Hydrothermal synthesis of luminescent niobate thin rods

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Luminescent columbite-type CaNb2O6 crystals undoped and doped with Eu3+ (CaNb2O6:Eu3+) and Tb3+ (CaNb2O6:Tb3+) have been synthesized at 240 °C using hydrothermal method from precursor solutions of inorganic salts. Microscopic examinations reveal that the morphology of the columbite crystals is like thin rods or needles (width: 0.1–0.3 μm, length 5–10 μm). The red, green, and blue light-emitting CaNb2O6-based materials have been prepared. Under the UV light excitation, the as-prepared CaNb2O6 presents a broad and blue photoluminescence (PL) peaked at 452 nm, originated from the niobate octahedral group [NbO6]7-. The columbite-type CaNb2O6 with 12 mol % Eu3+ synthesized hydrothermally at 240 °C shows the strongest PL: weak orange and strong red light, attributed to the 5D0→7F1 and 5D0→7F2 transitions of Eu3+, respectively. The intensities of blue–green and green PL bands originated from the 5D4→7F6 and 5D4→7F5 transitions of Tb3+, respectively for the as-prepared CaNb2O6:Tb3+ reach the maximum at 10 mol % Tb3+, and their PL intensities have been improved by heating at 1000 °C in air.

Key-words: CaNb2O6, Columbite, Eu3+, Tb3+, Photoluminescence, Hydrothermal synthesis

1. Introduction

Calcium niobate (CaNb2O6) is a best-known member of orthorhombic columbite group, MNb2O6 in which M is calcium, magnesium, or transition metal elements. The materials based on the columbite group have attracted considerable attention because of their high potentials and interesting characteristics such as microwave dielectric properties,1–4 photocatalytic activities5,6 including photocatalytic water splitting,7 and phosphors.8–12 As a coherent light source the niobate is useful in applications to holography and laser host material,13,14 on the other hand.

In order to improve the performance and properties of inorganic materials, the investigation on their synthesis techniques is an efficient way.15,16 Therefore, various investigations on the preparation of CaNb2O6 using solid-state reaction,4,7,12 flux growth,17 laser-heated pedestal growth,18 glycothermal,18 sol–gel,19 and coprecipitation method20 have been carried out. In recent years, from a viewpoint of green processing, great attention has also been devoted to a direct synthesis of fine inorganic materials at low temperatures. Hydrothermal synthesis technique is well known to be able to prepare inorganic materials as nanocrystals from aqueous precursor solutions at relatively low temperatures.21–24 As for the direct synthesis of CaNb2O6 using wet chemical synthesis method at low temperatures, there have been a very few studies. In the case of biphasic liquid method, heating at 700 °C in air was necessary for the crystallization of CaNb2O6 from amorphous niobate gels.25 The hydrothermal synthesis reaction can replace the calcination or heat treatment for crystallization. There are a few reports on the formation of crystalline CaNb2O6 via solvothermal5 and hydrothermal routes.6,26 The as-prepared samples with CaNb2O6 composition that were formed by the solvothermal method were amorphous, and subsequent heating at 600 °C in air was necessary for the crystallization of columbite phase.5 In that hydrothermal method,6 two times of long period of hydrothermal treatments more than 1 day and for 2 days were also necessary to synthesize crystalline CaNb2O6, on the other hand. Those studies were all done for the synthesis of pure CaNb2O6, moreover aiming at photocatalyst. Few studies have ever been conducted on the direct synthesis of luminescent CaNb2O6 columbite phosphors with high crystallinity doped with activators under hydrothermal conditions.

Here, we report on the hydrothermal synthesis of red, green, and blue light-emitting CaNb2O6-based thin rods. Luminescent columbite-type CaNb2O6 fine crystals undoped and doped with Eu3+ and Tb3+ have been synthesized under mild hydrothermal conditions from precursor solutions of inorganic salts, i.e., Ca(NO3)2, NbCl5, EuCl3,
and TbCl₃. The effects of hydrothermal treatment conditions and the concentrations of Eu⁺³ and Tb⁺³ on the crystallization, structure, and PL properties of CaNb₂O₆ with columbite phase have been investigated.

2. Experimental

Two CaNb₂O₆-based metal complex oxides whose cation ratios were Ca/Eu/Nb = 1.00 - x/x/2.00 and Ca/Tb/Nb = 1.00 - x/x/2.00 were formed under hydrothermal conditions. Reagent-grade Ca(NO₃)₂·4H₂O, EuCl₃·6H₂O, TbCl₃·6H₂O, and NbCl₅ were used as starting materials. An aqueous solution dissolving the starting materials selected from Ca(NO₃)₂, EuCl₃, and TbCl₃ and an ethanol solution dissolving NbCl₅ were mixed in a Teflon container while stirring, thus a precursor solution was prepared. The pH of the solution was controlled by the addition of aqueous ammonia to have acidic (pH 2.7) to weakly basic (pH 8.7) conditions. This precursor solution with total cation concentration of 0.10–0.30 mol/dm³ (Ca/Nb = 1/2) in the Teflon container was then placed in a stainless-steel vessel. In the preparation of samples doped with Eu⁺³ or Tb⁺³, the site of Ca in the chemical formula, CaNb₂O₆ was partially substituted with Eu or Tb (substitution atomic ratio is referred to as x). The vessel was tightly sealed and it was heated at 180–240°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 as-prepared powder was heated in an alumina crucible at heating rate 200°C/h, held at 1000–1300°C for 1 h in air, and then cooled to room temperature in a furnace. The powder sample after heating in air was pulverized in an alumina mortar.

The observation of morphology and structure of the samples was carried out using transmission electron microscopy (TEM; model JEM-2100Plus, JEOL, Tokyo, Japan) and selected area electron diffraction (SAED). The powder X-ray diffraction (XRD) measurements for sample powders were done using Cu Kα radiation (XRD; model RINT-2000, Rigaku, Tokyo, Japan). The measurement of the crystallite size of orthorhombic columbite phase was conducted from the line broadening of 131 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 \(\beta^2 = \beta_m^2 - \beta_i^2\), where \(\beta_m\) is the measured half-width and \(\beta_i\) is the half-width of a standard sample. The molar ratio (mole percent) of Eu/Ca and Tb/Ca in the samples was determined via an inductively coupled plasma emission spectrometer (ICP; model SPS-3100, SII NanoTechnology Inc., Japan).

The ultraviolet–visible (UV–Vis) absorption spectra of the prepared powders were recorded at room temperature in air 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 done using a spectrofluorimeter (F-2700, Hitachi High-Tech, Japan) with Xe lamp. Powder samples were excited with 260 or 393 nm radiation from a 150 W xenon lamp. The emission wavelength was scanned from 300 to 800 nm at a scanning rate of 60 nm/min. For the measurements of excitation spectra, the excitation wavelength was scanned from 220 to 400 nm at the same scanning rate, and emissions were monitored at 450 nm (for pure CaNb₂O₆), 610 nm (for CaNb₂O₆:Eu⁺³), and 546 nm (for CaNb₂O₆:Tb⁺³).

3. Results and discussion

3.1 Crystallization of columbite-type CaNb₂O₆ thin rods doped with Eu⁺³ and Tb⁺³

The hydrothermal treatment of precursor solutions added with different amounts of aqueous ammonia was conducted at 240°C for 5 h to investigate the effect of the pH condition of the precursor solutions on the preparation of CaNb₂O₆. Under the acidic hydrothermal condition, the formed solid precipitates were almost amorphous-like. Almost a single phase of orthorhombic CaNb₂O₆ columbite with relatively high crystallinity was detected in the sample formed under weakly basic conditions at pH 8.7, on the other hand. Thus, the hydrothermal treatment was carried out under weakly basic conditions at various temperatures for 5 h. The XRD patterns of precipitates formed hydrothermally at various treatment temperatures are shown in Fig. 1. The precipitates formed hydrothermally at 180 and 200°C were almost amorphous. At 220°C, the hydrothermal crystallization of CaNb₂O₆ phase from amorphous precipitate was observed. To promote the growth of columbite-type CaNb₂O₆ hydrothermal treatment at 240°C for 5 h under weakly basic condition is suggested to be necessary. It is known that CaNb₂O₆ has a columbite struc-
ture with the space group of Phen, in which the Ca and Nb cations are at the center of the octahedra CaO₆ and NbO₆ surrounded by six oxygen atoms, respectively.1) The TEM images and SAED pattern of columbite-type CaNb₂O₆ precipitates formed under weakly basic and hydrothermal conditions at 240 °C for 5 and 24 h are presented in Figs. 2(a) and 2(b), respectively. The thin rods which were sufficiently grown into elongated micron-sized crystals (width: 0.1–0.3 μm, length 5–10 μm) with needle-like morphology are observed in the figure. The SAED pattern of the area marked with a circle on the thin rod crystal in the TEM image of Fig. 2(b) shows that the preferential growth direction of the acicular crystals is along the b-axis.

The effect of hydrothermal treatment time on the crystallinity of columbite-type CaNb₂O₆ precipitates has been investigated. Hydrothermal treatments were conducted for 5–24 h at 240 °C. The differences in the crystalline phase could not be found for the XRD lines of the as-prepared samples that were formed via hydrothermal treatment for 5–24 h, as a result. The crystallite size of orthorhombic columbite-type CaNb₂O₆ samples formed under hydrothermal condition at 240 °C for 5 h was in the range of 80 nm. The crystallinity of the columbite, CaNb₂O₆ was a little improved by maintaining for 24 h at 240 °C. Thus, thin rod crystals of columbite-type CaNb₂O₆ composed of crystallites with a size in the range of nano-size were synthesized directly from the precursor solutions of inorganic salts, i.e., Ca(NO₃)₂ and NbCl₅ under weakly basic hydrothermal conditions at 240 °C for 5 h.

The columbite-type pure CaNb₂O₆ could be synthesized hydrothermally, therefore the hydrothermal crystallizations of Eu³⁺- and Tb³⁺-doped CaNb₂O₆ have also been carried out under similar weakly basic conditions at 240 °C for 5 h. The effect of the concentrations of Eu³⁺ and Tb³⁺ on the formation, crystalline phase, and optical properties of as-prepared solid precipitates has been investigated. Figures 3 and 4 show XRD patterns of solid precipitates synthesized hydrothermally and doped with Eu³⁺ and Tb³⁺, respectively. In Figs. 3 and 4, the atomic ratios of europium and terbium doped into CaNb₂O₆ are described as x = 0–0.20 and x = 0–0.30, respectively. The analytical concentrations of Eu, Tb, and Ca in the as-prepared samples determined using ICP are shown in Table 1. This result suggests that the analytical values of europium and terbium in the as-prepared samples are almost equal to their starting concentrations.

The XRD patterns show that the solid precipitates doped with Eu³⁺ and Tb³⁺ have orthorhombic columbite-type
structure with good crystallinity. As the concentration of Eu$^{3+}$ and Tb$^{3+}$ increased, the crystallite size of columbite-type phase slightly decreased from 81 to 62.5 nm and from 81 to 61 nm, respectively. In the present study, columbite-type CaNb$_2$O$_6$-based fine crystals doped with Eu$^{3+}$ and Tb$^{3+}$ were obtained after hydrothermal treatment at 240 °C for 5 h. In the formation of columbite-type solid solutions substitutionally doped with rare earth ions RE$^{3+}$:Eu$^{3+}$ or Tb$^{3+}$, it should be more natural to understand that cation vacancies are introduced in the structure in accordance with 3Ca$^{2+}$ ↔ 2RE$^{3+}$ + cation vacancy.

### 3.2 PL properties of CaNb$_2$O$_6$ doped with Eu$^{3+}$ and Tb$^{3+}$

The optical band gap value measured for the undoped columbite-type CaNb$_2$O$_6$ synthesized hydrothermally at 240 °C was 3.85 eV based on the absorption edge in the UV–Vis absorption spectrum of the sample. A large and relatively wide band at 240 to 280 nm in the UV region was located in the excitation spectrum of the pure CaNb$_2$O$_6$ formed hydrothermally at 240 °C. This broad band is attributed to the charge transfer band (C.T.B.) from O ligands to central Nb atoms in the NbO$_6$ octahedral group.

The PL spectra excited at 260 nm for the samples synthesized hydrothermally at various temperatures for 5 h are shown in Fig. 5. The CaNb$_2$O$_6$ acicular crystals formed at 240 °C for 5 h present a strong and broad blue emission peaked at 452 nm under excitation at 260 nm. This blue emission is originated from the niobate octahedral group [NbO$_6$]$^{7-}$ (self-trapped exciton luminescence). The PL intensities of those samples that were prepared at 180–220 °C for 5 h, which were mainly composed of amorphous phase, were very low, on the other hand. This means that the fully crystallization and high crystallinity of columbite phase are necessary to obtain intense emission. It should be noted that the luminescent CaNb$_2$O$_6$ fine crystals can be formed directly by means of hydrothermal treatment at 240 °C for 5 h without subsequent heat treatment in air, though heating at temperatures higher than 1000 °C for 1 h in air in addition to the hydrothermal treatment was necessary to obtain efficient emission in the case of another niobate, fergusonite-type YNbO$_4$ crystal based on the niobate [NbO$_4$]$^{3-}$ group.

The pure CaNb$_2$O$_6$ emits strong blue light, therefore the effect of the substitutional incorporation of Eu$^{3+}$ ions into CaNb$_2$O$_6$ crystal on the PL properties has been investigated to obtain red light-emitting CaNb$_2$O$_6$-based materials. Figure 6 shows PL excitation spectra of the as-prepared CaNb$_2$O$_6$ doped with various concentrations of Eu$^{3+}$, obtained by monitoring the emission at 610 nm. A large and broad band centered at 260 nm in the UV region is attributed to the C.T.B. of the CaNb$_2$O$_6$ crystal. Several sharp absorption bands in the near-UV region are corresponding to the f-f transitions of Eu$^{3+}$, for example.
7F0→5D4, 7F0→5L7, and 3F0→5L6. It is suggested from the data on the excitation spectra that the CaNb2O6:Eu3+ can be efficiently excited by both the UV-light around 260 nm and the lights corresponding to the f-f transitions of Eu3+, e.g., violet light at 393 nm (: the 7F0→5L6 transition).

The PL spectra excited at 260 nm (: C.T.B.) and at 393 nm (: the transition 7F0→5L6 of Eu3+) for the as-prepared columbite-type CaNb2O6:Eu3+ with various concentrations of Eu3+ are shown in Figs. 7 and 8, respectively. The spectra obtained at λex = 260 nm are composed of both a broad emission band around 450 nm originated from the niobate octahedral group [NbO6]7− and several sharp emission bands attributed to the transitions of Eu3+ ions (Fig. 7). The sharp emission bands in the spectra of Figs. 7 and 8 are weak orange and strong red luminescence with peaks at 590 and 610 nm originated from the 5D0→7F1 and 5D0→7F2 transitions of Eu3+, respectively. As the Eu3+ concentration increased, the intensity of the large broad band emission in Fig. 7 decreased and the intensities of both sharp emission peaks (: 5D0→7F1 and 5D0→7F2 transitions of Eu3+) increased. When excited at 260 nm, the energy is absorbed by the CaNb2O6 lattice, subsequently the energy of excited state is transferred from the NbO6 group to the excited state of the luminescent center Eu3+, and then emissions originated from the transitions 5D0→7F1 and 5D0→7F2 are given rise to.

It is known that electric dipole transitions corresponding to the 5D0→7F2 transition are sensitive to the local electric field and they are only allowed in the absence of inversion symmetry.28,29 These spectra show that Eu3+ ions are embedded in the sites without inversion symmetry in the columbite-type structure of CaNb2O6:Eu3+ because the 5D0→7F2 electric-dipole transition (: red emission) is dominant.

In general, an insufficiency of doping ratio of activators gives weak luminescence while an over-doping ratio brings concentration quenching of the luminescence. In the case of indirect excitation at 260 nm, as the concentration of Eu3+, the value of x increased, the luminescence intensity increased, it reached a maximum value at x = 0.12, and then decreased (Fig. 7). When excited at 393 nm, the PL intensity increased up to x = 0.30.
In Fig. 9, the Commission Internationale de l’Eclairage (CIE) chromaticity coordinates $x$ and $y$ for the PL of the as-prepared CaNb$_2$O$_6$:Eu$^{3+}$ ($x = 0.12$) and those for the PL of CaNb$_2$O$_6$:Tb$^{3+}$ ($x = 0.1$ and 0.2) samples before and after heating at 1000 °C for 1 h in air, 1: Eu$^{3+}$ $\lambda_{ex} = 260$ nm, (0.232, 0.217), 2: Eu$^{3+}$ $\lambda_{ex} = 393$ nm, (0.625, 0.340), 3: Tb$^{3+}$ ($x = 0.10$) As-prep. $\lambda_{ex} = 260$ nm, (0.180, 0.288), 4: Tb$^{3+}$ ($x = 0.20$) As-prep. $\lambda_{ex} = 260$ nm, (0.204, 0.360), 5: Tb$^{3+}$ ($x = 0.10$) 1000 °C $\lambda_{ex} = 260$ nm, (0.216, 0.438), 6: Tb$^{3+}$ ($x = 0.20$) 1000 °C $\lambda_{ex} = 260$ nm, (0.241, 0.543).

In Fig. 9, the Commission Internationale de l’Eclairage (CIE) chromaticity coordinates $x$ and $y$ for the PL of the as-prepared columbite-type CaNb$_2$O$_6$:Eu$^{3+}$ ($x = 0.12$) sample obtained at $\lambda_{ex} = 260$ nm (Fig. 7) and at $\lambda_{ex} = 393$ nm (Fig. 8) are shown as No. 1: $x = 0.232$, $y = 0.217$ and No. 2: $x = 0.625$, $y = 0.340$, respectively. When excited at 260 nm, the large and broad band emission at around 450 nm in the blue region originated from the host lattice effect on the total color chromaticity of the system, and its coordinates were in a region of blue, consequently (No. 1 in Fig. 9). On exciting at 393 nm, its coordinates fell in a region of red (No. 2) in the CIE chromaticity diagram, on the other hand.

The effect of the substitutional incorporation of Tb$^{3+}$ ions in CaNb$_2$O$_6$ crystal on the PL properties has been investigated to prepare green light-emitting CaNb$_2$O$_6$-based materials. The PL excitation spectra of the as-prepared CaNb$_2$O$_6$:Tb$^{3+}$ samples synthesized hydrothermally at 240 °C are shown in Fig. 10. Both broad absorption bands in the short UV region and relatively narrow PL excitation peaks assigned to the $f$-$f$ transitions of Tb$^{3+}$ in the longer UV wavelength region are observed. The largest absorption band centered at 260 nm in the short UV region is corresponding to the self-absorption (C.T.B.) of CaNb$_2$O$_6$ crystal, originated from the $O^{2-} \rightarrow$ Nb$^{5+}$ ($\rightarrow$ Tb$^{3+}$) charge transfer transition. Tb-activated phosphors show 4$f$-5$d$ transition band absorption around 300 nm. The second broad band around 300–320 nm corresponds to the $4f^8\rightarrow 4f^75d^1$ transition of Tb$^{3+}$. The additional several absorption bands and small peaks are attributed to the $f$-$f$ transitions of Tb$^{3+}$, e.g. $^7F_6\rightarrow^3D_2$, $^7F_6\rightarrow^5G_{5/2}$, $^7F_6\rightarrow^5L_{9/2}$, and $^7F_6\rightarrow^5D_3$. It is suggested from these excitation spectra that the CaNb$_2$O$_6$ doped with Tb$^{3+}$ can be excited effectively using UV light around 260 nm corresponding to the C.T.B.

The PL spectra excited at 260 nm for the as-prepared CaNb$_2$O$_6$:Tb$^{3+}$ ($x = 0.05–0.30$) samples obtained under hydrothermal conditions at 240 °C for 5 h.

![Fig. 9](image-url) The CIE chromaticity coordinates $x$ and $y$ for the PL of the as-prepared CaNb$_2$O$_6$:Eu$^{3+}$ ($x = 0.12$) and those for the PL of CaNb$_2$O$_6$:Tb$^{3+}$ ($x = 0.1$ and 0.2) samples before and after heating at 1000 °C for 1 h in air, 1: Eu$^{3+}$ $\lambda_{ex} = 260$ nm, (0.232, 0.217), 2: Eu$^{3+}$ $\lambda_{ex} = 393$ nm, (0.625, 0.340), 3: Tb$^{3+}$ ($x = 0.10$) As-prep. $\lambda_{ex} = 260$ nm, (0.180, 0.288), 4: Tb$^{3+}$ ($x = 0.20$) As-prep. $\lambda_{ex} = 260$ nm, (0.204, 0.360), 5: Tb$^{3+}$ ($x = 0.10$) 1000 °C $\lambda_{ex} = 260$ nm, (0.216, 0.438), 6: Tb$^{3+}$ ($x = 0.20$) 1000 °C $\lambda_{ex} = 260$ nm, (0.241, 0.543).

![Fig. 10](image-url) Excitation spectra monitored at 546 nm for the as-prepared CaNb$_2$O$_6$:Tb$^{3+}$ ($x = 0–0.30$) samples obtained under hydrothermal conditions at 240 °C for 5 h.

![Fig. 11](image-url) PL spectra excited at 260 nm for the as-prepared CaNb$_2$O$_6$:Tb$^{3+}$ ($x = 0.05–0.30$) samples obtained under hydrothermal conditions at 240 °C for 5 h.
Tb$^{3+}$ ions are observed in Fig. 11. The two large and narrow emission bands are responsible for the characteristic blue green (around 490 nm) and green (around 545 nm) luminescence, originated from the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions of Tb$^{3+}$, respectively. Their emission intensity changed depending on the Tb$^{3+}$ concentration, the value of atomic ratio ($x$) of Tb. When excited at 260 nm, the charge transfer transition occurs in the CaNb$_2$O$_6$ crystal via the absorption of excitation energy corresponding to around 260 nm (C.T.B.), and the transfer of the excitation energy from the NbO$_6$ group to the excited state of the neighboring activator Tb$^{3+}$ ions occurs, and then returns to the ground state by the emission of characteristic luminescent radiations (correspondent to the $f$-$f$ transitions of Tb$^{3+}$ ions). When the concentration of Tb$^{3+}$ increased from 5 to 20 mol%, the intensity of the broad band emission decreased, and the intensities of the both sharp emission bands correspondent to the $f$-$f$ transitions of Tb$^{3+}$ ions increased. The concentration dependence of the PL intensity corresponding to the $^5D_4 \rightarrow {}^7F_6$ transition of Tb$^{3+}$ is plotted against Tb$^{3+}$ concentration in Fig. 12. The as-prepared CaNb$_2$O$_6$ containing 10 mol% Tb$^{3+}$ exhibits the maximum emission intensity.

The as-prepared CaNb$_2$O$_6$:Tb$^{3+}$ samples doped with 10 mol% Tb were heated at 1000–1300 °C for 1 h in air. The XRD patterns of CaNb$_2$O$_6$:Tb$^{3+}$ samples after heating in air are indicated in Fig. 13. Significant changes in crystalline phases were hardly observed in the samples after heating in air. The XRD patterns of these samples after heating at 1000–1300 °C inform that these samples are composed of columbite phase. The PL spectra excited at 260 nm for the CaNb$_2$O$_6$:Tb$^{3+}$ ($x = 0.10$) after heating at 1000 and 1300 °C are shown in Fig. 14. Under excitation at 260 nm, similar characteristic PL spectra that are composed of both a large broad band attributed to the NbO$_6$ niobate group and the multiple sharp emission bands assigned to the $^5D_4 \rightarrow {}^7F_6$ and $^5D_4 \rightarrow {}^7F_5$ transitions of Tb$^{3+}$ are observed. The emission intensity of the columbite, CaNb$_2$O$_6$:Tb$^{3+}$ has been improved effectively by heating in air. Heating at 1000 °C was more effective for the enhancement of the PL intensity of the CaNb$_2$O$_6$:Tb$^{3+}$ than that at 1300 °C.

The color chromaticity coordinates for the PL spectra of CaNb$_2$O$_6$:0.10Tb$^{3+}$ and 0.20Tb$^{3+}$ samples are also shown in Fig. 9. Since the emission spectra excited at 260 nm for the columbite-type CaNb$_2$O$_6$:Tb$^{3+}$ were composed of both a broad band at 450 nm in the blue region and the narrow emission bands attributed to the $f$-$f$ transitions of Tb$^{3+}$ ions in the green region, the color chromaticity coordinates $x$ and $y$ were shifted gradually and tunable from light blue to
green region with the increase in the Tb³⁺ concentration and by means of heating at 1000 °C. The present materials, CaNb₂O₆:Eu³⁺, CaNb₂O₆:Tb³⁺, and pure CaNb₂O₆ emitted red (R), green (G) and blue (B) lights, respectively. The present results that the columbite-type CaNb₂O₆-based materials with characteristic morphology like thin rods or needles can be easily formed by hydrothermal crystallization at 240 °C may provide useful hints for future material research.

4. Summary

Luminescent pure, Eu³⁺-doped, and Tb³⁺-doped columbite-type CaNb₂O₆ fine crystals have been synthesized hydrothermally under weakly basic conditions at 240 °C. They are thin rod shaped crystals (width: 0.1–0.3 μm, length 5–10 μm) with needle-like morphology, and their crystallite sizes are in the range of 60–80 nm. The as-prepared pure CaNb₂O₆ shows a strong and broad blue emission peaked around 450 nm under excitation at 260 nm, which is originated from the niobate octahedral group [NbO₆]⁷⁻ (self-trapped exciton luminescence). The as-prepared CaNb₂O₆ doped with Eu³⁺ presents relatively strong characteristic emissions, i.e., weak orange and strong red light corresponding to the $5D_{0}→3F_{1}$ and $5D_{0}→7F_{2}$ transitions of Eu³⁺, and the emission intensity reaches the maximum at 12 mol% Eu under excitation at 260 nm. When the material is excited directly at 393 nm, the color chromaticity coordinates fall in a red region of the CIE chromaticity diagram, but the blue and broad band emission from the host crystal effects on the total color chromaticity coordinates of the system under excitation at 260 nm. Upon the excitation at 260 nm, CaNb₂O₆ doped with Tb³⁺ presents characteristic blue-green to green PL emission corresponding to the $5D_{4}→7F_{5}$ and $5D_{4}→7F_{5}$ transitions. The as-prepared columbite-type CaNb₂O₆ containing 10 mol% Tb³⁺ exhibits the maximum emission intensity. The PL intensity of CaNb₂O₆:Tb³⁺ has been improved by heating at 1000 °C in air. The columbite-type materials, CaNb₂O₆:Eu³⁺, CaNb₂O₆:Tb³⁺, and pure CaNb₂O₆ that emit red (R), green (G) and blue (B) lights, respectively have been obtained.

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