

Formation and characterization of luminescent nanocrystalline solid solutions based on YNbO_4 through hydrothermal route

* Masanori Hirano¹⁾ and Hayato Dozono²⁾

^{1), 2)} Department of Applied Chemistry, Aichi Institute of Technology, Toyota 470-0392, Japan

¹⁾ hirano@aitech.ac.jp

ABSTRACT

Nanocrystalline solid solutions based on YNbO_4 having luminescence properties were synthesized through mild hydrothermal route. The solid solution particle had a distinguishing feature of ellipsoidal morphology. The photoluminescence of the nanocrystalline solid solutions showed the predominant green emission corresponding to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition and the other emission peaks, $^5\text{D}_4 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_4$ transitions (Tb^{3+}) under excitation at 240 nm. The solid solution with composition of $\text{Y}_{0.90}\text{Tb}_{0.10}\text{NbO}_4$ showed the highest luminescence intensity. A dominant red emission at 610 nm and a weak orange emission at 590 nm assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transitions of Eu^{3+} , respectively were observed in the samples containing europium under excitation at 395 nm. The luminescence intensity of the as-prepared solid solution was improved by heat treatment at temperatures more than 1000 °C in air.

1. INTRODUCTION

Rare earth compounds have been used in many fields of application such as optical, magnetic, catalytic, electrical, structural, and chemical fields due to their excellent properties. An intermediate compound, YNbO_4 which has fergusonite-related crystal structure with a monoclinic phase at room temperature exists in the $\text{Y}_2\text{O}_3\text{-Nb}_2\text{O}_5$ system. The pure YNbO_4 shows a broad-band emission at 400 nm under excitation at 260 nm (Buth 1981), and it has been investigated for the application as luminescent materials by doping rare earth ions. Many preparation techniques of niobates, $\text{LnNbO}_4\text{: Re}$ (Re= rare earth ions) such as co-precipitation (Xiao 2006), solid state reaction (Massabni 1998), and flux method (Nazarov 2010) have been reported. In recent years, much attention has been devoted to the low-temperature synthesis of nanocrystalline inorganic materials. The hydrothermal route, which is one of building up processes from aqueous precursor solution at low temperatures, is superior to other techniques in terms of ecological and economical view point. It is well known that the direct synthesis

¹⁾ Professor

²⁾ Graduate Student

of crystalline inorganic materials is achieved at lower temperature through hydrothermal route in comparison with the solid-state reaction. The luminescent nanocrystalline solid solutions based on YNbO_4 have been formed through hydrothermal route. (Hirano 2014)

In the article, the compositional dependence of the formation, structure, and luminescence properties of nanocrystalline solid solutions based on YNbO_4 has been reviewed.

2. EXPERIMENTAL PRECEDURE

An aqueous solution of reagent-grade $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, and ethanol solution of NbCl_5 in different ratios of Y/Tb/Nb (that was controlled to be the composition: $\text{Y}_{1-x}\text{Tb}_x\text{NbO}_4$, $x=0\sim 1.0$) were mixed in a Teflon container. On the other hand, in a Teflon container, a mixture of an aqueous solution of reagent-grade $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, and ethanol solution of NbCl_5 in different ratios of Y/Eu/Nb (that was controlled to be the composition: $\text{Y}_{1-x}\text{Eu}_x\text{NbO}_4$, $x=0\sim 1.0$) was also prepared. The solution mixture added with aqueous ammonia was controlled to have a weak basic condition after hydrothermal treatment. This solution mixture with total cation concentrations of 0.2 mol/dm^3 in the Teflon container was then placed in a stainless-steel vessel. After the vessel was tightly sealed, it was heated at $240 \text{ }^\circ\text{C}$ for 5 h under rotation 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 $60 \text{ }^\circ\text{C}$. The powders thus prepared were heated in an alumina crucible at $600\sim 1300 \text{ }^\circ\text{C}$ for 1 h in air.

The crystalline phases of the as-prepared and heat-treated powders were examined by X-ray diffractometry (XRD; RINT-2000, Rigaku, Japan) using $\text{CuK}\alpha$ radiation. The crystallite size of monoclinic phase was calculated from the line broadening of -121 and 121 diffraction peaks, according to the Scherrer equation. The lattice parameters were measured using silicon as the internal standard. The morphology of the as-prepared and heat-treated samples was observed using transmission electron microscopy (TEM; model JEM-2010, JEOL, Tokyo, Japan). The optical absorption of these prepared powders was measured using an ultraviolet-visible spectrophotometer (V-560, Nihon Bunko, Japan). The photoluminescence (PL) emission and excitation spectra of samples were measured using a spectrofluorometer (F-2700, Hitachi High-Tech, Japan) with Xe lamp. Powder samples were excited with 240 or 395 nm radiation from a 150 W Xe lamp.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Nanocrystalline Solid Solutions

The crystallization of monoclinic phase corresponding to the fergusonite structure was observed in the samples obtained at temperatures higher than $180 \text{ }^\circ\text{C}$. The precipitates formed in the composition range of $x=0\sim 1.0$ in both systems, YNbO_4 - TbNbO_4 and YNbO_4 - EuNbO_4 were all detected as a single phase corresponding to monoclinic fergusonite structure, and no diffraction peaks due to another crystalline phases was detected as shown in the XRD patterns of precipitates with various

compositions: $x=0\sim 1.0$ formed at 240 °C (Fig. 1 (a) and (b)). The crystallite sizes of the monoclinic (Y, Tb)NbO₄ and (Y, Eu)NbO₄ phases were in the range of 10~20 nm. The particles observed in the TEM images had distinctive ellipsoidal or spindle-like morphology and those are considered to be single crystals since the particle sizes observed in the TEM relatively well corresponded to the crystallite sizes estimated from the XRD line broadening.

The lattice parameters of the as-prepared samples estimated as a monoclinic structure plotted as a function of the value x roughly corresponded to the Vegard's Law. These results suggest the formation of composite nanostructure, i.e. solid solution nanoparticles in the overall composition range in the YNbO₄-TbNbO₄ and YNbO₄-EuNbO₄ systems under hydrothermal conditions.

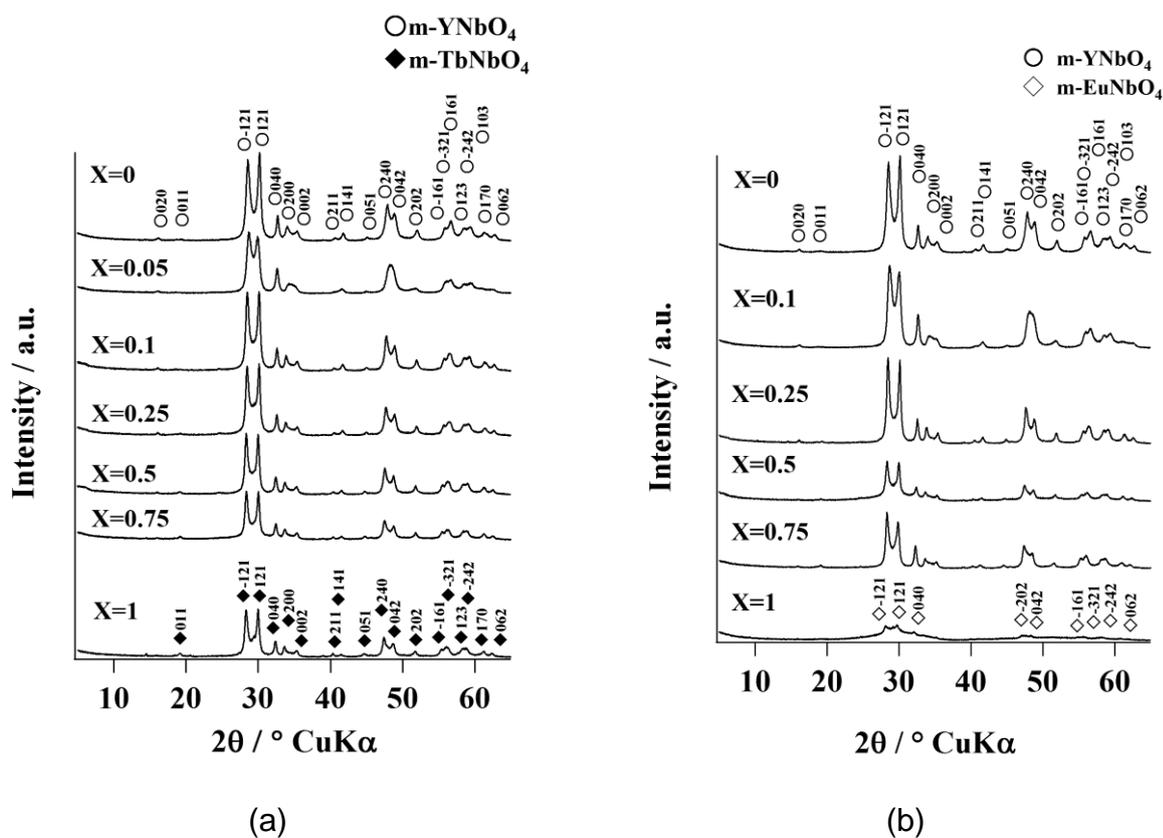


Fig. 1 X-ray diffraction patterns of precipitates obtained at various compositions of $x=0\sim 1.0$ in (a) Y_{1-x}Tb_xNbO₄ and (b) Y_{1-x}Eu_xNbO₄ under hydrothermal conditions at 240 °C for 5 h.

3.2 Optical Properties of Nanocrystalline Solid Solutions

The optical properties of as-prepared solid solutions were investigated. The absorption edge observed in the diffuse reflectance spectra of the samples changed according to their compositions. The photoluminescence spectra of the as-prepared solid solutions in the YNbO₄-TbNbO₄ system measured under excitation at 240 nm and in the YNbO₄-EuNbO₄ system measured under excitation at 395 nm are shown in Fig.

2 (a) and (b), respectively. A broad band in the short wavelength region centered at 400 nm corresponding to the niobate group $[\text{NbO}_4]^{3-}$ (recombination luminescence) in the pure YNbO_4 and the narrow emission bands corresponding to $4f \rightarrow 4f$ transitions within Tb^{3+} ions are observed in Fig. 2 (a). The sample with composition $x=0.10$, i.e. $\text{Y}_{0.90}\text{Tb}_{0.10}\text{NbO}_4$ solid solution showed the highest intensity of photoluminescence. On the other hand, the major emission bands which are orange and red luminescence with peaks at 590 and 610 nm corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transitions of Eu^{3+} , respectively were observed in the $\text{YNbO}_4\text{-EuNbO}_4$ system as shown in Fig. 2 (b). The luminescence intensity reached a maximum value at $x=0.25$, and then decreased with the increase of Eu concentration.

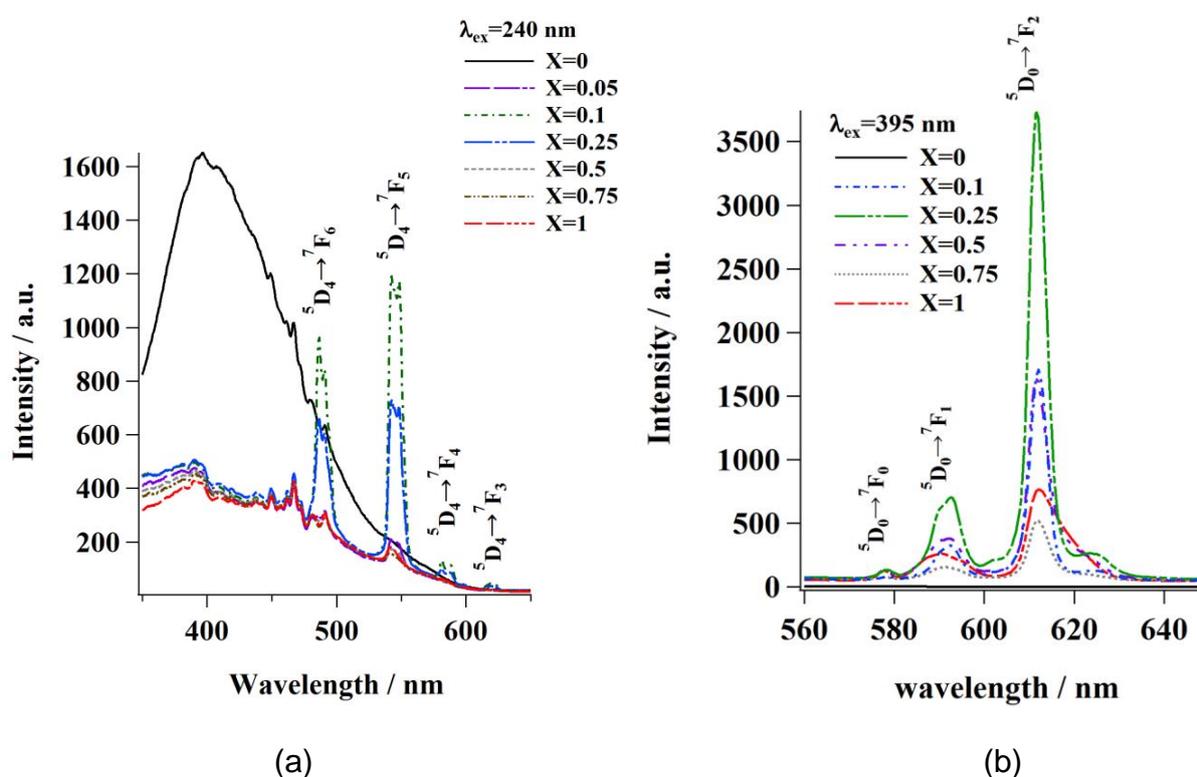


Fig. 2 Emission spectra for the as-prepared samples (a) $\text{Y}_{1-x}\text{Tb}_x\text{NbO}_4$ measured under excitation at 240 nm and (b) $\text{Y}_{1-x}\text{Eu}_x\text{NbO}_4$ measured under excitation at 395 nm.

3.2 Effect of Heat Treatment on Luminescence Properties

The as-prepared monoclinic solid solutions were heat treated at various temperatures in air. The XRD patterns showed that the crystalline phases of the solid solutions after heat treated at high temperatures were almost the same as those before the heat treatment. The crystallinity of the monoclinic phase in the solid solutions was pretty improved after the reversible monoclinic \rightleftharpoons tetragonal phase transition via heat treatment. The emission spectra of the samples: $\text{YNbO}_4:\text{Tb}^{3+}$ (solid solution $x=0.10$) and $\text{YNbO}_4:\text{Eu}^{3+}$ (solid solution $x=0.25$), before and after heat treatment at various

temperatures are shown in Fig. 3 (a) and (b), respectively. The heat treatment through the phase transformation (monoclinic \leftrightarrow tetragonal) at temperatures more than 1000 °C was pretty effective for the improvement in the photoluminescence intensity of the as-prepared solid solutions, which may be mainly due to the enhancement in the crystallinity and crystallite growth of the monoclinic phase. The strongest green and red emissions have been obtained via heat treatment at 1300 °C.

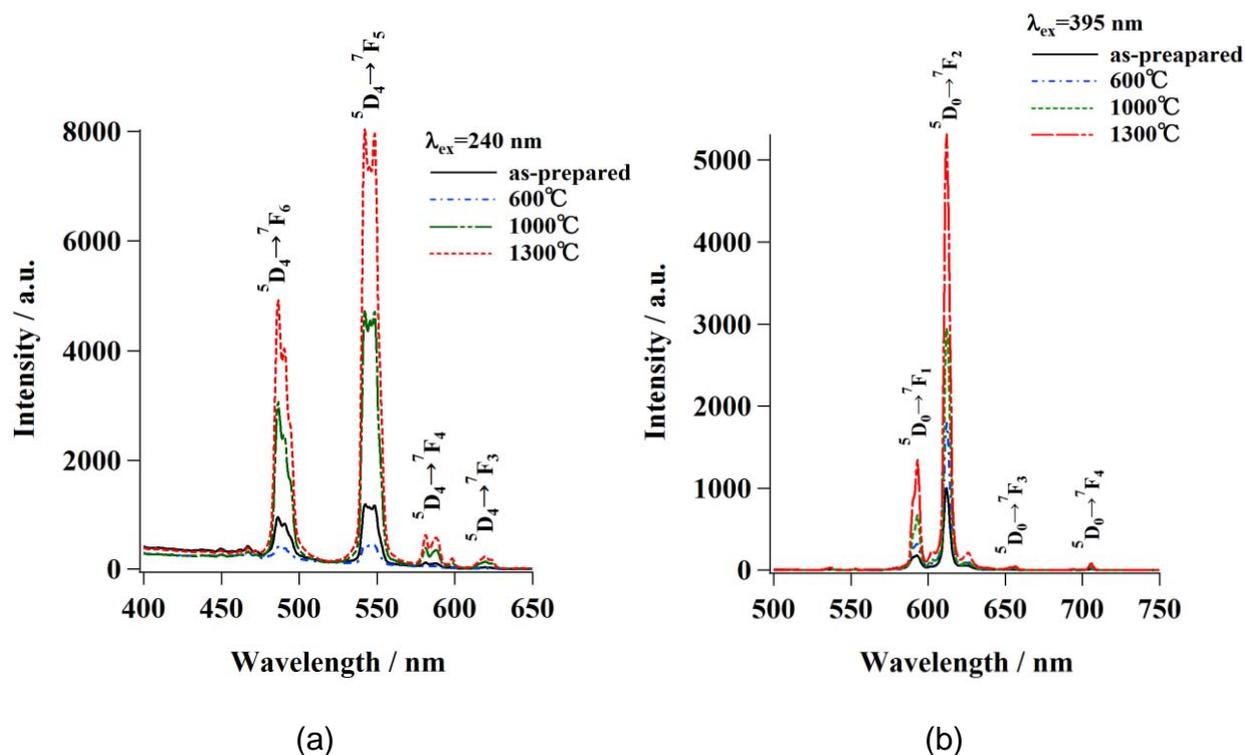


Fig. 3 Emission spectra for samples as-prepared and after heated at various temperatures for 1 h: (a) $Y_{0.9}Tb_{0.1}NbO_4$ measured under excitation at 240 nm and (b) $Y_{0.75}Eu_{0.25}NbO_4$ measured under excitation at 395 nm.

4. CONCLUSIONS

Luminescent solid solutions having monoclinic fergusonite structure in the $YNbO_4$ - $TbNbO_4$ and $YNbO_4$ - $EuNbO_4$ systems were directly formed as nanocrystalline particles from the precursor solutions of inorganic salts under mild hydrothermal conditions at 240 °C. The photoluminescence of the solid solutions $YNbO_4: Tb^{3+}$ showed the predominant green emission corresponding to the $^5D_4 \rightarrow ^7F_5$ transition and the other emission peaks, $^5D_4 \rightarrow ^7F_6$ and $^5D_4 \rightarrow ^7F_4$ transitions (Tb^{3+}) under excitation at 240 nm. The photoluminescence of the solid solutions $YNbO_4: Eu^{3+}$ was composed of strong red luminescence with main emission band at 610 nm corresponding to $^5D_0 \rightarrow ^7F_2$ transition of Eu^{3+} and small orange luminescence with band at 590 nm ($^5D_0 \rightarrow ^7F_1$ transition of Eu^{3+}) under excitation at 395 nm. The heat treatment through the phase transformation

(monoclinic ↔ tetragonal) at temperatures more than 1000 °C was pretty effective for the improvement in the photoluminescence intensity of the as-prepared solid solutions.

REFERENCES

- Buth, A.H. and Blasse, G. (1981), "Luminescence and energy transfer in yttrium niobate (YNbO₄)," *Phys. Stat. Sol. (a)*, **64** (2), 669-676.
- Hirano, M. and Dozono, H. (2014), "Synthesis of luminescent nanocrystals and solid solutions in the YNbO₄ - EuNbO₄ system via hydrothermal route," *Mater. Res. Bull.*, **50**, 213-220.
- Hirano, M. and Dozono, H. (2014), "Hydrothermal formation and characteristics of rare-earth niobate phosphors and solid solutions between YNbO₄ and TbNbO₄," *Mater. Chem. Phys.*, **143** (2), 860-866.
- Massabni, A.M.G., Montandon, G.J.M. and Santos, M.A.C. (1998) "Synthesis and luminescence spectroscopy of YNbO₄ doped with Eu(III)," *Mater. Res.*, **1** (1), 1-4.
- Nazarov, M., Kim, Y.J., Lee, E.Y., Min, K.I., Jeong, M.S., Lee, S.W. and Noh, D.Y. (2010) "Luminescence and Raman studies of YNbO₄ phosphors doped by Eu³⁺, Ga³⁺, and Al³⁺," *J. Apply. Phys.*, **107** 103104-103106.
- Xiao, X. and Yan, B. (2006) "Hybrid precursors synthesis and optical properties of LnNbO₄:Bi³⁺ blue phosphors and Bi³⁺ sensitizing of on Dy³⁺'s luminescence in YNbO₄ matrix," *J. Alloy. Comp.*, **421** (1-2), 252-257.