

## Yttriaite-(Y): The natural occurrence of $Y_2O_3$ from the Bol'shaya Pol'ya River, Subpolar Urals, Russia

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### ABSTRACT

Yttriaite-(Y), ideally  $Y_2O_3$ , is a new mineral (IMA2010-039) from the alluvial deposits of the Bol'shaya Pol'ya River, Subpolar Urals, Russia. The new mineral occurs as isolated crystals, typically cubo-octahedra  $<6 \mu\text{m}$  in size, embedded in massive native tungsten. Associated minerals include: copper, zircon, osmium, gold, and pyrite. The main forms observed are  $\{100\}$  and  $\{111\}$ . Due to the crystal size, physical properties could not be determined; however, the properties of synthetic  $Y_2O_3$  are well known. Synthetic  $Y_2O_3$  crystals are colorless to white with a white streak; crystals are transparent with an adamantine luster, while massive  $Y_2O_3$  is typically translucent with an earthy luster. Synthetic  $Y_2O_3$  has a Vickers hardness of 653.91, which corresponds to 5.5 on the Mohs scale. Synthetic  $Y_2O_3$  crystals have good cleavage on  $\{111\}$ . Yttriaite-(Y) is isotropic; the refractive index measured at 587 nm on synthetic  $Y_2O_3$  is  $n = 1.931$ . The empirical chemical formula (mean of 4 electron microprobe analyses) calculated on the basis of 3 O is:  $Y_{1.98}Dy_{0.01}Yb_{0.01}O_3$ . Yttriaite-(Y) is cubic, space group  $Ia\bar{3}$ , with parameters  $a = 10.6018(7) \text{ \AA}$ ,  $V = 1191.62(7) \text{ \AA}^3$ , and  $Z = 16$ . The five strongest lines in the powder X-ray diffraction pattern (measured on synthetic  $Y_2O_3$  using synchrotron radiation) are [ $d_{\text{obs}}$  in  $\text{Å}$  ( $hkl$ )]: 3.0646 (100) (222), 1.8746 (55) (440), 1.5984 (38) (622), 2.6537 (26) (400), and 4.3356 (14) (211). The mineral name is based on the common name for the chemical compound, yttria.

**Keywords:** Yttriaite-(Y), new mineral, yttria, tungsten, Bol'shaya Pol'ya River, Subpolar Urals, Raman spectroscopy, electron back scatter diffraction

### INTRODUCTION

Yttrium(III) oxide (also known as yttria, diyttrium trioxide, yttrium sesquioxide, and  $Y_2O_3$ ) is an air-stable, water-insoluble oxide that has various applications in material sciences and inorganic chemistry. It is a starting material for the manufacture of  $YVO_4:Eu$  and  $Y_2O_3:Eu$  phosphors used to produce the red color in television tubes (Palilla and Levine 1966; Hong et al. 1999); it is used to create yttrium iron garnets (YIG) used in microwave filters (Geschwind 1961); and it is used to make the high-temperature semiconductor  $YBa_2Cu_3O_7$  (Jorgensen et al. 1990). The natural occurrence of  $Y_2O_3$  was first described by Novgorodova et al. (1995) from the Bol'shaya Pol'ya River, Subpolar Urals, Russia (Fig. 1) [unnamed mineral UM1995-19-O:Y, Smith and Nickel (2007)]. Herein, we report the complete characterization of this material as a new mineral.

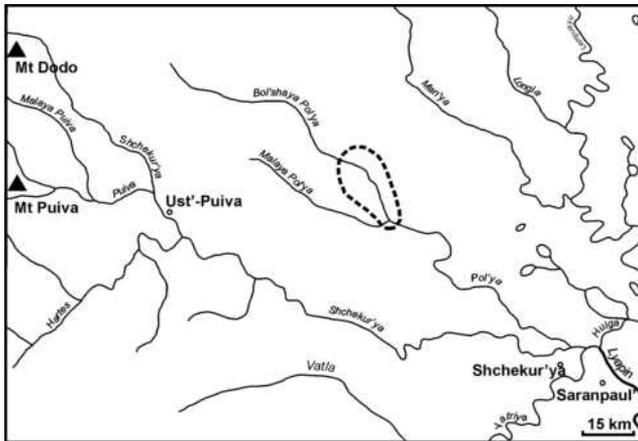
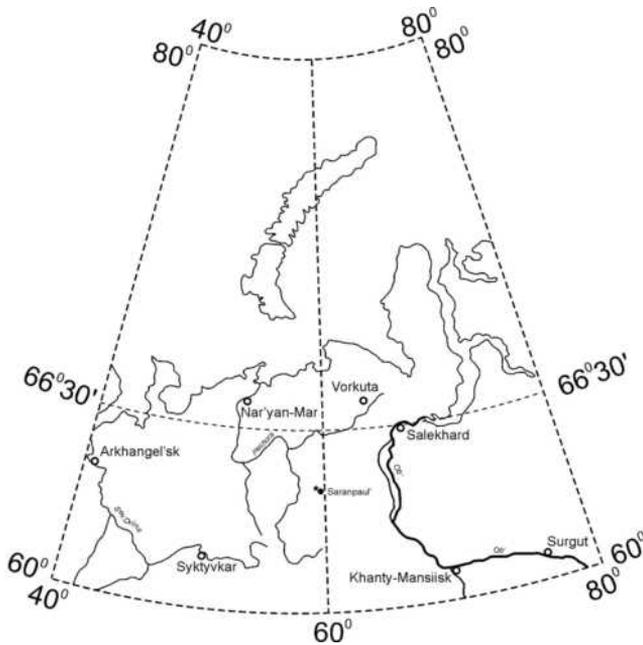
The mineral and name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA 2010-039). The mineral name is based on the common name for the chemical compound, yttria. Because no single specimen provided all of the data for the description, no specimen qualifies as the holotype; however, one co-type specimen is housed in the collections of Mineral Sciences Department, Natural History Museum of Los Angeles County (California, U.S.A.), catalog number 63272, and one is in the collections of Fersman Mineralogical Museum (Moscow, Russia), registered number 4147/1.

### OCCURRENCE AND GEOLOGY

Yttriaite-(Y) is very rare and occurs exclusively as micro-inclusions within native tungsten<sup>1</sup> grains (Fig. 2). Quartz and "phengite" are also found as inclusions in the W grains. Yttriaite-(Y) and native W were discovered during a geological survey

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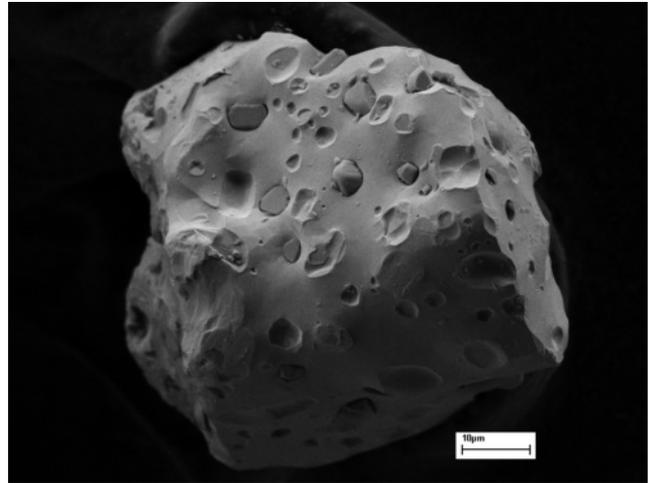
<sup>1</sup> Tungsten has recently been accepted as a new mineral (IMA2011-004).



**FIGURE 1.** Location map for the Bol'shaya Pol'ya River Basin, Subpolar Urals, Russia. Regional map (**top**) and local map (**bottom**). Dashed outline shows the area rich in W and yttriaite-(Y).

for gold placers in the Bol'shaya Pol'ya River Valley. The river valley is characterized by a 30 m thick sequence of friable sediments composed of inter-layered sandstones, alewives and pebbly sands of Pleistocene-Holocene age. These sediments are typical in the Ural erosion-structural depressions. Modern alluvial deposits in the Bol'shaya Pol'ya River were formed by erosion of these friable strata and also by erosion of basement gneisses, amphibolites, quartzites, and conglomerates of Upper Proterozoic-Cambrian age, schists, sandstones, and gravellites of Ordovician age, gabbros of Silurian age, and small bodies of serpentinites. Gold placers, known in the region since the beginning of the 20th Century, are derived from gold-sulfide-quartz veins within diabases and diabase porphyries. Other minerals, which occur with the yttriaite-(Y)/W in the placer, include copper, zircon, osmium, gold, and pyrite.

Initial drilling, conducted by the Severo-Sos'vinskaya geological survey expedition in the early 1980s showed the presence



**FIGURE 2.** SEM-SE photomicrograph of yttriaite-(Y) inclusions in tungsten. The grain is about 30  $\mu\text{m}$  across.

of grains of native W along all vertical sections (up to at least 30 m in depth) of modern and ancient friable sediments. In some drill holes, native W concentrations were estimated to be as high as hundreds of milligrams per cubic meter. Contamination of these holes can be excluded because metallic W and its alloys and composites were not used in any of the drilling equipment. The region is also geographically located quite far from any industrial plants/enterprises, oil pipelines, and other possible sources of contaminants. Contamination from the Soviet aerospace program can also be discounted, because different W alloys were used in their space equipment and the Bol'shaya Pol'ya River Valley is away from any flight or blast pathways. These placers have also never been exploited by mining. Native W has also been observed in situ [but without yttriaite-(Y) inclusions] at the nearby Mt. Dodo locality (Fig. 1).

Although  $\text{Y}_2\text{O}_3$ -W alloys have been recently described (e.g., Aguirre et al. 2009; Ishiwata et al. 1995; Kim et al. 2000, 2006) in the material sciences literature, we are unable to make a convincing argument for their manufacture and incorporation in these sediments in Siberia prior to the 1980s in the volume that has been found (hundreds of milligrams per cubic meter over 30 m in depth). It is, therefore, concluded that the drill cores represent undisplaced strata of age up to 0.5 million years old.

In addition, a sample of synthetic tungsten containing 0.5 wt%  $\text{Y}_2\text{O}_3$  from the study of Aguirre et al. (2009) was subjected to the same SEM-EBS and Raman studies that were used for the yttriaite-(Y). In the case of the synthetic composite, the yttrium-containing phases were found to contain significant amounts of tungsten and presented different electron diffraction and Raman patterns from the yttriaite-(Y). Thus, the synthetic W- $\text{Y}_2\text{O}_3$  composite was considered to be unrelated to natural sample and its properties were not examined further.

Inclusions of rock-forming minerals (quartz and "phengite") within native tungsten with yttriaite-(Y) supply us with very important genetic information. We can infer from this association that it was formed within hydrothermal quartz veins below a temperature of 400  $^{\circ}\text{C}$  (the upper limit of thermal stability of "phengite"). Both quartz and "phengite" are the most common

constituents of the Ordovician schists and associated with these schists are alpine-type veins, which are very abundant in the area.

### PHYSICAL AND OPTICAL PROPERTIES

Yttriaite-(Y) occurs as isolated crystals, typically  $<6\ \mu\text{m}$  in diameter, embedded in massive native tungsten. Some crystals have a rounded globular shape, however, most are cubo-octahedra (Fig. 2), exhibiting the forms  $\{100\}$  and  $\{111\}$ . Because of the small grain size, physical properties could not be determined on the natural material. Synthetic  $\text{Y}_2\text{O}_3$  has been widely studied and most properties have been previously determined. Synthetic  $\text{Y}_2\text{O}_3$  is colorless to white and has a white streak. Crystals are transparent with an adamantine luster, while massive material is typically translucent with an earthy luster. The fluorescence of synthetic  $\text{Y}_2\text{O}_3$  is variable, depending on the presence of trace amounts of other REE ions (e.g., Krupke 1966). The Vickers hardness is 653.91 (Cha et al. 2009), which corresponds to 5.5 on the Mohs scale. Synthetic crystals exhibit good cleavage on  $\{111\}$  (Hanic et al. 1984). Parting, fracture, and density of the natural material could not be determined due to size of the crystals; however, the calculated density on the basis of the empirical formula and an  $a$  cell dimension of  $10.60\ \text{\AA}$  is  $5.073\ \text{g/cm}^3$ .

Yttriaite-(Y) is isotropic; because of the small size of the crystals, we could not measure the index of refraction. The refractive index for synthetic  $\text{Y}_2\text{O}_3$  measured at  $587\ \text{nm}$  is 1.931 (Bass et al. 2010).

### CHEMICAL COMPOSITION

Quantitative wavelength-dispersive electron-microprobe analyses (4 points) were carried out using a JSM-5610LV with an INCA-450 EDS attachment at IGM, Russia. Operating conditions were 25 kV and 20 nA with a  $1\ \mu\text{m}$  beam diameter. No other elements were detected. The results, as well as the standards used, are shown in Table 1. The empirical formula (based on three O atoms) is:  $\text{Y}_{1.98}\text{Dy}_{0.01}\text{Yb}_{0.01}\text{O}_3$ . The simplified end-member formula is  $\text{Y}_2\text{O}_3$ . Trace elements are highly variable in yttriaite-(Y) and are near the limit of detection of a microprobe. Unfortunately, due to the small grain size, we were unable to obtain LA-ICMP-MS data, which would have enabled a discussion of possible REE fractionation effects.

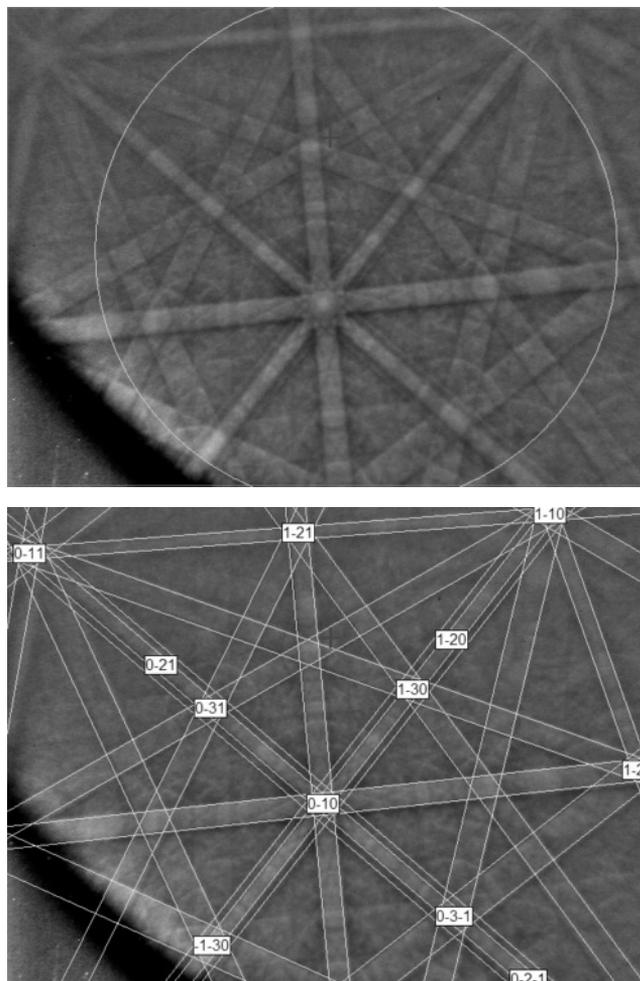
### X-RAY DIFFRACTION

#### Electron backscatter diffraction (EBSD)

Single-crystal X-ray studies could not be carried out due to the nature and size of the yttriaite-(Y) crystals. EBSD analyses (Fig. 3) confirmed an exact match to synthetic  $\text{Y}_2\text{O}_3$  (e.g., Ishibashi et al. 1994) and the unit-cell data obtained below, with mean angular deviations as low as 0.21, using the methods described in Ma and Rossman (2008, 2009). An HKL system on a ZEISS

**TABLE 1.** Analytical data for yttriaite-(Y)

Constituent	wt%	Range	St.dev.	Probe standard
$\text{Y}_2\text{O}_3$	98.27	97.49–98.72	0.56	Synthetic $\text{YPO}_4$
$\text{Tb}_2\text{O}_3$	0.20	0–0.31	0.14	Synthetic $\text{TbPO}_4$
$\text{Dy}_2\text{O}_3$	0.47	0.24–0.74	0.25	Synthetic $\text{DyPO}_4$
$\text{Ho}_2\text{O}_3$	0.29	0–0.74	0.36	Synthetic $\text{HoPO}_4$
$\text{Er}_2\text{O}_3$	0.05	0–0.18	0.09	Synthetic $\text{ErPO}_4$
$\text{Tm}_2\text{O}_3$	0.09	0–0.35	0.18	Synthetic $\text{TmPO}_4$
$\text{Yb}_2\text{O}_3$	0.64	0.35–1.25	0.42	Synthetic $\text{YbPO}_4$
Total	100.01			



**FIGURE 3.** EBSD pattern for yttriaite-(Y) (top) and the pattern indexed with the synthetic  $\text{Y}_2\text{O}_3$  structure (bottom).

1550VP scanning electron microscope, operated at 20 kV and 6 nA in a focused beam with a  $70^\circ$  tilted stage, was used for the in situ EBSD analysis.

#### Powder diffraction

We were unable to obtain powder diffraction of yttriaite-(Y) crystals using conventional Gandolfi-style techniques due to the low volume compared to the native W. Instead, we report the powder diffraction data obtained on synthetic  $\text{Y}_2\text{O}_3$  (Alfa Chemicals), which was used as a calibration standard for the diffraction experiments of parwanite (Birch et al. 2007a) and pittongite (Grey et al. 2006; Birch et al. 2007b). Powder-diffraction data were recorded using synchrotron radiation in a high-resolution powder diffractometer at the Photon Factory (KEK), Tsukuba, Japan. Partial diffraction rings were collected on three concurrent image plates, located 573 mm from the axially spinning sample. Data were collected at a wavelength of  $0.800\ \text{\AA}$  (Table 2). Unit-cell parameters, derived from whole pattern fitting using JADE 9.1 software are:  $a = 10.5897(2)\ \text{\AA}$ ,  $V = 1187.6(2)\ \text{\AA}^3$ , and  $Z = 16$ . The data are consistent with the unit cell [ $a = 10.60(3)\ \text{\AA}$ ] based on SAED images given by Novgorodova et al. (1995) and older determinations for synthetic  $\text{Y}_2\text{O}_3$  (e.g., Brauer and Gradinger 1954).

**TABLE 2.** X-ray powder diffraction data for synthetic  $Y_2O_3$  (synchrotron radiation, wavelength 0.800 Å)

<i>hkl</i>	<i>d</i> <sub>obs</sub> (Å)	<i>d</i> <sub>calc</sub> (Å)	<i>I</i> <sub>obs</sub>
<b>211</b>	<b>4.3356(4)</b>	<b>4.3386</b>	<b>14</b>
<b>222</b>	<b>3.0646(1)</b>	<b>3.0646</b>	<b>100</b>
<b>400</b>	<b>2.6537(1)</b>	<b>2.6531</b>	<b>26</b>
411	2.5017(2)	2.5011	6
420	2.3730(6)	2.3724	1
332	2.2623(2)	2.2618	8
422	2.1658(5)	2.1654	1
134	2.0807(1)	2.0803	11
125	1.9360(13)	1.9364	3
<b>440</b>	<b>1.8748(1)</b>	<b>1.8748</b>	<b>55</b>
433	1.8187(2)	1.8187	3
600	1.7672(6)	1.7674	1
611	1.7200(1)	1.7202	7
026	1.6764(2)	1.6766	2
145	1.6365(5)	1.6361	4
<b>622</b>	<b>1.5983(1)</b>	<b>1.5984</b>	<b>38</b>
136	1.5631(1)	1.5633	9
444	1.5302(1)	1.5303	7
543	1.4992(1)	1.4993	3
046	1.4701(2)	1.4702	2
721	1.4425(1)	1.4427	5
642	1.4165(1)	1.4166	2
156	1.3462(1)	1.3463	3
800	1.3250(1)	1.325	7
811	1.3047(1)	1.3048	6
820	1.2854(1)	1.2854	3
356	1.2669(1)	1.2669	3
822	1.2492(1)	1.2492	2
831	1.2322(1)	1.2322	6
662	1.2159(1)	1.2158	13
048	1.1851(1)	1.185	9
833	1.1706(1)	1.1704	3

Note: Five strongest lines are in bold face.

**TABLE 3.** Minerals of the bixbyite group

Bixbyite, (Mn,Fe) <sub>2</sub> O <sub>3</sub>
Avicennite, Ti <sub>2</sub> O <sub>3</sub>
Yttriaite-(Y), Y <sub>2</sub> O <sub>3</sub>

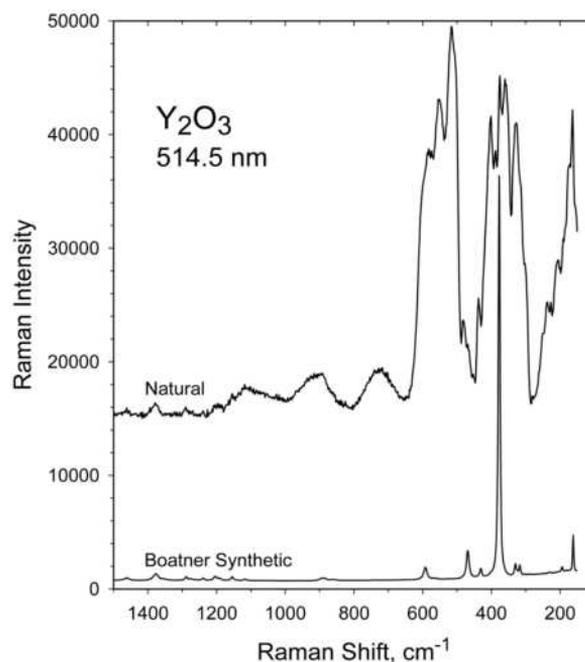
### CRYSTAL STRUCTURE AND GROUP NOMENCLATURE

Yttriaite-(Y) has a bixbyite-type crystal structure, (Y<sub>2</sub>A<sub>2</sub>)(Y<sub>2</sub>O<sub>3</sub>), which is body-centered cubic (e.g., Hanic et al. 1984). Although yttrium is not a lanthanoid element, it is usually found in nature together with the lanthanoids in various rare-earth minerals and is commonly grouped with the rare-earth elements in mineralogy. Thus, as the first naturally occurring “rare-earth” oxide with the formula REE<sub>2</sub>O<sub>3</sub>, the mineral yttriaite-(Y) contains the suffix “-(Y),” which designates the dominant REE in the phase.

In the yttriaite-(Y) structure, Y<sup>3+</sup> ions occupy positions at (1/4, 1/4, 1/4) and (x, 0, 1/4) while the O atom occupies a general position (x, y, z). The structure of yttriaite-(Y) is related to the fluorite structure-type by reducing the A<sup>2+</sup> cation from eightfold coordination to sixfold, when A is 3+. Group nomenclature has not been set out for minerals with the bixbyite structure (Table 3), it is appropriate to do so following the rules of Mills et al. (2009). Because bixbyite is the oldest known mineral with the bixbyite structure, the group takes this name.

### RAMAN SPECTROSCOPY

Raman spectroscopic microanalysis was carried out using a Renishaw M1000 micro-Raman spectrometer system. Spectra were obtained with both a 514.5 nm argon ion laser and a 783.5 nm solid-state laser with a 100× objective, producing a spot about 0.9 μm in diameter with about 2.5 mW power at the



**FIGURE 4.** Raman spectra of yttriaite-(Y) taken with 514.5 nm laser excitation compared to a synthetic crystal of  $Y_2O_3$  from Lynn Boatner.

sample. Peak positions were calibrated against a silicon standard. A dual-wedge polarization scrambler was used in the laser beam for all spectra to minimize the effects of polarization. Literature Raman data were obtained from Schaack and Koningstein (1970) and Gajovic et al. (2005). Spectra of laboratory standards were obtained from Aldrich Chemical Company yttria powder and a single crystal provided by Lynn Boatner. The main feature of the yttria spectrum, the band at 378  $cm^{-1}$ , is seen in all the spectra, including the yttriaite-(Y) spectra taken with both 514.5 and 783.5 nm lasers. The yttriaite-(Y) spectra, in particular (Fig. 4), show significant interference from fluorescence, presumably from other rare-earth elements (Dy and Yb) (e.g., Tanner and Wong 2004). While the yttriaite-(Y) Raman spectrum is not particularly diagnostic, it is compatible with a mineral that is yttrium oxide containing lanthanoids.

### ACKNOWLEDGMENTS

Associate Editor Fernando Colombo, referee Igor Pekov, and an anonymous reviewer provided helpful comments on the manuscript, which are greatly appreciated. NSERC Canada is thanked for a Discovery Grant to M.R. Parts of this study were funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County and the White Rose Foundation at Caltech. The collection of synchrotron data was undertaken at the Australian National Beamline Facility with support from the Australian Synchrotron Research Program, which is funded by the Commonwealth of Australia under the Major National Research Facilities Program. SEM-EBSD analysis was carried out at the Caltech Geological and Planetary Sciences Division Analytical Facility, which is supported in part by NSF Grant EAR-0318518 and the NSF MRSEC Program under grant DMR-0080065. Lynn Boatner (Oak Ridge National Laboratory) is thanked for donation of the synthetic  $Y_2O_3$  crystal standards. Jose Ygnacio Pastor (Universidad Politécnica de Madrid) is thanked for providing a specimen of synthetic  $W+Y_2O_3$  for further study.

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MANUSCRIPT RECEIVED NOVEMBER 14, 2010

MANUSCRIPT ACCEPTED FEBRUARY 1, 2011

MANUSCRIPT HANDLED BY FERNANDO COLOMBO