Photoluminescence Properties of $\text{LaNbO}_4\text{:Eu}^{3+}$ Phosphors Prepared by a Solid-state Reaction

Iori Sakakibara and Kazunori Matsui

College of Engineering, Kanto Gakuin University, 1-50-1, Mutsuurahigashi, Kanazawa-ku, Yokohama 236-8501, Japan
Fax: 81-45-784-8153, e-mail: matsui@kanto-gakuin.ac.jp

$\text{LaNbO}_4\text{:Eu}^{3+}$, Dy^{3+} phosphors prepared by a solid-state reaction were characterized by X-ray diffraction (XRD) and photoluminescence spectra. The XRD patterns of LaNbO_4 doped with Eu^{3+} and Dy^{3+} essentially agreed with those of LaNbO_4 , indicating that the doping of Eu^{3+} and Dy^{3+} ions does not change the host crystal structure. From the strong emission peak at 615 nm corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_2$, Eu^{3+} was thought to occupy the sites with lower symmetry. In addition to the usual emission transitions from $^5\text{D}_0$, the emission transitions from the higher $^5\text{D}_1$ and $^5\text{D}_2$ levels were observed. The transitions from the higher levels were explained by the reduced multi-phonon relaxation from the $^5\text{D}_1$ and $^5\text{D}_2$ to the lowest excited level $^5\text{D}_0$ due to the lower vibrational energy of NbO_4^{3-} . The relative emission intensity of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition decreased with an increase in the amount of Dy^{3+} . This was attributed to energy transfer to the Dy^{3+} ions.

Key words: Phosphors, Photoluminescence, Rare earth, LaNbO_4 , Eu^{3+} , Dy^{3+} , XRD

1. INTRODUCTION

Advanced luminescent materials are in great demand for various applications such as lamps, signing and display devices [1]. Persistent luminescence (afterglow) is the light emission which remains for an appreciable time after stopping excitation. It is one of the important features for advanced luminescent materials. Since the pioneering work of Matsuzawa *et al.* on a very bright and long persistence $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, Dy^{3+} phosphor [2], a large number of new phosphors with persistent luminescence have been developed and widely used for safety uses in emergencies, traffic signaling, structural damage sensors, and medical diagnostics [3-5].

Lanthanum niobate (LaNbO_4) is expected to find use as a multifunctional material for various purposes such as dielectric resonators, ferroelastic materials, and optical materials [6-10]. The band gap of LaNbO_4 is around 4.8 eV and this material shows photoluminescence at 400 nm [9, 10]. Therefore, the luminescence properties of pure and doped LaNbO_4 are quite interesting. However, there are few reports about the luminescence of LaNbO_4 doped with rare earth ions [11]. In addition, persistent luminescence in LaNbO_4 is a challenging problem. In this report, the photoluminescence of LaNbO_4 doped with Eu^{3+} and Dy^{3+} was studied.

2. EXPERIMENTAL

The $\text{LaNbO}_4\text{:Eu}^{3+}$, Dy^{3+} phosphors were prepared by a solid-state reaction by mixing of La_2O_3 (Wako, 99.99%), Nb_2O_5 (Wako, 99.9%), Eu_2O_3 (ShinEtsu), and Dy_2O_3 (ShinEtsu) in a ball mill (Fritsch P-7) for 12 min. Then, the resultant mixtures were sintered from 1100 to 1300 °C in a reducing environment of 3 % H_2 in N_2 for 3 h. The obtained phosphors were characterized by X-ray diffraction (XRD, Rigaku RINT 2200) using $\text{Cu K}\alpha$ radiation. The emission and the excitation spectra

were taken with a JASCO FP-6500 spectrometer.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of $\text{La}_{0.8}\text{NbO}_4\text{:Eu}^{3+}_{0.1}\text{Dy}^{3+}_{0.1}$ phosphors sintered at different temperatures. In general, the XRD patterns of the phosphors are in good agreement with that of the monoclinic phase of LaNbO_4 (PDF#01-083-1911). The widths of the peaks become sharper and the intensity of the peaks become stronger with an increase in the sintering temperature. This is attributed to an increased crystallinity; the sizes of the crystallites obtained by the Sherrer equation are 37, 36, and 67 nm for sintering at 1100, 1200, and 1300 °C, respectively.

Fig. 1. XRD patterns of $\text{La}_{0.8}\text{NbO}_4\text{:Eu}^{3+}_{0.1}\text{Dy}^{3+}_{0.1}$ phosphors sintered at different temperatures. The numbers indicate the size of the crystallite obtained by Sherrer's equation. The lines are the XRD of the LaNbO_4 (PDF#01-083-1911).

Fig. 2. Excitation ($\lambda_{\text{ex}} = 435 \text{ nm}$) and emission ($\lambda_{\text{ex}} = 258 \text{ nm}$) spectra of LaNbO_4 calcined at 1200°C .

The XRD patterns of LaNbO_4 doped with Eu^{3+} and Dy^{3+} essentially agree with those of LaNbO_4 , indicating that the doping of Eu^{3+} and Dy^{3+} ions does not change the host crystal structure for the present preparation conditions. From the ionic radii of La^{3+} (0.116 nm), Nb^{5+} (0.048 nm), Eu^{3+} (0.107 nm), and Dy^{3+} (0.103 nm), Eu^{3+} and Dy^{3+} ions are expected to occupy the La^{3+} sites in LaNbO_4 [11].

Figure 2 shows the excitation and emission spectra of LaNbO_4 calcined at 1200°C . The emission spectrum of the sample has a peak at 435 nm, which is shifted toward the red compared with previous results such as 400 nm [9] and 408 nm [10]. The peak of the excitation spectrum monitored at 435 nm is seen at 258 nm. This peak corresponds to those previously observed at 240 nm [9] and 260 nm [10] and is ascribed to the charge transfer band of $[\text{NbO}_4]^{3-}$ ($\text{O}^{2-}-\text{Nb}^{5+}$) in LaNbO_4 [8, 10]. A previous paper reported that the excitation peak exhibited a red shift from 247 to 260 nm and a new peak appeared at 300 nm

with increase in the calcination temperatures from 700 to 1200°C [10]. The latter peak was attributed to the formation of $[\text{NbO}_6]^{7-}$ groups in LaNbO_4 [10]. As seen in Fig. 2, there is no peak at 300 nm in this sample. This is most probably because the phosphor in this experiment was sintered in a reducing environment of 3 % H_2 in N_2 , while the phosphors showing an excitation peak at 300 nm were sintered in air [10].

Figure 3 shows the emission spectra of phosphors sintered at 1200°C : (a) $\text{La}_{0.9}\text{NbO}_4:\text{Eu}^{3+}_{0.1}$, (b) $\text{La}_{0.8}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.1}$ and (c) $\text{La}_{0.7}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.2}$. The strong peaks were observed at 615 and 595 nm, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions of Eu^{3+} , respectively. The former, which is originally electrical dipole forbidden, becomes allowed by lowering the site symmetry of Eu^{3+} while the latter, which is magnetic dipole allowed, has the same intensity regardless of the site symmetry [12]. Therefore, Eu^{3+} is considered to occupy the sites with lower symmetry, because the peak intensity at 615 nm is much stronger than that at 595 nm.

The relative emission intensities at $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition are 390, 230, and 1 for $\text{La}_{0.9}\text{NbO}_4:\text{Eu}^{3+}_{0.1}$, $\text{La}_{0.8}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.1}$, and $\text{La}_{0.7}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.2}$, respectively, indicating a decrease in the emission intensity of Eu^{3+} with an increase in the amount of Dy^{3+} . When the above spectra are normalized by the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition at 595 nm, the relative peak intensities at 615 nm for the three phosphors are identical with each other, as seen in Fig. 4 (the spectrum of $\text{La}_{0.7}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.2}$ is not shown here), indicating the same site symmetry around Eu^{3+} for different Dy^{3+} concentrations. Therefore, the decreased peak intensity with an increase in Dy^{3+} in Fig. 3 is not caused by the site symmetry. In addition, bands are seen at 576 nm due to Dy^{3+} ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$), and 480 and 490 nm due to Dy^{3+} ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) for the Dy^{3+} -doped phosphors [13]. These results suggest that the quenching of Eu^{3+} emission by Dy^{3+} occurs by energy

Fig. 3. Emission spectra of phosphors sintered at 1200°C and excited at 395 nm: (a) $\text{La}_{0.9}\text{NbO}_4:\text{Eu}^{3+}_{0.1}$, (b) $\text{La}_{0.8}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.1}$, and (c) $\text{La}_{0.7}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.2}$.

Fig. 4. Emission spectra normalized at 595 nm for phosphors sintered at 1200°C and excited at 395 nm: (a) $\text{La}_{0.9}\text{NbO}_4:\text{Eu}^{3+}_{0.1}$ and (b) $\text{La}_{0.8}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.1}$.

transfer from Eu^{3+} to Dy^{3+} .

Another interesting characteristic is the presence of emission from higher energy levels in addition to $^5\text{D}_0$; the emission transitions observed are from $^5\text{D}_1$ to $^7\text{F}_1$ and $^7\text{F}_2$ at 538 and 555 nm, and from $^5\text{D}_2$ to $^7\text{F}_0$ and $^7\text{F}_3$ at 467 and 512 nm, respectively in Figs. 3 and 4. The transitions from the higher levels are caused by the reduced multi-phonon relaxation from the $^5\text{D}_1$ and $^5\text{D}_2$ to the lowest excited level $^5\text{D}_0$ due to the lower vibrational energy of NbO_4^{3-} , as previously discussed in the emission spectrum of $\text{YNbO}_4:\text{Eu}^{3+}$ [14].

As for the effect of sintering temperature on the emission of $\text{La}_{0.9}\text{NbO}_4:\text{Eu}^{3+}_{0.1}$, $\text{Dy}^{3+}_{0.1}$, the emission spectra showed a similar one to that seen in Fig. 3 for 1100, 1200, and 1300 °C, while the sizes of the crystallites were 37, 36, and 67 nm for sintering at 1100, 1200, and 1300 °C, respectively as shown in Fig. 1. These results indicate that Eu^{3+} can form an effective luminescent center at the sintering temperatures and that the crystalline size has little influence on the emission spectra.

Fig. 5. Excitation spectra of phosphor sintered at 1200 °C: (a) $\text{La}_{0.9}\text{NbO}_4:\text{Eu}^{3+}_{0.1}$ monitored at 615 nm and (b) $\text{La}_{0.8}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.1}$ monitored at 615 nm.

Figure 5 shows the excitation spectra of (a) $\text{La}_{0.9}\text{NbO}_4:\text{Eu}^{3+}_{0.1}$ monitored at 615 nm and (b) $\text{La}_{0.8}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.1}$ monitored at 615 nm. The excitation spectra showed peaks at around 280 nm with shoulders at around 260 nm for (a) and (b). The shoulders at 260 nm are ascribed to the charge transfer band of $[\text{NbO}_4]^{3-}$ ($\text{O}^{2-}-\text{Nb}^{5+}$), as discussed above. The peak position and width of the broad band did not change when Dy^{3+} was added. Therefore the broad peaks around 280 nm are considered to be the charge transfer bands of $\text{O}^{2-}-\text{Eu}^{3+}$ and $\text{O}^{2-}-\text{Nb}^{5+}$ [11]. The line spectra are attributed to the transitions of Eu^{3+} such as $^7\text{F}_0-^3\text{L}_6$ at 395 nm, $^7\text{F}_0-^5\text{D}_2$ at 465 nm and so on. The intensities of the broad bands at around 280 nm are stronger than those of the lines, suggesting that the most effective excitation process is from the host LaNbO_4 to Eu^{3+} .

The Eu^{3+} -doped LaNbO_4 phosphors did not show Eu^{2+} luminescence, indicating no reduction from Eu^{3+} to Eu^{2+} in LaNbO_4 , while reduction occurred in SrAl_2O_4 , BaAl_2O_4 , and CaAl_2O_4 host crystals under the same sintering conditions employed in our laboratory. This

result confirms one of the necessary conditions for reduction of Eu^{3+} to Eu^{2+} ; the dopant trivalent Eu^{3+} ion substitutes for the divalent cation in the host [15]. As mentioned previously, Eu^{3+} and Dy^{3+} ions are considered to occupy the La^{3+} sites in LaNbO_4 . Eu^{3+} was not reduced under our experimental conditions, because it is very difficult to change the charge balance of the LaNbO_4 host.

Afterglow luminescence was examined for LaNbO_4 doped with various concentrations of Eu^{3+} and Dy^{3+} and sintering conditions. So far, unfortunately, afterglow luminescence could not be measured for these phosphors. Further studies are still in progress.

4. CONCLUSIONS

The following phosphors were prepared by the solid-state reaction method using a ball mill and high temperature heat treatments in a reduced atmosphere: $\text{La}_{0.9}\text{NbO}_4:\text{Eu}^{3+}_{0.1}$, $\text{La}_{0.8}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.1}$, and $\text{La}_{0.7}\text{NbO}_4:\text{Eu}^{3+}_{0.1}, \text{Dy}^{3+}_{0.2}$. The phosphors showed red emission lines of Eu^{3+} corresponding to the $^5\text{D}_0-^7\text{F}_2$ transition at 615 nm, which becomes allowed by lowering the Eu^{3+} site symmetry. Emission transitions were also observed from $^5\text{D}_1$ to $^7\text{F}_1$ and $^7\text{F}_2$ and from $^5\text{D}_2$ to $^7\text{F}_0$ and $^7\text{F}_3$, which were attributed to the reduced multi-phonon relaxation due to the lower vibrational energy of NbO_4^{3-} . With an increase in the amount of Dy^{3+} , the emission intensity of Eu^{3+} decreased and the relatively weak emissions due to Dy^{3+} increased. Afterglow luminescence could not be detected for these phosphors.

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