Takanawaite-(Y), a new mineral of the *M*-type polymorph with Y(Ta,Nb)O₄ from Takanawa Mountain, Ehime Prefecture, Japan

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Takanawaite-(Y), a new mineral of the *M*-type polymorph with an generalized formula of Y(Ta,Nb)O₄, is identified from Takanawa Mountain, Ehime Prefecture, Japan. It is dark brown in color and occurs as a single crystal with a tabular habit (up to 5 mm) or a radial aggregate of fine crystals. The hardness is 5½ on Mohs scale. The empirical formula of takanawaite-(Y) is (Y_{0.75}Dy_{0.08}Yb_{0.05}Gd_{0.02}U_{0.03}Ti_{0.02}Fe_{0.02})_{Σ0.97}(Ta_{0.57}Nb_{0.45})_{Σ1.02}O₄, leading to a simplified formula of Y(Ta,Nb)O₄. The Ta/(Ta + Nb) ratio varies between 0.55 and 0.57. Takanawaite-(Y) naturally occurs in a submetamict state, and a heating treatment is required to determine the crystal structure. The heating experiment revealed the consistency of takanawaite-(Y) and its *M*-type polymorph. The mineral crystallizes in a monoclinic *M*-type structure with a space group *I*2/*a*, unit cell parameters *a* = 5.3182(8), *b* = 10.9583 (13), *c* = 5.0595 (7) Å, β = 94.993(14)°, and *V* = 293.74(7) Å³, and *Z* = 4, with a calculated density 6.97 g/cm³. The eight strongest lines in the powder XRD pattern [*d* (Å), (*I*/*I*₀), *hkl*] are 3.1334 (100) 121̄, 2.9525 (85) 121̄, 2.7391 (29) 040, 2.6494 (21) 200, 1.9115 (24) 202̄, 1.9050 (39) 240, 1.8546 (26) 042, and 1.5681 (19) 242̄. Takanawaite-(Y) is a distinct mineral compared to iwashiroite-(Y), yttrotantalite-(Y), and formanite-(Y).

Keywords: Takanawaite-(Y), YTaO₄, YNbO₄, New mineral, Takanawa Mountain

INTRODUCTION

Three polymorphs, *T* (tetragonal *I*4₁/*a*), *M* (monoclinic *I*2/*a*), and *M'* (monoclinic *P*2/*a*), have been reported for synthetic tantalates of rare earth elements, REETaO₄, except the tantalates of Sc, La, Ce, and Pr (e.g., Brixner and Chen, 1983; Stubičan, 1964). Recently, Mather and Davies (2005) reported a fourth, a metastable *T'* phase with tetragonally-distorted fluorite-like structure (*P*4₂/*nmc*) for REETaO₄ via a sol-gel route. The *T* phase is a high-temperature form with a scheelite structure. This phase is unquenchable to ambient conditions and converts to the *M* phase upon cooling. The *M'* phase appears as a low temperature form when REETaO₄ compounds are synthesized below the *T*-*M* transition temperature (e.g., Stubičan, 1964; Wolten, 1967; Graham and Thornber, 1974; Brixner, 1987). REENbO₄ compounds have both *T* and *M* structures at high temperatures and show isomorphous substitution of Nb for Ta. However, formation of the *M'* phase strongly depends on the Ta-Nb composition rather

than variation in REE (e.g., Stubičan, 1964; Brixner, 1987). In a Y(Ta_xNb_{1-x})O₄ system, the *M'* phase appears as a single phase in only a limited compositional range of *x* = 1–0.85 at 1000–1100 °C (Brixner and Chen, 1983).

Among naturally-occurring Y(Ta,Nb)O₄ compounds, three mineral species have been identified and approved: iwashiroite-(Y), yttrotantalite-(Y), and formanite-(Y). The structure of iwashiroite-(Y) corresponds to a synthetic *M'* polymorph (Hori et al., 2006). Yttrotantalite-(Y) and formanite-(Y) are thought to have as yet synthetically undetermined orthorhombic and tetragonal phases (Palache et al., 1944), respectively, while a monoclinic form has been suggested for the latter mineral (Kornetsova and Kazakova, 1964; Lima de Faria, 1964). Voloshin et al. (2003) reported a metamict Y(Ta,Nb)O₄ mineral from Russia and conducted a heating experiment. They identified this mineral as formanite-(Y), but the result was inconsistent with previously described formanite-(Y). As such, the *T* and *M* polymorphs of Y(Ta,Nb)O₄ have never been identified and approved as mineral species.

During a mineralogical investigation at Takanawa Mountain, in Ehime Prefecture, Shikoku, Japan, we found a submetamict Y(Ta,Nb)O₄ mineral. Here, we investigate

the crystallographic behavior of this mineral during a heating procedure using X-ray diffraction (XRD) and transmission electron microscopy (TEM). According to experimental evidence, we conclude that this mineral crystallized in the *M* phase (*I*2/*a*) in its original state before metamictization. The $Y(Ta,Nb)O_4$ mineral in *M* phase is named takanawaite-(Y) after its discovery location and its composition. The mineral data and the name have been approved by the Commission on New Minerals, Nomenclature and Classification, of the International Mineralogical Association (no. 2011-099). The type specimen is deposited at the National Museum of Nature and Science, Tokyo, under the registered number NSM M-43517. Here, we report takanawaite-(Y), identified by heating experiment and XRD and TEM observation.

OCCURRENCE

Takanawa Mountain forms part of the Takanawa peninsula in the northwest of Shikoku, and is located near to Matsuyama City, Ehime Prefecture, Japan (33°56'N 132°51'E). The geological setting of this area corresponds to that of the Ryoke Terrane, and Takanawa Mountain mainly consists of granite. Pegmatites within this granite

are characterized by two types of mineral assemblage: a gadolinite-zircon-muscovite assemblage, and an allanite-fergusonite-zircon-biotite assemblage. The former and the latter types occur at mid-elevations and at the foot of the mountain, respectively (e.g., Minakawa et al., 1999; 2001). The takanawaite-(Y) reported here was identified from the former type of pegmatite. Takanawaite-(Y) occurs in close association with gadolinite-(Y) and zircon at the boundary between quartz and K-feldspar (Fig. 1). Muscovite also occurs in this pegmatite as an accessory mineral, and allanite-(Ce) is also found in rare cases.

Takanawaite-(Y) forms as a single crystal with a tabular morphology, or as radial aggregates up to 5 mm across, consisting of fine crystals. The mineral shows microscopic internal cracks, which are filled by Ca- and Ta-rich oxide or hydroxide in the present state (Fig. 1). The crystal faces {100}, {010}, and {001} of an *M*-type lattice were observed, and the prominent crystal face is {010}. Striation in the [101] direction is also observed on the {010} face given monoclinic settings. No cleavage was observed as a result of the metamictization, and the fracture was conchoidal. Takanawaite-(Y) has a Mohs hardness of 5½, and its density is calculated to be 6.97 g/cm³ on the basis of the empirical formula and the lattice

Figure 1. Photomicrographs of takanawaite-(Y) showing (a) tabular morphology, (b) radial aggregates, and (c) striations on {010}. (d) A BSE image of takanawaite-(Y) shows cracks of Ca- and Ta-rich phase(s) (dark gray) in the domain (pale gray). Gdl, gadolinite-(Y); Tk, takanawaite-(Y); Zir, zircon. Color version is available online from <http://japanlinkcenter.org/DN/JST.JSTAGE/jmps/120513a>.

Table 1. Chemical data for takanawaite-(Y)

	wt %	Range (5)
Y ₂ O ₃	27.07	26.46 – 27.67
Gd ₂ O ₃	1.16	0.36 – 2.50
Dy ₂ O ₃	4.64	3.60 – 5.50
Yb ₂ O ₃	2.90	1.40 – 4.50
UO ₂	2.77	2.40 – 3.31
TiO ₂	0.51	0.37 – 0.68
FeO	0.39	0.26 – 0.58
Nb ₂ O ₅	19.22	18.43 – 19.63
Ta ₂ O ₅	40.49	40.10 – 41.27
Total	99.15	
	O = 4	
Y	0.745	
Gd	0.020	
Dy	0.077	
Yb	0.046	
U	0.032	
Ti	0.020	
Fe	0.017	
Nb	0.449	
Ta	0.570	
Total	1.976	

parameters for the sample recrystallized by heating.

CHEMICAL COMPOSITION

Chemical analyses were carried out by a JEOL JSM-5600 electron microscope using an EDX microprobe analyzer (Oxford) at the Institute for Solid State Physics (ISSP) of the University of Tokyo. Settings of 15 kV, 0.4 nA, and 1 μ m beam diameter were used, and the ZAF method was employed for corrections.

Table 1 shows the chemical composition for takanawaite-(Y). The empirical formula for takanawaite-(Y) is (Y_{0.75}Dy_{0.08}Yb_{0.05}Gd_{0.02}U_{0.03}Ti_{0.02}Fe_{0.02}) Σ 0.97(Ta_{0.57}Nb_{0.45}) Σ 1.02O₄, leading to a simplified formula of Y(Ta,Nb)O₄. The Ta/(Ta + Nb) ratio varies between 0.55 and 0.57. The end-member formula is written as YTaO₄, which requires Y₂O₃ 33.82, Ta₂O₅ 66.18, giving a total 100.00 wt%.

X-RAY DIFFRACTION AND TRANSMISSION ELECTRON MICROSCOPY OBSERVATION

Experimental methods

We investigated the variations in structure upon heating in order to reveal the formation of takanawaite-(Y). The samples were heated in air at 600–1000 °C for 24 h in an electrical muffle furnace. The products before and after heating were investigated by X-ray diffraction (XRD) and transmission electron microscope (TEM). The aims of these experiments were to determine the stable phases at

each temperature, because a transition between several phases is expected in the investigated compositional system, and it is also well known that crystallization from an amorphous state induced by low temperature heating often forms a metastable phase.

Angle-dispersive XRD measurements were conducted at room temperature using MoK α radiation with 5.4 kW from a Rigaku rotating anode generator equipped with a 100 μ m collimator in Debye-Scherrer geometry at ISSP. The XRD spectra were recorded using an imaging plate. Synchrotron radiation XRD measurements were also conducted at the NE1 beam line of the Photon Factory-Advanced Ring, High Energy Accelerator Research Organization (PF-AR, KEK), where monochromatic X-ray (wavelength, 0.411 Å) and a 30 μ m collimator were used. The sample-to-detector distance and inclination of the imaging plate were calibrated using a standard material (CeO₂). The XRD spectra were also recorded using an imaging plate. Two-dimensional XRD images in both XRD experiments were integrated as a function of 2 θ to obtain conventional one-dimensional diffraction profiles using IPAnalyzer and PDIndexer software developed by Seto et al. (2010). Rietveld refinement was performed using the RIETAN-FP software (Izumi and Momma, 2007). Peak profiles were fitted with pseudo-Voigt functions.

The samples for TEM investigation were thinned using an argon-ion mill (RES010, BAL-TEC) in a voltage of 3.5 kV and a current of 1.0 mA under a low beam angle of 10–15°. Transmission electron images, selected area diffraction patterns, and chemical mapping were obtained using a TEM (JEOL JEM-2010F), operating at a voltage of 200 kV with EDX system (Oxford) at ISSP.

X-ray diffraction

Experimental results are shown in Table 2. The phases of the compounds and minerals in the YTaO₄–YNbO₄ system are summarized in Table 3. Representative XRD patterns are shown in Figure 2. The XRD pattern of the raw sample before heating is extremely broad due to the metamictization, while several intensities were observed around d = 3.0, 2.6, 1.8, and 1.6 Å. Although peak separation is impossible for this XRD pattern, these positions and intensities roughly coincide with the basal reflections from a fluorite-type structure. Since the *M* phase basically corresponds to a fluorite-type superstructure (Graham and Thornber, 1974; Graham, 1974), the broadening of an XRD pattern of an *M* (*I*2/a) structure may ultimately result in a fluorite-like XRD pattern. Thus, the fluorite-like trace observed in this XRD pattern can be regarded as a significant broadening pattern of an *M* phase.

After heating the sample at 600 °C for 24 h, the

Table 2. List of products before and after the heating experiment on takanawaite-(Y) and the phases appearing during the procedure

Condition	Color	Result
Prior to heating	Dark brown	Submetamict*
600 °C, 24 h	Reddish brown	<i>T'</i> phase†
1000 °C, 24 h	Dull, pale green	<i>M</i> phase‡
1000 °C, 24 h to 600 °C, 24 h	Dull, pale green	<i>M</i> phase§

* Nano-crystallites (*M* phase trace?) are found rarely using TEM.

† Formed metastably from the starting metamict state.

‡ Formed from the high temperature *T* phase upon cooling.

§ True stable form at 600 °C.

XRD pattern changed to give reflections (Fig. 2b) in which peaks can be indexed with a tetragonal unit cell (Table 4). However, it differs from previously seen tetragonal phases such as formanite-(Y) and the *T* phase, in respect to its volume and space group. The XRD pattern after heating at 600 °C can be explained by a tetragonal symmetry such as that in the *T'* phase, which is consistent with previous experimental findings. Mather and Davies (1995) reported that the *T'* phase was formed by low temperature heating of a starting material in an amorphous state. Lima de Faria (1964) reported the appearance of an unidentified cubic phase after heating to 700 °C, but it was not seen in our experiment. In all cases, YTaO₄ polymorphs (*T*, *M*, and *M'* phases) did not re-crystallize with this heating.

After heating at 1000 °C for 24 h, the XRD pattern again changed and a number of new peaks appeared. These agree with a monoclinic unit cell of the *M* phase (Fig. 2c). The extinction of $h + k + l = 2n$ for hkl and $h = 2n$ for $h0l$ for the space group *I*2/a (the *M* phase) was completely confirmed using data from the synchrotron ra-

Figure 2. Representative X-ray diffraction patterns (MoK α source) made using takanawaite-(Y) (a) before and (b) after heating at 600 °C, (c) 1000 °C, and (d) 600 °C after heating at 1000 °C. Intensities for the *T'* phase were calculated as Atoms(*x*, *y*, *z*, *occ.*): Y(3/4, 1/4, 3/4, 1/2), Ta(3/4, 1/4, 3/4, 1/2), O(1/4, 1/4, 0.42, 1) on *P*4₂/*n*mc (No. 137-2). Those for the *M* phase were simulated using the data in Table 6.

diation X-ray diffraction pattern (Table 5). Figure 3 shows a Rietveld refinement plot based on the *M* phase structural model for the synchrotron radiation data of the sample heated at 1000 °C. The final structural parameters are listed in Table 6. This is the first observation of incontestable *M* phase formation from a natural metamict Y(Ta,Nb)O₄. Again, the *M'* phase did not appear in this

Table 3. Mineral names and corresponding phases in the YTaO₄-YNbO₄ system

Phase	Mineral	Symmetry	Space group	References
YTaO ₄ <i>T</i>	—	Tetragonal*	<i>I</i> 4 ₁ / <i>a</i>	presumed from phase relationship
<i>M</i>	Takanawaite-(Y)	Monoclinic†	<i>I</i> 2/ <i>a</i>	Ferguson (1957); This study
<i>M'</i>	Iwashiroite-(Y)	Monoclinic‡	<i>P</i> 2/ <i>a</i>	Wolten et al. (1967); Hori et al.(2006)
<i>T'</i>	—	Tetragonal§	<i>P</i> 4 ₂ / <i>n</i> mc	Mather and Davies (1995); This study
Unknown Formanite-(Y)	—	Tetragonal	<i>P</i> 4/ <i>m</i> , <i>P</i> 4 ₃ / <i>m</i> , <i>P</i> 4/ <i>n</i> , or <i>P</i> 4 ₂ / <i>n</i>	Palache et al. (1944)
Unknown Yttrotantalite-(Y)	—	Orthorhombic	Unknown	Palache et al. (1944)
YNbO ₄ <i>T</i>	Fergusonite-(Y)	Tetragonal*	<i>I</i> 4 ₁ / <i>a</i>	Komkov (1959)
<i>M</i>	β-fergusonite-(Y)	Monoclinic*	<i>I</i> 2/ <i>a</i>	Gorshevskaya et al. (1961)

* The *T* phase is stable only at high temperatures and commonly reverts to the *M* phase upon cooling.

† Stable at 600 °C.

‡ Occurs in a crystalline state without heating.

§ Metastable phase formed at 600 °C from amorphous or metamict material.

|| Unknown among synthetic compounds.

Table 4. Powder X-ray diffraction data based on a MoK α X-ray source for the T' phase ($P4_2/nmc$) after initial heating to 600 °C

hkl	$d_{\text{calc.}} (\text{\AA})$	$d_{\text{obs.}} (\text{\AA})^*$	I/I_0	Impurity
		6.10		Ct 002
101	3.027	3.023	100	
002	2.697	2.694	24	
110	2.586	2.603	29	
102	2.171			
112	1.867	1.867	27	
200	1.829			
201	1.732			
103	1.614	1.613	11	
211	1.565	1.570	15	
202	1.514			
212	1.399			
004	1.348			
220	1.293	1.291	3	
203	1.281			
104	1.265			
213	1.210	1.210	4	
$a = 3.658(4), c = 5.393(9) \text{\AA}, V = 72.16(19) \text{\AA}^3$				

* broad pattern.

Ct, calcicotantite

heating, although the M' phase is stable at 1000 °C for pure YTaO_4 (e.g., Brixner and Chen, 1983; Mather and Davies, 1995).

A consecutive re-heating procedure was carried out at 600 °C for 24 h, following the previous heating at 1000 °C (Table 2). After the re-heating, the XRD pattern shows the M phase alone (Fig. 2d). The T' phase did not reappear, indicating its metastability.

Transmission electron microscope observations

Figure 4 shows bright field transmission electron microscopic images and selected area electron diffraction (SAED) patterns for the samples before and after heating. Although the SAED pattern of the sample before heating was generally broad due to metamictization, some reflections were uncommonly remained (Fig. 4a). The broad ring ($d = 3.0 \text{\AA}$) and reflections ($d = 2.6$ and $1.8 \text{\AA}$) correspond to the first sharp diffraction peak (FSDP) from the metamict and crystalline phases, respectively. The high-resolution transmission electron microscopic (HRTEM) image also revealed some crystallites showing a lattice image with $2.6 \text{\AA}$ spacing. Although indexing of the reflections is difficult due to the metamictization, 040, 200, or 002 of the M phase can be observed at around $2.6 \text{\AA}$ spacing.

After heating at 600 °C for 24 h, spheroidal particles with metamict portions were observed in the sample (Fig. 4b). These spheroidal particles consist of fine crystallites

with low crystallinity, and their impure texture indicates their instability. Although the SAED pattern from the spheroidal particle is broad due to its low crystallinity, all reflections can be indexed with the T' phase, consistent with the XRD result.

After heating at 1000 °C for 24 h, the sample shows a lamellar texture (Fig. 4c). No compositional difference was observed between the layers (Fig. 5) and the lamellar boundary is inconsistent with the grain boundary, indicating that the lamellae formed after grain growth. The SAED pattern from the two layers can be indexed as twins of M phase crystallinity. Since the crystal structure of the M phase corresponds to monoclinic distortion of that of the T phase, the lamellar texture is derived from the difference in the distortion direction in the transition from tetragonal to monoclinic cells (e.g., Quinn and Wusirika, 1991).

The lamellar texture disappeared after subsequent re-heating at 600 °C. The SAED pattern from an individual crystal corresponds to the M phase (Fig. 4d), and the adjoining crystals are not twins.

DISCUSSION

Stable phase at high temperature based on the experimental result using takanawaite-(Y)

The results are summarized in Table 2. XRD and TEM observations revealed that the sample before heating was almost entirely in a metamict state (Fig. 2a), with slight remains of fine crystallites (Fig. 4a). Although exact indexing is not possible due to the metamictization, XRD pattern and SAED reflections can be regarded as a trace of the M phase. At the first 600 °C heating, the T' phase appeared (Fig. 2b), while the M phase was not found. However, the texture of the T' phase shows it to be unstable (Fig. 4b.). Since Mather and Davies (1995) demonstrated that the T' phase was metastably formed from an amorphous starting material by heating at low temperatures, the rapid formation of the metastable phase may inhibit recovery of the M phase from the metamict state in the process of thermal treatment. The M phase was later found in the sample after heating at 1000 °C (Fig. 2c), where it shows a lamellar texture (Fig. 4c). Since the T phase at high temperature is unquenchable to room temperature and the sample is instead recovered as M phase lamella (e.g. Stubičan, 1964; Quinn and Wusirika, 1991), the lamellar texture in the sample indicates the formation not of the M phase but of the T phase at such high temperatures. Therefore, the stable phase at 1000 °C is determined in this study to be the T phase. However, it is noted that this temperature was not a part of the crystallization

Table 5. Powder X-ray diffraction data based on a synchrotron X-ray source for the *M* phase (*I2/a*) after heating to 1000 °C

<i>hkl</i>	<i>d</i> _{calc.} (Å)	<i>d</i> _{obs.} (Å)	<i>I</i> / <i>I</i> ₀	Impurity	<i>hkl</i>	<i>d</i> _{calc.} (Å)	<i>d</i> _{obs.} (Å)	<i>I</i> / <i>I</i> ₀	Impurity
		6.1320	0.2	Ct 002	2 4 2	1.5672	1.5681	19.3	
		6.0026	0.9	MI 111	3 2 1	1.5563	1.5569	15.0	
0 2 0	5.4791	5.4771	5.3		0 3 3	1.5264	1.5260	1.4	
		5.3805	0.8	Ct 100	2 6 0	1.5036	1.5024	16.8	
		4.9229	0.5	Ct 101	1 7 0	1.5013			
1 1 0	4.7698	4.7708	9.9		3 1 2	1.4952			
0 1 1	4.5792	4.5994	0.3		0 7 1	1.4950	1.4952	4.3	
		4.0472	0.4	Ct 102	2 4 2	1.4756	1.4761	8.3	
		3.6714	0.3	MI 220	2 1 3	1.4649			
1 2 $\bar{1}$	3.1345	3.1334	100.0		3 4 $\bar{1}$	1.4530	1.4534	1.2	
1 3 0	3.0073						1.4509	1.3	MI 711
		2.9998	14.2	MI 222	1 4 $\bar{3}$	1.4092	1.4092	1.1	
0 3 1	2.9577				3 4 1	1.3965	1.3959	0.3	
1 2 1	2.9512	2.9525	84.9		3 3 $\bar{2}$	1.3949			
		2.7701	1.9	Ct 112	3 1 2	1.3794			
0 4 0	2.7396	2.7391	28.8		3 5 0	1.3751	1.3749	1.9	
2 0 0	2.6490	2.6494	20.8		2 3 $\bar{3}$	1.3702	1.3698	3.5	
		2.5966	2.4	MI 400	0 8 0	1.3698			
0 0 2	2.5202	2.5207	15.1		1 4 3	1.3575			
		2.4733	0.6	Ct 113	2 1 3	1.3556	1.3553	0.2	
2 2 0	2.3849						1.3529	0.2	MI 731
		2.3840	0.8	MI 331	0 5 3	1.3334	1.3336	0.5	
2 1 $\bar{1}$	2.3758	2.3774	0.8		4 0 0	1.3245	1.3245	3.8	
		2.2309	0.3	Ct 105	2 6 $\bar{2}$	1.3203			
1 1 $\bar{2}$	2.3041	2.3014	0.3		2 7 $\bar{1}$	1.3166	1.3172	1.6	
0 2 2	2.2896	2.2899	0.7		1 7 $\bar{2}$	1.3040	1.3038	1.4	
1 4 $\bar{1}$	2.2266				4 1 $\bar{1}$	1.3001			
2 1 1	2.2182	2.2194	0.5		3 3 2	1.2995			
1 1 2	2.1595	2.1581	8.4		1 8 $\bar{1}$	1.2895	1.2887	3.5	
1 4 1	2.1579				2 7 1	1.2878			
2 3 $\bar{1}$	2.0253	2.0253	2.9		4 2 0	1.2874			
1 5 0	2.0252				2 3 3	1.2795			
0 5 1	2.0099	2.0091	4.2		1 7 2	1.2760	1.2757	1.5	
		1.9998	1.2	MI 333	1 8 1	1.2757			
1 3 $\bar{2}$	1.9803	1.9808	0.4		2 6 2	1.2741			
2 3 1	1.9250	1.9250	5.3		0 0 4	1.2601	1.2605	3.9	
2 0 $\bar{2}$	1.9108	1.9115	23.8		3 6 $\bar{1}$	1.2498	1.2495	3.6	
2 4 0	1.9043	1.9050	39.1		4 1 1	1.2463			
1 3 2	1.8862	1.8890	5.9		3 5 $\bar{2}$	1.2431			
0 4 2	1.8547	1.8546	25.9		1 1 4	1.2426			
		1.8369	3.1	MI 440	3 2 $\bar{3}$	1.2408	1.2414	5.4	
0 6 0	1.8264	1.8263	1.7		4 3 $\bar{1}$	1.2325			
2 2 $\bar{2}$	1.8042	1.8046	0.5		0 2 4	1.2280			
		1.7950	0.8	Ct 300	2 5 $\bar{3}$	1.2255			
2 0 2	1.7513	1.7518	1.2		1 6 $\bar{3}$	1.2216	1.2213	6.0	
3 1 0	1.7435				4 0 $\bar{2}$	1.2169	1.2164	9.2	
		1.7069	0.5	Ct 116	2 8 0	1.2167			
		1.6945	0.1	Ct 214	3 6 1	1.2133	1.2132	6.8	
2 2 2	1.6682	1.6674	0.6		0 8 2	1.2035	1.2035	3.6	
0 1 3	1.6607				1 1 4	1.1954			
1 6 $\bar{1}$	1.6479	1.6471	14.8		4 4 0	1.1924	1.1921	5.4	
3 2 $\bar{1}$	1.6357	1.6359	18.0		4 2 $\bar{2}$	1.1879			
2 5 $\bar{1}$	1.6286				1 6 3	1.1874	1.1873	5.3	
1 6 1	1.6194	1.6195	12.8		1 9 0	1.1866			
1 5 $\bar{2}$	1.6049	1.6048	3.1		4 3 1	1.1864			
3 3 0	1.5899				0 9 1	1.1835	1.1837	4.0	
2 5 1	1.5751				1 3 4	1.1832			
1 2 $\bar{3}$	1.5740	1.5731	18.3		2 0 4	1.1784	1.1787	2.2	

M phase: *a* = 5.3182(8) Å, *b* = 10.9583(13) Å, *c* = 5.0595(7) Å, β = 94.993(14)°, *V* = 293.74(7) Å³. Calciotantite (Ct): *a* = 6.2162(10) Å, *c* = 12.254(3) Å, *V* = 410.06(15) Å³. Microlite (MI): *a* = 10.382(5) Å, *V* = 1119.1(16) Å³.

The occupancies are constrained in reference to the chemical composition, such that $Y1 = 0.78Y + 0.08Dy + 0.05Yb + 0.02Gd + 0.03U + 0.02Ti + 0.02Fe$ and $Ta1 = 0.56Ta + 0.44Nb$.

In conclusion, experimental results using takana-

Figure 5. Bright field TEM image and compositional mapping images of takanawaite-(Y) after heating at 1000 °C. No compositional zoning is observed between the lamellae. Color version is available online from <http://japanlinkcenter.org/DN/JST.JSTAGE/jmps/120513a>.

waite-(Y) as a starting material reveal that the *M* phase is stable at 600 °C and that the *T* phase is formed at 1000 °C. We note that appropriate heating treatment and observations are necessary in order to determine the stable phases at each temperature, because of the rapid formation of the metastable phase at low temperatures and the unquenchable behavior of the *T* phase in this compositional system. We also show that the *M'* phase does not appear in our sample with $x = 0.55\text{--}0.57$ in $\text{Y}(\text{Ta}_x\text{Nb}_{1-x})\text{O}_4$, which is consistent with the previous experimental findings that the *M'* phase composition is limited to the range $x = 1\text{--}0.85$ at 1000–1100 °C (Brixner and Chen, 1983).

Original crystal structure of takanawaite-(Y)

Although the crystal structure of takanawaite-(Y) when it formed in-situ is indeterminable by just the experimental results, its morphology and occurrence help to indicate its formation. If the mineral naturally crystallized in the *T* phase, then the morphology probably retains a tetragonal shape identical to the *T* phase, like scheelite. For example, fergusonite-(Y) (YNbO_4) has a scheelite structure (*T* phase) and it occurs in a tetragonal columnar shape even if later occurring in a metamict state. In contrast, takanawaite-(Y) shows a tabular morphology, suggesting that the pre-metamict, original takanawaite-(Y) did not crystallize in a scheelite structure (the *T* phase). Although two monoclinic forms (*M* and *M'* phases) are known in

the $\text{Y}(\text{Ta}_x\text{Nb}_{1-x})\text{O}_4$ compositional system, we observe only the *M* phase in the heated samples of takanawaite-(Y) and the *M'* phase does not appear, even in metastable form, throughout the thermal experiment carried out here. Moreover, we also confirmed grain growth in the *M* phase at 600 °C, which is comparable to the temperature of pegmatite formation. The pegmatite containing the takanawaite-(Y) is rich in Be and Ta, because gadolinite-(Y) and muscovite also occur. These features correspond to a LCT subtype pegmatite, which has been estimated to form at 500 to 650 °C (Černý, 1991). The concordance of the experimental results and the conditions of the mineral's occurrence suggests that the original takanawaite-(Y) is an *M* phase of $\text{Y}(\text{Ta},\text{Nb})\text{O}_4$. After crystallization as the *M* phase during its original formation, the takanawaite-(Y) suffered radiation damage, leaving only a relict trace of the *M* phase in the metamict sample at the present time.

Comparison between takanawaite-(Y) and other $\text{Y}(\text{Ta},\text{Nb})\text{O}_4$ minerals

Among naturally-occurring $\text{Y}(\text{Ta},\text{Nb})\text{O}_4$ compounds, four minerals have been identified as independent species: takanawaite-(Y), iwashiroite-(Y), yttrotantalite-(Y), and formanite-(Y). Iwashiroite-(Y) corresponds to the *M'* polymorph (Hori et al., 2006), and yttrotantalite-(Y) has been thought to be an orthorhombic phase on the basis of morphological analysis (Palache et al., 1944). Takanawaite-(Y) (the *M* phase) apparently differs from iwashiroite-(Y) (the *M'* phase) and yttrotantalite-(Y), but the precise description of formanite-(Y) is ambiguous and thus it is necessary to compare takanawaite-(Y) with formanite-(Y).

Palache et al. (1944) described formanite-(Y) from Cooglegong, Western Australia, citing data of Ta-dominant 'fergusonite' (Simpson, 1909) and private communications with Berman and Frondel in 1941. Palache et al. (1944) pointed out that formanite-(Y), as well as fergusonite-(Y), are found in a metamict state, but could be crystallized on ignition. They classed the tetragonal *P*-type lattice ($P4/m$, $P43/m$, $P4/n$, or $P42/n$) of formanite-(Y) as analogous with fergusonite-(Y). However in later years, it was shown that fergusonite-(Y) could be classified into two polymorphs: fergusonite-(Y), in the *T* phase ($I4_1/a$), noting that it has an *I*-type lattice with a different setting, and β -fergusonite-(Y), in the *M* phase ($I2/a$). Kornetsova and Kazakova (1964) reported the occurrence of a metamict YTao_4 mineral in Siberia, which they described as formanite-(Y) and summarized the X-ray diffraction *d*-table of a sample heated to 900 °C. They suggested a monoclinic cell for the sample, but cell dimensions were not applied to index the *d*-space data in

their study. Instead, indexing was carried out based on a tetragonal P -type lattice for the X-ray diffraction data given by Kornetsova and Kazakova (1964) in a later edition of ICDD #26-1478. In addition, Mather and Davies (1995) synthesized YTao_4 and determined the crystal structure to be T' phase ($P4_2/nmc$). Since no tetragonal phase having a Palache-type unit cell has been reported in any synthetic REETaO_4 – REENbO_4 system, its conditions of formation are still unresolved. Moreover, it should be noted that a Palache-type tetragonal phase was never found in any of the products of the thermal treatment of the takanawaite-(Y) specimen.

Lima de Faria (1964) reported a metamict mineral having a YTao_4 composition from the type locality of formanite-(Y). The metamict mineral crystallized into the monoclinic M' phase (described as a ' YTao_4 -like phase' in the literature), different from the M phase (' YNbO_4 -like phase' in the literature) after heating to 1000 °C, but the work did not make mention of the unit cell parameters and space group for this YTao_4 -like phase. The M and M' phases are indistinguishable using the incomplete d -value list in that paper, since the data can be indexed with unit cells of both M and M' phases, which have similar crystal structures. The synthetic experiment demonstrated that the M' phase appeared only in the limited compositional range of $x = 1-0.85$ in $\text{Y}(\text{Ta}_x\text{Nb}_{1-x})\text{O}_4$ at 1000–1100 °C (Brixner and Chen, 1983). The sample of Lima de Faria (1964) has quite a high Ta content of $x = 0.9$. This strongly suggests that his monoclinic phase probably corresponds to the M' phase, as monoclinic tantalate, namely ' YTao_4 ', is always in the M' phase in the experimental studies. The formation of the M' phase at 1000 °C in Lima de Faria (1964) also suggests the absence of the T phase at this temperature, because it is stable at a higher temperature than that at which the M' phase is stable. In contrast, in our takanawaite-(Y) sample, which has composition of $x = 0.55-0.57$, the T phase is already stable at 1000 °C and the M' phase does not appear in any of the heating treatments.

Voloshin et al. (2003) reported a metamict $\text{Y}(\text{Ta,Nb})\text{O}_4$ mineral from Russia, which underwent a crystallization process upon heating to 900 °C. They claimed that the mineral crystallized to the T and the M phases after heating at 600–800 °C and 900 °C, respectively and they subsequently named this mineral 'formanite-(Y)'. This is a misidentification, however, because their mineral never crystallized to give the tetrahedral unit cell of formanite-(Y), as reported by Palache et al. (1944). Therefore, Voloshin's mineral is not identical to formanite-(Y). Moreover, Voloshin's identification of T and M phases has some problems. The formation of the T phase at temperatures below that of M phase formation, and the quench-

able behavior of the T phase in their study contradict the results of other thermal examinations of $\text{Y}(\text{Ta,Nb})\text{O}_4$. The T phase is the highest temperature form in the $\text{Y}(\text{Ta}_x\text{Nb}_{1-x})\text{O}_4$ system and is unquenchable to room temperature (e.g., Stubičan, 1964; Wolten, 1967; Graham and Thornber, 1974; Brixner, 1987). Voloshin et al. (2003) also made an inadequate identification of the M phase in their X-ray diffraction work; they defined the M phase ($I2/a$) in spite of a violation of the extinction rule for an I -type lattice. However, despite the contradiction in the T phase behavior and the inadequate indexing for the M phase, their work may be worth comparing with our study. Our study and other experimental work (Mather and Davies, 1995) have confirmed that the T' phase (tetragonal; $P4_2/nmc$) is metastably formed from low temperature heating of an amorphous (metamict) starting material. The d -value for Voloshin's T phase is quite similar to this phase. The axial ratio of their monoclinic phase may correspond to the M phase and its composition ($x = 0.61-0.67$) also falls within the compositional range for M phase formation, according to experimental studies (Brixner and Chen, 1983). Therefore, we suggest that Voloshin's mineral is not formanite-(Y), but is instead possibly identical to takanawaite-(Y) as defined here.

It therefore is concluded that takanawaite-(Y) is a new mineral species, distinct from iwashiroite-(Y), yttrotantalite-(Y), and formanite-(Y).

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DEPOSITORY MATERIALS

Color version of Figures 1, 3, 4 and 5 is available online from <http://japanlinkcenter.org/DN/JST.JSTAGE/jmps/120513a>.

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