Formation and luminescence properties of GdTiNbO$_6$:Er$^{3+}$/Yb$^{3+}$ through the hydrothermal route

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Up-converting of GdTiNbO$_6$-based complex oxide co-doped with 5 mol% Er$^{3+}$ and 10 mol% Yb$^{3+}$ (GdTiNbO$_6$: Er$^{3+}$/Yb$^{3+}$) was conducted through a mild hydrothermal route. A single phase of aeschynite-type GdTiNbO$_6$: Er$^{3+}$/Yb$^{3+}$ was crystallized under weak basic hydrothermal conditions at 240°C for 5 h. The aeschynite-type structure was maintained after heating up to 1050°C for 1 h in air. A single phase of euxenite-type GdTiNbO$_6$: Er$^{3+}$/Yb$^{3+}$ was formed by heating at 1300°C for 1 h through phase transformation. The GdTiNbO$_6$: Er$^{3+}$/Yb$^{3+}$ emitted luminescence in the green spectral region from 515 to 560 nm ($^{2}H_{11}$/2 and $^{6}S_{3}$/2 levels) under direct and indirect excitation of Er$^{3+}$ at wavelengths of 377 and 277 nm, respectively, in addition to up-converted luminescence under excitation at 980 nm. The luminescence intensity was enhanced by high-temperature heating.

Key-words: GdTiNbO$_6$, Hydrothermal synthesis, Luminescence, Aeschynite, Euxenite

1. Introduction

The complex oxides RETiNbO$_6$, where RE is a rare-earth ion, are reported to be useful materials with characteristics showing potential for use as miniature solid-state lasers,1,2) dielectric resonator,3) and luminescent materials.6)−9) The compound GdTiNbO$_6$ in the ternary system Gd$_2$O$_3$−TiO$_2$−Nb$_2$O$_5$ that crystallizes in the orthorhombic structure falls into the category of compounds belonging to the RETiNbO$_6$ group. RETiNbO$_6$ compounds have been synthesized through various preparation routes, e.g., conventional solid-state reaction of oxides,8)−10) and the sol-gel combustion route.9) In recent years, aqueous solution routes such as mild hydrothermal synthesis techniques at low temperature have been used for synthesis of crystalline inorganic materials.12)−15) RETiNbO$_6$ compounds comprise two types of orthorhombic structures, i.e., euxenite and aeschynite. In rare-earth titanium niobate solid solutions (Pr$_{1-x}$Gd$_x$TiNbO$_6$, Nd$_{1-x}$DY$_x$TiNbO$_6$, and Sm$_{1-x}$Y$_x$TiNbO$_6$), RETiNbO$_6$ compounds are crystallized in the euxenite form when the average ionic radius of RE < 0.0945 nm and in the aeshynite form when RE > 0.0945 nm.10) It has also been reported that their orthorhombic structures change depending on the ionic radius and atomic number of RE.10,16) Recently, the development of luminescent inorganic materials for improved optoelectronic devices and advanced electronic and photonic technologies has attracted considerable attention due to their applications in solid-state lasers, luminescent lamps, optical data storage, infrared optical amplifiers, and various displays.17)−19) Up-conversion is a process in which the adsorption of two or more lower-energy photons leads to emission of a higher-energy photon. Much more attention has been paid to rare-earth-doped materials due to their up-conversion emission for applications in biological fluorescence labeling devices, luminescent solar converters, biosensors, and up-conversion lasers.20)−24)

To date, a large number of investigations on up-converting materials has been carried out. An investigation has been conducted on the energy up-conversion process in Er$^{3+}$ and Nd$^{3+}$ doped RETiNbO$_6$ crystals.25) Up-conversions of GdTiNbO$_6$-based materials have been quite few in number, however, and the number of investigations of the formation of up-converted GdTiNbO$_6$-based metal complex oxides using hydrothermal method is also small. In this paper, we report the formation of GdTiNbO$_6$ co-doped with Er$^{3+}$/Yb$^{3+}$ using the hydrothermal method and its photoluminescence and up-converted luminescence properties.

2. Experimental procedures

2.1 Preparation of samples

A metal complex oxide with a composition of Gd$_{0.25}$Er$_{0.05}$Yb$_{0.10}$TiNbO$_6$ was synthesized using a mild hydrothermal method. A mixture of an aqueous solution of reagent-grade GdCl$_3$·6H$_2$O, ErCl$_3$·6H$_2$O, YbCl$_3$·6H$_2$O, TiOSO$_4$ and an ethanol solution of NbCl$_5$ in a ratio of Gd:Er:Yb:Ti:Nb = 0.85:0.05:0.10:1.00:1.00 was prepared in a Teflon container. This solution mixture was controlled by the addition of aqueous ammonia to obtain a weak
basic condition. The solution mixture in the Teflon container was then placed in a stainless-steel vessel. The vessel was tightly sealed and heated at 150–240°C for 5 h while rotating at 1.5 rpm. After hydrothermal treatment, the precipitates were washed with distilled water, separated from the solution by centrifugation, and dried in an oven at 60°C. The powders thus prepared were heated in an alumina crucible at a heating rate 200 °C/h, kept at 800–1300°C for 1 h in air, and then cooled to room temperature in a furnace.

2.2 Characterization of samples

Powder X-ray diffraction (XRD) measurements were carried out using Cu Kα radiation (XRD; model RINT-2000, Rigaku, Tokyo, Japan). The crystallite size of the aeschynite phase was estimated from the line broadening of the 112 diffraction peak, according to the Scherrer equation. The microstructure of the samples was observed using a field emission scanning electron microscope (SEM; model JSM-6335FM, JEOL, Tokyo, Japan). Fourier transform infrared spectroscopy (FTIR) was conducted to characterize the presence of impurities, i.e., specific chemical groups in the materials. FTIR powder spectra were recorded from 4000 to 600 cm⁻¹ by means of FTIR microscopy (Nicolet iS50, Nicolet/Continuum, Thermo Fisher Scientific, Waltham, MA, USA).

Ultraviolet–visible (UV–Vis) absorption spectra measurements for powder samples were made using an ultraviolet–visible spectrophotometer (V-560, Nihon Bunko, Tokyo, Japan). The measurements of the photoluminescence (PL) emission and excitation spectra of the samples were performed using a spectrofluorometer (F-2700, Hitachi High-Tech, Japan) with a xenon (Xe) lamp. The powder samples were excited with both 277 and 377 nm radiation from a 150 W Xe lamp. For measurements of the excitation spectra, the excitation wavelength was scanned from 220 to 500 nm and the emission monitored at 555 nm. The up-conversion luminescence of the samples was recorded under excitation with a 980 nm laser. All measurements were carried out at room temperature.

3. Results and discussion

3.1 Preparation of GdTiNbO₆:Er³⁺/Yb³⁺

The XRD pattern of the precipitates (Gd₀.₈₅Er₀.₀₅-Yb₀.₁₀TiNbO₆) formed under hydrothermal conditions at 240°C for 5 h is shown in Fig. 1. In the present study, the formation of the aeschynite-type phase through crystallization from amorphous solid precipitates was observed at hydrothermal temperatures higher than 210°C. The crystalline phase precipitated at 240°C was detected as almost a single phase corresponding to an aeschynite-type structure, and no diffraction peaks due to other crystalline phases were detected. The lattice parameters and crystallite size of the as-prepared aeschynite-type sample (Gd₀.₈₅Er₀.₀₅Yb₀.₁₀TiNbO₆) are listed in Table 1 in comparison with those of pure GdTiNbO₆ shown in the JCPDS data. A slight increase in the lattice parameters was observed in the as-prepared sample in comparison with those of GdTiNbO₆ in the JCPDS data. After heating at 800 or 1050°C for 1 h in air, the values of the lattice parameters, especially \( b_0 \) and \( c_0 \), were slightly decreased, as shown in Table 1. This is considered to be due to the presence of OH⁻ as an impurity in the aeschynite lattice of the as-prepared sample formed hydrothermally. It is suggested that the single phase of aeschynite-type GdTiNbO₆ solid solution with sufficient crystallinity is formed directly by the substitutional incorporation of 5 mol% Er³⁺ and 10 mol% Yb³⁺ under weak basic hydrothermal conditions at 240°C for 5 h.

Table 1. Lattice parameters, crystallite size, and optical band gap of aeschynite-type sample (Gd₀.₈₅Er₀.₀₅Yb₀.₁₀TiNbO₆) formed under hydrothermal conditions at 240°C for 5 h and after heating at 800 and 1050°C for 1 h

| Sample            | Lattice parameter (nm) | Crystallite size (nm) | Band gap (eV) |
|-------------------|------------------------|-----------------------|---------------|
| As-prepared at 240°C | \( a_0 \) 0.5237 \quad \( b_0 \) 1.1046 \quad \( c_0 \) 0.7472 | 96.7 | 3.41 |
| After heating at 800°C | \( a_0 \) 0.5238 \quad \( b_0 \) 1.0979 \quad \( c_0 \) | 0.7431 | 3.35 |
| After heating at 1050°C | \( a_0 \) 0.5241 \quad \( b_0 \) 1.0978 \quad \( c_0 \) | 0.7422 | 3.41 |

*GdTiNbO₆ (JCPDS 20-1257) 0.5235 1.0990 0.7465 — —

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Figure 1 also shows the changes in the crystallinity and crystalline phase of as-prepared samples (Gd₀.₈₅Er₀.₀₅-Yb₀.₁₀TiNbO₆) caused by heating at various temperatures...
for 1 h in air. The crystalline phase of the aescynite-type GdTiNbO₆ co-doped with Yb³⁺ and Er³⁺, which was directly formed under hydrothermal condition, was maintained after heating at 1050°C for 1 h. The phase transformation from an aescynite- to euxenite-type structure proceeded during heat treatment between 1050 and 1300°C, and a single euxenite-type phase appeared after heating at 1300°C for 1 h. The XRD pattern of the sample after heating at 1300°C shows that the euxenite-type phase formed by the phase transition has improved crystallinity. Figure 2 shows an SEM image of the sample after heating at 1300°C. The SEM image and the results obtained from the change in XRD patterns indicate that the hydrothermally formed aescynite-type phase grew and developed into euxenite-type micron-sized crystals through crystal growth and phase transition after heating at 1300°C.

3.2 Photoluminescence and up-converted luminescence of GdTiNbO₆:Er³⁺/Yb³⁺

The UV–Vis absorption spectra of samples as-prepared and after heating at 800 to 1300°C are shown in Fig. 3. In the spectra, a broad absorption band is observed at around 250–300 nm in the low wavelength UV region. There are also small sharp absorbance peaks, corresponding to the f-f transitions of Er³⁺ in the spectra, which provide sufficient evidence that the Er component exists in the GdTiNbO₆ structure. A slight change in the absorption edge among the samples is also observed in Fig. 3. The optical band gap value (3.41 eV) of the as-prepared sample (listed in Table 1) is changed slightly to 3.49 eV after heating at 1300°C in air.

In Fig. 4, the excitation spectra of the as-prepared sample and the samples after heating at 800–1300°C are presented. The intensity of the excitation spectrum for the as-prepared sample was very low. In the low wavelength UV region, a broad absorption band appearing at around 280 nm is attributed to the charge transfer band (C.T.B.) of the host crystal, GdTiNbO₆. In addition to the broad absorption band, there are also sharp absorbance peaks corresponding to the f-f transitions of Er³⁺, e.g., $^4I_{15/2} \rightarrow ^2G_{15/2}$, $^4I_{15/2} \rightarrow ^4G_{11/2}$, $^4I_{15/2} \rightarrow ^2H_{15/2}$, $^4I_{15/2} \rightarrow ^4F_{3/2}$, $^4I_{15/2} \rightarrow ^4F_{5/2}$, in the near-UV and visible light regions.
characteristic broad-band emission coexisted in the sample with the green emission spectra in the visible region after heating at 1300°C (Fig. 5). This broad-band emission is responsible for the recombination luminescence associated with the [(Nb,Ti)O₆] polyhedron from the host lattice in GdTiNbO₆. The green emission bands observed in both Figs. 5 and 6 correspond to the f-f transitions of Er³⁺, i.e., \( {^2H_{11/2}} \rightarrow {^4I_{15/2}} \) and \( {^4S_{3/2}} \rightarrow {^4I_{15/2}} \).

In the case of the indirect excitation at 277 nm, the [(Nb,Ti)O₆] polyhedron absorbs excited energy, and the energy of the excited state is subsequently transferred to the luminescent center Er³⁺, i.e., the transitions from \( {^2H_{11/2}} \) and \( {^4S_{3/2}} \) to the ground state \( {^4I_{15/2}} \) and the transition from \( {^4F_{9/2}} \) to \( {^4I_{15/2}} \), occur with emissions. Under excitation at 377 nm, on the other hand, the electrons of Er³⁺ are directly excited from the \( {^4I_{15/2}} \) level to the \( {^4G_{11/2}} \) level. The excited electrons decay to the luminescent levels \( {^2H_{11/2}}, {^4S_{3/2}}, \) and \( {^4F_{9/2}} \) through multiphonon relaxation. Emissions corresponding to the f-f transitions from the luminescent levels to the ground state \( {^4I_{15/2}} \) then arise.

The green emission intensity under direct excitation of Er³⁺ ions increased as the heating temperature rose from 800 to 1300°C, although emission was scarcely observed from the as-prepared aeschynite sample (Fig. 6). The red emission attributed to the transition from \( {^4F_{9/2}} \) to \( {^4I_{15/2}} \) is scarcely visible. The euxenite-type phase formed through phase transition by heating at 1300°C presented the highest emission intensity.

Figure 7 shows the up-converted emission spectra of the samples. Green emission bands corresponding to the f-f transitions of Er³⁺, i.e., \( {^2H_{11/2}} \rightarrow {^4I_{15/2}} \) and \( {^4S_{3/2}} \rightarrow {^4I_{15/2}} \), are also observed in the samples after heating at temperatures higher than 800°C. The materials formed under hydrothermal conditions are thought to contain a substantial amount of OH⁻ species that may be among the luminescent quenchers in their structures. The FT-IR spectra of as-prepared and heat-treated samples were measured as shown in Fig. 8. The presence of OH groups is clearly detected in the as-prepared sample. The characteristic vibration bands originating from H₂O molecules and OH groups are not observed, on the other hand, in the sample after heating. The phenomenon of improvement of luminescent efficiency through removal of impurities that may act as luminescent quenchers has been demonstrated in many phosphors. High-temperature heating in air is considered to be an effective means of removing those impurities. In the present case, the red emission (from \( {^4F_{9/2}} \) to \( {^4I_{15/2}} \) at around 660–670 nm was extremely weak.

With a 980 nm photon, energy-transfer up-conversion generally arises while Yb³⁺ is excited from the ground state \( {^2F_{7/2}} \rightarrow {^2F_{5/2}} \), and energy transfer to a neighboring Er³⁺ ion by cross-relaxation occurs. The electrons of Er³⁺ are excited to the \( {^4I_{11/2}} \) level and then to the \( {^4F_{7/2}} \) level. Because the absorption cross-section of the \( {^2F_{7/2}} \rightarrow {^2F_{5/2}} \) transition of Yb³⁺ is much larger than that of the \( {^4I_{11/2}} \rightarrow {^4I_{15/2}} \) transition of Er³⁺, most of the excitation energy is absorbed by the Yb³⁺. Nonradiative processes
enable the excited electrons to relax to the luminescent levels $^2H_{11/2}$, $^4S_{1/2}$, and $^4F_{9/2}$. Green emissions (at around 515–530 and 540–560 nm, respectively) arise with the transitions from $^2H_{11/2}$ and $^4S_{1/2}$ to the ground state $^4I_{15/2}$. The up-converted emission intensity increased with increases in the heating temperature. The sample after heating at 1050°C showed maximum emission intensity. The present study suggests that RETiNbO$_6$ compounds exhibit potential for use as luminescent materials.

4. Summary

Aeschynite-type GdTiNbO$_6$:Er$^{3+}$/Yb$^{3+}$ (Gd$_{0.85}$Er$_{0.05}$Yb$_{0.10}$TiNbO$_6$) fine crystals were formed by the mild hydrothermal method conducted at 240°C for 5 h. The as-prepared aeshynite-type structure was maintained after heating at 1050°C for 1 h in air. Heating at 1300°C led to a phase transformation from an aeshynite to an euxenite structure. The photoluminescence and up-converted luminescence, e.g., the green emission bands corresponding to the f-f transitions of Er$^{3+}$, i.e., $^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$, are observed under excitation at wavelengths of 277 or 377 and 980 nm, respectively. The photoluminescence and up-converted emission intensity increased with increases in the heating temperature. A single phase of euxenite-type GdTiNbO$_6$:Er$^{3+}$/Yb$^{3+}$ showed relatively intense photoluminescence and up-converted luminescence.

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