration. The intensity of these up-converted emissions are increased as the dopant Er<sup>3+</sup> ions concentration increases to 3 mol%. Especially, the luminescence intensity of SrTiO<sub>3</sub>: Er<sup>3+</sup> 3% is several times higher than that of SrTiO<sub>3</sub>: Er<sup>3+</sup> 1%. In Er<sup>3+</sup>-doped SrTiO<sub>3</sub> system, a resonant cross-relaxation mechanism of the type <sup>4</sup>F<sub>7/2</sub> → <sup>4</sup>F<sub>9/2</sub> and <sup>2</sup>I<sub>11/2</sub> → <sup>4</sup>F<sub>9/2</sub> type could directly populate the red emitting <sup>4</sup>F<sub>9/2</sub> state when exciting the <sup>2</sup>I<sub>11/2</sub> state with 980 nm. This cross-relaxation mechanism is depending on the concentration, so the increasing content of Er<sup>3+</sup> ions would increase the efficiency of the mechanism. However, when the doping concentration reaches to 5 mol%, the up-converted emissions reduce sharply. This may be due to the interionic interactions as the substitution concentration of Er<sup>3+</sup> ions increasing. Therefore, an optimum concentration of Er<sup>3+</sup> ions to realize the intense up-converted luminescence is approximately 3 mol% in SrTiO<sub>3</sub> matrix.

In order to understand the upconversion mechanism of the observed luminescence bands, the power dependent UC intensity in SrTiO<sub>3</sub>: Er<sup>3+</sup> 3% has been provided in Fig. 1b. The results are excited by the 980 nm diode laser with the power from 500 mW to 900 mW. And the interval of power is 50 mW. In up-conversion process,  $I$  is proportional to the  $n$ th power of  $P$ ,  $I \propto P^n$ . Where  $n$  is the number of pump photons absorbed per up-conversion photon emitted. A plot of  $\log I$  versus  $\log P$  yields a straight line with slope  $n$ . The slopes  $n$  are 1.88, 1.69 and 1.52 for 525, 550 and 670 nm emissions, respectively. These results vividly show that the green and red emission of Er<sup>3+</sup>-doped SrTiO<sub>3</sub> are two photon process.

Fig. 2a presents XRD patterns of Er-doped SrTiO<sub>3</sub> samples. As shown in Fig. 1a, when Er dopant concentration is ranging from 1 mol% to 5 mol%, all the diffraction peaks can be indexed as the

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