Up- and Down-Conversion Luminescence of $\text{LuNbO}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ Phosphors

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ABSTRACT

Up-conversion (UC) and down-conversion (DC) luminescence of $\text{LuNbO}_4\text{:0.18Yb}^{3+}, x\text{Er}^{3+}$ ($x = 0.01\text{--}0.07$) powders were investigated. Post-annealed powders were composed of a single LuNbO_4 phase with a monoclinic fergusonite structure, whereas as-calcined powders contained a small amount of the Li_3NbO_4 impurity phase. Under near infrared radiation, the UC spectra of the post-annealed powders exhibited the strong green and weak red emission peaks assigned to the transition of $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ to the ground state ($^4\text{I}_{15/2}$) of Er^{3+} ions, respectively; the green and red emission intensities were approximately 330 and 270% stronger, respectively, than those of the as-calcined powders. A two-photon UC process was involved in the emission as a result of an energy transfer from Yb^{3+} to Er^{3+} . Under ultraviolet radiation, the DC spectra exhibited broad blue and sharp green emission bands. The DC mechanism was explained using self-activated $[\text{NbO}_4]^{3-}$ niobates and an energy transfer from $[\text{NbO}_4]^{3-}$ to Er^{3+} .

Key words : Lutetium niobate, Luminescence, Phosphors, Up-conversion

1. Introduction

LuNbO_4 is a niobate compound with an MNbO_4 (M: La^{3+} , Y^{3+} , and Lu^{3+}) formula. YNbO_4 and LaNbO_4 phosphors doped with rare-earth (RE) elements have been widely investigated for use in various optical applications.¹⁻⁵⁾ On the other hand, only a few studies on the luminescence of LuNbO_4 doped with RE ions have been carried out. For instance, the photoluminescence (PL) spectra of $\text{LuNbO}_4\text{:Eu}^{3+}$ exhibit strong red emission peaks, which are assigned to f-f transitions of the Eu^{3+} ions.⁶⁻⁸⁾ Furthermore, the up-conversion (UC) luminescence of LuNbO_4 has been rarely studied.

For UC luminescence, sensitizer and activator ions are co-doped into the host materials. Yb^{3+} ions are typically used as sensitizers owing to their strong absorption of 980 nm, while Er^{3+} , Tm^{3+} , and Ho^{3+} ions are co-doped as activators, resulting in various UC spectra.^{9,10)} In the case of the $\text{Yb}^{3+}\text{--}\text{Er}^{3+}$ system, under infrared (IR) radiation (980 nm), the energy absorbed by the sensitizers (Yb^{3+} ions) is transferred to the activators (Er^{3+} ions), leading to a multistep excitation of the Er^{3+} ions: ground-state absorption (GSA) and excited-state absorption (ESA).¹¹⁾ For UC phosphors co-doped with the Yb^{3+} and Er^{3+} ions, the UC emission spectra typically exhibit multiple-emission peaks in the green and red regions; the emission ratio of green to red closely depends on the host materials.¹²⁻¹⁶⁾

In this study, we prepared LuNbO_4 powders co-doped with Yb^{3+} and Er^{3+} and then investigated their UC and down-con-

version (DC) luminescence. Under near IR (NIR) radiation, the UC spectra exhibited strong green and weak red emission bands, whose intensities dramatically increased after a post-annealing process. Under ultraviolet (UV) radiation, the DC spectra consisted of blue and green emission bands. This dual-mode emission (DC and UC) suggests that $\text{LuNbO}_4\text{:Yb}^{3+}, \text{Er}^{3+}$ has high potential for use in various optical applications including sensing devices, security printing, electronic displays, etc.

2. Experimental Procedure

$\text{Lu}_{0.82-x}\text{Yb}_{0.18}\text{Er}_x\text{NbO}_4$ (LYE_xNO) powders ($x = 0.01\text{--}0.07$) were prepared using a conventional solid-state reaction process with Lu_2O_3 (Molycorp, 99.99%), Nb_2O_5 (Kojundo Chemical Lab., 99.9%), Yb_2O_3 (Kojundo Chemical Lab., 99.99%), and Er_2O_3 (Kojundo Chemical Lab., 99.9%). Stoichiometric starting mixtures with flux of 7 wt% LiCl were calcined at 1300°C for 12 h under a nitrogen atmosphere. Thereafter, the as-calcined powders were ground in an agate mortar and post-annealed under the same conditions as used in the calcination process. An X-ray diffractometer (XRD, Rigaku, Miniflex II) using $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.5406 \text{ \AA}$) was used to determine the crystal structure. The UC and DC PL spectra were measured at room temperature using a PL (PSI, Darsa-5000) system with an external 200 mW NIR laser diode ($\lambda = 980 \text{ nm}$) and a 500 W xenon lamp, respectively.

3. Results and Discussion

Almost all the XRD patterns of the as-calcined LYE_xNO powders (Fig. 1(a)) corresponded to those of ICSD #98-010-9182 (LuNbO_4 with a monoclinic fergusonite structure);

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Fig. 1. XRD patterns of (a) as-calcined and (b) post-annealed LYE_xNO powders.

very weak peaks of an impurity phase of Li_3NbO_4 were also observed. However, after the post-annealing process, the XRD peaks of the Li_3NbO_4 impurity phase disappeared completely (Fig. 1(b)), indicating that the synthesized powders were composed entirely of single phase LuNbO_4 , and that the Yb^{3+} and Er^{3+} ions were incorporated completely into the Lu^{3+} sites. With regard to the ionic radius (r), it is reasonable to infer that the Yb^{3+} ($r = 0.985 \text{ \AA}$) and Er^{3+} ($r = 1.004 \text{ \AA}$) ions can be substituted for the Lu^{3+} ions ($r = 0.977 \text{ \AA}$).

Under NIR radiation, the UC spectra of the post-annealed LYE_xNO powders were measured, with results shown in Fig. 2(a); these spectra consisted of strong green and weak red peaks. The emission intensities (I_{em}) at 556 and 673 nm were measured as a function of the input (excitation) power P ; the measurement results for $x = 0.05$ are representatively plotted on a log-log scale, as shown in the inset of Fig. 2(a). In the linear region, I_{em} is proportional to P^n , where n is the number of photons required for the UC process.¹¹ For $x = 0.01, 0.03, 0.05$, and 0.07 , the slopes n of the 556 nm peak were 2.33, 2.31, 2.26, and 2.32, while those of the 673 nm peak were 2.56, 2.09, 2.32, and 2.64, respectively. These findings demonstrate that a two-photon process was involved in the UC emission. The two-photon UC process is

Fig. 2. (a) UC spectra and (b) variations of the emission intensities of LYE_xNO powders under 980 nm radiation. Inset of (a) shows the emission intensity (I_{em}) of $\text{LYE}_{0.05}\text{NO}$ as a function of the input power (P).

a well-known mechanism,¹¹⁻¹³ and we only briefly explain it as follows.

The Yb^{3+} ions in the ground state ($^2\text{F}_{7/2}$) absorb the energy of the 980 nm radiation and switch into the excited state ($^2\text{F}_{5/2}$). Then, the absorbed energy of the Yb^{3+} ions is transferred to the Er^{3+} ions; this is an energy transfer (ET) process. As a result, a two-photon UC process, involving the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ (ground-state absorption, GSA) and $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$ (excited-state absorption, ESA) transitions of the Er^{3+} ions, occurs. Subsequently, nonradiative multiphoton relaxation from $^4\text{F}_{7/2}$ to $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, and $^4\text{F}_{9/2}$ levels of the Er^{3+} ions occurs, resulting in the green (526/556 nm) and red emission (673 nm) assigned to the transitions of the $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ levels to the ground state ($^4\text{I}_{15/2}$) of the Er^{3+} ions, respectively. Besides the main emission peaks at 526, 556, and 673 nm, weak emission peaks were also observed owing to large Stark splitting, because one Er^{3+} ion has a coordination of eight oxygen atoms in a distorted cube.¹²

The variations of the UC emission intensities at 556 and 673 nm for the LYE_xNO powders are shown in Fig. 2(b). The strongest emission intensity was obtained at $x = 0.05$; there-

Fig. 3. SEM micrographs of (a) as-calcined and (b) post-annealed $\text{LYE}_{0.05}\text{NO}$ powders.

after, the intensity decreased owing to a concentration quenching effect. In comparison with the emission intensities of the as-calcined powders, those of the post-annealed powders dramatically increased to approximately 330 and 270% for the 556 and 673 nm emissions, respectively. This behavior could be explained by the fact that the post-annealing process led to an elimination of the impurity phase, as shown in Fig. 1, and a diminution of internal defects of the as-calcined powders that could act as luminescence killers. SEM micrographs of the as-calcined and post-annealed $\text{LYE}_{0.05}\text{NO}$ powders, which exhibited the strongest green emissions, are shown in Fig. 3(a) and 3(b). There were no significant differences in particle shape or size between the two samples; the powders consisted of irregularly shaped-particles of different sizes. However, nano-sized particles on the surface of the large particles of the as-calcined powders almost disappeared after the post-annealing treatment. This phenomenon might contribute partly to the enhancement of the emission intensity of the post-annealed powders. In addition, the full width at half maximum (FWHM) values of the as-calcined (post-annealed) powders were obtained for $02\bar{1}$ at $2\theta = 28.864^\circ$; they were approximately 0.17 (0.15), 0.18 (0.15), 0.17 (0.15), and 0.17 (0.15) for $x = 0.01, 0.03, 0.05$, and 0.07 , respectively; these values were found to be independent of the Er content. However, the FWHM values of the post-annealed powders were apparently lower than those of the as-calcined powders. This revealed that the crystallinity of the post-annealed powders was higher than that of the as-calcined powders, causing the enhancement of the emission intensity in addition to other effects. The intensities of the green emissions of the synthesized powders far surpassed those of the red emissions, resulting in the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates in the green region, as shown in Fig. 4.

In addition to the UC emissions, the DC luminescence of the LYE_xNO powders was also investigated, with results shown in Figs. 5(a) - (c). Under UV (271 nm) excitation, the PL spectra exhibit strong broad blue emission bands peaking at approximately 412 nm, as shown in Fig. 5(a); weak emission peaks are observed in the green region as well. Corresponding PL excitation (PLE) spectra are shown in Fig. 5(b). The PLE spectra for the 412 nm emission (blue lines) consist of strong and weak bands at 271 and 309 nm, respectively; these bands are called charge transfer bands

Fig. 4. CIE chromaticity coordinates of LYE_xNO powders activated by 980 nm radiation.

Fig. 5. (a) PL ($\lambda_{\text{ex}} = 271$ nm) and (b) PLE spectra of LYE_xNO powders. (c) PLE (red line) and PL spectra (black line) of un-doped LuNbO_4 powders. Inset of (a) shows the PL spectra activated by 380 nm radiation.

Fig. 6. Variations of the emission intensities at 556 (green line) and 412 nm (blue line) of LYE_xNO powders activated by 271 nm (CTB) radiation.

(CTBs); they occur through a CT mechanism between a ligand (oxygen 2p-like states) and a metal (Nb 4d-like states) of $[\text{NbO}_4]^{3-}$. As shown in Fig. 5(c), the PL spectrum of un-doped LuNbO_4 exhibits a blue emission band peaking at 412 nm; a corresponding PLE band was observed at 271 nm. This finding confirmed that the blue emission bands and the CTBs of the LYE_xNO powders (Figs. 5(a) and 5(b), respectively) originated from $[\text{NbO}_4]^{3-}$ niobates. As shown in Fig. 5(b), the PLE spectra (red lines) for the 556 nm emission exhibit strong and sharp peaks at 380 nm; these peaks originate from the Er^{3+} ions. In addition, weak broad bands were also observed at 271 nm; these bands corresponded to CTBs. These behaviors indicate that the green emission (556 nm) by 271 nm (CTB) excitation (Fig. 5(a)) originated from the Er^{3+} ions through an ET process from $[\text{NbO}_4]^{3-}$ to Er^{3+} . Accordingly, it was evident that the CTB excitation mainly caused the blue emission (412 nm) associated with $[\text{NbO}_4]^{3-}$ and partly activated the Er^{3+} ions through the ET process, resulting in the green emission (556 nm). The DC PL spectra activated by 380 nm radiation are shown in the inset of Fig. 5(a): the sharp emission peaks in the green region are assigned to the characteristic energy transitions of the Er^{3+} ions; the strongest peak appears at 556 nm.

Variations of the blue (412 nm) and green emission intensities (556 nm) for the LYE_xNO powders activated by CTB (271 nm) are shown in Fig. 6. Increasing x can lead to an increase in the ET probability from $[\text{NbO}_4]^{3-}$ to Er^{3+} , resulting in a continuous decrease in the emission intensity at 412 nm, which is associated with $[\text{NbO}_4]^{3-}$. On the other hand, with increasing x values, the number of Er^{3+} ions, which can absorb the transferred energy from $[\text{NbO}_4]^{3-}$, increased. As a result, the emission intensity at 556 nm, which originated from the Er^{3+} ions, increased to $x = 0.03$; it then decreased at $x = 0.05$ and at higher values of x due to the concentration quenching effect. Accordingly, corresponding CIE chromaticity coordinates (Fig. 7) shifted from the blue region to the green region as the x values increased.

Fig. 7. CIE chromaticity coordinates of LYE_xNO powders activated by 271 nm radiation.

4. Conclusions

Under NIR radiation, the UC spectra of the post-annealed powders consisted of strong green and weak red peaks assigned to the transition of $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ to the ground state ($^4\text{I}_{15/2}$) of the Er^{3+} ions, respectively. The UC emission occurred through a two-photon ET process from Yb^{3+} to Er^{3+} . The post-annealing process caused a dramatic increase in the green and red emission intensities to approximately 330 and 270%, respectively, compared to those of the as-calcined powders. These phenomena were attributed to the phase purity and the diminution in the internal defects of the as-calcined powders. Under UV excitation, the DC spectra consisted of broad blue and sharp green emission bands, which originated from $[\text{NbO}_4]^{3-}$ niobates and the Er^{3+} ions, respectively. The DC spectra and the variation of the emission intensities indicated an ET process from $[\text{NbO}_4]^{3-}$ to Er^{3+} . The effective UC and DC emission of the LYE_xNO powders suggest that they have a high possibility for use in various optical applications.

Acknowledgements

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