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Upconversion photoluminescence and dielectric properties in Er³⁺ and Yb³⁺ co-doped Sr₄La₂Ti₄Nb₆O₃₀

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ABSTRACT

Filled tetragonal tungsten bronze (TTB) structure Sr₄La₂Ti₄Nb₆O₃₀ co-doped by Er³⁺ and Yb³⁺ (SLTN: xEr³⁺-yYb³⁺) ceramics with different x and y were synthesized, and their crystal structure, upconversion photoluminescence (UC-PL), and dielectric permittivity were investigated for the first time. Under 980 nm infrared (IR) excitation, bright single-band UC green (515–570 nm) emission was observed for SLTN: xEr³⁺-yYb³⁺ (x=0.05, y=0), however, featured two-bands UC emission (515–570 nm and 640–690 nm) was confirmed for all SLTN: xEr³⁺-yYb³⁺ (x=0.05, y≠0) samples. Two-photon energy transfer process was proved through pumping laser power dependence of emission intensity measurement. It is believed that energy back transfer (EBT) process should be mainly responsible for the two-bands UC emission. In addition, the dielectric properties were also discussed for SLTN: xEr³⁺-yYb³⁺ system.

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1. Introduction

The up-conversion (UC) spectroscopic process can generate higher energy photon with shorter wavelength from lower energy photons with longer wavelength through multi-photon absorptions or energy transfers process [1,2]. The development of new UC materials has recently attracted much attention due to their great potential in a multitude of possible applications [1,2].

Filled tetragonal tungsten bronze (TTB) oxides, (A₂)₄(A₁)₂(C)₄-(B₁)₂(B₂)₈O₃₀, where A₁-, A₂-, B₁-, and B₂-sites are occupied while C-sites are unfilled, have greatly focused recently due to their interesting dielectric and ferroelectric properties [3–5]. Filled TTB structure consists of a complex array of distorted (B₁/B₂)O₆ octahedra sharing corners in such a way that three different types of interstices (square A₁, pentagonal A₂, and trigonal C) are available as shown in Fig. 1 [3–5].

Amusingly, the variety of crystallographic sites of filled TTB structure provides degrees of freedom to tailor the novel physical feature of the materials for potential multi-functional device applications. Up to now, though a lot of work concerning with electric properties has been carried out on filled TTB materials, few work has been reported on other physical features of this materials [3–5]. It should be noted that the rare earth ions (A₁-sites)

inside filled TTB materials can be explored to design the luminescence properties [3–5], especially the UC photoluminescence (UC-PL) properties. The realization of UC-PL in filled TTB materials will shed light on the future integrated optoelectronic materials designing.

In this work, Er³⁺ was explored to design the UC-PL properties in typically filled TTB Sr₄La₂Ti₄Nb₆O₃₀. Referring to the low absorption cross-section of the ⁴I_{11/2} excited state of Er³⁺ in the IR region, Yb³⁺ was deliberately introduced owing to the larger absorption cross-section and efficient energy transfer between Er³⁺ and Yb³⁺ [6,7]. Therefore, Er³⁺ and Yb³⁺ co-doped filled TTB Sr₄La₂Ti₄Nb₆O₃₀ (SLTN: xEr³⁺-yYb³⁺, where Er³⁺ and Yb³⁺ ions were used to substitute for La³⁺-sites) ceramics were prepared, and the UC-PL and dielectric properties were explored for the first time.

2. Experimental details

The investigated SLTN: xEr³⁺-yYb³⁺ ceramics were prepared through a solid state processing [8,9]. SrCO₃(99%), La₂O₃(99.99%), and Nb₂O₅(99.5%) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. Er₂O₃(99.9%), Yb₂O₃(99.9%), and TiO₂(99%) were supplied by Aladdin Industrial Corporation. All chemicals were mixed in stoichiometric rations, ground, and then calcined at 1200 °C for 3 h. The resultant powders were reground and pelletized under 10 MPa

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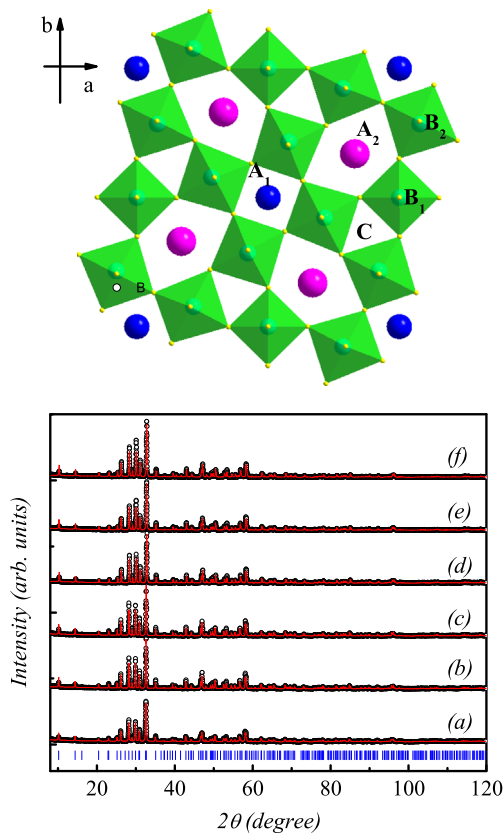


Fig. 1. Schematic diagram of the filled TTB structure in a – b plane. The measured XRD (open circle dots) and Rietveld refinement results (solid lines) with reliability factors $4\% < R_p < 6\%$ and $7\% < R_w < 9\%$ for all samples, ErOYb0 (a), Er0.05Yb0 (b), Er0.05Yb0.1 (c), Er0.05Yb0.2 (d), Er0.05Yb0.4 (e), Er0.05Yb0.5 (f). The short vertical solid lines correspond to standard Bragg positions.

pressure into disks of 13 mm in diameter and sintered at 1300 °C for 3 h. The phase identification was determined by an X-ray diffractometer (XRD) (X'pert-MPD, Philips) using Cu $K\alpha$ radiation, with working current and voltage of 40 mA and 40 kV, respectively. XRD measurements were carried out over an angular range from 8° to 120° with scanning step of 0.02° and a fixed counting time of 20 s. The general structure analysis system (GSAS) program was used for Rietveld structural refinement [10]. In UC-PL experiments, a 980 nm power-controllable infrared (IR) diode laser (Hi-Tech Optoelectronics Co., Ltd) with a maximum of 2 W was used to pump the samples. UC-PL was collected by a Zolix SBP300 spectrofluorometer (SBP300, Zolix Instruments Co. Ltd) with multiplier phototube as detector. The resolution of detectors is within ± 1 nm. Silver electrodes were deposited on the surfaces to perform electrical measurements. Dielectric characteristics were measured with dielectric spectrometer (TH2828S, Tonghui electronic Co. Ltd) [8,9].

3. Results and discussions

Fig. 1 gives the room temperature XRD pattern of SLTN: $x\text{Er}^{3+} - y\text{Yb}^{3+}$ ceramics with different x and y (hereafter, labeled as Er_xYb_y in this section for clear), where the open circle dots represent the measured XRD reflections and the solid lines are the Rietveld refinement results. The short vertical solid lines guide for eyes the corresponding standard Bragg positions. Very small difference is shown between the measured and refined pattern. The diffraction peaks of Er_xYb_y can be well indexed to the single TTB phase in the space group $P4/mbm$ [3–5]. No other lines of X-ray diffraction arising from a secondary phase are present.

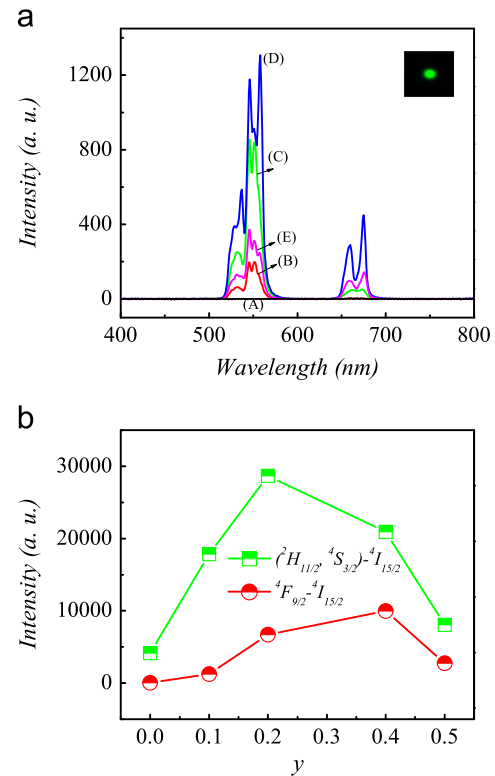


Fig. 2. UC-PL spectra of ErOYb0 (A), Er0.05Yb0 (B), Er0.05Yb0.1 (C), Er0.05Yb0.2 (D), and Er0.05Yb0.5 (E) under the 980 nm IR excitation (a). The inset shows the typical photograph for Er0.05Yb0. Variation of UC-PL intensity (${}^2\text{H}_{11/2}$ – ${}^4\text{S}_{3/2}$ – ${}^4\text{I}_{15/2}$ and ${}^4\text{F}_{9/2}$ – ${}^4\text{I}_{15/2}$) versus y (b).

The Rietveld refined data suggest that high fitting reliability is obtained given that the Sr^{2+} ions fully occupy the A_2 -sites (pentagonal interstices) in the TTB structure, while the A_1 -sites (tetragonal interstices) are occupied by La^{3+} , Yb^{3+} , and Ho^{3+} ions in random order. Furthermore, as generated by the Rietveld fitting, the lattice parameters $a=b=12.30759(32)$ Å, $c=3.86760(12)$ Å for sample ErOYb0 and $a=b=12.29403(21)$ Å, $c=3.86445(21)$ Å for sample Er0.05Yb0.4, indicating the lattice shrinkage of host lattice. It is reasonable since the effective ionic radius of La^{3+} (1.160 Å, CN8) is larger than that of Er^{3+} (1.004 Å, CN8) and Yb^{3+} (0.985 Å, CN8) [11]. In addition, the inter atomic distances (bond lengths) and angles (bond angles) show also obvious variation with increasing Yb^{3+} and Er^{3+} -substitution at the A_2 -sites according to the Rietveld refinement.

Fig. 2(a) shows the room-temperature UC spectra of Er_xYb_y under NIR 980 nm laser excitation. No UC emission is observed for ErOYb0. When Er^{3+} ions are introduced into the SLTN host lattice, intense intrinsic single-band green UC emission locating around 515–570 nm region is observed for Er0.05Yb0 as shown in Fig. 2(a) [12,13]. The green UC emission arising from the intra f–f transition of Er^{3+} is assigned to the ${}^2\text{H}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ transitions [6,7,14,15]. The intense UC green luminescence can be easily seen by the naked eye at room temperature as shown in the inset of Fig. 2(a). Furthermore, we examined the UC emission behavior of Er^{3+} and Yb^{3+} co-doped SLTN as a function of Yb^{3+} content. Significantly, the single-band emission feature of Er0.05Yb0 disappears on modifying the Yb^{3+} content. Interestingly, all samples co-doped with Er^{3+} and Yb^{3+} exhibit Er^{3+} -related two distinct emission bands, locating around green 515–570 nm region and red 640–690 nm region, respectively. The new UC red emission corresponds to the ${}^4\text{F}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transition of Er^{3+} [6,7,14,15]. Moreover, obvious variation of the relative intensity of UC-PL

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