Direct synthesis of nanocrystalline GdNbO₄ and GdNbO₄-based phosphors doped with Eu³⁺ through hydrothermal route

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Nanocrystalline gadolinium niobate, GdNbO₄ with fergusonite structure was directly formed from the precursor solution mixtures of GdCl₃ and NbCl₅ under weakly basic conditions at temperatures higher than 210°C for 5 h in the presence of aqueous ammonia via hydrothermal route. The as-prepared GdNbO₄ nanocrystals and those after heating at 1000–1300°C showed UV-blue and broad-band emission centered at 435 nm under excitation at 266 nm due to the blue recombination luminescence, associated with charge transfer transitions involving the tetrahedral NbO₄ group. The fergusonite-type complete solid solution nanocrystals having good luminescence in the red spectral region in the GdNbO₄–EuNbO₄ system were directly formed under hydrothermal conditions at 240°C. The photoluminescence spectra of the as-prepared nanocrystalline solid solutions containing europium under excitation at 240 nm were responsible for the characteristic weak orange luminescence (592 nm) and strong red emission spectrum at 612 nm. The intra-4f-shell down-conversion allowed transition (5D₀ → 7F₂) of Eu³⁺ ions is electric dipole allowed transition (7F₁ → 5D₀) and the red emission at 612 nm originates from the magnetic dipole transition (5D₀ → 7F₂). The red emission is hypersensitive to structure changes and is influenced by the local symmetry of the crystal field around the Eu³⁺ ions, which has been reported for various host materials.13-14 Among rare earth elements, Eu³⁺ doped oxide phosphors have been intensively investigated due to their intense sharp red emission centered at 611 nm. The intra-4f-shell down-conversion transitions (5D₀ → 7Fⱼ (ⱼ = 1, 2, 3, 4)) of Eu³⁺ ions are dependent on the crystal structure of the host materials. The orange emission spectrum at 590 nm originates from the magnetic dipole allowed transition (5D₀ → 7F₁) and the red emission at 612 nm corresponding to 5D₀ → 7F₂ is electric dipole allowed transition (5D₀ → 7F₂). The red emission is hypersensitive to structure changes and is influenced by the local symmetry of the crystal field around the Eu³⁺ ions, which has been reported for various host materials.13-14

Recently, wet chemical routes to synthesize nanometer-sized particles of inorganic materials have received extensive attention because their structures, crystalline phases, morphologies, characteristics, and performances can be designed by controlling their compositions and preparation conditions.15 Hydrothermal synthesis techniques,16 which fall into a category of the aqueous solution routes and building up processes of inorganic materials, have attracted considerable attention from a view point of green processing, because the hydrothermal routes are most suitable for the direct formation of nanosized-particles,17 solid solutions,18 and metastable phases19 of complex oxide and oxide ceramics with homogeneity, controlled composition, and variously designed morphological structures. Rare-earth niobates RNbO₄ (R=Y, rare earth) crystallize in the two forms of the crystal structure, that is, scheelite-type (high temperature tetragonal phase) and fergusonosite-type (low temperature monoclinic phase). The fergusonosite-type phase transforms into scheelite-type structure via the reversible phase transition in the temperature range 500–800°C depending on the rare earth ion.20,21 The rare-earth niobate has been of much interest due to its potential properties, e.g., luminescence,22 ionic conductivity,23 photocatalytic activity,24 and magnetic properties.25 Many studies on the synthesis and characterization of rare earth niobate have been done using several preparation methods such as solid state reaction,26,27 flux method,28,29 combustion synthesis,30 the method based on complexes,31 hydrothermal method,32,33 and co-precipitation.34 But, there have been a few studies on the direct synthesis of GdNbO₄ nanocrystals doped with Eu³⁺ through hydrothermal route. We have reported on the formation, structure, and optical properties of solid solution nanocrystals in the YNbO₄–EuNbO₄ system.35 The ionic radius of Gd³⁺ is rather similar to that of Eu³⁺ in comparison with that of Y³⁺. The solid solutions in the GdNbO₄–EuNbO₄ system are considered to be easily formed. In the present study, hydrothermal technique has been applied to the direct formation of luminescent fergusonosite-type GdNbO₄ nanocrystals doped with Eu³⁺. The effect of the composition on their structure and luminescence properties has also been investigated.

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2. Experimental

2.1 Sample Preparation

In a Teflon container (volume: 100 cm³), a mixture of an aqueous solution of reagent-grade GdCl₃·6H₂O, EuCl₃·6H₂O, and ethanol solution of NbCl₃ in different ratios of Gd/Eu/Nb (that was controlled to be the composition: Gd₁₋ₓEuₓNbO₄, x = 0–1.00) was prepared. The solution mixture was controlled by the addition of aqueous ammonia to have a weakly basic condition in the end stage of hydrothermal treatment. This solution mixture (volume: 90 cm³) with cation concentration of 0.200 mol/dm³ (Gd + Eu = 0.200 mol/dm³, Nb = 0.200 mol/dm³) in the Teflon container was then placed in a stainless-steel vessel. The vessel was tightly sealed and it was heated at 180–240°C for 5 h under rotation at 1.5 rpm. After hydrothermal treatment, the precipitates 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 prepared powders were heated in an alumina crucible at heating rate 300°C/h, held at 1000–1300°C for 1 h in air, and then cooled to room temperature in a furnace.

2.2 Characterization

The powder X-ray diffraction (XRD) measurements were performed at room temperature for the as-prepared and heat-treated powders using Cu Kα radiation (XRD; model RINT-2000, Rigaku, Tokyo, Japan). The crystallite size of monoclinic phase was estimated from the line broadening of 0 0 4 diffraction peak, according to the Scherrer equation, \[ D_{\text{XRD}} = \frac{K \lambda}{\beta \cos \theta} \]
where \( \theta \) is the Bragg angle of diffraction lines, \( K \) is a shape factor (\( K = 0.9 \) in this work), \( \lambda \) is the wavelength of incident X-rays, and \( \beta \) is the corrected half-width given by \( \beta = \beta_m - \beta_r \), where \( \beta_m \) is the measured half-width and \( \beta_r \) is the half-width of a standard sample. The lattice parameter was measured using silver as the internal standard. The morphology of the precipitates was observed using transmission electron microscopy (TEM; model JEM-2010, JEOL, Tokyo, Japan).

The UV–vis absorption spectra of the prepared powders were recorded at room temperature and in air by means of ultraviolet–visible spectrophotometer with an integrating sphere attachment (V-560, Nihon Bunko, Tokyo, Japan). The photoluminescence (PL) emission and excitation spectra of samples were measured using a spectrofluorometer (F-2700, Hitachi High-Tech, Tokyo, Japan) with Xe lamp. Powder samples were excited with 240 or 266 nm radiation from a 150 W xenon lamp. The emission wavelength was scanned from 500 to 750 nm at a scanning rate of 60 nm/min. For the measurements of excitation spectra, the excitation wavelength was scanned from 220 to 500 nm at the same scanning rate, and emission monitored at 611 nm.

3. Results and discussion

3.1 Synthesis and photoluminescence properties of fergusonite-type GdNbO₄

The precursor solution of GdCl₃ and NbCl₃ was hydrothermally treated under weakly basic condition at various temperatures for 5 h. Figure 1 shows the XRD patterns of precipitates formed under hydrothermal conditions at 180–240°C. The appearance of sharp XRD lines, that is, crystalline phase of fergusonite-type in the broad XRD line corresponding to amorphous precipitate is observed in the sample treated at 180°C for 5 h. The precipitates formed at temperatures higher than 210°C were detected as a single phase of monoclinic fergusonite-type GdNbO₄, and no diffraction peaks due to another crystalline phases was detected. When the treatment temperature rose from 210 to 240°C the XRD lines of fergusonite-type phase became sharp, that is, its crystallinity enhanced. Direct formation of fergusonite-type GdNbO₄ was achieved via crystallization from amorphous precipitate phase under hydrothermal conditions at temperatures higher than 210°C.

The effect of heat treatment in air on the crystalline phase and the change in the crystallinity of GdNbO₄ has been investigated. The XRD patterns before and after heating at 1000 and 1300°C for 1 h in air.
temperature rose, the intensity of monoclinic fergusonite phase and its crystallinity increased. The crystalline phase of GdNbO$_4$ after heating at temperatures higher than 1150°C was almost a single phase of monoclinic fergusonite. The crystallite sizes of monoclinic phase for GdNbO$_4$ before and after heating are shown in Table 1.

The optical band gap values obtained for the GdNbO$_4$ with fergusonite-type structure as-prepared and after heating at 1150 and 1300°C, which were evaluated by the plots of transformed Kubelka–Munk function vs. the energy of light absorbed of samples, are listed in Table 1. The optical band gap value of samples increased via heating at 1150 and 1300°C. The photo-luminescence spectra measured under excitation at 266 nm at room temperature for the GdNbO$_4$ before and after heat treatment at various temperatures are shown in Fig. 3. The pure GdNbO$_4$ exhibited a UV-blue and broad emission band centered at 435 nm under excitation at 266 nm. It is evident that heating in air is pretty effective for the improvement in the intensity of the emission spectrum. Especially, the photoluminescence intensity was improved via heating at 1300°C in air, which is considered to be due to the enhancement of crystallinity of GdNbO$_4$ and the removal of impurities that act as luminescent quenchers. These UV-blue-light emissions from the GdNbO$_4$ are considered to be responsible for the blue recombination luminescence, associated with [NbO$_4$]$^{3-}$ groups from the crystalline lattice in GdNbO$_4$.

### 3.2 Synthesis of fergusonite-type Gd$_{1.00-x}$Eu$_x$NbO$_4$ solid solutions

To investigate the effect of the composition on the synthesis, structure, and properties of precipitates in the GdNbO$_4$–EuNbO$_4$ system and to form Gd$_{1.00-x}$Eu$_x$NbO$_4$ solid solutions, samples formed via hydrothermal treatment at 240°C 5 h were used, because the hydrothermal treatment at 240°C brought the GdNbO$_4$ nanocrystals with the most sharp XRD lines of fergusonite-type phase. XRD patterns of precipitates obtained at various compositions of $x = 0$–1.0 in Gd$_{1.00-x}$Eu$_x$NbO$_4$ under hydrothermal conditions at 240°C for 5 h are shown in Fig. 4. In the whole composition range $x = 0$–1.0, a single phase corresponding to monoclinic fergusonite-type structure was detected, and no diffraction peaks due to another crystalline phases was detected.

The TEM image of sample with a composition $x = 0.20$ formed under hydrothermal condition at 240°C is indicated in Fig. 5. The particles with monoclinic fergusonite-type structure have ellipsoidal morphology with size of approximately 40 nm-length and 20 nm-width. The observed particles were a little larger than the crystallite size estimated from the line broadening of 0.040 diffraction peak. In Fig. 6 are shown the lattice parameters of the precipitates evaluated as monoclinic structure plotted against $x$: the substitution amount of Gd with Eu. On the whole, the lattice parameters of the monoclinic phase of the precipitates
almost linearly changed with increase the Eu content $x$ in the sample corresponding to the Vegard’s Law. This result is one of pieces of evidence that the monoclinic fergusonite-type solid solutions at the whole composition range in the GdNbO$_4$–EuNbO$_4$ system can be directly formed as nanocrystals from the precursor solutions under hydrothermal condition at 240°C for 5h, which is similar to the case in the YNbO$_4$–EuNbO$_4$ system.\textsuperscript{32}

### 3.3 Optical properties of fergusonite-type Gd$_{1.00-x}$Eu$_x$NbO$_4$ solid solutions

In Fig. 7, the UV–vis absorption spectra of the as-prepared Gd$_{1.00-x}$Eu$_x$NbO$_4$ solid solutions are indicated. In the samples containing europium, the presence of small absorbance peaks are clearly observed at 395 nm ($^7F_0 \rightarrow ^5L_6$), 466 nm ($^7F_0 \rightarrow ^3D_2$), and others, which supports the presence of Eu$^{3+}$ in the solid solutions with monoclinic structure. A broad absorption band peak in the low wavelength UV region (230–270 nm) appeared in the samples is ascribed to the charge transfer corresponding to O$^{2-} \rightarrow$ Nb$^{5+}$. According to the change in the composition of the samples, the onset of absorption slightly changed. The evaluated optical band-gap values of the samples are plotted in Fig. 8. The optical band gap values of as-prepared samples were in the range of 3.4–3.5 eV and slightly changed depending on the composition.

The excitation spectra of the as-prepared samples scanned from 220 to 500 nm, and emission monitored at 611 nm are shown in Fig. 9. In the excitation spectra, a broad absorption band existed in the low wavelength UV region which is attributed to a charge transfer band (C.T.B.), corresponding to O$^{2-} \rightarrow$ Nb$^{5+}$ charge transfer transition. The coexistence of several sharp absorption bands in the near-UV and visible light region corresponding to
the f-f transitions of Eu\(^{3+}\) that includes peaks, for example, \(^7F_0 \rightarrow ^5D_4\), \(^7F_0 \rightarrow ^7L_7\), \(^7F_0 \rightarrow ^5L_6\), \(^7F_0 \rightarrow ^5D_3\), and \(^7F_0 \rightarrow ^7D_2\) are clearly observed in the spectra. The most intense excitation spectrum was observed in the sample with the composition \(x = 0.20\). The excitation spectra of the nanocrystals suggest that the compounds can be excited by both ultraviolet light around 230–270 nm and visible light corresponding to the f-f transitions of Eu\(^{3+}\), for example, a sharp peak wavelength of \(^7F_0 \rightarrow ^7L_6\) transition at 395 nm with the highest intensity.

The compositional dependence of the emission spectra of samples has been investigated. The emission spectra of the as-prepared Gd\(_{1.00}\)Eu\(_{0.20}\)NbO\(_4\) solid solution nanocrystals that were formed at 240°C, measured at room temperature under excitation at 240 nm are shown in Fig. 10. Under excitation at 240 nm, the [NbO\(_4\)]\(^{3-}\) groups can absorb excitation energy through \(O^{2-} \rightarrow \text{Nb}^{5+}\) charge transfer transition, and can transfer the energy to neighboring activator Eu\(^{3+}\) ions; the f-f transition of Eu\(^{3+}\) exhibits red emission corresponding to intra-4f-shell down-conversion transitions \((^5D_0 \rightarrow \gamma ^7F_\lambda)\). In the spectra, several emission bands corresponding to the \(^5D_0 \rightarrow \gamma ^7F_\lambda (\lambda = 0, 1, 2)\) transitions of Eu\(^{3+}\) ions are observed. It is well known that the major emission bands, that is, orange and red luminescence with peaks at 592 and 611 nm corresponding to \(^5D_0 \rightarrow \gamma ^7L_\alpha\) and \(^5D_0 \rightarrow \gamma ^7F_\beta\) transitions, respectively exist in the photoluminescence spectra of the materials containing Eu\(^{3+}\) ions in the structure of the host materials. The orange emission at 592 nm corresponding to \(^5D_0 \rightarrow \gamma ^7F_2\) is the magnetic dipole allowed transition and the red emission at 611 nm is electric dipole allowed transition \((^5D_0 \rightarrow \gamma ^7F_\beta)\). In general, as reported for various host materials, the red emission is influenced by the local symmetry of the crystal field around the Eu\(^{3+}\) ions. In all samples, intense red emissions corresponding to the electric dipole allowed transition \((^5D_0 \rightarrow \gamma ^7F_\beta)\) were observed. According to the Judd–Ofelt theory, electric dipole transitions are sensitive to the local electric field and they are only allowed in the absence of inversion symmetry.\(^{35-37}\) When Eu\(^{3+}\) ions are situated in a site without inversion symmetry, for example, in the case of fergusonite-type structure in this study, \(^5D_0 \rightarrow \gamma ^7F_2\) electric-dipole (red) transition is the strongest.\(^{37}\)

The compositional dependence of the intensity of the red emission corresponding to the electric dipole allowed transition \((^5D_0 \rightarrow \gamma ^7F_2)\) is shown in Fig. 11. The red emission intensity increased as the content of the substitutional incorporation of Eu into GdNbO\(_4\) increased. At the composition \(x = 0.20\), Gd\(_{0.80}\)Eu\(_{0.20}\)NbO\(_4\) the emission intensity reached the maximum, and then decreased with increased Eu content due to an overlapping ratio bringing concentration quenching of the luminescence. The most appropriate composition of the Gd\(_{1.00}\)Eu\(_{0.20}\)NbO\(_4\) solid solution for red phosphor nanocrystals is suggested to be Gd\(_{0.80}\)Eu\(_{0.20}\)NbO\(_4\) based on these results. The Red-to-Orange \((^5D_0 \rightarrow \gamma ^7F_\beta / ^5D_0 \rightarrow \gamma ^7F_1) (R/O)\) emission intensity ratio of the as-prepared Gd\(_{0.80}\)Eu\(_{0.20}\)NbO\(_4\) nanocrystals with the highest emission intensity that were formed at 240°C was \(R/O = 5.0\).

The effect of heat treatment on the crystalline phase and photoluminescence properties of Gd\(_{1.00}\)Eu\(_{0.20}\)NbO\(_4\) solid solutions has been investigated. The as-prepared sample with the composition Gd\(_{0.80}\)Eu\(_{0.20}\)NbO\(_4\) that showed the highest emission intensity was heat-treated for 1 h in air. The XRD patterns of Gd\(_{0.80}\)Eu\(_{0.20}\)NbO\(_4\) nanocrystals before and after heat treatment at 1000 and 1300°C for 1 h in air are also shown in Table 1. The improvement in crystallinity of mono-

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**Fig. 10.** Emission spectra excited at 240 nm for the as-prepared Gd\(_{1.00}\)Eu\(_{0.20}\)NbO\(_4\) samples: \(x = 0–1.00\).

**Fig. 11.** The intensity of red luminescence \((^5D_0 \rightarrow \gamma ^7F_\lambda)\) for the as-prepared Gd\(_{1.00}\)Eu\(_{0.20}\)NbO\(_4\) samples plotted as a function of composition.

**Fig. 12.** The XRD patterns of Gd\(_{0.80}\)Eu\(_{0.20}\)NbO\(_4\) nanocrystals before and after heat treatment at 1000 and 1300°C for 1 h in air.
clinic fergusonite phase via heating was clearly observed though the coexistence of a small amount of the metastable tetragonal scheelite phase was observed in the sample heated at 1000°C. The optical band gap values obtained for Gd$_{0.80}$Eu$_{0.20}$NbO$_4$ samples with fergusonite-type structure as-prepared and after heating at 1300°C are listed in Table 1. Although the optical band gap values of as-prepared samples (GdNbO$_4$ and Gd$_{0.80}$Eu$_{0.20}$NbO$_4$) were a little small in comparison with the values reported in the literatures, those values increased after heating at temperatures higher than 1000°C in air. As it has been suggested that the materials formed under hydrothermal conditions hold substantial amount of OH$^-$ species in their structures,\cite{17,19} the increase in the optical band gap values after heating listed in Table 1 is supposed to be due to the removal of the presence of hydroxyl group incorporated into the fergusonite-type crystals that were formed through hydrothermal method. In Fig. 13, is shown the emission spectra of samples with the composition Gd$_{0.80}$Eu$_{0.20}$NbO$_4$ before and after heat treatment at 1000 and 1300°C. Although the as-prepared Gd$_{0.80}$Eu$_{0.20}$NbO$_4$ nanocrystals already showed sufficient high emission intensity, remarkable enhancement in the intensity of emission is evidently achieved via heat treatment. The most intense emission was obtained in the sample at 1300°C for 1 h. An over-doping ratio bringing concentration quenching of the luminescence is evidently achieved via heat treatment at 1300°C for 1 h.

4. Summary

Nanocrystals with red luminescence based on the solid solutions having monoclinic fergusonite structure in the GdNbO$_4$–EuNbO$_4$ system were directly synthesized under hydrothermal conditions at 240°C for 5 h. UV-blue and broad-band emission centered at 435 nm under excitation at 266 nm was observed in the as-prepared pure GdNbO$_4$ nanocrystals before and after heating at 1000–1300°C because of the blue recombination luminescence, associated with charge transfer transitions attributed to the niobate group [NbO$_4$]$^{3-}$\cite{12,13}. The as-prepared Gd$_{0.80}$–Eu$_{0.20}$NbO$_4$ solid solution nanocrystals containing europium emitted the characteristic orange (592 nm) luminescence with weak intensity and red (611 nm) luminescence with strong intensity, attributed to $^2D_0 \rightarrow ^2F_1$ and $^2D_0 \rightarrow ^2F_2$ transitions, respectively. The emission intensity of the as-prepared solid solution nanocrystals reached the maximum at the composition, Gd$_{0.80}$Eu$_{0.20}$NbO$_4$, and then decreased with increased Eu content due to an over-doping ratio bringing concentration quenching of the luminescence. The intensity of the red emission of as-prepared Gd$_{0.80}$Eu$_{0.20}$NbO$_4$ was even more improved through heat treatment at 1300°C for 1 h.

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