Synthesis, photoluminescence, and up-conversion luminescence of niobates co-doped with Er\(^{3+}\) and Yb\(^{3+}\)

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Niobates, CaNb\(_2\)O\(_6\) with columbite-type structure doped with Er\(^{3+}\) (CaNb\(_2\)O\(_6\):Er\(^{3+}\)) and co-doped with Er\(^{3+}\) and Yb\(^{3+}\) (CaNb\(_2\)O\(_6\):Er\(^{3+}\)/Yb\(^{3+}\)) were synthesized from precursor solutions using inorganic salts under mild hydrothermal conditions at 240°C. The as-prepared niobates appeared to be a sheaf of aligned acicular particles. At 3 mol % Er\(^{3+}\), the as-prepared CaNb\(_2\)O\(_6\):Er\(^{3+}\) showed the strongest photoluminescence (PL) in the characteristic green spectral region corresponding to the \(2H_{11/2} \rightarrow 2I_{5/2}\) and \(2S_{3/2} \rightarrow 2I_{5/2}\) transitions of Er\(^{3+}\). The green PL intensity of the sample doped with 5 mol % Er\(^{3+}\) after heating at 1300°C in air was more than 10 times stronger than that before heating when exciting directly at 377 nm. The effect of the concentration of the sensitizer Yb\(^{3+}\) on the up-conversion emission of CaNb\(_2\)O\(_6\):Er\(^{3+}\)/Yb\(^{3+}\) was investigated using samples after heating in air. The up-conversion emission intensity of CaNb\(_2\)O\(_6\):Er\(^{3+}\)/Yb\(^{3+}\) became the maximum at 5 mol % Er\(^{3+}\) and 20 mol % Yb\(^{3+}\) under excitation at 980 nm.

Key-words : Columbite, CaNb\(_2\)O\(_6\), Er\(^{3+}\), Yb\(^{3+}\), Photoluminescence, Up-conversion, Hydrothermal synthesis

1. Introduction

Calcium niobate (CaNb\(_2\)O\(_6\)) is known to be one of the members of columbite group with orthorhombic-type structure. CaNb\(_2\)O\(_6\) has attracted attention due to its potential for microwave dielectric material\(^1\)-\(^4\), photocatalyst\(^5\),\(^6\) photocatalytic water splitting,\(^7\) laser host material,\(^8\),\(^9\) and one of host crystals for luminescent phosphors doped with several activators.\(^10\)-\(^13\)

To investigate on the synthesis technique and processing of inorganic materials is useful for the improvement of their performance and characteristics.\(^14\),\(^15\) Thus, many researches have been conducted on the synthesis of CaNb\(_2\)O\(_6\) using various methods (e.g., solid-state reaction,\(^4\),\(^5\),\(^13\) flux growth,\(^16\) laser-heated pedestal growth,\(^12\) glyothermal technique,\(^17\) sol–gel process,\(^18\) and coprecipitation method\(^19\)). Recently, wet-chemical synthesis techniques such as hydrothermal formation technique at relatively low temperatures have been focused on.\(^20\)-\(^23\) However, there have been a very few studies on the direct formation of CaNb\(_2\)O\(_6\) at low temperatures using wet chemical synthesis method.\(^24\) Although, a few investigations on the formation of crystalline CaNb\(_2\)O\(_6\) via solvothermal\(^5\) and hydrothermal routes\(^6\),\(^25\) have been reported, these studies are all focused on the formation of non-doped (pure) CaNb\(_2\)O\(_6\) for photocatalysis applications. The hydrothermal technique is advantageous for doping and dispersing homogeneously small amount of selective additives into nanomaterials in the stage of hydrothermal crystallization, in general. Few studies have ever been done on the synthesis of luminescent CaNb\(_2\)O\(_6\) columbite phosphors doped with Er\(^{3+}\) (CaNb\(_2\)O\(_6\):Er\(^{3+}\)) or co-doped with Er\(^{3+}\) and Yb\(^{3+}\) (CaNb\(_2\)O\(_6\):Er\(^{3+}\)/Yb\(^{3+}\)) using hydrothermal method.

In the present study, luminescent columbite-type niobates, CaNb\(_2\)O\(_6\):Er\(^{3+}\) and CaNb\(_2\)O\(_6\):Er\(^{3+}\)/Yb\(^{3+}\) have been synthesized as homogeneous fine crystals from precursor solutions of inorganic salts under mild hydrothermal conditions. The effect of the concentrations of activator and sensitizer on their structures and optical properties, i.e., PL and up-conversion properties has been investigated.

2. Experimental

The metal complex oxides based on CaNb\(_2\)O\(_6\) with atomic ratios of Ca/Er/Yb/Nb = 1.00 – x – y/x/y/2.00 were synthesized hydrothermally. In the preparation of samples doped with Er\(^{3+}\) and co-doped with Er\(^{3+}\) and Yb\(^{3+}\), the site of Ca\(^{2+}\) in the chemical formula, CaNb\(_2\)O\(_6\) was partially substituted with Er\(^{3+}\) and Er\(^{3+}\)/Yb\(^{3+}\), respectively. A solution mixture of an aqueous solution selected from Ca(NO\(_3\))\(_2\), 4H\(_2\)O, ErCl\(_3\), 6H\(_2\)O, Yb(NO\(_3\))\(_3\), 3H\(_2\)O, and

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an ethanol solution of NbCl₅ was prepared in a Teflon container while stirring as an precursor solution. The pH of the solution was controlled by the addition of aqueous ammonia to have weakly basic condition. This precursor solution in the Teflon container was then placed in a stainless-steel vessel. The vessel was tightly sealed and it was heated at 240 °C for 24 h while rotating at 1.5 rpm. After 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 1300 °C for 1 h in air, and then cooled to room temperature in a furnace.

The powder X-ray diffraction (XRD) measurement was conducted for sample powders using Cu Kα radiation (XRD; model RINT-2000, Rigaku, Tokyo, Japan). The morphology and structure of the samples were observed using field emission 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 crystallite size of columbite phase was measured from the line broadening of 131 diffraction peak, according to the Scherrer equation, $D_{\text{XRD}} = K \lambda / \beta \cos \theta$, 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-ray, and $\beta$ is the corrected half-width given by $\beta^2 = \beta_m^2 - \beta_s^2$, where $\beta_m$ is the measured half-width and $\beta_s$ is the half-width of a standard sample. The fourier transform infrared spectroscopy (FTIR) was used to characterize the presence of impurities, i.e., specific chemical groups in the materials. The FTIR powder spectra were recorded from 4000 to 600 cm⁻¹ by means of FTIR microscopy (Nicolet iS50, Nicolet/Continum, Thermo Fisher Scientific, Waltham, MA, USA).

The ultraviolet–visible (UV–Vis) absorption spectra of sample powders were measured using UV–Vis spectrophotometer with an integrating sphere attachment (V-560, Nihon Bunko, Tokyo, Japan). The photoluminescence (PL) and excitation spectra of samples were recorded using a spectrofluorometer (F-2700, Hitachi High-Tech, Japan) with Xe lamp. The powder samples of CaNb₂O₆:Er³⁺ and CaNb₂O₆:Er³⁺/Yb³⁺ were excited with 257 or 377 nm radiation from a 150 W xenon lamp, respectively. The up-conversion luminescence of samples was recorded under excitation of a 980 nm laser (Laser Diode) using an absolute quantum yield spectrometer (Quantaurus-QY Plus C13534-02, Hamamatsu Photonics K.K., Hamamatsu, Japan).

3. Results and discussion

3.1 Synthesis and characteristics of CaNb₂O₆:Er³⁺ and CaNb₂O₆:Er³⁺/Yb³⁺

To synthesize CaNb₂O₆ doped with activator and sensitizer the hydrothermal treatment of the precursor solutions has been conducted at 240 °C under weakly basic conditions at pH 9 in the presence of aqueous ammonia. The effect of Er and Yb atomic ratios (concentrations) on the formation and structure of CaNb₂O₆-based materials has been investigated. There was no presence of residual unreacted metal cation components in ultrafiltrated solutions separated from precipitates after hydrothermal treatment in all the samples. XRD patterns of as-prepared precipitates doped with Er³⁺ and co-doped with Er³⁺ and Yb³⁺ after hydrothermal treatment at 240 °C are shown in Figs. 1 and 2, respectively. The structure of CaNb₂O₆ is known to be a columbit-type with the space group of Pbcn, in which Ca and Nb cations are at the center of the octahedra CaO₆ and NbO₆, respectively surrounded by six oxygen atoms. Both of the XRD patterns shown in

Fig. 1. XRD patterns of precipitates obtained from the precursor solution mixtures with various atomic ratios $x = 0–0.30$ in Ca/Er/Nb = 1.00 – $x$/x/2.00 under hydrothermal conditions at 240 °C for 24 h.

Fig. 2. XRD patterns of precipitates obtained from the precursor solution mixtures with various atomic ratios $y = 0–0.35$ in Ca/Er/Yb/Nb = 0.95 – y/0.05/y/2.00 under hydrothermal conditions at 240 °C for 24 h.
Figs. 1 and 2 suggest that solid precipitates formed under hydrothermal conditions at 240 °C were all detected as almost a single phase corresponding to the columbite-type CaNb2O6 structure in all of the compositions. There have been studies on the synthesis of metastable phases and the formation of wide range of solid solutions of metal oxide based materials under hydrothermal conditions.26,27 The ionic radii of Er3+ and Yb3+ are relatively similar to the radius of Ca2+, and the sites of Ca2+ in the columbitetype CaNb2O6 were partially substituted with up to 30 mol% Er3+ or 5 mol% Er3+ + 35 mol% Yb3+ under hydrothermal conditions, in the present study. For example, in the case of periclase (MgO) solid solution formed by doping Al2O3, cation vacancy is produced in the periclase solid solution in accordance with 3Mg2+ → 2Al3+ + cation vacancy. When Al2O3 is doped into p-type semiconductor NiO, the charge compensation is brought about by decreasing in the amount of oxygen vacancy. In the third case of BaTiO3 doped with rare earth ion RE3+, the system becomes in a mixed valence state in accordance with Ti4+ → Ti3+. In the present case of columbite-type CaNb2O6 solid solutions doped with Er3+ or Er3+ + Yb3+, the formation of cation vacancy is suggested as is in the case of periclase solid solution. In the samples doped with more than 5 mol% Er3+ or Er3+ + Yb3+, the decrease in the intensity of 200 diffraction peak is observed, which suggests that the presence of rare earth ions more than 5 mol% in the precursor solution mixtures reduce the crystal growth of 200 plane in Miller index. In the present study, CaNb2O6-based materials doped with Er3+ and Er3+/Yb3+ were synthesized hydrothermally at 240 °C as columbite-type crystals with crystallite in the order less than 100 nm.

A SEM image of the pure CaNb2O6 sample that was synthesized hydrothermally at 240 °C is presented in Fig. 3. The as-prepared CaNb2O6 crystals appear to be a sheaf of aligned acicular particles which are well grown and have the length of 5–10 μm and the width of 0.1–0.3 μm. Images of TEM-EDS mapping of the as-prepared CaNb2O6 co-doped with 5 mol% Er3+ and 20 mol% Yb3+ are presented in Fig. 4. These elemental mapping images of Ca, Nb, Er, and Yb demonstrate that those samples that were crystallized under hydrothermal conditions possess high homogeneity in element distribution.

The effect of the concentration of Er3+ on the PL properties of as-prepared columbite-type CaNb2O6:Er3+ that was synthesized hydrothermally at 240 °C has been investigated. The excitation spectra of the as-prepared samples that have various concentrations of Er3+ monitored at 553 nm are shown in Fig. 5. In the spectra, a broad and large absorption band at around 260 nm in the low wavelength UV region, which is attributed to the charge-transfer band (CTB) corresponding to the absorption edge of columbite-type host crystal, is observed. In addition to the large broad absorption band several sharp excitation bands in the near-UV region which correspond to the 4f-4f transitions of Er3+. Figure 6 indicates the PL spectra of the as-prepared CaNb2O6:Er3+ containing various concentrations of Er3+ obtained by indirect excitation at 257 nm, i.e., by the charge-transfer of the excitation energy absorbed by the host lattice. Pure CaNb2O6 (x = 0) host crystal prepared hydrothermally presented a strong and broad blue PL centered at 452 nm. The PL spectra of CaNb2O6:Er3+ excited indirectly at 257 nm corresponding to the C.T.B.
are composed of the combination of a large broad band emission around 400 to 500 nm based on the emission attributed to the \([\text{NbO}_6]^{7-}\) of the host lattice and several sharp and small green emission bands at around 520–530 and 540–560 nm that are originated from the \(f-f\) transitions of Er\(^{3+}\), i.e., \(2H_{11/2} \rightarrow 4I_{15/2}\) and \(4S_{1/2} \rightarrow 4I_{15/2}\), respectively. The peak intensity of the PL spectra centered around 450 nm decreased as the concentration of Er\(^{3+}\) increased.

The paths of excitation, energy transfer (ET) and emission for CaNb\(_2\)O\(_6\):Er\(^{3+}\) are presented as a schematic diagram in Fig. 7. When the materials are excited at 257 nm, Nb–O band of the host crystal absorbs excited energy through charge-transfer transition, subsequently, the energy...
of excited state is transferred to luminescent center Er\textsuperscript{3+}, and then emissions corresponding to the transitions from \(^2\text{H}_{11/2}\) and \(^4\text{S}_{3/2}\) to the ground state \(^4\text{I}_{15/2}\) are given rise to, in general. In this study, the light blue green and large broadband emissions centered around 450 nm, which are responsible for the recombination luminescence, attributed to the \([\text{NbO}_6]\)\textsuperscript{7-} group in the crystalline lattice of Ca\text{Nb}_2O\text{O}_6 are observed in addition to the \(f\rightarrow f\) transitions of Er\textsuperscript{3+} under excitation at 257 nm.

The PL spectra according to the Stokes shift excited at 377 nm (the transition \(^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}\) of Er\textsuperscript{3+}) are shown in Fig. 8. In the PL spectra, characteristic green emission bands corresponding to the \(f\rightarrow f\) transitions of Er\textsuperscript{3+}, i.e., \(^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}\) and \(^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}\) are observed. When the material is excited at 377 nm, the electrons of Er\textsuperscript{3+} are transformed from the \(^4\text{I}_{15/2}\) level to the \(^4\text{G}_{11/2}\) level. The excited electrons decay to the luminescent levels \(^2\text{H}_{11/2}\), and \(^4\text{S}_{3/2}\) through multiphonon relaxation. Then emissions from the luminescent levels to the ground state \(^4\text{I}_{15/2}\) arise. It should be noted that the red emission corresponding to the \(f\rightarrow f\) transition of Er\textsuperscript{3+} from the luminescent level \(^4\text{F}_{9/2}\) to the ground state \(^4\text{I}_{15/2}\) was hardly observed at lower wavelength position around 650–675 nm in the PL spectra excited at both 257 and 377 nm. This phenomenon suggests that the initial \(^4\text{F}_{9/2}\) state responsible for the red emission is not populated. It is found that the as-prepared Ca\text{Nb}_2O\text{O}_6:Er\textsuperscript{3+} doped with 3 mol\% Er\textsuperscript{3+} showed the maximum PL intensity.

The effect of the presence of Yb\textsuperscript{3+} on the PL properties of Ca\text{Nb}_2O\text{O}_6:Er\textsuperscript{3+} was investigated. The PL spectra of Ca\text{Nb}_2O\text{O}_6:Er\textsuperscript{3+}/Yb\textsuperscript{3+} obtained by excitation at 257 nm (C.T.B.) and direct excitation at 377 nm (the transition \(^4\text{I}_{15/2} \rightarrow ^4\text{G}_{11/2}\) of Er\textsuperscript{3+}) were almost similar to those shown in Figs. 6 and 8, respectively. In both cases the PL intensity decreased gradually as Yb\textsuperscript{3+} concentration increased.

The materials synthesized hydrothermally include substantial amount of OH\textsuperscript{-} species in their structures, in general. The removal of impurities in the phosphor materials that may act as luminescent quenchers is important to improve their efficiency. Especially, OH radicals are very efficient quenchers of Er\textsuperscript{3+} up-conversion luminescence. The measurement of FTIR spectra was done for the samples. Figure 9 shows the FTIR spectra. The presences of large band corresponding to the stretching mode region of \(\text{H}_2\text{O}\) molecule and OH group at around 3429 cm\textsuperscript{-1} and the bending mode region of \(\text{H}_2\text{O}\) molecule at around 1636 cm\textsuperscript{-1} are detected in the as-prepared sample. Although the up-conversion luminescence was recorded under excitation of a 980 nm laser for the as-prepared Ca\text{Nb}_2O\text{O}_6:Er\textsuperscript{3+}/Yb\textsuperscript{3+} samples, the up-conversion spectra was hardly detected, which is due to the existence of OH\textsuperscript{-} species as impurities included in the as-prepared samples.
3.2 PL and up-conversion luminescence properties of CaNb$_2$O$_6$:Er$^{3+}$/Yb$^{3+}$

The PL and up-conversion luminescence properties of the columbite-type CaNb$_2$O$_6$:Er$^{3+}$/Yb$^{3+}$ were investigated using the samples after heating in air. The XRD patterns of CaNb$_2$O$_6$ co-doped with $5 \text{ mol}\% \text{ Er}^{3+}$ and various concentrations of $\text{Yb}^{3+}$ after heating at $1300 \degree C$ for $1 \text{ h}$ in air are shown in Fig. 10. The crystalline phases in the samples before and after heating in air were hardly changed in those samples doped with less than $10 \text{ mol}\% \text{ Yb}^{3+}$. Figure 11 shows a SEM image of the microstructure for the sample after heating at $1300 \degree C$ for $1 \text{ h}$. The morphology of the acicular columbite-type particles changed into the aggregation of fine particles after heating in air. Almost a single phase of columbite-type was observed in those samples though an appearance of very small amount of $\text{YbNbO}_4$ phase in addition to a main columbite phase was detected in the samples doped with more than $20 \text{ mol}\% \text{ Yb}^{3+}$. This heating was done to diminish the presence of absorbed species, e.g., $\text{OH}^-$ or defects that act as very efficient quenchers in the excited states because up-conversion luminescence is very sensitive to nonradiative processes.

The excitation spectra of CaNb$_2$O$_6$:Er$^{3+}$/Yb$^{3+}$ samples containing $5 \text{ mol}\% \text{ Er}^{3+}$ and various concentrations of sensitizer $\text{Yb}^{3+}$ that were obtained by monitoring the emission at $553 \text{ nm}$ are shown in Fig. 12. The intensity of excitation spectra consisting of a large broad absorption band (C.T.B.) at around $260 \text{ nm}$ and several sharp absorption bands correspond to the $f-f$ transitions of $\text{Er}^{3+}$ fairly increased after heating in air.

The PL spectra of CaNb$_2$O$_6$:Er$^{3+}$/Yb$^{3+}$ samples, which contain $5 \text{ mol}\% \text{ Er}^{3+}$ and various concentrations of sensitizer $\text{Yb}^{3+}$, obtained by excitation at $257$ and $377 \text{ nm}$ are shown in Figs. 13 and 14, respectively. On exciting at $257 \text{ nm}$ corresponding to the C.T.B. by indirect excitation,
larger PL spectra than those obtained before heating in air are observed. The spectra are composed of both a large broad band around 400 to 600 nm that are originated from the host lattice and sharp green emission bands corresponding to the $f$-$f$ transitions of Er$^{3+}$ at around 520–530 nm and 540–560 nm. The PL intensity decreased as the concentration of Yb$^{3+}$ increased. As shown in Fig. 14, the intensities of the green PL ($^2H_{11/2} \rightarrow ^4I_{15/2}$ and $^2S_{3/2} \rightarrow ^4I_{15/2}$) obtained by direct excitation at 377 nm were also improved after heating at 1300 °C in air. When exciting directly at 377 nm, the PL intensity of the sample ($y = 0$ in Fig. 14) doped with 5 mol% Er$^{3+}$ after heating was more than 10 times stronger than that ($x = 0.05$ in Fig. 8) before heating.
The concentration quenching of Yb$^{3+}$ ions is observed when the material CaNb$_2$O$_6$:Er$^{3+}$/Yb$^{3+}$ contains more than 20 mol % Yb$^{3+}$ at the concentration of 5 mol % Er$^{3+}$. A small amount of Yb which was added into columbite-type CaNb$_2$O$_6$ was precipitated as second phase, YbNbO$_4$ out of a main columbite phase in the sample, $y = 0.20$ (Fig. 10). The precipitation of YbNbO$_4$ second phase suggests that the incorporation of more than 20 mol % Yb$^{3+}$ is inefficient for the role of ET for up-conversion in comparison with the ideal case that all of the Yb$^{3+}$ ions are present in the same sites as Er$^{3+}$ ions in the columbite structure. In the heavily doped case such as the 35 mol % Yb$^{3+}$, the up-conversion luminescence has been found to be quenched significant. The balance between the ET and its backward process may be achieved in the sample incorporated with 20 mol % Yb$^{3+}$.

The pathways corresponding to the excitation, ET and subsequent emission for the case of up-conversion emission excited at 980 nm are also indicated schematically in Fig. 7. The dominant procedure of up-conversion luminescence can be described as follows. In the Er$^{3+}$-Yb$^{3+}$ co-doped system energy-transfer up-conversion occurs when a ytterbium ion is excited from the ground state ($^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$) by a 980 nm photon, and undergoes nonradiative decay via the transfer of energy of its excited state to a neighboring erbium ion within the lattice, i.e., via the cross relaxation mechanism $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$ (Yb$^{3+}$): $^{4}I_{15/2} \rightarrow ^{4}I_{11/2}$ (Er$^{3+}$). In addition to this cross relaxation, a second cross relaxation from Yb$^{3+}$ to a previously excited Er$^{3+}$ ion leads to the excitation of the Er$^{3+}$ ion to the upper levels via a new transfer process $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$ (Yb$^{3+}$) $^{2}I_{11/2} \rightarrow ^{2}F_{7/2}$ (Er$^{3+}$). The electrons of Er$^{3+}$ are excited to the $^{4}I_{11/2}$ level and then to the $^{4}F_{7/2}$ level. Not only Yb$^{3+}$ but also Er$^{3+}$ ions are affected when the excitation is tuned at 980 nm. Therefore, additional up-conversion mechanisms, i.e., the occurrence of direct Er$^{3+}$ excited state absorption ($^{4}I_{15/2} \rightarrow ^{4}I_{11/2} \rightarrow ^{4}F_{7/2}$) can take place.$^{28}$ The absorption cross section of the $^{2}F_{7/2} \rightarrow ^{2}F_{5/2}$ transition of Yb$^{3+}$ is very larger than that of the $^{4}I_{15/2} \rightarrow ^{4}I_{11/2}$ transition of Er$^{3+}$. Therefore, most of the excitation energy is absorbed by the Yb$^{3+}$. Through nonradiative processes, the excited electrons decay to the luminescent levels $^{2}H_{11/2}$, $^{2}S_{5/2}$. Then, the green emissions (around 520–530 and 540–560 nm, respectively) are given rise to via the transitions from $^{2}H_{11/2}$ and $^{2}S_{5/2}$ to the ground state $^{4}I_{15/2}$. Meanwhile, Er$^{3+}$ ions excited on the $^{4}I_{11/2}$ can nonradiatively relax to its lower level, $^{4}I_{13/2}$. Thereafter, the red emitting energy level of $^{4}F_{9/2}$ can be populated by the ET process, $^{2}F_{5/2}$ (Yb$^{3+}$) $^{4}I_{13/2}$ (Er$^{3+}$) $^{4}F_{7/2}$ (Yb$^{3+}$) $^{4}F_{9/2}$ (Er$^{3+}$). Additionally, $^{4}F_{9/2}$ energy level can also be populated by the nonradiative multi-phonon relaxation came on the heels of the process, $^{2}F_{5/2}$ (Yb$^{3+}$) $^{4}I_{11/2}$ (Er$^{3+}$) $^{4}F_{7/2}$ (Yb$^{3+}$) $^{4}F_{9/2}$ (Er$^{3+}$), in general. By the transition from $^{4}F_{9/2}$ to $^{4}I_{13/2}$, the red emission (around 660–670 nm) also arises. Although the red emission gives rise to as mentioned above in the up-conversion process, the initial $^{4}F_{9/2}$ state responsible for the red emission is not populated in the PL because all of the excited electrons in the luminescent levels, $^{2}H_{11/2}$ and $^{2}S_{5/2}$ return back to its ground state with emitting green light. These results suggest that the initial $^{4}F_{9/2}$ state for the red emission occurs not via $^{2}H_{11/2}$, $^{2}S_{5/2}$ levels, but via the up-conversion process, i.e., the ET process, $^{2}F_{3/2}$ (Yb$^{3+}$) $^{4}I_{13/2}$ (Er$^{3+}$) $^{4}F_{7/2}$ (Yb$^{3+}$) $^{4}F_{9/2}$ (Er$^{3+}$) in this material system.

The color chromaticity coordinates $x$ and $y$ of the PL and up-conversion emission spectra for CaNb$_2$O$_6$:Er$^{3+}$/Yb$^{3+}$ samples after heating at 1300 °C that contain 5 mol % Er$^{3+}$ and 20 mol % sensitizer Yb$^{3+}$ are plotted in the CIE chromaticity diagram of Fig. 17. When the samples are excited indirectly at 257 nm by the charge-transfer absorption corresponding to the band gap energy of the host crystal, their emission colors fall in the light blue region due to the broadband emission centered around 450
nm from the host CaNb$_2$O$_6$ crystal. On excitation with light at 377 and 980 nm, the color chromaticity coordinates of the PL and up-conversion emission were shifted in the green region.

4. Summary

Columbite-type CaNb$_2$O$_6$ fine crystals doped with Er$^{3+}$ and co-doped with Er$^{3+}$ and Yb$^{3+}$ were synthesized hydrothermally as aligned acicular particles (width: 0.1–0.3 μm, length 5–10 μm) under weakly basic conditions at 240 °C. When exciting at 377 nm, the as-prepared columbite-type CaNb$_2$O$_6$:Er$^{3+}$ showed PL in the characteristic green spectral regions corresponding to the $^4I_{15/2} \rightarrow ^4I_{11/2}$ and $^4S_{3/2} \rightarrow ^4I_{15/2}$ transitions of Er$^{3+}$, and the emission intensity reached a maximum value at Er atomic ratio $x = 0.03$. The intensities of the PL and up-conversion luminescence were improved by heating the samples in air, which is mainly due to the removal of OH$^-$ species as impurities included in the as-prepared samples. The up-conversion emission intensity for the material co-doped with Er$^{3+}$/Yb$^{3+}$ became more than 100-times higher than that of CaNb$_2$O$_6$:Er$^{3+}$ doped without sensitizer Yb$^{3+}$. At the concentration of 5 mol% Er$^{3+}$, the material CaNb$_2$O$_6$:Er$^{3+}$/Yb$^{3+}$ that contained 20 mol% Yb$^{3+}$ showed the highest up-conversion emission intensity.

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