Preparation and characteristics of YTiTaO$_6$ and YTiTaO$_6$:Er$^{3+}$/Yb$^{3+}$: Synthesis, aeschynite phase, and photoluminescence of YTiTaO$_6$

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Aeschynite-type fine crystals of YTiTaO$_6$ and Er$^{3+}$- and Yb$^{3+}$-co-doped YTiTaO$_6$ (YTiTaO$_6$:Er$^{3+}$/Yb$^{3+}$) were synthesized for the first time using hydrothermal method at 240°C. The effects of Yb$^{3+}$ and Er$^{3+}$ concentrations and heating temperature in air on their crystalline phases were investigated. The images of transmission electron microscope (TEM) and energy dispersive X-ray spectrometry (EDS) elemental mapping showed that their metal cations were dispersed homogeneously in the cube-like crystals in the range of 200–300 nm. A single phase of aeschynite appeared in all of the as-prepared YTiTaO$_6$ and YTiTaO$_6$:Er$^{3+}$/Yb$^{3+}$ samples synthesized hydrothermally at 240°C and samples after heating at 1100 and 1200°C in air although YTiTaO$_6$ is known to possess euxenite-type structure. The lattice constants of the orthorhombic aeschynite phase decreased slightly according to the Vegard’s law as the concentration of Yb$^{3+}$ was increased from $y = 0$ to 0.30 in the Er$_{0.10}$Yb$_{0.90}$-YTiTaO$_6$ system. Under excitation at 270 nm the pure YTiTaO$_6$ showed light blue green and broadband photoluminescence centered at 520 nm. The aeschynite-to-euxenite phase transition occurred completely in the whole Yb$^{3+}$ concentration range, $y = 0$–0.30 in Er$_{0.10}$Yb$_{0.90}$-YTiTaO$_6$ and pure YTiTaO$_6$ as a consequence of heating at 1400°C for 1 h in air.

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1. Introduction

Inorganic compounds based on metal complex oxides MTiM'O$_6$ (M = trivalent cations; M' = pentavalent cations) in the M$_2$O$_7$-2TiO$_2$-M'$_2$O$_5$ system possess unique and potential properties. In particular, some of complex oxides RETiM'O$_6$, where RE is a rare earth and M' is Nb or Ta, have useful properties in the fields of solid-state laser materials, dielectric materials, and phosphors. The crystalline phase of RETiM'O$_6$ is known to possess mainly two types of orthorhombic structures and the change in the structure from an euxenite- to an aeschynite-phase occurs as the cell volume increases.

The hydrothermal synthesis technique is useful for the direct synthesis of nanocrystalline inorganic materials based on metal complex oxides, on the other hand. This wet chemical synthesis route is especially advantageous to gain homogeneous dispersion of numbers of dopant cations in multi-component systems. An investigation on the Stokes fluorescence of euxenite-type YTiTaO$_6$ doped with Er$^{3+}$ that was synthesized using conventional solid-state reaction was reported. However, no study has been done on the formation of pure YTiTaO$_6$ and YTiTaO$_6$-based materials using hydrothermal synthesis route. There have been no reports on the formation of Er$^{3+}$/Yb$^{3+}$-co-doped YTiTaO$_6$ (YTiTaO$_6$:Er$^{3+}$/Yb$^{3+}$). And moreover, it has not been reported on the appearance and the formation of aeschynite-type YTiTaO$_6$ up to date, because YTiTaO$_6$ is known to possess euxenite-type structure in general. The crystalline phases appeared in those RETiM'O$_6$ materials are supposed to depend on their processing conditions in addition to the ionic radius of rare-earth dopant, RE and M', but the information on their properties and structures is limited.

In the present study, new aeschynite-type and cube-like crystals of YTiTaO$_6$ and YTiTaO$_6$:Er$^{3+}$/Yb$^{3+}$ in the range of 200–300 nm have been synthesized directly using hydrothermal method. Their aeschynite phase has been proved to be stable up to at least 1200–1250°C in air. Their aeschynite-to-euxenite phase transitions and the PL property of YTiTaO$_6$ have been investigated.

2. Experimental

2.1 Sample preparation

Transition-metal complex oxides, YTiTaO$_6$ and Er$_x$Yb$_{1-x}$TiTaO$_6$ were synthesized at 240°C by means of hydrothermal method. The reagent-grade ErCl$_3$·6H$_2$O, Yb(NO$_3$)$_3$·3H$_2$O, YCl$_3$·6H$_2$O, TiOSO$_4$ and TaCl$_5$ were used as starting raw materials. A solution mixture of

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aqueous solutions of their raw materials and an ethanol solution of TaCl_5 in a ratio of Y/Ti/Ta = 1.00/1.00/1.00 or in different ratios of Er/Yb/Y/Ti/Ta = x/y/1.00 – (x + y)/1.00/1.00, x = 0.10 and 0.20, y = 0–0.30 was prepared in a Teflon container. The solution mixture was controlled to have a weak basic condition by the addition of aqueous ammonia while stirring. This precursor 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 24 h while rotating at 1.5 rpm. After the hydrothermal treatment, precipitates formed in the Teflon container were washed with distilled water, separated from the solution by centrifugation, and dried in an oven at 60 °C. The powders thus prepared hydrothermally were heated in an alumina crucible at a heating rate 200 °C/h, kept at 1100–1400 °C for 1 h in air, and then cooled to room temperature in a furnace.

### 2.2 Characterization

The X-ray diffraction (XRD) patterns of the as-prepared powders and samples after heating were recorded using Cu Kα radiation (XRD: RINT-2000, Rigaku, Tokyo, Japan). The lattice parameters of the aeschynite phase were measured using silicon as the internal standard. The microstructures of the samples were characterized using transmission electron microscope (TEM) (JEM-2100Plus, JEOL, Tokyo, Japan) equipped with X-ray spectrometry (EDS).

The measurements of the ultraviolet–visible (UV–Vis) absorption spectra of prepared powders were performed using UV–Vis spectrophotometer with an integrating sphere attachment (V-560, Nihon Bunko, Tokyo, Japan). A spectrofluorometer (FP-8500, Nihon Bunko, Tokyo, Japan) with a xenon lamp was used for recording the PL and excitation spectra of samples. The YTiTaO_6 samples were excited with 270 nm radiation from a 150 W xenon lamp. All measurements were carried out at room temperature. The emission wavelength was scanned from 300 to 750 nm at a scanning rate of 60 nm/min. For the measurements of the excitation spectra, the excitation wavelength was scanned from 220 to 500 nm at the same scanning rate, and emission monitored at 525 nm for YTiTaO_6.

### 3. Results and discussion

#### 3.1 Hydrothermal crystallization of YTiTaO_6 and YTiTaO_6:Er^{3+}/Yb^{2+}

The effect of hydrothermal treatment temperature on the crystallization and crystallinity of solid products obtained from the precursor solution mixture (composition: YTiTaO_6) has been investigated. The hydrothermal treatment was conducted under weakly basic conditions at 150–240 °C for 24 h. Figure 1 shows XRD patterns of precipitates obtained under hydrothermal conditions at various temperatures. A broad peak with low intensity around 2θ = 30° suggests that the solid precipitate obtained at 150 °C is amorphous. The appearance of many sharp diffraction lines in the broad peak corresponding to the amorphous phase around 2θ = 30°, that is, the crystallization of an aeschynite-type phase is observed in the XRD pattern of the precipitate formed at 180 °C. The XRD data and calculated data based on the Rietveld analysis for as-prepared YTiTaO_6 sample obtained at 240 °C are shown in Fig. 2. The precipitate synthesized at 240 °C was detected to be a single phase of aeschynite-type YTiTaO_6 structure (Pnma space group). The crystalline phase of YTiTaO_6 prepared using the conventional solid-state reaction of the mixture of 1/2Y_2O_3, TiO_2, and 1/2Ta_2O_5, for example, by heating at high temperature around 1400–1500 °C for 10 h in air was reported to be orthorhombic euxenite-type with Pnma space group. The crystal structure of YTiTaO_6 formed by polymerizable complex method and heat-treatment at 1200 °C for 5 h was also reported to be euxenite-type. The appearance of the aeschynite-type phase with Pnma space group in YTiTaO_6 is interesting and has not been reported. Since the stable phase in YTiTaO_6 at room temperature and under normal pressure must be euxenite, the aeschynite-type phase appeared hydrothermally in the as-prepared YTiTaO_6 sample is suggested to be metastable one.
The hydrothermal synthesis of YTiTaO$_6$-based crystals co-doped with Er$^{3+}$ and Yb$^{3+}$ was also carried out under weakly basic conditions at 240 °C. The effect of the concentrations of Er$^{3+}$ and Yb$^{3+}$ on the crystalline phase of precipitates has been investigated in the Er$_x$Yb$_y$Y$_{1-x-y}$TiTaO$_6$ system. Figures 3 and 4 show XRD patterns of precipitates synthesized from the precursor solution mixtures with various concentrations of Yb$^{3+}$ ($y = 0.0$–$0.30$) and different Er$^{3+}$, $x = 0.10$ and $x = 0.20$, respectively. In both cases of $x = 0.10$ and $x = 0.20$, the precipitates, Er$_x$Yb$_y$Y$_{1-x-y}$TiTaO$_6$ in the whole Yb$^{3+}$ concentration range were detected as a single phase corresponding to orthorhombic aeschynite-type structure (pmma space group).

The TEM images of the precipitates, Er$_x$Yb$_y$Y$_{1-x-y}$TiTaO$_6$, with compositions $(x, y) = (0.20, 0)$ and $(0.20, 0.05)$ are shown in Figs. 5(a) and 5(b), respectively. The particles that were grown hydrothermally are observed to be cube or rectangular-like characteristic morphology in the range of 200–300 nm in the TEM images. Figure 6 shows the TEM-EDS mapping for the as-prepared Er$_{0.20}$Yb$_{0.10}$Y$_{0.70}$TiTaO$_6$ crystallized hydrothermally at 240 °C. The elemental mapping images of Er, Y, Yb, Ti, and Ta show the evidence that the rare earth ions, i.e., Er$^{3+}$, Y$^{3+}$, and Yb$^{3+}$ and the other metal cations are homogeneously and very well dispersed in the crystals synthesized directly by the hydrothermal method at 240 °C.

In the XRD patterns of the precipitates corresponding to Figs. 3 and 4, a slight and gradual shift of XRD lines into higher $2\theta$ values in accordance with the increase in Yb$^{3+}$ concentration was observed, which suggests a slight decrease in lattice parameters of orthorhombic aeschynite-type samples. Figure 7 indicates the lattice parameters of the as-prepared Er$_x$Yb$_y$Y$_{1-x-y}$TiTaO$_6$ that were calculated as an orthorhombic aeschynite structure and were plotted against the value $y$, the ytterbium atomic ratio. The slight and gradual declining trend in lattice parameters of the orthorhombic aeschynite phase according to the Vegard’s law can be observed as the concentration of ytterbium is increased from 0 to 30 mol %, because Yb$^{3+}$ (0.0985 nm) has a smaller ionic radius than Y$^{3+}$ (0.1019 nm).29)

### 3.2 Phase stability of YTiTaO$_6$ and YTiTaO$_6$: Er$^{3+}$/Yb$^{3+}$

The effect of heating in air on the crystalline phase of the as-prepared aeschynite-type YTiTaO$_6$ and Er$_x$Yb$_{1-x}$Y$_{1-x-y}$TiTaO$_6$ has been investigated. The XRD patterns...
of YTiTaO$_6$ samples after heating at various temperatures in air are shown in Fig. 8. The as-prepared sample and samples after heating at 1100 and 1200 °C are detected as orthorhombic aeschynite-type structure. The aeschynite-type phase of YTiTaO$_6$ synthesized hydrothermally was maintained up to 1200 °C. In the sample after heating at 1300 °C, the appearance of the euxenite phase caused by the aeschynite-to-euxenite phase transition is observed in addition to the residual aeschynite phase. Since a single phase of euxenite is observed in the sample after heating at 1400 °C, the aeschynite-to-euxenite phase transition in YTiTaO$_6$ is completed by heating at 1400 °C for 1 h.

Figure 9 shows the XRD patterns after heating at 1400 °C for 1 h in air for the samples Er$_x$Yb$_y$Y$_{1-(x+y)}$TiTaO$_6$, x = 0.10 and y = 0–0.30 that were synthesized hydrothermally at 240 °C for 24 h. The as-prepared aeschynite-type phase completely transformed into the euxenite structure in consequence of heating at 1400 °C in all samples. In Fig. 10, the crystalline phases of the samples, Er$_{0.10}$Yb$_{y}$-
less than 1250 °C, the appearance of the euxenite phase was not observed. But heating at 1300 °C for 1 h promoted the phase transition from the aeschynite to euxenite structure, and the phase transformation was completed as a consequence of heating at 1400 °C for 1 h. The average ionic radii of rare earth ions that are constituent of Er\(^{3+}\)Yb\(^{3+}\)Y\(^{3+}\)(x+y)TiTaO\(_6\) are estimated according to the following equation:

\[ x(0.1004 \text{ nm} = \text{Er}^{3+}) + y(0.0985 \text{ nm} = \text{Yb}^{3+}) + (1 - (x + y))(0.1019 \text{ nm} = \text{Y}^{3+}) \]

Since those estimated values of ionic radii of rare earth ions are smaller than the ionic radius of Dy\(^{3+}\) (0.1027 nm\(^2\)), the aeschynite structure is suggested to be unstable based on the Ref. 27).

The boundary between the aeschynite and the euxenite phases was already shown in the paper about RETiTaO\(_6\),\(^4\) though the ionic radius was different from the Ref. 27). Thorogood et al.\(^{27}\) proposed on the boundary of the aeschynite to euxenite phase as follows. Where the lanthanide is larger than Dy\(^{3+}\) (0.1027 nm\(^2\)) the aeschynite structure is stabilized. The boundary of the aeschynite to euxenite phase change lies between Dy\(^{3+}\) (0.1027 nm\(^2\)), DyTiTaO\(_6\) and Ho\(^{3+}\) (0.1015 nm\(^2\)), HoTiTaO\(_6\). Since the single phase of euxenite existed in YTiTaO\(_6\) via the aeschynite-to-euxenite phase transition by heating at 1400 °C for 1 h in the present study and it appeared in YTiTaO\(_6\) synthesized via the solid state reaction at high temperatures,\(^{24,28}\) the boundary of the aeschynite to euxenite phase change is suggested to lie between Dy\(^{3+}\) (0.1027 nm\(^2\)), DyTiTaO\(_6\) and Y\(^{3+}\) (0.1019 nm\(^2\)), YTiTaO\(_6\) more precisely.

### 3.3 PL properties of YTiTaO\(_6\)

The excitation spectra and room-temperature PL spectra of YTiTaO\(_6\) samples before and after heating at various temperatures up to 1400 °C are shown in Figs. 11(a) and 11(b), respectively. The excitation spectra shown in Fig. 11(a) suggest that the material can be excited using UV light around 270 nm. Under excitation at 270 nm the pure YTiTaO\(_6\) shows light blue green and broadband emission centered around 520 nm. The intensity of PL spectra gradually increases as heating temperature in air rises up to 1400 °C. It is obvious that heating in air is effective for the improvement in the PL intensity. The YTiTaO\(_6\) material after heating at 1400 °C is composed of euxenite as shown in Fig. 8. The characteristic light blue green PL of YTiTaO\(_6\) is responsible for the recombination luminescence, associated with the \([(\text{Ta,Ti})\text{O}_6]\) polyhedron from the crystalline lattice in YTiTaO\(_6\). The PL color of the YTiTaO\(_6\) sample after heating at 1400 °C is shown in Fig. 12, which lies at light blue green region (1  ●  of the CIE-1931 chromaticity diagram. The compound YTiTaO\(_6\) with light blue green PL is suggested to be useful and a candidate for the host crystal of rare-earth ion-doped phosphor materials. The up-conversion luminescence properties of YTiTaO\(_6\):Er\(^{3+}\)/Yb\(^{3+}\) prepared hydrothermally have been investigated and discussed elsewhere.

### 4. Conclusions

Aeschynite-type pure YTiTaO\(_6\) and YTiTaO\(_6\)-based fine crystals doped with Er\(^{3+}\) and Yb\(^{3+}\) were synthesized directly using hydrothermal method. The crystallization of an aeschynite phase was observed at 180 °C. To obtain a single phase of aeschynite-type YTiTaO\(_6\) and YTiTaO\(_6\):Er\(^{3+}\)/Yb\(^{3+}\) with sufficient crystallinity a hydrothermal treatment at 240 °C was necessary. The TEM and elemental
mapping images of Er, Y, Yb, Ti, and Ta proved homogeneously dispersion of the metal elements in the cube-like crystals in the range of 200–300 nm synthesized directly using hydrothermal method. The pure YTiTaO₆ showed light blue green and broadband PL centered around 200 nm under excitation at 270 nm. The aeschynite phase shownly was maintained after heating at 1250 °C for 1 h in air. The aeschynite-type Y₁.₀₀ ±₀.₃₀Er₀.₂₀Yb₀.₈₀TiTaO₆ co-doped with 0, 10, and 20 mol % Er³⁺ and with 0–30 mol % Yb³⁺ fully transformed into euxenite-type structure caused by heating at 1400 °C for 1 h in air.

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References
1) C. H. Holcombe, J. Mater. Sci., 14, 2255–2260 (1979).
2) V. V. Kazantsev, E. I. Krylov, A. K. Borisov and A. I. Chupin, Russ. J. Inorg. Chem., 19, 506–507 (1974).
3) G. Blasse, Mater. Res. Bull., 2, 497–502 (1967).
4) K. P. Surendran, S. Solomon, M. R. Varma, P. Mohanan and M. T. Sebastian, J. Mater. Res., 17, 2561–2566 (2002).
5) R. Mani, S. N. Achary, K. R. Chakraborty, S. K. Deshpande, J. E. Joy, A. Nag, J. Gopalakrishnan and A. K. Tyagi, J. Solid State Chem., 183, 1380–1387 (2010).
6) L. Jacob, H. P. Kumar, K. G. Gopchandran, J. K. Thomas and S. Solomon, J. Mater. Sci.-Mater. El., 18, 831–835 (2007).
7) R. Mani, S. N. Achary, K. R. Chakraborty, S. K. Deshpande, J. E. Joy, A. Nag, J. Gopalakrishnan and A. K. Tyagi, Adv. Mater., 20, 1348–1352 (2008).
8) X. Qi, T. P. J. Han, H. G. Gallagher, B. Henderson, R. Illingworth and I. S. Ruddock, J. Phys.-Conden. Mat., 8, 4837–4845 (1996).
9) X. Qi, R. Illingworth, H. G. Gallagher, T. P. J. Han and B. Henderson, J. Cryst. Growth, 160, 111–118 (1996).
10) M. T. Sebastian, R. Ratheesh, H. Sreemoolananthan, S. Solomon and P. Mohanan, Mater. Res. Bull., 32, 1279–1284 (1997).
11) M. T. Sebastian, S. Solomon, R. Ratheesh, J. George and P. Mohanan, J. Am. Ceram. Soc., 84, 1487–1489 (2001).
12) S. Solomon, M. Kumar, K. P. Surendran, M. T. Sebastian and P. Mohanan, Mater. Chem. Phys., 67, 291–293 (2001).
13) D. B. Dhwajam, J. K. Thomas, K. Joy and S. Solomon, J. Mater. Sci.-Mater. El., 22, 384–388 (2011).
14) K. P. Surendran, P. Mohanan and M. T. Sebastian, J. Eur. Ceram. Soc., 23, 2489–2495 (2003).
15) Y. Lei, I. M. Reaney, Y. C. Liu, Y. S. Yin and G. H. Chen, Adv. Mat. Res., 197–198, 285–289 (2011).
16) G. Blasse, J. Inorg. Nucl. Chem., 28, 1122–1124 (1966).
17) B. V. Shul`gin, A. K. Borisov, E. I. Krylov, V. K. Sleipukhin and V. I. Rogovich, Zh. Prikl. Spektrosk., 15, 431–435 (1971).
18) Q. Ma, Y. Zhou, A. Zhang, M. Lu, G. Zhou and C. Li, Solid State Sci., 11, 1124–1130 (2009).
19) Q. Ma, M. Lu, P. Yang, A. Zhang and Y. Cao, J. Lumin., 29, 386–392 (2014).
20) M. Hirano, T. Iwata, K. Komaki, H. Iwata and K. Tanaka, J. Ceram. Soc. Jpn., 128, 875–882 (2020).
21) M. Hirano and K. Ishikawa, J. Am. Ceram. Soc., 100, 2814–2821 (2017).
22) M. Hirano and T. Okamoto, Nano Struct. Nano. Obj., 13, 139–145 (2018).
23) M. Hirano and M. Hara, J. Ceram. Soc. Jpn., 126, 178–183 (2018).
24) Y. Zhang, D. Geng, X. Li, J. Fan, K. Li, H. Lian, M. Shang and J. Lin, J. Phys. Chem. C, 118, 17983–17991 (2014).
25) M. Hirano and S. Sato, J. Am. Ceram. Soc., 99, 2607–2614 (2016).
26) M. Hirano and Y. Takagi, Mater. Res. Bull., 105, 13–20 (2018).
27) G. J. Thorogood, M. Avdeev and B. J. Kennedy, Solid State Sci., 12, 1263–1269 (2010).
28) K. Watanabe, P. Valery and M. Kakihana, Abstract of SCEJ 72nd Annual Meeting, Kyoto, Japan, B315 (2007).
29) R. D. Shannon, Acta Crystallogr. A, 32, 751–767 (1976).