



Enhanced upconversion luminescence induced by structural evolution of lanthanum niobate phosphor

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Abstract

A series of Yb^{3+} - Er^{3+} coactivated $\text{La}(\text{Nb}_{1-x}\text{V}_x)\text{O}_4$ ($0 \leq x \leq 1$) upconversion (UC) emission phosphors are prepared by high-temperature solid-state reaction method. Experimental results demonstrate that the introduction of V^{5+} expands and distorts the unit cell volume of LaNbO_4 , and induces structural transformation of LaNbO_4 from Phase 1 with monoclinic fergusonite structure ($0 < x \leq 0.2$) to Phase 2 with tetragonal scheelite structure ($0.25 \leq x \leq 0.5$) to Phase 3 with monoclinic monazite structure ($x = 1$). Under 976 nm excitation, continuously enhanced green UC emission is observed in Phase 1 with gradual replacement of Nb^{5+} with the V^{5+} ($0 < x \leq 0.2$). At $x = 0.2$, the luminescence intensity is enhanced 1.3 times than that of the pristine sample. In Phase 2 and Phase 3, the intensity of green UC emission is decreased gradually with increasing the V^{5+} concentration. Based on the XRD results and crystal structural analysis, the enhanced luminescence is attributed to the lowered symmetry around La^{3+} ions (Er^{3+} ions), which relaxes the parity-forbidden selection rules of Er^{3+} luminescent centers. This study provides a useful approach in developing UC luminescence materials with controllable optical properties based on variations in local coordination environments through composition substitutions.

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1. Introduction

Trivalent lanthanide ($\text{Ln}^{3+} = \text{Er}^{3+}$, Tm^{3+} , Pr^{3+} and Ho^{3+}) ions activated UC luminescent materials have attracted extensive attention for their applications in biological sensing [1–4], security printing [5,6], novel 3D optical display technologies [7,8], as well as spectral conversion in solar cells [9]. As known, Yb^{3+} ion is the most frequently used sensitizer for Ln^{3+} activators for intensifying UC luminescence, since it has a large absorption cross-section at 980 nm [10,11]. Generally, in order to obtain efficient UC luminescence from Ln^{3+} activators, a key point is choosing an appropriate host material, because host materials with low phonon energies is helpful to minimize nonradiative loss and maximize radiative emission [12]. Recently, inorganic fluorides are

often employed as efficient host materials for their advantage of intrinsic low phonon energy, although their harsh preparation condition still need to be optimized further [13–16]. Alternatively, inorganic oxides as host materials for Ln^{3+} ions show many advantages such as high chemical stability, mechanical stability, simple preparation, and low-toxicity, which have been prepared into glass, ceramics and luminescent powders for diverse applications [3].

Lanthanum niobate (LaNbO_4) has been of great interest for their good mechanical behavior, dielectric and proton conduction properties [17–20]. It has been well known that LaNbO_4 is able to generate structural transformation induced by temperature and composition substitution. For example, Stubčian et al. reported that lanthanum niobate with monoclinic structure can change into a tetragonal structure when the temperature was elevated to ~ 500 °C [21]. Grande et al. and Aldrend et al. reported that the structural transformation can also take place from monoclinic to tetragonal phase of lanthanum niobate by substituting Nb^{5+} with

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Ta⁵⁺/V⁵⁺ [22,23]. The structural transformation in lanthanum niobate makes it possible to fine-tune the specific physical property or to design a new useful material. In addition, it possesses a much lower phonon energy (811 cm⁻¹) than conventional oxides such as silicates, borates and phosphates [20,24]. All these properties behavior make lanthanum niobate attractive for several important technological applications, such as lasers, optical fiber communication, optical information storage and displays. However, to the best of our knowledge, there are very few reports on Yb³⁺-Er³⁺ codoped LaNbO₄ as potential luminescent materials for these technological applications. Therefore, the present investigation aims at the synthesis of Yb³⁺-Er³⁺ co-activated LaNbO₄ phosphors, as well as the study of the effect of V⁵⁺ substitution induced host structural transformation on luminescence properties of Er³⁺ ions [25–28]. In our case, Yb³⁺-Er³⁺ codoped LaNbO₄ phosphors are synthesized by high-temperature solid-state reaction. At optimal concentration of 0.16 and 0.04 for Yb³⁺ and Er³⁺, the green UC emission assigning to the transition of ²H_{11/2}→⁴I_{15/2} and ⁴S_{3/2}→⁴I_{15/2} reaches a maximum value. Substituting Nb⁵⁺ with V⁵⁺ results in expansion and distortion of the unit cell volume of La(Nb_{1-x}V_x)O₄ (0 < x ≤ 0.2), induces structural transformation from monoclinic fergusonite-type LaNbO₄ (0 ≤ x ≤ 0.2) to tetragonal scheelite-type LaNb_{0.7}V_{0.3}O₄ (0.25 ≤ x ≤ 0.5) and then to monoclinic monazite-type LaVO₄ (x=1). At a V⁵⁺ concentration of x=0.1, the intensity of green UC emission is enhanced by a factor of 1.31 relative to that of x=0 under 976 nm excitation. Enhanced UC emission is ascribed to the lowered symmetry around La³⁺ ions, which causes the relaxation of parity-forbidden selection rules for Er³⁺ luminescent centers. In short, the La(Nb_{1-x}V_x)O₄ material is a promising UC emission materials for Yb³⁺-Er³⁺ luminescent centers.

2. Experimental section

(La_{0.8}Yb_{0.16}Er_{0.04})(Nb_{1-x}V_x)O₄ [LNVO] (0 ≤ x ≤ 1) phosphors were prepared by a high-temperature solid-state reaction using stoichiometric amounts of high-purity La₂O₃, Nb₂O₅, NH₄VO₃, Yb₂O₃, Er₂O₃ powders. The reactant powders were ground in an agate mortar together with a small amount of boric acid flux. Then the mixture of reactant powders were placed in a sintering furnace preheated to 1350 °C for 3 h. The obtained pink pellets were ground into powder and sintered at 1350 °C again for one hour. This procedure was observed to play an important role in improving UC emission properties of LNVO (0 ≤ x ≤ 1) phosphors.

Phase identification and characterization of the as-prepared phosphors were performed on a Rigaku D/max-2500 X-ray diffractometer (XRD) with Cu K_α radiation (λ=1.5406 Å). Lattice parameters of the LNVO (0 ≤ x ≤ 0.2) powders were calculated using UnitCell program (general cell parameters analysis system) [26]. Luminescence spectra were measured at room temperature with a home-made photoluminescence measurement setup, using a 20 mW near-Infrared (NIR) laser diode (976 nm emission) as excitation source and an miniature fiber optic spectrometer (Ocean Optics USB4000, 1.25 nm resolution) as the detector. The NIR laser was focused on phosphor powders which were pressed into a glass cell (1.5 × 1.5 cm), and the UC emission was collected at an angle of 45° to the excitation beam. All the samples were measured with the home-made setup under the same conditions.

3. Results and discussion

Fig. 1 presents the XRD patterns of the La_{1-y-z}NbO₄: Yb_y, Er_z (0 ≤ y ≤ 0.24; 0 ≤ z ≤ 0.04) phosphors. The XRD patterns of

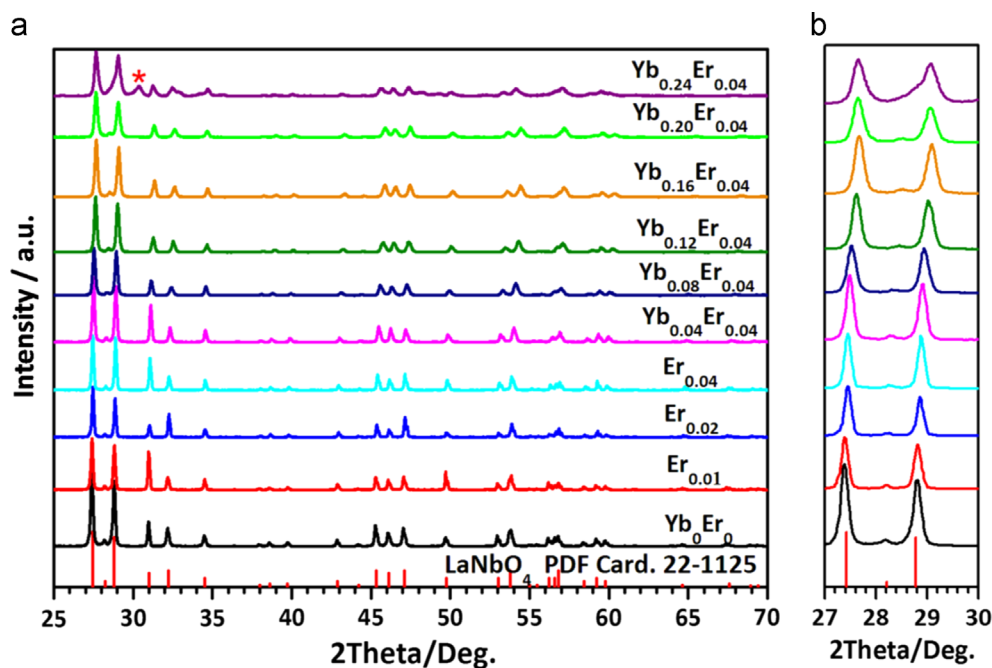


Fig. 1. a) XRD patterns of the as-prepared La_{1-y-z}NbO₄: Yb_y, Er_z (0 ≤ y ≤ 0.24; 0 ≤ z ≤ 0.04) phosphors. Bottom shows monoclinic LaNbO₄ crystal indexed in PDF #22–1125 as a reference. b) Magnified XRD patterns in the region between 27–30° of La_{1-y-z}NbO₄: Yb_y, Er_z phosphors.

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