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Upconversion luminescence of (Lu,M)NbO_4:Yb^{3+},Er^{3+} (M: Al^{3+}, Ga^{3+})

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ABSTRACT

The effects of substitution of Al^{3+} and Ga^{3+} ions on the upconversion luminescence of (Lu,M)NbO_4:Yb^{3+}, Er^{3+} (M: Al^{3+}, Ga^{3+}) were studied for the first time. Under infrared (980 nm) radiation, the upconversion spectra consisted of strong green and weak red emission bands, which were assigned to the transition of the $^2H_{11/2}$/$^4S_{3/2}$ and $^4F_{9/2}$ levels, respectively, to the ground state ($^4I_{15/2}$) of the Er^{3+} ions through an energy transfer process from Yb^{3+} to Er^{3+}. A two-photon upconversion process was involved in the upconversion emission of (Lu,M)NbO_4:Yb^{3+},Er^{3+}. Substitution of Al^{3+} and Ga^{3+} ions increased the green (red) emission intensity to approximately 120% (120%) and 135% (130%), respectively. These behaviors were explained in terms of the crystal field asymmetry and energy transfer probability.

1. Introduction

Niobate compounds doped with some rare-earth (Re) ions (Eu^{3+}, Sm^{3+}, and Tb^{3+}) having the form of $XNbO_4$:Re (X: Y^{3+}, La^{3+}, Gd^{3+}, and Lu^{3+}) are well known as optical materials for use in various applications including lasers, solid-state lighting, and X-ray phosphors [1–11]. Among them, $YNbO_4$:Re has been widely investigated as a downconversion (DC) phosphor [1–5], and the upconversion (UC) luminescence of $YNbO_4$ co-doped with Yb^{3+} and Er^{3+} (or Tm^{3+}) ions was also recently reported [12,13]. However, for $LuNbO_4$ (LuNO), there are only a few studies of the DC luminescence [9–11].

LuNO has two isomorphs: a monoclinic fergusonite structure (M-fergusonite) at low temperatures and a tetragonal scheelite structure (T-scheelite) at high temperatures. M-fergusonite is also called distorted T-scheelite [14–17]. A Lu atom is coordinated with eight oxygen atoms. A Nb atom is coordinated with four oxygen atoms in a highly distorted tetrahedron, forming a $[NbO_4]^{3-}$ niobate, but, if more nearest-neighbor oxygen atoms are considered, it is six-coordinated in a highly distorted octahedron. When LuNO is doped with Eu^{3+} ions, the photoluminescence (PL) excitation spectra of LuNO:Eu^{3+} consist of a broad band (~268 nm) and sharp peaks in the near-ultraviolet (NUV) region, which originate from self-activated $[NbO_4]^{3-}$ niobates and the f–f transitions of the Eu^{3+} ions, respectively [9,11]. Under NUV radiation, the PL spectra of LuNO:Eu^{3+} exhibit sharp red emission peaks.

It was suggested that Yb^{3+} and Er^{3+} ions can be fully incorporated into the $YNbO_4$ lattices, resulting in UC luminescence with strong green-emitting bands under near-infrared (NIR, 980 nm) radiation [12,13]. For highly efficient UC, Yb^{3+} and Er^{3+} are typically used as a sensitizer and an activator, respectively. In addition, the DC luminescence of $YNbO_4$:Eu^{3+} could be greatly enhanced by substitution of Al^{3+} and Ga^{3+} ions [5]. Accordingly, on the basis of a similarity in the crystal structures of $YNbO_4$ and LuNO, it is reasonable to consider that LuNO co-doped with Yb^{3+} and Er^{3+} (LuNO:Yb,Er) can also be an effective UC phosphor. However, to the best of our knowledge, the UC luminescence of LuNO:Yb,Er has not been reported yet, even though the UC luminescence has recently attracted considerable attention because of its high potential for use in many applications [18–25]. In this study, we successfully synthesized LuNO:Yb,Er powders with a single phase of M-fergusonite, and strong UC luminescence could be obtained in the green region. Furthermore, the incorporation of Ga^{3+} and Al^{3+} ions significantly enhanced the UC emission intensity.

2. Experimental

$Lu_{1-x}Al_xNbO_4$:0.18Yb,0.05Er (LuA_xNO:Yb,Er) and $Lu_{1-y}Ga_yNbO_4$:0.18Yb,0.05Er (LuG_yNO:Yb,Er) powders (x, $y = 0–0.2$) were synthesized by a conventional solid-state reaction process using Lu_2O_3 (Molycorp, 99.99%), Nb_2O_5 (Kojundo Chemical Lab., 99.9%), Yb_2O_3 (Grand Chemical & Material, 99.99%), Er_2O_3 (Grand Chemical & Material, 99.9%), Al_2O_3 (Kojundo Chemical Lab., 99.99%), and Ga_2O_3 (Kojundo Chemical Lab., 99.99%) as raw materials. In our preliminary experiment, we found that the LuNO powders co-doped with $0.18Yb^{3+}$ and $0.05Er^{3+}$ contained no impurity phases,

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and that their UC spectra exhibited strong emission intensities. Starting mixtures with stoichiometric compositions were calcined at 1350 °C for 12 h under nitrogen atmosphere. A flux of 7 wt% LiCl (Sigma-Aldrich, >99.99%) was added to promote the reaction kinetics for the formation of the compounds. An X-ray diffractometer (XRD, Rigaku Miniflex II) using $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å) 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 IR laser diode ($\lambda = 980$ nm) and a 500 W xenon lamp, respectively.

3. Results and discussion

The XRD patterns of LuA$_x$NO:Yb,Er and LuG$_y$NO:Yb,Er powders (x, $y = 0$–0.2) are shown in Fig. 1a and Fig. 1b, respectively. The patterns agree with those of ICSD #98-010-9182. This indicates that the synthesized powders were composed of a LuNO single phase and that the dopant ions (Yb^{3+}, Er^{3+}, Al^{3+}, and Ga^{3+}) were fully incorporated into the LuNO lattices. On the basis of the ionic size and valence, it was reasonable to consider that all the dopants were substituted for Lu^{3+} ions. For a coordination number (CN) of eight, Yb^{3+} and Er^{3+} have ionic radii of 0.985 and 1.004 Å, respectively, and can be readily substituted for Lu^{3+} ions ($r = 0.977$ Å). On the other hand, the ionic radii of Al^{3+} and Ga^{3+} for CN = 6 are 0.535 and 0.62 Å, respectively, which are significantly smaller than that of Lu^{3+}. As a result, it was inferred that the crystal structure would be modified as Al^{3+} and Ga^{3+} ions replaced Lu^{3+} ions. However, the positions of the XRD peaks of the synthesized powders did not change significantly, as shown in Fig. 1. These findings implied that the dimensions of a unit cell were rarely modified, but that local distortion might occur at the host lattices to permit the inclusion of the much smaller substitutes, Al^{3+} and Ga^{3+} ions. In addition, the intensities of the XRD peaks of the synthesized powders were significantly different from those of the reference (ICSD #98-010-9182). The integrated intensity of each diffraction peak is determined by some factors including the structure, multiplicity, temperature factor, etc. For example, the structure factor mainly depends on the positions of the atoms in the unit cell. Accordingly, the difference in the peak intensity between the synthesized powders and the reference might be attributed to the different atomic positions owing to the distortion of the local structure. A correlation between the local lattice distortion and the UC luminescence will be discussed when the PL spectra are explained. Fig. 2 shows SEM micrographs of the LuA$_x$NO:Yb,Er and LuG$_y$NO:Yb,Er powders; the powders consisted of irregular particles. The addition of Al^{3+} or Ga^{3+} did not affect the particle morphologies.

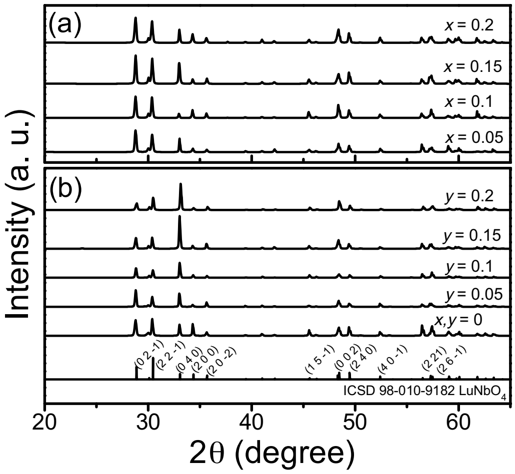

Fig. 1. XRD patterns of (a) LuA$_x$NO:Yb,Er and (b) LuG$_y$NO:Yb,Er powders prepared with various amounts of Al (x) and Ga (y).

The UC emission spectra of the synthesized powders were measured under 980 nm radiation. Among them, Fig. 3a shows the spectrum of the LuNO:Yb,Er powders; it consists of strong green and weak red emission peaks. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinate (0.3372, 0.6493) lies in the green region because the green peaks had greater emission intensity than the red peaks. The emission peaks originated from the Er^{3+} ions via an energy transfer UC (ETU) process from Yb^{3+} to Er^{3+}; the main peaks are assigned to the transitions of the $^2H_{11/2}/^4S_{3/2}$ (526 nm/556 nm) and $^4F_{9/2}$ levels (673 nm) to the ground state ($^4I_{15/2}$) of the Er^{3+} ions. The Er^{3+} ions are coordinated with eight oxygen atoms in a distorted cube, leading to large Stark splitting; thus, several additional peaks at 521, 535, 545, and 658 nm are observed, as well as the main emission peaks. To verify the UC mechanism, the emission intensities (I_{em}) at 556 and 673 nm are plotted as functions of the input (excitation) power P on a log–log scale, as shown in Fig. 3b. In the linear region, I_{em} is proportional to P^n, where n is the number of photons required for a UC process [19]. The slopes n are 2.01 and 1.84 for the 556 and 673 nm emission, respectively, revealing that a two-photon process is predominantly responsible for the UC emission.

Accordingly, the sequential ETU process between Yb^{3+} and Er^{3+} can be explained using a schematic energy diagram of the two-photon UC process (Fig. 4) as follows [18–20,24]. Under NIR (980 nm) radiation, the Yb^{3+} ions are activated to the excited state ($^2F_{5/2}$), and then the absorbed energy at $^2F_{5/2}$ is transferred to the Er^{3+} ions, leading to two ET processes, $W1$ and $W2$, which result in the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ (ground-state absorption, GSA) and $^4I_{11/2} \rightarrow {}^4F_{7/2}$ (excited-state absorption, ESA) transitions, respectively. Subsequently, nonradiative multiphoton relaxation processes from the $^4F_{7/2}$ to $^2H_{11/2}$, $^4S_{3/2}$, and $^4F_{9/2}$ levels of the Er^{3+} ions occur. Finally, the green (526 nm/556 nm) and red emission (673 nm) occur as a result of the transitions of the $^2H_{11/2}/^4S_{3/2}$ and $^4F_{9/2}$ levels, respectively, to the ground state ($^4I_{15/2}$) of the Er^{3+} ions. The following route for the red emission is also possible.

(i) Cross-relaxation: $^4I_{11/2}(Er^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+})$
(ii) ET ($W3$): $^4I_{13/2}(Er^{3+}) + {}^2F_{5/2}(Yb^{3+}) \rightarrow {}^4F_{9/2}(Er^{3+})$
(iii) Red emission: $^4F_{9/2}(Er^{3+}) \rightarrow {}^4I_{15/2}(Er^{3+})$

For LuNO:Yb,Er, the stronger green emission demonstrated that the excited $^2H_{11/2}$ and $^4S_{3/2}$ levels had much higher electron populations than the $^4F_{9/2}$ level. Detailed explanations are given in earlier reports [18–20,24].

The effects of Al^{3+} and Ga^{3+} substitution on the ETU process of the LuA$_x$NO:Yb,Er and LuG$_y$NO:Yb,Er powders are studied. Log–log graphs of I_{em} *vs.* P are shown in Fig. 5. The slopes n are in the ranges of 2.0–2.9 and 1.75–2.05 for the 556 and 673 nm emission, respectively, indicating that the two-photon process is responsible for the UC emission of the powders. These findings indicate that Al^{3+} and Ga^{3+} substitution did not affect the ETU mechanism of LuNO:Yb,Er. The variation of the UC emission intensity is shown in Fig. 6. As x or y increased from 0 to 0.1, the intensity of the green emission (556 nm) gradually increased to approximately 120% and 135% for LuA$_x$NO:Yb,Er and LuG$_y$NO:Yb,Er, respectively. In the same way, the intensity of the red emission (673 nm) also increased to approximately 120% and 130% for $x = 0$–0.1 and $y = 0$–0.1, respectively. Thereafter, both the green and red emission intensities decreased for $x \geq 0.1$ and $y \geq 0.1$. The variation of the emission intensity was attributed to modification of the ETU process and the crystal field environment of the Er^{3+} ions. ETU is accomplished through a multistep process consisting mainly of energy transfer, nonradiative relaxation, GSA, ESA, and the electron population of each excited energy level. In addition, the UC emission depends on

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