**Oxyyttrobeta-(Y), Y$_2$Ti$_2$O$_6$O, a new mineral of the pyrochlore supergroup in a pegmatite from Souri Valley, Komono, Mie Prefecture Japan**

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Oxyyttrobeta-(Y) is the first member in the betafite group of the pyrochlore supergroup found in albite-rich pegmatite from Souri Valley, Mie Prefecture, Japan. This new mineral occurs as small anhedral grains with sizes of 20 to 200 µm in cylinder-shaped aggregates with a substrate of thalénite-(Y) and synchysite-(Y). Small amounts of aeshynite-(Y), thorianite, and thorite are also associated in the same occurrence with oxyyttrobeta-(Y), and gadolinite-(Y) is also included at the boundary between the aggregate and albite. The physical properties are: brown in color, brittle, transparent, non-fluorescent, vitreous luster, white streak with a Mohs hardness of 5, and a calculated density of 5.54 g·cm$^{-3}$. Oxyyttrobeta-(Y) has the strongest peaks in the powder X-ray diffraction pattern $d$ [Å] ($I/I_{hkl}$) were 2.918(100) 222, 2.527(18) 400, 2.321(13) 331, 1.788(53) 440, 1.525(46) 622, and 1.162(13) 662, and 1.033(9) 844 with unit cell parameters of $a = 10.113(10)$ Å, $V = 1033.64(3)$ Å$^3$, and $Z = 8$. The crystal structure was refined to $R_1 = 0.018$ for 159 observed reflections with the criteria of $I > 2σ(I)$. Oxyyttrobeta-(Y) is characterized by Y dominance at the A sites, Ti dominance at the B sites, and O dominance at the X and Y sites in the $A_2B_2X_6Y$ pyrochlore-type formula.

Keywords: Oxyyttrobeta-(Y), Betafite group, Pyrochlore supergroup, New mineral, Mie Prefecture, Japan

INTRODUCTION

Betafite was first found in Betafo, Madagascar and reported as a new species in 1912 because it was rich in U and Ti compared to the known niobate pyrochlore mineral (Lacroix, 1912). However, the amount of Ti did not exceed that of Nb, and the distinction from pyrochlore was uncertain, which caused confusion in later generations. Hogarth (1961) confirmed that betafite contains large amounts of U and Nb is predominant. Based on these characteristics, he proposed the name betafite for pyrochlore containing more than 15% metallic U by weight. The first nomenclature, developed by the pyrochlore subcommittee over a ten-year period, was published in 1977, which defined a betafite subgroup as subordinate to a pyrochlore group (Hogarth, 1977). This nomenclature declared that $2Ti \geq Nb + Ta$ in the B site belongs to the betafite subgroup in the general formula $A_2mB_2O_6$ (O,OH,F)$_{1-x}$pH$_2$O. With this criterion, betafite by Lacroix (1912) existed as an independent species from pyrochlore. This was due to the preferential treatment of Ti based solely on empirical trends in chemical composition, but such biased classification received official approval because the pyrochlore subcommittee had a policy of re-
taining the old name (Hogarth, 2013). Later, the definition of mineral species and group hierarchy was defined more precisely (Nickel, 1992; Mills et al., 2009), and then the pyrochlore supergroup was established in 2010, where the dominant-valency rule was adopted (Atencio et al., 2010; Bosi et al., 2019). There, the betafite group was placed below the pyrochlore supergroup. However, modernized nomenclature has discredited all species with the root name of betafite described under past nomenclature (Atencio et al., 2010; Christy and Atencio, 2013; Atencio, 2021). For example, betafite by Lacroix (1912) should be classified as a member of the pyrochlore group. Conclusively, from 2010, there were no betafite group members until the present new mineral, oxyyttrobeta-(Y), was approved.

In the current nomenclature for the pyrochlore supergroup with $A_2B_2X_6Y$ composition, the betafite group is defined as the member for which Ti is predominantly in the $B$ site under the dominant-valency rule (Atencio et al., 2010). Species are classified from the contents of the $A$ and $Y$ sites, and the nomenclature requires that a name include one root name and two prefixes. If rare earth elements are predominant, then the Levinson rule is also applied to the name (Bayliss and Levinson, 1988). The mineral oxyyttrobeta-(Y) with the $Y_2Ti_2O_6O$ composition is dominated by Y at the $A$ sites, Ti at the $B$ sites, and O at the $X$ and $Y$ sites. Oxyyttrobeta-(Y) was found in a pegmatite from Souri Valley, Komono, Mie Prefecture, Japan. Both the mineral and name have been approved by the International Mineralogical Association, Commission on New Minerals, Nomenclature and Classification (IMA no. 2022–002). A type specimen was deposited in the collections of the National Museum of Nature and Science, Japan, specimen number NSM–M49380.

**OCCURRENCE**

Oxyyttrobeta-(Y) was found in a granite pegmatite block from Souri Valley, Komono, Mie Prefecture, Japan (Lat.35°0′35″N, Long.136°27′33″E). Magnesiorowlandite-(Y) (Matsubara et al., 2014) and miete-(Y) (Miyawaki et al., 2015) have also been found there in recent years as new minerals in the pegmatite blocks. Even before those discoveries, Souri Valley was known as a famous locality for pegmatite minerals such as gadolinite-(Y). The geology around Souri Valley consists of sedimentary rocks divided into the Komono formations (Harayama et al., 1989) and no granite outcrops have been found along the valley. However, the soil on sedimentary rocks contains small amounts of granite block, which suggests that the granite now distributed beyond the ridge was once supplied to the valley. The granite body is distributed 8 × 35 km from north to south and forms a mountain range that is named the Suzuka granite (Ogata, 1959). The igneous activity in the area is considered to have begun around 80 Ma and ended around 70 Ma, with an additional 10 to 15 Ma required for complete cooling (Harayama et al., 1989). The granite pegmatite blocks containing new minerals are considered to originate from the Suzuka granite (Matsubara et al., 2014; Miyawaki et al., 2015).

The sample was collected by the last author (S.I.) in August of 2016. Pegmatite containing oxyyttrobeta-(Y) is a separate block from the previously discovered pegmatite containing magnesiorowlandite-(Y) and miete-(Y). Oxyyttrobeta-(Y) has not yet been found together with those minerals. Oxyyttrobeta-(Y) occurs as small brown colored grains in a cylinder-shaped aggregate (2.5 × 0.6 cm) with a substrate of thalénite-(Y) and synchysite-(Y) in an albite-dominated pegmatite (Fig. 1). A small amount of aescynite-(Y), thorianite, and thorite with dark red to black color are also associated in the same occurrence with oxyyttrobeta-(Y). Gadolinite-(Y) is associated in the boundary between the aggregate and albite.

**PHYSICAL AND OPTICAL PROPERTIES**

The oxyyttrobeta-(Y) crystals are irregularly shaped grains with sizes ranging from 20 to 200 µm. The mineral has a transparent brown color with vitreous luster, while the streak is white. Oxyyttrobeta-(Y) is non-fluorescent, brittle, and uneven in fracture. No cleavage or parting has been observed. The Mohs scale hardness is 5. The density could not be measured because the mineral exceeds the density of available fluids, although the calculated density based on the empirical formula and single crystal X-ray diffraction (XRD) data is 5.54 g cm$^{-3}$. Oxyyttrobeta-(Y) is an optically isometric material with brown color under the microscope. The refractive index was determined to be in the range 1.78 < n < 2.30 with the available index media. This is consistent with the refractive index of n = 2.3 calculated by the Gladstone–Dale relationship using the k value in Mandarino (1981) and the calculated density.

**CHEMICAL COMPOSITION**

Analyses for oxyyttrobeta-(Y) were conducted using an electron microprobe (IT100, JEOL; EDS mode, 20 kV, 1 nA, and 5 µm beam diameter), and the ZAF method was used for data correction. The standards for each metal were Ti, Fe, Y, Nb, Sn, and Ta, while REEP$_5$O$_{14}$ was used for the rare-earth elements (REE). Analytical data are given in Table 1. Oxyyttrobeta-(Y) did not contain any radioactive
elements and no zoning structure was observed. For REE included in the mineral, Y was the most predominant, and heavy REEs (HREEs) were more abundant than light REEs. Ti was also dominant compared to Ta, Nb and other minor elements. F was not detected for oxyyttrobetafite–(Y). The empirical formula with rounding error calculated on the basis of $B = 2$ with $A_2B_2X_6Y$ composition was $(Y_{1.58}Dy_{0.13}Yb_{0.07}Er_{0.06}Tm_{0.05}Gd_{0.04}Ho_{0.03}Sm_{0.02}Tb_{0.02}Eu_{0.01}Lu_{0.01})_2(O_{2.02}(Ti_{1.85}Ta_{0.09}Fe_{0.05}Sn_{0.02}Nb_{0.00})_2O_{7.05}$. The simplified formula is $(Y,\text{HREE})(Ti,\text{Ta})_2O_7$, and the ideal formula is $Y_2Ti_2O_6O$, which requires TiO$_2$ 41.44 wt% and Y$_2$O$_3$ 58.56 wt%, total 100 wt%.

### CRYSTALLOGRAPHY

The single-crystal X-ray diffraction (XRD) experiment was performed using a Rigaku Synergy–Custom diffractometer equipped with a HyPix–6000He detector and monochromatized Mo Kα radiation. The CrysAlis Pro software package was used to process the diffraction data, including the application of a numerical absorption correction. The crystal structure was solved by the charge flipping method using Superflip software (Palatinus and Chapuis, 2007), by which the space group $Fd\overline{3}m$ and the pyrochlore-type structure were derived. SHELXL–2018/1 software (Sheldrick, 2015) was used for refinement of the crystal structure with neutral atom–scattering factors. A full-matrix least-squares refinement with anisotropic atomic displacement parameters was conducted. The A site was represented by Y and Dy, and the B site by Ti and Ta in the $A_2B_2O_6O$ formula because of the compositional complexity of oxyyttrobetafite–(Y). The refinement yielded 0.879(7)Y + 0.121(7)Dy and 0.993(3)Ti + 0.007Ta(3), which confirmed that Y and Ti are dominant in the A and B sites, respectively. The full refinement resulted in $R_I = 0.018$ for 159 observed reflections with the criteria of $I > 2\sigma(I)$. Details of the sample, data collection, and structure refinement are provided in Table 2. The final atom coordinates and equivalent isotropic atomic displacement parameters are summarized in Table 3. The refined unit cell parameters were $a = 10.11090(10)$ Å, $V = 1033.64(3)$ Å$^3$, and $Z = 8$. The CIF file has been deposited to the Crystallography Open Database (COD; ID 3000402).

Angle-dispersive powder XRD measurement was conducted at room temperature using Mo Kα (50 kV

### Table 1. Chemical composition of oxyyttrobetafite–(Y)

|        | Mean (range) in wt% | S.D. apfu |
|--------|---------------------|-----------|
| Y$_2$O$_3$ | 40.99 (40.37–41.39) | 0.37   |
| Sm$_2$O$_3$ | 0.78 (0.50–1.04) | 0.11   |
| Eu$_2$O$_3$ | 0.37 (0–0.74) | 0.12   |
| Gd$_2$O$_3$ | 1.80 (1.57–2.03) | 0.13   |
| Tb$_2$O$_3$ | 0.71 (0.39–1.31) | 0.17   |
| Dy$_2$O$_3$ | 5.57 (5.33–6.00) | 0.19   |
| Ho$_2$O$_3$ | 1.27 (0.93–1.71) | 0.15   |
| Er$_2$O$_3$ | 2.76 (2.39–3.40) | 0.17   |
| Tm$_2$O$_3$ | 2.19 (1.29–2.79) | 0.39   |
| Yb$_2$O$_3$ | 3.27 (2.95–3.48) | 0.25   |
| Lu$_2$O$_3$ | 0.34 (0.10–0.67) | 0.16   |
| TiO$_2$ | 33.91 (33.75–34.23) | 0.24   |
| SnO$_2$ | 0.61 (0.22–0.85) | 0.09   |
| Nb$_2$O$_5$ | 0.14 (0–0.39) | 0.14   |
| Ta$_2$O$_5$ | 4.38 (3.61–4.92) | 0.20   |
| FeO | 0.76 (0.57–0.89) | 0.09   |
| Total | 99.84 | Sn 0.02 Fe 0.05 |
|        | $\Sigma A = 2.02$ | $\Sigma B = 2$ |

Oxyyttrobetafite–(Y), a new mineral

Figure 1. Occurrence of oxyyttrobetafite–(Y) (Oyb–Y) in the cylindrical aggregate mainly composed of thalénite–(Y) (Tlé–Y) and synchysite–(Y) (Syn–Y). Gadolinite–(Y) (Gad–Y) is included at the boundary between the cylindrical aggregate and albite (Ab).
and 54 mA) radiation from a rotating anode generator (Rigaku) equipped with a 100 µm collimator in the Debye–Scherrer geometry and recorded on an imaging plate. Data are given in Table 4. The seven strongest lines of oxyyttrobeta-fite–(Y) in the powder XRD pattern \[d = \frac{10.11090(10)}{\AA}\] were 2.918(100) 222, 2.527(18) 400, 2.321(13) 331, 1.788(53) 440, 1.525(46) 622, 1.162(13) 662, and 1.033(9) 844. The refined unit-cell parameters were \[a = 10.1241(17) \ \AA, \ V = 1037.7(5) \ \AA^3, \text{ and } Z = 8. \]

Table 2. Data collection and structural refinement details

| Temperature | 293 K |
|-------------|-------|
| Radiation   | MoKα  |
| Crystal size| \[0.10 \times 0.07 \times 0.06 \ \text{mm}\] |
| Space Group | \[Fd\bar{3}m\] |
| Unit cell dimensions | \[a = 10.11090(10) \ \AA\] |
| Volume      | \[V = 1033.64(3) \ \AA^3\] |
| Z           | 8     |
| \[F(000)\]  | 1568  |
| Absorption coefficient \[m(MoKα)\] | 28.995 mm\(^{-1}\) |

| Diffractometer | Rigaku Synergy-Custom |
|----------------|-----------------------|
| Voltage, Current | 50 kV, 24 mA |
| 20 max | 76.2° |
| No. of Reflections Measured | 15203 |
| Independent reflections | 168 |
| Reflections with \[I > 2\sigma(I)\] | 159 (\[R_{int} = 0.033\]) |
| Refinement | Full-matrix least-squares on \[F^2\] |
| Function Minimized | \[Sw(F_o^2 - F_c^2)\] |
| Least Squares Weights | \[w = 1/\left[\sigma^2(F_o^2) + (0.0295P)^2 + 0.7993P\right]\] |
| Residuals: \[R1 (I > 2\sigma(I))\] | 0.018 |
| Residuals: \[wR2 (All reflections)\] | 0.050 |
| Goodness of Fit Indicator | 1.27 |
| Largest diff. peak and hole | 0.49 e/Å\(^3\) and −0.89 e/Å\(^3\) |

Table 3. Final atom coordinates and displacement parameters (Å\(^2\))

| \(x/a\) | \(y/b\) | \(z/c\) | \(U_{eq}\) | Occupancy |
|---------|---------|---------|---------|-----------|
| Y1      | 0       | 0       | 0       | 0.00811(15) | Y\(_{0.8797(7)}\)D\(_{0.121(7)}\) |
| Ti1     | 1/2     | 0       | 0       | 0.0048(3)   | Ti\(_{0.9933(3)}\)Ta\(_{0.07(3)}\) |
| O1      | 1/8     | 1/8     | 1/8     | 0.0068(5)   | O         |
| O2      | 7/8     | 3/8     | 0.07927(14) | 0.0085(3)   | O         |

| \(U_{11}\) | \(U_{22}\) | \(U_{33}\) | \(U_{12}\) | \(U_{13}\) | \(U_{23}\) |
|-------------|-------------|-------------|-------------|-------------|-------------|
| Y1          | 0.00811(15) | 0.00811(15) | 0.00811(15) | −0.00297(4) | −0.00297(4) | −0.00297(4) |
| Ti1         | 0.0048(3)   | 0.0048(3)   | 0.0048(3)   | −0.00008(7) | −0.00008(7) | −0.00008(7) |
| O1          | 0.0068(5)   | 0.0068(5)   | 0.0068(5)   | 0           | 0           | 0           |
| O2          | 0.0073(4)   | 0.0073(4)   | 0.0107(6)   | −0.0028(4)  | 0           | 0           |

Figure 2 shows the crystal structure of oxyyttrobeta-fite–(Y), which is equivalent to synthetic \[\text{Y}_2\text{Ti}_5\text{O}_{12}\] with pyrochlore structure (e.g., Matteucci et al., 2007). Y is located on the 16c sites and forms a distorted hexahedron with eight oxygens, while Ti is located on 16d sites and forms a rigid octahedron with six oxygens. In the depiction of the polyhedra, the connections between hexahedra, and between hexahedra and octahedra are edge-shared, and the connections between octahedra are corner-shared.
RELATION TO OTHER SPECIES

In the current nomenclature for the pyrochlore supergroup with \( A_2B_2X_6Y \) composition, seven groups have been established by the dominance in the \( B \) sites: the pyrochlore group (\( B = \text{Nb} \)), the microlite group (\( B = \text{Ta} \)), the betaefite group, the elsmoreite group (\( B = \text{Sb} \)), the ralstonite group (\( B = \text{Al} \)), and the coulsellite group (\( B = \text{Mg} \)) (e.g., Atencio et al., 2010; Christy and Atencio, 2013; Atencio, 2021). The pyrochlore supergroup consists of 32 species by July 2022; however, there has been no valid betaefite group member prior to this study. Therefore, oxyyttrobetaefite–(Y) is currently the only valid species in the betaefite group. On the other hand, based on previous studies for lunar samples (Meyer and Yang, 1988; Mokhov et al., 2008), oxycalcio– and oxyurano-type betaefite have already been noted as possible new species (Atencio et al., 2010; Christy and Atencio, 2013; Atencio, 2021). The former type betaefite has also been found in terrestrial samples. Ogoshi and Minakawa (2012) reported the occurrence of an oxycalcio–type betaefite without structural information in skarn from Yuge Island, Ehime Prefecture, Japan. Uehara et al. (2013) also found an oxycalcio–type betaefite in the pegmatite from Mitoko, Itoshima, Fukuoka Prefecture, Japan, which was in a metamict state, although a pyrochlore–type powder XRD pattern appeared upon heating. Under these circumstances, the existence of the oxycalcio–type betaefite is probably certain. The betaefite group will likely have a few more members.

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REFERENCES

Atencio, D. (2021) Pyrochlore-supergroup minerals nomenclature: an update. Frontiers in Chemistry, 9, 1–6.

Atencio, D., Andrade, M.B., Christy, A.G., Gieré, R. and Kartashov, P.M. (2010) The pyrochlore supergroup of minerals: nomenclature. The Canadian Mineralogist, 48, 673–698.

Bayliss, P. and Levinson, A.A. (1988) A system of nomenclature for rare-earth mineral species: revision and extension. American Mineralogist, 73, 422–433.

Bosi, F., Hatert, F., Hälenius, U., Pasero, M., et al. (2019) On the application of the IMA-CNMNC dominant-valency rule to complex mineral composition. Mineralogical Magazine, 83, 627–632.

Christy, A.G. and Atencio, D. (2013) Clarification of status of species in the pyrochlore supergroup. Mineralogical Magazine,
