FULL PAPER

Effect of processing conditions on crystallinity and luminescent characteristics of aeschynite-type complex oxide crystals doped with Dy^{3+} and Eu^{3+}

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Effect of processing conditions on the crystallinity and luminescent characteristics of aeschynite-type Dy^{3+} - and Eu^{3+} -doped GdTiNbO_6 formed under hydrothermal conditions from precursor solutions of inorganic salts, i.e. $\text{Dy}(\text{NO}_3)_3$, EuCl_3 , GdCl_3 , TiOSO_4 , and NbCl_5 was investigated. A processing condition using the hydrolysis of urea promoted the formation of aeschynite with finer crystallite due to an increase in nucleation number. The aeschynite-type solid solution was directly formed under hydrothermal conditions at 240°C because its lattice parameters changed according to the Vegard's Law. The photoluminescence (PL) emission intensity of aeschynite crystals depended on their crystallinity, which was closely related to their processing conditions. Without subsequent heat treatment in air, the as-prepared aeschynite-type solid solutions substitutionally doped with 5 mol % Dy^{3+} and 50 mol % Eu^{3+} showed the maximum and intense PL emissions under direct excitation of dopant ions. In the case of indirect excitation using energy transfer from the host absorption band at 280 nm, the characteristic blue and yellow PL emission intensities involved in the broad host emission of the Dy^{3+} -doped GdTiNbO_6 were improved dramatically after heating at 1300°C in air.

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1. Introduction

Materials based on metal complex oxides with general formula $\text{A}^{3+}\text{B}^{4+}\text{C}^{5+}\text{O}_6$ in ternary systems (i.e. A_2O_3 – 2BO_2 – C_2O_5) have attracted attention because of interesting characteristics and high potentials such as dielectric¹⁾ and microwave dielectric properties,²⁾ strong relaxor ferroelectric behavior,³⁾ and photoluminescence (PL) properties.⁴⁾ The single phase occurrence,⁵⁾ structures,⁶⁾ and properties of these complex oxides have been investigated by some researchers.⁷⁾ In these compounds, several complex oxides of RETiNbO_6 , where RE is a rare earth, have been studied for the development of dielectric resonators,^{8)–11)} solid-state laser materials,^{12),13)} and phosphors.^{7),14)–17)} RETiNbO_6 has mainly both structures, i.e. aeschynite and euxenite depending on the radius of RE^{3+} ion, and these phases are usually members of representative crystalline minerals containing rare earth element.

In recent years, luminescent rare earth ions-doped materials have attracted much attention because they can be used in many highly functional applications, e.g., display devices (: field emission displays, cathode ray tubes, and vacuum fluorescent displays), solid-state laser, biological

labeling devices, biochemical probes, and lighting apparatus such as white light-emitting diodes.^{18)–22)} Dy^{3+} doped materials are known to emit blue light at 470–500 nm and yellow light at 570–600 nm attributed to the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ transitions, respectively under UV excitation. Trivalent Eu^{3+} ion possesses a typical feature as a representative activator for red emission because its emission band is centered about the primary red color, on the other hand.²³⁾

RETiNbO_6 crystals among those complex oxide materials have been synthesized mostly by means of conventional solid-state reactions or processes such as solution combustion technique, i.e., Pechini method and polymerized complex method or sol–gel method,^{15),24)–27)} excluding a few techniques based on aqueous solutions,^{28),29)} in general. However, in those reactions and processes, subsequent heating at high temperatures (more than about 1000°C) in air is indispensable for the formation or crystallization of desired metal complex oxide crystals. Recently, from the view point of processing through energy consumption reduction, much attention has been devoted on green processing at low temperatures including wet chemical synthesis routes for the synthesis of fine inorganic crystals because those routes such as hydrothermal synthesis method are advantageous to obtain highly homogeneous materials and to control the crystallinity and

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particle size of fine powders based on metal oxides, complex oxides, new compounds, solid solutions, and metastable phases.^{30)–34)} Since GdTiNbO₆-based compounds crystallize into euxenite-type structure by means of heat-treatment at high temperatures of 1000–1400°C in air in the case of the solid-state reactions, in general, almost all of reports and literatures published on GdTiNbO₆-based compounds up to now are studies and data concerning the euxenite-type GdTiNbO₆³⁵⁾ with the exception of our study. Therefore, there are few reports and data that are available on the aeschynite-type GdTiNbO₆-based materials, e.g. Dy³⁺-doped GdTiNbO₆. Because there are only a few studies on the low-temperature synthesis of fine GdTiNbO₆-based crystals, on the other hand, the relationship between processing and properties of fine GdTiNbO₆ phosphor materials using hydrothermal route at low temperatures less than 250°C has not been sufficiently clarified.

In this study, the effect of processing conditions on the direct synthesis, structure, and luminescence properties of aeschynite-type Dy³⁺-doped GdTiNbO₆ and Eu³⁺-doped GdTiNbO₆ fine crystals has been investigated using a green processing under mild hydrothermal conditions from precursor solutions of inorganic salts.

2. Experimental procedures

2.1 Preparation of samples

Two metal complex oxides [composition: Dy_xGd_{1-x}TiNbO₆ ($x = 0-0.20$) and Eu_xGd_{1-x}TiNbO₆ ($x = 0-1.00$)] were synthesized using hydrothermal method. A solution mixture of an aqueous solution selected from reagent-grade Dy(NO₃)₃·5H₂O, EuCl₃·6H₂O, GdCl₃·6H₂O, TiOSO₄, and an ethanol solution of NbCl₅ in different ratios of Dy/Gd/Ti/Nb = $x/1.00 - x/1.00/1.00$, $x = 0-0.20$, or Eu/Gd/Ti/Nb = $x/1.00 - x/1.00/1.00$, $x = 0-1.00$ was prepared in a Teflon container (100 cm³) while stirring. Two-types of precursor solutions were prepared by the addition of (i) aqueous ammonia or (ii) aqueous solution of urea into the solution mixture while stirring. These solutions were controlled to obtain weak basic conditions after hydrothermal treatment by the addition of aqueous ammonia or hydrolysis of urea. The precursor solution (90 cm³) with total cation concentration of 0.500 mol/dm³ (: Dy + Gd + Ti + Nb or Eu + Gd + Ti + Nb = 0.500 mol/dm³) in the Teflon container was then placed in a stainless-steel vessel. The vessel was tightly sealed and heated at 200–240°C for 5–24 h while rotating at 1.5 rpm. After the hydrothermal treatment, precipitates formed in the Teflon container were washed with distilled water until the pH value of the rinsed water became 7.0, separated from the solution by centrifugation, and dried in an oven at 60°C. The powders thus prepared hydrothermally were heated in an alumina crucible at a heating rate 200 °C/h, kept at 1000–1300°C for 1 h in air, and then cooled to room temperature in a furnace.

2.2 Characterization

X-ray diffraction (XRD) patterns of as-prepared pow-

ders were recorded using Cu K α radiation (XRD; model RINT-2000, Rigaku, Tokyo, Japan). The crystallite size of the orthorhombic aeschynite phase was estimated from the line broadening of 020 diffraction peak, according to the Scherrer equation, $D_{\text{XRD}} = K\lambda/\beta \cos \theta$, where θ is the Bragg angle of diffraction lines; K is a shape factor ($K = 0.9$ in this work); λ is the wavelength of incident X-rays, and β is the corrected half-width given by $\beta^2 = \beta_m^2 - \beta_s^2$, where β_m is the measured half-width and β_s is the half-width of a standard sample. The lattice parameters were measured using silicon as the internal standard. The observation of the morphology of as-prepared samples was carried out using scanning electron microscope (FESEM; model JSM-6335FM, JEOL, Tokyo, Japan) and transmission electron microscope (TEM; model JEM-2100Plus, JEOL, Tokyo, Japan) equipped with an energy dispersive X-ray spectrometry (EDS).

The ultraviolet-visible (UV-Vis) absorption spectra of the prepared powders were recorded at room temperature by means of UV-Vis spectrophotometer with an integrating sphere attachment (V-560, Nihon Bunko, Tokyo, Japan). The measurements of the PL emission and excitation spectra of samples were performed using a spectrofluorometer (F-2700, Hitachi High-Tech, Tokyo, Japan) with a Xe lamp. Powder samples doped with Dy³⁺ and Eu³⁺ were excited with 280, 387 and 317, 394 nm radiation from a 150 W xenon lamp, respectively. All measurements were carried out at room temperature. The emission wavelength was scanned from 500 to 750 nm at a scanning rate of 60 nm/min. For the measurements of the excitation spectra, the excitation wavelength was scanned from 220 to 500 nm at the same scanning rate, and emission monitored at 483 nm for GdTiNbO₆:Dy³⁺ and 611 nm for GdTiNbO₆:Eu³⁺, respectively. The absolute PL quantum yield of the samples was measured under excitation at 394 and 464 nm using an absolute quantum yield spectrometer (Quantaury-QY Plus C13534-02, Hamamatsu Photonics K.K., Hamamatsu, Japan). The fluorescence decay curves were measured using a Quantaury-tau C11367 fluorescence lifetime spectrometer (Hamamatsu Photonics K.K., Hamamatsu, Japan).

3. Results and discussion

3.1 Effect of processing conditions on the formation of aeschynite-type fine crystals

The hydrothermal treatment of the precursor solution was performed under weak basic conditions in the presence of aqueous ammonia or urea for 5–24 h. **Figure 1** shows the XRD patterns of precipitates (composition: Eu_{0.50}Gd_{0.50}TiNbO₆) formed under hydrothermal conditions in the presence of aqueous ammonia or urea at 200–240°C for 5 h. After hydrothermal treatment at 200°C, the product was amorphous. The hydrothermal crystallization of an aeschynite phase from amorphous precipitate was occurred around 220°C. When the treatment temperature is raised to 240°C, almost a single phase of aeschynite with high crystallinity was formed in the presence of aqueous ammonia. As suggested from the line broadening of the

Fig. 1. XRD patterns of precipitates ($\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$) obtained under hydrothermal conditions in the presence of urea or aqueous ammonia at 200–240°C for 5 h.

Table 1. Crystallite size, emission ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) intensity at 510 nm, and absolute quantum yield (excitation at 394 nm) of aeschynite-type $\text{Gd}_{1.00-x}\text{Eu}_x\text{TiNbO}_6$ formed under several processing conditions at 240°C using hydrothermal method

Processing condition	As-prepared sample (composition $x = 0.50$)		
	Urea 5 h	Ammonia 5 h	Ammonia 24 h
Crystallite size (nm)	18	53	58
Emission Intensity (a.u.)	4691	8409	9768
Quantum yield (%)	21	37	32

XRD peak, finer aeschynite crystals were formed when using the hydrolysis of urea, on the other hand. In **Table 1**, the crystallite sizes of these aeschynite phases are shown. The crystallite size of the aeschynite prepared by using the hydrolysis of urea was one-third of that obtained in the presence of aqueous ammonia. This is considered to be mainly due to an increase in the nucleation number for the crystallization of aeschynite. The nucleation of aeschynite may be accelerated by homogeneous and rapid generation of hydroxide ions by hydrolysis of urea at more than about 90°C.

Figures 2(a) and 2(b) present the XRD patterns of precipitates, $\text{Dy}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$, $x = 0\text{--}0.10$ and $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$, $x = 0\text{--}1.00$, respectively, which were formed from the precursor solutions with various compositions under hydrothermal conditions at 240°C in the presence of aqueous ammonia. The XRD patterns suggest that all of the precipitates were synthesized as a single phase corresponding to the aeschynite-type structure. The RETiNbO_6 oxides are known to possess two characteristic crystalline forms of orthorhombic structure depending on the ionic radius of RE^{3+} . One is the aeschynite structure with a space group symmetry $Pnma$ and the other is the euxenite structure belonging to a $Pbcn$ symmetry. According to the

Fig. 2. XRD patterns of precipitates obtained at various compositions (a) $x = 0\text{--}0.10$ in the $\text{Dy}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ system under hydrothermal conditions in the presence of aqueous ammonia at 240°C for 24 h and (b) $x = 0\text{--}1.00$ in the $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ system under hydrothermal conditions in the presence of aqueous ammonia at 240°C for 5 h.

literatures,^{[12],[13],[36],[37]} GdTiNbO_6 [at the composition $x = 0$ in Figs. 2(a) and 2(b)] and DyTiNbO_6 are suggested to belong to the euxenite-type phase and EuTiNbO_6 [in the

Fig. 3. FESEM images of samples formed hydrothermally at various conditions: (a) GdTiNbO_6 at 240°C for 5 h, using aqueous ammonia (b) $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ at 240°C for 5 h, using aqueous ammonia, (c) $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ at 240°C for 24 h, using aqueous ammonia, and (d) $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ at 240°C for 5 h, using urea.

composition $x = 1.00$ in Fig. 2(b)] is supposed to possess the aeschynite-type structure as the most stable phase at room temperature under normal pressure. It is noted that a single phase corresponding to the aeschynite-type phase, that is, orthorhombic CaTa_2O_6 -type structure belonging to the $Pnma$ space group was formed directly in all of the compositions including pure GdTiNbO_6 under these hydrothermal conditions.

The FESEM images of precipitates corresponding to the composition GdTiNbO_6 , $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$, and $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ that were obtained at 240°C in the presence of aqueous ammonia are shown in Figs. 3(a)–3(c), respectively. The images of the products suggest that those particles possess rectangular-like morphology, and that they are micron-sized in the range of 1.5–5 μm -length and 1–2 μm -width and well-crystallized. The length of each product is about two-times larger than its width. The x letter-like morphology is also observed in the FESEM images. In the samples formed under the same hydrothermal condition, the particle size of Eu^{3+} -doped sample [Fig. 3(b)] became a little bit large in comparison with that of pure GdTiNbO_6 [Fig. 3(a)]. The Dy^{3+} -doped sample [Fig. 3(c)] that was synthesized by hydrothermal treatment for 24 h grew larger than those formed by treatment for 5 h. Those products are considered to be polycrystalline because the crystallite size value for the $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ sample evaluated from the XRD line broadening is 53 nm (Table 1). Figure 3(d) shows the FESEM image of $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ precipitate obtained by hydrothermal treatment at 240°C for 5 h in the presence of urea. Relatively homogeneous and submicron-sized particles less than 0.4 μm are observed when using the hydrolysis of urea. Their crystallite size was 18 nm as shown in Table 1. These FESEM observation results relatively well corre-

sponded to their features of XRD patterns shown in Fig. 1. The TEM-EDS mapping of the as-prepared GdTiNbO_6 sample are presented in Fig. 4. The elemental mapping images of Ti, Nb, and Gd demonstrate that these samples formed directly under hydrothermal conditions possess homogeneity in elemental distribution.

The effect of hydrothermal treatment time on the crystallinity of product was investigated. The prolonged hydrothermal treatment for 24 h was conducted at 240°C to improve the crystallinity of aeschynite-type (Eu,Gd)- TiNbO_6 . The crystalline products formed after hydrothermal treatment for 24 h were compared with those obtained after hydrothermal treatment for 5 h. The XRD patterns of precipitates (composition: $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$) obtained under hydrothermal conditions at 240°C for 5 and 24 h are shown in Fig. 5. Both the precipitates were identified as aeschynite-type phase with good crystallinity. The crystallite sizes evaluated from the XRD line broadening of 020 diffraction peak of aeschynite phase formed by hydrothermal treatment for 5 and 24 h were 53 and 58 nm, respectively as shown in Table 1. It is obvious that the aeschynite-type product formed via prolonged hydrothermal treatment possess higher crystallinity because the sharper/higher the peaks are, the more crystalline the sample become, in general.

The prolonged hydrothermal treatment for 24 h was carried out at 240°C for precursor solutions (composition: $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$, $x = 0\text{--}1.00$) to measure precisely lattice parameters of samples. All of the precipitates were formed as aeschynite phase. The detail observation of the XRD patterns, together with the XRD lines of the internal standard Si showed that the XRD lines gradually shifted to lower degree of 2θ corresponding to an increase in Eu^{3+} concentration. This observed shift into lower 2θ values

Fig. 4. (a)–(f) TEM-EDS mapping of GdTiNbO_6 sample formed by hydrothermal treatment using aqueous ammonia at 240°C for 5 h.

Fig. 5. XRD patterns of precipitates ($\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$) obtained under hydrothermal conditions in the presence of aqueous ammonia at 240°C for 5 and 24 h.

with an increase in Eu^{3+} suggests an increase in lattice parameters. The lattice parameters of the as-prepared aeschynite-type $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ precipitates evaluated as orthorhombic structure plotted against x : the concentration of Eu^{3+} are presented in Fig. 6. The lattice parameters a_0 and c_0 of the orthorhombic aeschynite phase gradually and linearly increased in particular as the concentration of substitution with Eu^{3+} increased. This change in the lattice parameters of aeschynite phase in the as-prepared nanocrystals nearly corresponded to the Vegard's Law, which is due to the increase of ionic radius from 0.1053 nm for Gd^{3+} to 0.1066 nm for the Eu^{3+} .³⁸⁾ It is

Fig. 6. Lattice parameters plotted against Eu^{3+} concentration, x for $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ prepared under hydrothermal conditions in the presence of aqueous ammonia at 240°C for 24 h.

evident that a complete solid solution with aeschynite-type structure in the EuTiNbO_6 – GdTiNbO_6 system was formed directly under hydrothermal conditions at 240°C .

Similar change in the lattice parameters of aeschynite-type precipitates is considered to occur in the DyTiNbO_6 – GdTiNbO_6 system. However, the concentration range of Dy^{3+} substitutionally doped into GdTiNbO_6 was one-tenth of that in the EuTiNbO_6 – GdTiNbO_6 system in this experiment. Therefore the corresponding lattice parameter changes would become small and to find the changes in the lattice parameters is considered to be difficult because the concentration change ratio is small. In this study, certain existence of Dy^{3+} dopant in the sample doped with the lowest Dy^{3+} , i.e. the sample $x = 0.02$ in the DyTiNbO_6 – GdTiNbO_6 system was confirmed by the measurements of the excitation spectra and PL emission spectra in the sample $x = 0.02$ in the next section [Figs. 8(a) and 9(a)]. Since

Fig. 7. XRD patterns of $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ samples before and after heating at 1000–1300°C for 1 h in air.

GdTiNbO_4 (in the composition $x = 0$) has a euxenite-type structure as a stable phase, the aeschnite-type phase in the composition range rich in GdTiNbO_4 is suggested to be metastable one. What needs to be emphasized is that the aeschnite-type phase is formed in the whole composition range under this hydrothermal condition.

The formation of GdTiNbO_6 -based compound substitutionally doped with 5 mol % Dy^{3+} was done hydrothermally at 240°C for 24 h. Then, the as-prepared precipitate doped with 5 mol % Dy^{3+} was heated at 1000–1300°C for 1 h in air. The XRD patterns of the as-prepared sample correspond to the composition $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ and samples after heating in air are also indicated in Fig. 7. The as-prepared sample and samples after heating at 1000 and 1150°C were detected as orthorhombic aeschnite-type structure. However, heating at 1300°C in air promoted the occurrence and progression of the phase transition from aeschnite to euxenite structure. The main crystalline phase of $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ formed by heating at 1300°C was euxenite. The euxenite structure is suggested to be stable phase for $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$. This result is suggested to be reasonable according to the literatures^{(12),(13),(36),(37)} because the average ionic radius of $(\text{Dy}_{0.05}\text{Gd}_{0.9})^{3+}$ was smaller than that of Gd^{3+} . The dependences of phase transition upon both Eu^{3+} concentration and heating temperature in air were already investigated, on the other hand.⁽³⁹⁾

3.2 Optical and luminescence properties of as-prepared aeschnite-type fine crystals

The UV–Vis absorption spectra of the as-prepared aeschnite-type $\text{Dy}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ and $\text{Eu}_x\text{Gd}_{1.00-x}$

Fig. 8. Excitation spectra measured by (a) monitoring at 483 nm for $\text{Dy}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ samples and by (b) monitoring at 611 nm for $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ samples formed under hydrothermal conditions in the presence of aqueous ammonia at 240°C for 24 and 5 h, respectively.

TiNbO_6 precipitates formed at 240°C were recorded. In the spectra, the appearances of several small absorbance peaks attributed to the f–f transitions of Dy^{3+} and Eu^{3+} in the samples containing dysprosium or europium provide one of pieces of evidence that the Dy^{3+} and Eu^{3+} is doped in the as-prepared samples respectively. For the determination of optical band gap, the Kubelka–Munk (K–M) function^{(40),(41)} and Tauc plot⁽⁴²⁾ were used. A very slight change in the absorption edge in the spectra was observed. The optical band-gap values of the aeschnite-type samples doped with Dy^{3+} and Eu^{3+} were in the range around 3.5–3.6 eV.

Fig. 9. (a) PL emission spectra measured under excitation at 387 nm for Dy_xGd_{1.00-x}TiNbO₆ formed under hydrothermal conditions in the presence of aqueous ammonia at 240°C for 24 h. (b) Relationship between Dy³⁺ concentration, x and PL ($^4F_{9/2} \rightarrow ^6H_{15/2}$) emission intensity measured under excitation at 280, 350, and 387 nm for as-prepared Dy_xGd_{1.00-x}TiNbO₆. PL emission spectra measured under excitation at (c) 387 and (d) 280 nm for Dy_{0.50}Gd_{0.95}TiNbO₆ as-prepared and after heating at 1000–1300°C for 1 h in air.

The excitation spectra of the as-prepared aeschynite-type Dy_xGd_{1.00-x}TiNbO₆, x = 0–0.10 and Eu_xGd_{1.00-x}TiNbO₆, x = 0–1.00 samples measured by monitoring at λ_{em} = 483 and 611 nm are shown in Figs. 8(a) and 8(b), respectively. A broad band appearing at around 280–320 nm is attributed to a charge transfer band (C.T.B.) for the host aeschynite-type crystal. Several high intense and sharp absorption bands attributed to the characteristic intra-4f transitions, i.e., the $^6H_{15/2} \rightarrow ^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$,

$^4G_{11/2}$, $^4I_{15/2}$ transitions of Dy³⁺ ions and the $^7F_0 \rightarrow ^5D_4$, 5L_7 , 5L_6 , 5D_3 , 5D_2 transitions of Eu³⁺ ions are appeared in the spectra of the samples doped with Dy³⁺ and Eu³⁺, respectively. These measurement results suggest that those materials can be effectively excited using the UV light at 350 and visible light at 387 nm corresponding to the $^6H_{15/2} \rightarrow ^6P_{7/2}$ and $^6H_{15/2} \rightarrow ^4I_{13/2}$ transitions of Dy³⁺, respectively and using the visible light at 394 nm corresponding to the $^7F_0 \rightarrow ^5L_6$ transition of Eu³⁺, for example,

in addition to UV-B light corresponding to the C.T.B. for the host crystal.

The PL emission spectra of $\text{Dy}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$, $x = 0-0.10$ are recorded in the range of 400–650 nm under excitation at 280, 350, and 387 nm corresponding to the C.T.B., the ${}^6H_{15/2} \rightarrow {}^6P_{7/2}$, and ${}^6H_{15/2} \rightarrow {}^4I_{13/2}$ transitions of Dy^{3+} , respectively. Figure 9(a) shows the PL emission spectra measured under excitation at 387 nm for the as-prepared $\text{Dy}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$, $x = 0-0.10$ samples. In the spectrum there are mainly two dominating groups of lines lying in blue and yellow region centered at around 480 and 575 nm, respectively. The blue emission bands at 480 nm are attributed to the ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition corresponding to magnetic dipole transition, whereas the yellow emission bands at 575 nm are attributed to the ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, which is a hypersensitive electric dipole transition of Dy^{3+} . Both depend on the chemical environment of Dy^{3+} ion. Therefore the ratio of yellow to blue emission depends on host material. In Fig. 9(a), the yellow/blue emission intensity ratio is found to be almost constant with variation in Dy^{3+} ion concentration in the same aeschynite-type host crystal. The variation of PL emission intensity with varying Dy^{3+} ion concentration in the aeschynite-type GdTiNbO_6 lattice is presented in Fig. 9(b). The improvement in PL emission intensity for as-prepared samples associated to both blue as well as yellow emission bands with increment in Dy^{3+} ion concentration is visible up to 5 mol%. The occurrence of the possible non-radiative cross-relaxation among various Dy^{3+} ions at above this concentration causes the cancel of the generation of ${}^4F_{9/2}$ site of Dy^{3+} , which may be responsible for the concentration quenching phenomenon.

The PL emission spectra measured under excitation at 387 and 280 nm for the as-prepared sample doped with 5 mol % Dy^{3+} and those samples after heating at 1000, 1150, and 1300°C for 1 h in air corresponding to the XRD patterns shown in Fig. 7 are presented in Figs. 9(c) and 9(d), respectively. When fine-grained materials consisting of crystalline metal oxides are exposed to high temperatures less than melting temperature in air, a decrease in specific surface area, crystal growth, enhancement in crystallinity, grain growth, or sintering are brought about, in general,^{43,44} and the size measurement of large crystallite more than 100 nm using XRD line broadening becomes impossible. After high-temperature heating in air, defects or impurities that may act as luminescent quenchers such as OH^- species, which might be included in hydrothermal precipitates, might have been removed.⁴⁵ Although relatively high PL emission intensity was obtained for the as-prepared $\text{Dy}_{0.50}\text{Gd}_{0.95}\text{TiNbO}_6$ sample under excitation by means of direct excitation using 387 nm (the ${}^6H_{15/2} \rightarrow {}^4I_{13/2}$ transition of Dy^{3+}), the PL emission intensity gradually increased with increasing heating temperature in air, which may be due to the enhancement in crystallinity and in purity of materials. In the spectrum of the sample after heating at 1300°C, the change in the yellow/blue emission intensity ratio is also observed, which may be related to the change in the environment of Dy^{3+} ion in the host lattice

Fig. 10. The CIE chromaticity coordinates x and y for the PL emission of the as-prepared aeschynite-type $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ and $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ samples as-prepared and after heating at 1300°C for 1 h in air evaluated under excitation at 387 and 394 nm, respectively.

caused by the phase transformation from aeschynite to euxenite structure (as shown in Fig. 7). The PL emission spectra measured under excitation at 280 nm [Fig. 9(d)] shows that heating the Dy^{3+} -doped GdTiNbO_6 sample at 1300°C in air enhances dramatically its blue and yellow emission intensities involved in the broad host emission especially in the case under indirect excitation using energy transfer from the host absorption band at 280 nm. The color chromaticity coordinates x and y for the emission of the as-prepared aeschynite-type $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ samples as-prepared and after heating at 1300°C in air evaluated under direct excitation at 387 nm were $x = 0.393$, $y = 0.423$ and $x = 0.412$, $y = 0.437$, respectively, which fall in a green-yellow region of the CIE-1931 chromaticity diagram (Fig. 10, No. 1 and 2).

Using the Eu^{3+} -doped GdTiNbO_6 samples the effect of hydrothermal processing conditions, that is, the crystallinity of products on the luminescence property was investigated, on the other hand. Figure 11(a) shows the PL emission spectra measured under excitation at 395 nm (corresponding to the ${}^7F_0 \rightarrow {}^5L_6$ transition of Eu^{3+}) for the as-prepared aeschynite-type $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ samples formed by hydrothermal treatment in the presence of aqueous ammonia or urea for 5 or 24 h. The PL emission spectra are mainly composed of the ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) transition lines of Eu^{3+} , i.e., weak orange emission lines (${}^5D_0 \rightarrow {}^7F_1$ transition) and strong red emission lines (${}^5D_0 \rightarrow {}^7F_2$ transition). The PL emission intensity of the as-prepared aeschynite-type $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ prepared using aqueous ammonia was stronger than that using urea, and it clearly increased with increase in the hydrothermal treatment time, which was well corresponded to the

Fig. 11. PL emission spectra measured under excitation at (a) 394 nm for $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ formed under hydrothermal conditions in the presence of urea or aqueous ammonia at 240°C for 5 or 24 h and those measured under excitation at (b) 394 nm for $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ formed under hydrothermal conditions in the presence of aqueous ammonia at 240°C for 5 h. (c) Relationship between Eu^{3+} concentration, x and PL ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) emission intensity measured under excitation at 317 and 394 nm for as-prepared $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$.

increase in their crystallinity (i.e. crystallite size) as shown in Figs. 1, 5, and Table 1. It is certain that to improve crystallinity brought about the enhancement in the PL emission intensity.

The Eu^{3+} concentration dependence of PL property was investigated for the samples formed at 240°C for 5 h. The PL emission spectra of the as-prepared $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ evaluated under excitation at 394 nm (corresponding to the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition of Eu^{3+}) are shown in Fig. 11(b). The PL emission intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in the spectra evaluated under excitation both at 317 nm and at 394 nm are plotted against the concentration of Eu^{3+} , x in Fig. 11(c). In the case of as-prepared samples, the PL emission intensities of the f–f transitions of Eu^{3+} in the system ($\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$) measured under direct excitation using 394 nm (the $^7\text{F}_0 \rightarrow ^5\text{L}_6$ transition of Eu^{3+} ion)

[in Fig. 11(b)] were nearly four times stronger than those obtained under indirect excitation, i.e. indirect energy transfer from the host absorption band using 317 nm. Although the $\text{Nb}(\text{Ti})\text{O}_6$ polyhedron can absorb excitation energy corresponding to 317 nm and can transfer the energy to the neighboring activator Eu^{3+} ions, it is noted that the as-prepared ($\text{Eu},\text{Gd})\text{TiNbO}_6$ materials obtained hydrothermally can be excited effectively by direct excitation. In the case using indirect excitation and energy transfer from the host absorption band, we have already reported about the effect of heating in air on the PL emission and phase transition of $\text{GdTiNbO}_6:\text{Eu}^{3+}$.³⁹⁾ As the Eu^{3+} concentration increased, the emission intensity of the as-prepared $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ gradually increased, reached a maximum value at $x = 0.50$, and then decreased in both cases as shown in Fig. 11(c). It is evident that the emission

Fig. 12. Decay lifetime of as-prepared aeschynite-type $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ for the emission band at 483 nm measured under excitation at 365 nm.

intensity of the $\text{Eu}_x\text{Gd}_{1.00-x}\text{TiNbO}_6$ solid solution becomes the strongest by the incorporation of 50 mol % Eu^{3+} ($x = 0.50$). The color chromaticity coordinates x and y for the emission of the as-prepared aeschynite-type $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ samples as-prepared and after heating at 1300°C in air evaluated under direct excitation at 394 nm were $x = 0.652$, $y = 0.342$ and $x = 0.645$, $y = 0.341$, respectively, which lies in a slight orangey red region of the CIE-1931 chromaticity diagram (Fig. 10, No. 3 and 4).

The Judd–Ofelt theory shows that the electric dipole transitions ($^5D_0 \rightarrow ^7F_2$) are sensitive to the local electric field and they are only allowed in the absence of inversion symmetry.^{46,47} When Eu^{3+} ions are situated in a site without inversion symmetry, the $^5D_0 \rightarrow ^7F_2$ electric-dipole transition is the strongest.⁴⁸ Because the $^5D_0 \rightarrow ^7F_2$ transition is dominant in these results [in Figs. 11(a) and 11(b)], Eu^{3+} ions are located in a site without inversion symmetry in the $(\text{Eu,Gd})\text{TiNbO}_6$ materials. The absolute quantum yield measured for the as-prepared samples is also shown in Table 1. The values of the absolute quantum yield of the as-prepared $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ (: Ammonia 5 h) measured under excitation at 394 and 464 nm were 37 and 30%, respectively. Note that the as-prepared GdTiNbO_6 doped with Eu^{3+} showed strong red emission without subsequent heat treatment in air.

Heat-treatment at temperatures higher than 1000°C in air is reported to be necessary for the crystallization and synthesis of RETiNbO_6 compounds using conventional techniques, e.g., solid-state reaction, in general.⁹ Hence these results in this study suggest that the present technique is beneficial and moreover important from the view point of processing through energy consumption reduction, “green processing”. Figure 12 shows the fluorescence decay kinetic for the 483 nm emission of the as-prepared aeschynite-type sample $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ measured under direct excitation at 365 nm. The decay lifetime (for the emission band at 483 nm) of $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ as-prepared and after 1300°C was determined to be 162 and 156 μs , respectively. The decay lifetime (for the emission band at 615 nm) of the aeschynite-type $\text{Eu}_{0.5}\text{Gd}_{0.5}\text{TiNbO}_6$ as-prepared and after 1300°C mea-

sured under direct excitation at 405 nm was found to be 570 and 571 μs , respectively, on the other hand.

4. Conclusions

Aeschynite-type fine crystals with high crystallinity were formed directly as solid solutions in the $\text{Dy}_x\text{Gd}_{1-x}\text{TiNbO}_6$ and $\text{Eu}_x\text{Gd}_{1-x}\text{TiNbO}_6$ systems from weak basic precursor solutions using $\text{Dy}(\text{NO}_3)_3$, EuCl_3 , GdCl_3 , TiOSO_4 , and NbCl_5 under hydrothermal conditions at 240°C for 5–24 h. The aeschynite-type crystals formed hydrothermally in the presence of aqueous ammonia were well-crystallized and micron-sized. Submicron-sized finer aeschynite crystals were formed when using the hydrolysis of urea, on the other hand, which is suggested to be due to an increase in the nucleation number for the crystallization of aeschynite. The aeschynite-type $\text{GdTiNbO}_6:\text{Dy}^{3+}$ showed blue and yellow PL emissions attributed to the $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ transitions of Dy^{3+} ion, respectively. The aeschynite-type $\text{GdTiNbO}_6:\text{Eu}^{3+}$ presented characteristic weak orange and strong red PL emissions corresponding to the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions of Eu^{3+} ion, respectively. The PL emission intensity of aeschynite crystals increased with increasing in their crystallinity, which was closely related to their processing conditions. The as-prepared aeschynite-type $\text{Dy}_{0.05}\text{Gd}_{0.95}\text{TiNbO}_6$ and $\text{Eu}_{0.50}\text{Gd}_{0.50}\text{TiNbO}_6$ provided the strongest PL emission intensity under direct excitation of dopant ions without subsequent heat treatment in air.

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