Solid-state reaction synthesis and optical property analysis of LaF$_3$–LaOF:Yb$^{3+}$/Ho$^{3+}$ upconversion phosphors

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In this study, LaF$_3$–LaOF:Yb$^{3+}$/Ho$^{3+}$ upconversion (UC) phosphors were synthesized via a solid-state reaction and their optical properties were analyzed. The analysis of photoluminescence (PL) characteristics revealed strong emission at a wavelength of 543 nm for molar ratios of La:Yb:Ho = 1:x:y, where x = 0.04–0.06 and y = 0.01–0.03. The pump power dependence of phosphor PL and the fluorescence lifetime were then measured, and the mechanism of UC PL is discussed.

Key-words : Upconversion, LaF$_3$, LaOF, Yb$^{3+}$, Ho$^{3+}$

[Received July 14, 2022; Accepted August 1, 2022]

1. Introduction

Downconversion, also known as the Stokes shift, is a technique for converting short-wavelength electromagnetic waves, such as UV light, into longer-wavelength electromagnetic waves. Upconversion (UC), or the anti-Stokes shift, on the other hand, is a technique for converting longer-wavelength electromagnetic waves, such as near-IR (NIR), into shorter-wavelength electromagnetic waves.$^{1}$ Studies on UC have been conducted since 1966; UC phosphors have been synthesized by introducing rare-earth elements into the host material.$^{2}$ In recent years, rare-earth ions have been doped at higher concentrations than before with the aim of avoiding concentration quenching.$^3$

UC phosphors have attracted considerable attention in bioimaging applications owing to the high tissue penetration depth of NIR excitation and the low autofluorescence background at NIR wavelengths.$^4$ In addition, UC phosphors are expected to increase the efficiency of solar cells and to be used in noncontact temperature sensors.$^5$–$^8$

Fluoride has attracted attention as a host material for UC phosphors because of its low phonon energy; in particular, NaYF$_4$ and NaGdF$_4$ have been studied as promising host materials.$^9$–$^{12}$ In this study, LaF$_3$ was used as a host material.$^1$–$^3$ In addition to its low phonon energy, LaF$_3$ has another useful property as a host material: doping with rare-earth ions does not distort the crystal lattice because the ionic radius of La in the rare-earth ions does not distort the crystal lattice because

various combinations of doping elements in UC phosphors have been reported, such as Yb–Er and Yb–Tm.$^{17}$–$^{20}$ In this study, we used the Yb–Ho combination; Ho can be used to obtain green ($^5$S$_4$, $^5$I$_8$ → $^5$I$_6$) and red ($^5$F$_5$, $^5$F$_5$ → $^5$I$_6$) emissions.$^{21,22}$

We previously synthesized LaOF:Yb$^{3+}$/Er$^{3+}$ UC phosphors and analyzed their optical properties.$^{23}$ The photoluminescence (PL) intensity of LaOF was lower than that of LaF$_3$, indicating that practical applications for a host material made from LaOF alone would be limited. Also, in general, LaF$_3$ is considered to have low chemical stability, and it is thought that there will be challenges in practical application if the host material is only LaF$_3$. Therefore, the aim of this study is to synthesize a LaF$_3$–LaOF:Yb$^{3+}$/Ho$^{3+}$ UC phosphor with excellent PL intensity and chemical stability and to analyze its optical properties. The phonon energy of LaF$_3$ is lower than that of LaOF, and LaF$_3$–LaOF:Yb$^{3+}$/Ho$^{3+}$ is considered to emit at a higher intensity than LaOF:Yb$^{3+}$/Ho$^{3+}$. Also, LaF$_3$–LaOF composites are considered to be more chemically stable than LaF$_3$.

In previous studies on LaF$_3$:Yb$^{3+}$/Ho$^{3+}$, the samples were synthesized in solution,$^{28}$–$^{30}$ and there have been no reports of solid-phase synthesis. We describe the UC properties of LaF$_3$–LaOF:Yb$^{3+}$/Ho$^{3+}$ synthesized using a solid-state reaction.

2. Experimental conditions

To synthesize the sample by a solid-state reaction, LaF$_3$, Yb$_2$O$_3$, and Ho$_2$O$_3$ powders, obtained from Kojundo...
Chemical Lab Co., were mixed to achieve molar ratios of La:Yb:Ho = 1:x:y (x = 0.03, 0.04, 0.05, 0.06, and 0.07 and y = 0.01, 0.02, 0.03, 0.04, and 0.05). Then, the powder mixture was pressurized into pellets, which were placed in an Al₂O₃ crucible and heated in air at 1100 °C for 1 h.

The PL characteristics, crystal structure, pump power dependence of PL intensity, and fluorescence lifetime were analyzed. For the PL characteristics, an NIR laser (wavelength = 980 nm; output = 200 mW) was used as the excitation source. A Flame series spectrometer (Ocean Optics) was used for the analysis. PL characteristics were measured five times for each sample and the average value was calculated. An Ultima IV X-ray diffractometer (XRD) (Rigaku Corporation) was used for the crystal structure analysis. Neutral density (ND) filters were used to modify the excitation light output when measuring the pump power dependence of PL intensity. ND filters with transmittances of 12.5, 25, and 50 % were placed in front of the excitation light source to modify its pump power.

The fluorescence lifetime was measured using the method reported by Zhu. An electric motor (Mabuchi Motor Co. model FA-130RA) was used to rotate the samples. An iPhone 8 (Apple Inc.) digital camera was used to obtain fluorescence images, and the iOS version of Lightroom software (Adobe) was used for image processing. The sample was fixed to the motor shaft with double-sided tape and imaged during and after excitation by NIR while being rotated by the motor at 4800 rpm. After the images were taken, they were analyzed using the free software ImageJ. Images were divided into the three primary colors of light, and the fluorescence lifetime was calculated by measuring the rate of decay of luminance in the green and red spectral bands after NIR excitation had ceased.

3. Results and discussion

XRD patterns of LaF₃-LaOF:Yb³⁺/Ho³⁺ UC phosphors with differing concentrations of Yb³⁺ dopant are shown in Fig. 1. The molar ratios are La:Yb:Ho = 1:x:0.01, where x = 0.03, 0.04, 0.05, 0.06, and 0.07. The bottom part of Fig. 1 shows the XRD patterns of LaOF (01-089-5168) and LaF₃ (01-082-0684) for reference, which were obtained from the Inorganic Crystal Structure Database (ICSD). The crystal structures of LaOF (01-089-5168) and LaF₃ (01-082-0684) are tetragonal and hexagonal, respectively. Major peaks of LaOF and LaF₃ were observed at 2θ = 26.6° and 2θ = 27.6° in all samples, respectively, indicating that each sample is primarily composed of LaOF and LaF₃.

Figure 2 illustrates the PL characteristics of the samples. The horizontal and vertical axes in Fig. 2(a) are wavelength and emission intensity, respectively, and each spectrum shows the result for a different Yb³⁺ doping level. For all samples, peaks were observed at wavelengths of 543 nm (²F₄, ⁵S₂ → ⁵I₈) and 654 nm (²F₅ → ⁵I₈). The
The standard patterns are shown for LaOF (01-089-5168) and are La:Yb:Ho phors with different doping concentrations of Ho3+. The molar ratio of La:Yb:Ho is 1:0.06:0.01. For comparison, the unit cell parameters and volume of ICSD are also listed.

The analysis result of the peak positions in LaF3 by Yb3+ doping are shown in Table 1. The molar ratio is La:Yb:Ho = 1:0.06:0.01. For comparison, the unit cell parameters and volume of ICSD are also listed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>V [Å³]</th>
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<td>4.089</td>
<td>5.83</td>
<td>97.5</td>
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<td>4.0910</td>
<td>5.8360</td>
<td>97.673</td>
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<tr>
<td>LaF3 (This study)</td>
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<td>7.175</td>
<td>7.345</td>
<td>327.5</td>
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<td>7.2000</td>
<td>7.3760</td>
<td>331.144</td>
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</table>

Table 1. The unit cell parameters and volume of LaF3-LaOF: Yb3+/Ho3+ UC phosphor. The molar ratio is La:Yb:Ho = 1:0.06:0.01. For comparison, the unit cell parameters and volume of ICSD are also listed.

The highest PL emission intensity was observed at the molar ratio of La:Yb:Ho = 1:0.06:0.01. The horizontal and vertical axes in Fig. 2(b) respectively show the Yb3+ doping level and the ratio of PL emission intensity (G/R ratio) at wavelengths of 543 nm (°F{sub}5, 5S{sub}2 → 5I{sub}8) and 654 nm (°F{sub}5 → 5I{sub}8). In the range of Yb3+ mole fractions used in the experiment, the green emission intensity at 543 nm was dominant and was more than 10 times stronger than the red emission intensity at 654 nm. The G/R ratio of samples with Yb = 0.04–0.06 was ~14.

XRD patterns of LaF3-LaOF:Yb3+/Ho3+ UC phors with differing concentrations of Ho3+ dopant are shown in Fig. 3(a). The molar ratios of the samples are La:Yb:Ho = 1:0.06:γ, where γ = 0.01, 0.02, 0.03, 0.04, and 0.05. The XRD patterns of LaOF (01-089-5168) and LaF3 (01-082-0684) from ICSD are shown in Fig. 3(a) for reference. Results indicate that each sample primarily comprises LaOF and LaF3. The peak value of LaF3 was greater than that of LaOF in the samples with Ho = 0.01 and 0.02.

The analysis result of the peak positions in LaF3-LaOF:Yb3+/Ho3+ UC phosphor is shown in Fig. 3(b). Figure 3(b) shows the results for the sample with the molar ratio of La:Yb:Ho = 1:0.06:0.01. The main peaks are LaF3 and LaOF. The weight ratio of LaF3 to LaOF was 63.3:36.7. The peaks that could not be identified suggest the formation of impurity phases.

The unit cell parameters and volume of LaF3-LaOF: Yb3+/Ho3+ UC phosphor are shown in Table 1. The molar ratio is La:Yb:Ho = 1:0.06:0.01. The lattice parameters of LaF3-LaOF:Yb3+/Ho3+ UC phosphor are refined by the least-squares method. For comparison, Table 1 also includes the unit cell parameters and volume of ICSD. Comparing the ICSD with the analysis of this study, it can be seen that the rate of decrease in the volume of LaF3 is greater than the rate of decrease in the volume of LaOF. The ion radii of La3+ (coordination number = 8), Ho3+ (coordination number = 8), and Yb3+ (coordination number = 8) are 1.160, 1.015, and 0.985 Å, respectively. Therefore, it is assumed that the replacement of La3+ in LaF3 by Yb3+ and Ho3+ caused the decreased volume of LaF3.

The resulting PL characteristics are shown in Fig. 4. Each spectrum in Fig. 4(a) shows the dependence on the Ho3+ doping level. Peaks at wavelengths of 543 nm (°F{sub}5, 5S{sub}2 → 5I{sub}8) and 654 nm (°F{sub}5 → 5I{sub}8) were observed for all samples, with the same spectral distribution as in Fig. 2. Figure 4(b) shows the G/R ratio versus the Ho3+ doping level. At molar ratios of Ho = 0.01–0.03, the emission, dominated by the 543 nm peak similarly to in Fig. 2, showed a G/R ratio of ~1; however, the G/R ratio then decreased substantially when the Ho concentration was >0.04. The G/R ratio at Ho = 0.05 was found to be about one-fifth of that at Ho = 0.03.

To examine the UC mechanism, we analyzed the dependence of PL intensity on pump power. The PL intensity I_{UP} of UC depends on the output P and is expressed by

\[ I_{UP} \propto P^n, \]

where n indicates the number of pumping photons required for excitation from the ground state to the excited state.\(^{22}\) The pump power dependence of PL intensity is shown in Fig. 5. Figure 5(a) shows the results for a sample with a molar ratio of La:Yb:Ho = 1:0.06:0.01. The slopes at...
Fig. 4. (a) PL characteristics of LaF₃–LaOF:Yb³⁺/Ho³⁺ UC phosphors. The molar ratios are La:Yb:Ho = 1:0.06:y (y = 0.01, 0.02, 0.03, 0.04, 0.05). (b) G/R ratio versus Ho³⁺ concentration.

Fig. 5. (a) Pump power dependence of PL intensity of LaF₃–LaOF:Yb³⁺/Ho³⁺ UC phosphor. The molar ratio is La:Yb:Ho = 1:0.06:0.01. (b) Dependence of slope on Yb³⁺ concentration. (c) Dependence of slope on Ho³⁺ concentration. (d) Energy level diagram of Yb³⁺ and Ho³⁺ in LaF₃–LaOF and UC mechanisms.
wavelengths of 543 and 654 nm were observed to be 1.63 and 1.42, respectively. Both slopes are between 1 and 2, indicating that the PL emission is a two-photon process.\(^{32}\) The reason that both slope values are <2 is the energy loss due to cross-relaxation (CR) effects and non-radiative (NR) transitions.\(^{33}\) The results of similar measurements on other samples with different molar ratios are shown in Figs. 5(b) and 5(c). The changes in the slope in Figs. 5(b) and 5(c) were close to the trends in the G/R ratios in Figs. 2(b) and 4(b), respectively. For the molar ratios of Yb = 0.04–0.06 and Ho = 0.01–0.02, it is inferred that the energy loss due to CR effects and NR transitions is smaller than that of the other samples. The slope could not be calculated for the molar ratio of Ho = 0.05, which is therefore absent from Fig. 5(c), because the PL emission intensity was too low.

The energy level diagram of Yb\(^{3+}\) and Ho\(^{3+}\) in LaF\(_3\)–LaOF and UC mechanisms under 980 nm excitation are shown in Fig. 5(d). In the green emission \(\{5F_{4,5}S_2(Yb^{3+}) \rightarrow 5I_6(Ho^{3+})\}\), two successive energy transfer (ET) processes \(\{5I_6(Ho^{3+}) + 2F_{5/2}(Yb^{3+}) \rightarrow 5I_6(Ho^{3+}) + 2F_{7/2}(Yb^{3+})\}\) and \(\{5I_6(Ho^{3+}) + 2F_{7/2}(Yb^{3+}) \rightarrow 5F_{4,5}S_2(Ho^{3+}) + 2F_{5/2}(Yb^{3+})\}\) may be involved in the population of the \(5F_{4,5}S_2\) excited states. This green UC emission is a two-photon process, consistent with the results in Figs. 5(a)–5(c). On the other hand, in the red emission \(\{5F_{3}(Ho^{3+}) \rightarrow 5I_6(Ho^{3+})\}\), there are two pathways to populate in the excited state \(F_{3}\) level of Ho\(^{3+}\). The first is the NR transition from the upper \(5F_{4,5}S_2\) level to the \(F_{3}\) level. The second is the relaxation from the \(5I_6\) level to the \(5I_7\) level by the NR process and the excitation to the \(F_{5}\) level by the ET process \(\{5I_6(Ho^{3+}) + 2F_{5/2}(Yb^{3+}) \rightarrow 5F_3(Ho^{3+}) + 2F_{7/2}(Yb^{3+})\}\). In addition, the population of \(5I_6\) level via the CR process \(\{5F_{4,5}S_2(Ho^{3+}) + 5I_6(Yb^{3+}) \rightarrow 5F_3(Ho^{3+}) + 5I_6(Ho^{3+})\}\) can’t be neglected at relatively high concentrations.\(^{32}\)

The fluorescence lifetime \(\tau\) was calculated by analyzing the images using

\[
z = A_0 + A_1 e^{-t/\tau},
\]

where \(z\) is PL intensity, \(t\) is delay time, and \(A_0\) and \(A_1\) are constants.\(^{25}\) The fluorescence lifetime results are shown in Fig. 6, where Fig. 6(a) shows the results for the sample with the molar ratio of La:Yb:Ho = 1:0.06:0.01. The vertical axis in Fig. 6(a) is linear scale. For this sample, the fluorescence lifetime was 0.70 ms. The results of similar measurements on other samples are shown in Figs. 6(b) and 6(c). The sample with the molar ratio of La:Yb:Ho = 1:0.06:0.01 displayed the longest fluorescence lifetime.

The decrease in fluorescence lifetime at Yb = 0.07 in Fig. 6(b) may be attributed to the enhanced energy back transfer (EBT) process between Yb\(^{3+}\) and Ho\(^{3+}\) ions: \(\{5F_{4,5}S_2(Yb^{3+}) + 2F_{7/2}(Yb^{3+}) \rightarrow 5I_6(Ho^{3+}) + 2F_{5/2}(Yb^{3+})\}\). Furthermore, the decrease in fluorescence lifetime with increasing Ho\(^{3+}\) concentration in Fig. 6(c) may be caused by CR among Ho\(^{3+}\) ions.\(^{33}\)

4. Conclusion

UC phosphors of LaF\(_3\)–LaOF:Yb\(^{3+}\)/Ho\(^{3+}\) were synthesized by a solid-state reaction. Several samples were synthesized with differing concentrations of rare-earth dopants. The crystal structure was analyzed via XRD, and LaF\(_3\) and LaOF peaks were detected in all samples. The analysis of PL characteristics revealed strong emission at the wavelength of 543 nm for the molar ratios of La:Yb:Ho = 1.04, \(x\) where \(x = 0.04–0.06\) and \(y = 0.01–0.03\). The pump power dependence of PL intensity showed that the PL emission of the samples is a two-photon process. Furthermore, samples with the highest G/R ratios had the smallest energy losses. This was due to CR effects and NR transitions. A decrease in fluorescence lifetime was observed at Yb = 0.07, which may be attributed to EBT. Moreover, a decrease in fluorescence lifetime was observed with increasing Ho\(^{3+}\) concentration owing to the CR of absorbed energy among Ho\(^{3+}\) ions.
Declarations
Conflict of interest  The authors declare that there is no conflict of interest in this work.

References
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