

BISMUTOTALITE FROM NORTHWESTERN ARGENTINA: DESCRIPTION AND CRYSTAL STRUCTURE

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ABSTRACT

Bismutotalite occurs in albite-rich cores of the La Elvirita granitic pegmatites, northwestern Argentina, associated mainly with bismuth, bismuthinite, ferrotapiolite, manganotalite, microlite, uranmicrolite, bismutomicrolite, hafnian zircon and montebrasite. A fresh, cm-sized crystal, dark grey with a greasy luster and $D = 8.809 \text{ g/cm}^3$, was examined. In reflected light, it is grey with very weak bireflectance; two phases can be distinguished. Electron-microprobe analysis gives the host bismutotalite [Bi] as $(\text{Bi}_{0.98}\text{Sb}_{0.02})(\text{Ta}_{0.89}\text{Nb}_{0.11})\text{O}_4$; the subsidiary phase [Bi,Sb], $(\text{Bi}_{0.68}\text{Sb}_{0.32})(\text{Ta}_{0.89}\text{Nb}_{0.11})\text{O}_4$, is enriched in Sb. Least-squares refinement of X-ray powder-diffraction data of [Bi] gave $a 4.968(1)$, $b 11.796(3)$, $c 5.646(1) \text{ \AA}$, $V = 330.85(9) \text{ \AA}^3$. The crystal structures of [Bi] and [Bi,Sb] were refined to R indices of 1.9 and 2.4%, based on 387 and 377 observed (4σ) reflections, respectively, measured with $\text{MoK}\alpha$ X-radiation. Both phases are orthorhombic, space group $Pcnn$, $Z = 4$; [Bi] has $a 4.9652(4)$, $b 11.7831(16)$, $c 5.6462(5) \text{ \AA}$, $V 330.32(6) \text{ \AA}^3$, and [Bi,Sb] has $a 4.9471(4)$, $b 11.7878(7)$, $c 5.6048(3) \text{ \AA}$, $V 326.83(4) \text{ \AA}^3$. These results show that the centrosymmetric structure of bismutotalite can accommodate up to ~40% Sb^{3+} substituting for Bi^{3+} without changing to the $Pc2_1n$ structure of stibiotantalite.

Keywords: bismutotalite, crystal-structure refinement, electron-microprobe analysis, granitic pegmatite, La Elvirita, Argentina.

SOMMAIRE

La bismutotalite est présente dans le coeur riche en albite des massifs de pegmatite granitique de La Elvirita, dans le nord-ouest de l'Argentine, en association surtout avec bismuth, bismuthinite, ferrotapiolite, manganotalite, microlite, uranmicrolite, bismutomicrolite, zircon hafnifère et montebrasite. Nous avons porté notre attention sur un cristal centimétrique non altéré, gris foncé, avec un éclat gras et une densité de 8.809 g/cm^3 . En lumière réfléchie, la bismutotalite est grise avec une bireflectance très faible; deux phases distinctes sont présentes. Une analyse à la microsonde électronique de la phase hôte [Bi] a donné $(\text{Bi}_{0.98}\text{Sb}_{0.02})(\text{Ta}_{0.89}\text{Nb}_{0.11})\text{O}_4$; la phase accessoire, que nous appelons [Bi,Sb], est enrichie en antimoine: $(\text{Bi}_{0.68}\text{Sb}_{0.32})(\text{Ta}_{0.89}\text{Nb}_{0.11})\text{O}_4$. Une affinement de données de diffraction X pour [Bi] par la méthode des poudres a donné $a 4.968(1)$, $b 11.796(3)$, $c 5.646(1) \text{ \AA}$, $V 330.85(9) \text{ \AA}^3$. Les structures cristallines de [Bi] et de [Bi,Sb] ont été affinées jusqu'à un résidu R de 1.9 et 2.4%, respectivement, en utilisant 387 et 377 réflexions observées (4σ), mesurées avec rayonnement $\text{MoK}\alpha$. Les deux phases sont orthorhombiques, groupe spatial $Pcnn$, $Z = 4$; les paramètres de [Bi] sont $a 4.9652(4)$, $b 11.7831(16)$, $c 5.6462(5) \text{ \AA}$, $V 330.32(6) \text{ \AA}^3$, tandis que ceux de [Bi,Sb] sont $a 4.9471(4)$, $b 11.7878(7)$, $c 5.6048(3) \text{ \AA}$, $V 326.83(4) \text{ \AA}^3$. Ces résultats montrent que la structure centrosymétrique de la bismutotalite peut accommoder jusqu'à ~40% de Sb^{3+} en substitution du Bi^{3+} sans transformation à la structure $Pc2_1n$ de la stibiotantalite.

(Traduit par la Rédaction)

Mots-clés: bismutotalite, affinement de la structure cristalline, analyse à la microsonde électronique, pegmatite granitique, La Elvirita, Argentine.

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INTRODUCTION

Bismutotantalite, ideally BiTaO_4 , is a fairly rare mineral that occurs usually in geochemically highly evolved granitic pegmatites (Foord 1982, Černý & Ercit 1989). Some of the physical and optical properties and the chemical composition have been reported in earlier studies (Wayland & Spencer 1929, Hurlbut 1957). The mineral was discovered in a granitic pegmatite at Gamba Hill, Kampala, Uganda (Wayland & Spencer 1929), where it occurs in crystals of up to several kilograms, associated with quartz, kaolinized K-feldspar and buff-colored mica; tourmaline and traces of cassiterite occur in the same pegmatite. Frenzel (1955) studied bismutotantalite from two localities in Brazil: Acary, Rio Grande do Norte, and Recife, Paraíba. Probably, these two localities are the same as those reported by Bhaskara Rao & Adusumilli (1966): Acari in Rio Grande do Norte, and Picui and Pedra Lavrada, Paraíba, Brazil. At all these Brazilian localities, bismutotantalite is found

as pebbles in gravel beds. Hurlbut (1957) studied samples of pebbles from Acari and determined the space group of bismutotantalite to be $Pcmm$ or $Pc2_1n$. Correia Neves *et al.* (1974) described bismutotantalite occurrences from Mozambique. Von Knorring & Fadipe (1981) mentioned that bismutotantalite occurs in the Wampewo and Mbele pegmatites, Uganda, where it is commonly altered to bismuthian microlite. Voloshin *et al.* (1983) reported the chemical composition of bismutotantalite from the granitic pegmatites of Koktokai, Sincizyan, China. In spite of all this work, the details of the structure of bismutotantalite still remain to be determined.

Ahlfeld & Angelelli (1948) reported the occurrence of powdery bismutotantalite from the El Quemado granitic pegmatites, northwestern Argentina. During a study of (Nb-Ta)-bearing minerals from pegmatites of the Pampean Ranges, a sample from La Elvirita mine, one of the pegmatites of the El Quemado pegmatite field, was identified as bismutotantalite. Here, we describe the paragenesis, physical and optical properties, chemical composition and crystal structure of bismutotantalite from this locality.

OCCURRENCE

The La Elvirita mine is located at $24^\circ 45' 11''$ S and $66^\circ 20' 44''$ W, 4040 m above sea level in Salta Province, northwestern Argentina. It is situated in one of the smaller pegmatites of the El Quemado pegmatite field (Fig. 1), the northernmost rare-element pegmatite field of the Pampean Pegmatite Province. La Elvirita consists of three small pegmatite dikes intruded into the northwestern side of an epizonal trondhjemite stock. The largest dike is 40 m long and 1.10 m wide, a tabular body that strikes $N20^\circ$ W and dips 45° SE. The pegmatite consists of border and wall zones and a core (Fig. 2). Quartz, albite and muscovite are the principal minerals of the border zone, and tourmaline is accessory. The wall zone is medium grained and consists of the same minerals plus apatite and manganocolumbite. The core consists of fine-grained albite, subordinate quartz of medium grain-size, and a completely altered pinkish

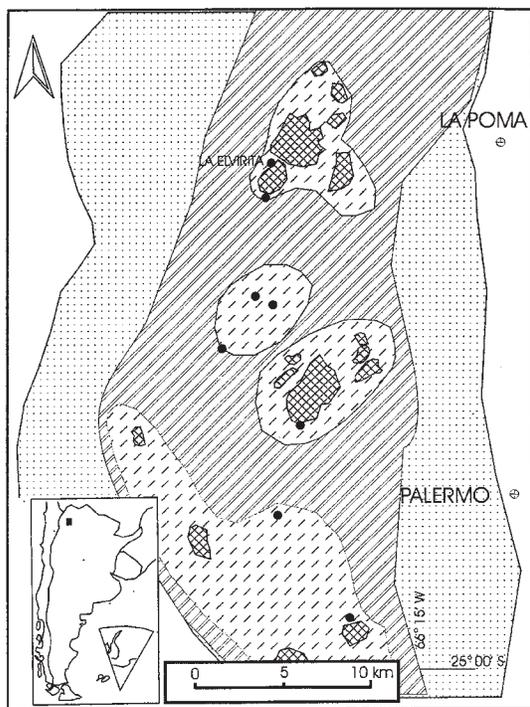


FIG. 1. Geological map of the El Quemado pegmatite field, modified from Galliski (1983a), with the location of La Elvirita pegmatite. Slates and phyllites are dotted, diagonal ruling denotes spotted-slates, phyllites and micaschists, and cordierite-spotted schists and K-feldspar-sillimanite-cordierite hornfels are dashed. Rectangular grid represents trondhjemite stocks, and solid circles are rare-element pegmatites.

TABLE 1. REFLECTANCE VALUES (%) IN AIR FOR BISMUTOTANTALITE

lnm	R_{\max}	R_{\min}	lnm	R_{\max}	R_{\min}
400	23.0	21.8	560	19.8	19.4
420	20.5	17.8	580	19.7	19.4
440	21.3	20.8	589	19.9	19.5
460	20.9	20.2	600	19.8	19.3
470	20.2	19.5	620	19.7	19.0
480	20.6	20.3	640	18.7	18.1
500	20.6	20.4	650	18.3	17.8
520	20.8	20.1	660	17.8	16.0
540	19.9	19.6	680	16.3	15.4
546	20.3	19.8	700	12.9	11.5(1)

white mineral. In the hanging-wall contact, the core carries montebrasite, hafnian zircon, bismuthinite, tantalite, uranmicrolite and triphylite-like minerals. In samples provided by the owner (collected when the mine was active), bismutotantalite, bismuthinite, bismuth, ferrotapiolite, microlite, uranmicrolite and sphalerite were recognized. Close to the south, in the same pegmatite field, there are some larger dikes of pegmatite with petalite transformed to pseudomorphs of spodumene + quartz, lepidolite, montebrasite, and fairly abundant columbite-group minerals that were mined in 1941–45 and 1957 (Galliski 1983b).

PHYSICAL AND OPTICAL PROPERTIES

Bismutotantalite occurs in two different samples. One sample consists of a 3-cm-long imperfect crystal with rough brown pyramidal faces. In polished section, this material is grey and consists of bismutotantalite cross-cut by a network of veinlets of tapiolite and minor bismuth. Microlite and bismutomicrolite are common in small grains and microveinlets as an alteration product. The second sample consists of a fresh-looking irregular $3 \times 2 \times 1.5$ cm fragment of a crystal of almost pure bismutotantalite. It is dark grey with a greasy luster (Fig. 3). Two cleavages are clearly visible, corresponding to {010} and {101} (perfect and fair, respectively). The density was measured with a Berman torsion balance on three different single grains; the average value is 8.809 g/cm^3 .

The optical properties and reflectance values were obtained using a Leitz microscope and one of the sili-

con samples tested for the paper of Pauly (1986) as a standard. In reflected light, bismutotantalite is grey; its birefractance is very weak, and pleochroism is not observable. The measured reflectance data are given in Table 1. Anisotropy is negligible in air, but distinct in oil. The colors under crossed nicols are grey to grey with an olive-greenish tint. Despite the weak anisotropy, bismutotantalite seems to show extinction parallel to the better cleavage, similar to that of columbite-tantalite. Internal reflections are scarce in air, but relatively abundant and darker in oil: yellow, yellowish brown and orange brown. Inclusions of bismuth, bismutomicrolite and Sb-bearing bismutotantalite are common. Bismuth occurs as 20–80 μm roundish or elongate inclusions, in some cases accentuating the pattern of cleavage. Bismutomicrolite occurs as 50 μm irregular grains. Antimony-bearing bismutotantalite forms roundish to elongate (< 2 mm) patches, which commonly contain small and irregular grains of bismuth (Fig. 4).

CHEMICAL COMPOSITION

Electron-microprobe analysis of bismutotantalite was done in wavelength-dispersion mode on a Cameca SX-50 instrument with a beam diameter of 1–2 μm , an acceleration potential of 15 kV, and a sample current of 20 nA measured on a Faraday cup. Counting times of 20 s were used for Fe, Mn, Sn, Ti, Nb and Ta; for Mg, Ca, Sb, As, Bi, Sc, Zr, Pb and U, 40 nA and 50 s were used. The following standards were used: manganotantalite ($\text{TaM}\alpha$), FeNb_2O_6 ($\text{FeK}\alpha$), MnNb_2O_6 ($\text{NbL}\alpha$, $\text{MnK}\alpha$), SnO_2 ($\text{SnL}\alpha$), rutile ($\text{TiK}\alpha$), ZrO_2 ($\text{ZrL}\alpha$), $\text{NaScSi}_2\text{O}_6$ ($\text{ScK}\alpha$), YAG ($\text{YL}\alpha$), gahnite ($\text{ZnK}\alpha$), MgNb_2O_6 ($\text{MgK}\alpha$), BiTaO_4 ($\text{BiM}\alpha$), CaWO_4 ($\text{WMB}\beta$), mimetite ($\text{AsL}\alpha$, $\text{PbM}\alpha$), CaNb_2O_6 ($\text{CaK}\alpha$), stibiotantalite ($\text{SbL}\alpha$), ThO_2 glass ($\text{ThM}\alpha$) and UO_2 ($\text{UM}\alpha$). Data were reduced using the PAP routine of Pouchou & Pichoir (1984,1985).

The chemical compositions of the La Elvirita bismutotantalite fall into two groups, representing the host near-end-member bismutotantalite [Bi], and a minor antimony-bearing bismutotantalite phase [Bi,Sb] (Table 2, Fig. 5). The [Bi] phase has a chemical composition close to that of end-member bismutotantalite, with only 3.3% Nb_2O_5 , less than 1% Sb_2O_3 , and local traces of W, Ti, Th, U, Sc, Mg, Ca, Mn, Fe and Pb. The antimony-bearing bismutotantalite [Bi,Sb] has a slightly higher content of Ta_2O_5 (Table 2) and, on average, 11.15% Sb_2O_3 . Comparison of chemical compositions with those given in Černý & Ercit (1989, Fig. 12) shows that the main phase is one of the most Ta- and Bi-rich members of the stibiotantalite group known to date. The average composition of the [Bi] phase is $(\text{Bi}_{0.98}\text{Sb}_{0.02})(\text{Ta}_{0.89}\text{Nb}_{0.11})\text{O}_4$, and the [Bi,Sb] phase averages $(\text{Bi}_{0.68}\text{Sb}_{0.32})(\text{Ta}_{0.89}\text{Nb}_{0.11})\text{O}_4$. The similar Ta:Nb ratio in the two phases and the textural relation with bismuth (Fig. 4) suggest that the [Bi,Sb] phase formed by local

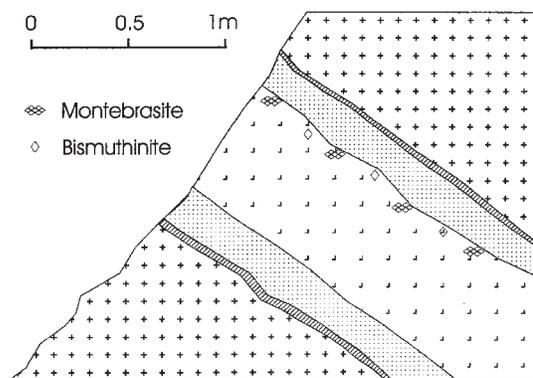


FIG. 2. Sketch of the internal structure of La Elvirita pegmatite. The host rock is trondhjemite, the border zone (with oblique lines) has quartz + albite + muscovite \pm tourmaline, the wall zone (represented by small dots) is composed of quartz + albite + muscovite \pm apatite \pm manganocolumbite. The core has albite, quartz and montebrasite, bismuthinite, and hafnian zircon close to the hanging wall.



FIG. 3. The sample of bismutotantalite selected for study. The white tabular crystals on the left are albite. Scale bar: 1 cm.

replacement of the main phase by a late Sb-rich solution.

X-RAY POWDER-DIFFRACTION DATA

X-ray powder-diffraction data were obtained for the [Bi] phase with a Philips 1710 automated powder diffractometer using $\text{CuK}\alpha$ X-radiation. The data were collected from 5 to $90^\circ 2\theta$ at 0.6° per minute. Silicon (Si batch 649b NBS, $a = 5.430825 \text{ \AA}$) was used as an internal standard, and intensities were measured at peak maxima. The cell parameters were refined with the CELREF program (Appleman & Evans 1973): a 4.968(1), b 11.796(3), c 5.646(1) \AA , V 330.85(9) \AA^3 . Table 3 gives the X-ray powder-diffraction pattern.

SPACE GROUP OF BISMUTOTALITE

Hurlbut (1957) showed that the cell dimensions of bismutotantalite from Uganda and Brazil are very similar ($a \approx 4.9$, $b \approx 11.8$, $c \approx 5.6 \text{ \AA}$). Reflection absences on Weissenberg photographs of Brazilian bismutotantalite led Hurlbut (1957) to suggest the space groups $Pcmm$ and $Pc2_1n$, and $Pcmm$ was assigned because the crystals did not show any pyroelectric or piezoelectric effect. Earlier work on the related phase, stibiotantalite (Penfield & Ford 1906), showed a strong pyroelectric effect, consistent with the polar space-group $Pc2_1n$. More recently, the crystal structure of $\alpha\text{-BiNbO}_4$ was



FIG. 4. Back-scattered electron image of bismutotantalite – stibian bismutotantalite; greyish white: native bismuth; pale grey: bismutotantalite; medium grey: stibian bismutotantalite; dark grey: microlite–bismutotantalite. Width of field of view: 1.1 mm.

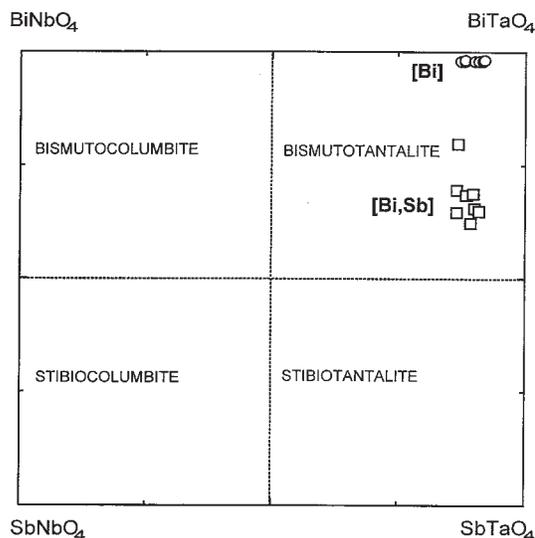


FIG. 5. Chemical composition of the two phases of La Elvirita bismutotantalite, plotted in the stibiotantalite-group quadrilateral.

TABLE 2. CHEMICAL COMPOSITION* (wt. %) AND UNIT FORMULAE (apfu)** OF BISMUTOTANTALITE

	MAIN PHASE [Bi] (N = 9)			MINOR PHASE [Bi,Sb] (N = 8)		
	Range	Mean	σ	Range	Mean	σ
WO ₃	0.00-0.58	0.09	0.19	0.00-0.34	0.09	0.12
Nb ₂ O ₅	2.40-5.03	3.24	0.83	2.49-4.26	3.50	0.69
Ta ₂ O ₅	41.64-45.19	44.33	1.16	46.09-48.57	47.05	0.84
TiO ₂	0.00-0.17	0.03	0.06	0.00-0.05	0.01	0.02
ThO ₂	0.00-0.13	0.03	0.04	0.00-0.03	0.01	0.01
UO ₂	0.00-0.10	0.03	0.03	0.00-0.13	0.02	0.05
Sb ₂ O ₃	0.59-0.70	0.63	0.03	6.76-13.14	11.15	1.95
Bi ₂ O ₃	50.49-52.24	51.30	0.67	34.79-42.33	37.63	2.42
MnO	0.00-0.09	0.03	0.04	0.00-0.02	0.00	0.01
FeO	0.00-0.08	0.03	0.03	0.00-0.08	0.02	0.03
PbO	0.00-0.26	0.06	0.10	0.00-0.24	0.05	0.09
Total	98.80-101.08	99.84	0.79	98.61-100.94	99.54	0.70
W	0.000-0.011	0.002	0.004	0.000-0.006	0.001	0.002
Nb	0.081-0.165	0.108	0.027	0.079-0.132	0.110	0.020
Ta	0.820-0.920	0.889	0.031	0.864-0.927	0.890	0.024
Ti	0.000-0.009	0.002	0.003	0.000-0.003	0.001	0.001
Zr	0.000-0.000	0.000	0.000	0.000-0.000	0.000	0.000
Th	0.000-0.002	0.000	0.001	0.000-0.000	0.000	0.000
U	0.000-0.001	0.000	0.000	0.000-0.002	0.000	0.001
Sb	0.018-0.021	0.019	0.001	0.200-0.374	0.319	0.053
Bi	0.972-0.978	0.975	0.002	0.620-0.783	0.675	0.051
Mn	0.000-0.006	0.002	0.002	0.000-0.001	0.000	0.000
Fe ₂	0.000-0.005	0.002	0.002	0.000-0.005	0.001	0.002
Pb	0.000-0.005	0.001	0.002	0.000-0.004	0.001	0.001
Total	1.999-2.005	2.003		1.994-2.004	1.999	

* Sn, Sc, Mg, Ca, Zn, Zr, As, Y not detected

** calculated on the basis of four O atoms,

reported in *Pnna* [$\equiv Pcnm$] (Subramanian & Calabrese 1993). The space groups *Pc2₁n* and *Pcmm* can be differentiated only on the basis of dissimilarity between Friedel pairs of reflections. However, (*Pc2₁n*, *Pcmm*) and the uniquely determined *Pcnn* can be distinguished on the basis of systematic absences of reflections.

To help resolve the correct space-group for bismutotantalite, we extracted single crystals from the [Bi] and [Bi,Sb] phases and collected long-exposure precession photographs down the 11 Å axis. For both crystals, all observed (*h0l*) reflections were found to be consistent with the condition $h + l = 2n$, in accord with *Pcnn* symmetry.

TABLE 3. X-RAY POWDER-DIFFRACTION DATA FOR BISMUTOTANTALITE

<i>l</i>	d_{obs} (Å)	d_{calc} (Å)	<i>h k l</i>	<i>l</i>	d_{obs} (Å)	d_{calc} (Å)	<i>h k l</i>
2	5.905	5.898	0 2 0	3	1.967	1.966	2 3 1
4	4.584	4.578	1 1 0	15	1.899	1.900	2 4 0
5	3.731	3.730	1 0 1	8	1.864	1.865	2 0 2
25	3.556	3.556	1 1 1	10	1.841	1.842	2 1 2
100	3.151	3.152	1 2 1	4	1.809	1.810	0 5 2
5	3.082	3.083	1 3 0	7	1.778	1.778	2 2 2
40	2.951	2.949	0 4 0	9	1.760	1.760	1 0 3
12	2.823	2.823	0 0 2	20	1.740	1.739	1 6 1
10	2.746	2.745	0 1 2	8	1.685	1.685	2 3 2
9	2.705	2.706	1 3 1	4	1.612	1.613	0 6 2
9	2.547	2.546	0 2 2	4	1.608	1.606	1 3 3
15	2.483	2.484	2 0 0	8	1.575	1.576	2 4 2
1	2.398	2.403	1 1 2	10	1.534	1.534	3 2 1
5	2.311	2.313	1 4 1	8	1.512	1.511	1 4 3
4	2.294	2.293	0 3 2	3	1.488	1.488	2 1 3
4	2.289	2.289	2 2 0	6	1.476	1.474	0 8 0
2	2.266	2.266	1 2 2	6	1.473	1.473	3 3 1
2	2.232	2.233	2 1 1	3	1.463	1.463	2 5 2
2	2.083	2.082	1 3 2	3	1.446	1.447	0 7 2
10	2.039	2.039	0 4 2	2	1.420	1.418	3 1 2
5	1.994	1.994	1 5 1	3	1.411	1.411	1 5 3

TABLE 4. RESULTS OF CRYSTAL-STRUCTURE REFINEMENT FOR BISMUTOTANTALITE

	[Bi] phase	[Bi,Sb] phase
<i>a</i> (Å)	4.9652(4)	4.9471(4)
<i>b</i>	11.7831(6)	11.7878(7)
<i>c</i>	5.6462(5)	5.6048(3)
<i>V</i> (Å ³)	330.32(6)	326.83(4)
Space group	<i>Pcnn</i>	<i>Pcnn</i>
<i>Z</i>	4	4
Crystal size (mm)	0.14 x 0.10 x 0.15	0.10 x 0.08 x 0.04
Radiation	MoK α /Graphite	MoK α /Graphite
No. of F_o^2	450	434
R_i ($ F_o > 4\sigma$) %	1.9	2.4
wR_2 (F_o^2) %	4.1	6.1
Site occupancies		
Bi site	0.96(2) Bi + 0.04(2) Sb	0.62(2) Bi + 0.38(2) Sb
Ta site	0.84(2) Ta + 0.16(2) Nb	0.92(2) Ta + 0.08(2) Nb

TABLE 5. ATOM COORDINATES AND DISPLACEMENT PARAMETERS ($U = U \times 10^4$) FOR BISMUTOTANTALITE

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
[Bi] phase										
<i>Bi</i>	0.22147(6)	1/2	1/4	0.0083(2)	0.0112(2)	0.0108(2)	0.0011(1)	0	0	0.0101(1)
<i>Ta</i>	1/4	3/4	0.64078(5)	0.0066(2)	0.0068(2)	0.0069(2)	0	0	-0.0001(1)	0.0068(2)
O(1)	0.49543(85)	0.69489(41)	0.36094(57)	0.0136(17)	0.0138(21)	0.0142(16)	-0.0007(15)	0.0040(13)	-0.0006(20)	0.0139(9)
O(2)	0.08657(78)	0.59742(36)	0.58723(52)	0.0143(18)	0.0082(18)	0.0105(12)	0.0005(15)	0.0035(14)	-0.0040(17)	0.0110(9)
[Bi,Sb] phase										
<i>Bi</i>	0.21854(11)	1/2	1/4	0.0079(3)	0.0078(3)	0.0096(3)	0.0016(1)	0	0	0.0084(2)
<i>Ta</i>	1/4	3/4	0.63557(6)	0.0016(3)	0.0043(3)	0.0048(3)	0	0	0.0002(1)	0.0035(2)
O(1)	0.49292(124)	0.69680(41)	0.35839(77)	0.0093(30)	0.0091(25)	0.0110(22)	0.0006(17)	0.0044(19)	-0.0050(24)	0.0098(13)
O(2)	0.08608(116)	0.59692(39)	0.58587(78)	0.0070(29)	0.0075(21)	0.0099(18)	-0.0015(19)	0.0043(23)	-0.0010(23)	0.0081(12)

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR BISMUTOTANTALITE

	[Bi] phase	[Bi,Sb] phase		[Bi] phase	[Bi,Sb] phase
<i>Bi</i> -O(1),b	2.742(5)	2.756(5) x2	<i>Ta</i> -O(1)e,f	1.888(4)	1.890(5) x2
<i>Bi</i> -O(2)a,c	2.122(4)	2.103(5) x2	<i>Ta</i> -O(1),d	2.098(4)	2.062(5) x2
<i>Bi</i> -O(2),b	<u>2.322(3)</u>	<u>2.297(5)</u> x2	<i>Ta</i> -O(2),d	<u>1.996(4)</u>	<u>1.998(5)</u> x2
< <i>Bi</i> -O>	2.395	2.385	< <i>Ta</i> -O>	1.994	1.983
O(2)- <i>Bi</i> -O(1)	62.7(2)	62.7(2) x2	O(2)- <i>Ta</i> -O(1)	81.0(2)	81.8(2) x2
O(2)- <i>Bi</i> -O(1)b	138.1(2)	137.7(2) x2	O(2)- <i>Ta</i> -O(1)d	85.9(2)	86.2(2) x2
O(2)- <i>Bi</i> -O(2)a	72.8(2)	73.0(2) x2	O(2)- <i>Ta</i> -O(1)e	93.6(2)	93.8(2) x2
O(2)- <i>Bi</i> -O(2)c	83.1(2)	83.3(2) x2	O(2)- <i>Ta</i> -O(1)f	97.9(2)	96.8(2) x2
O(1)- <i>Bi</i> -O(2)c	90.2(2)	89.5(2) x2	O(1)- <i>Ta</i> -O(1)e	90.0(2)	90.3(2) x2
O(1)- <i>Bi</i> -O(1)a	120.5(2)	121.0(2)	O(1)- <i>Ta</i> -O(1)d	82.3(2)	82.2(2)
O(2)a- <i>Bi</i> -O(2)c	87.7(2)	88.4(2)	O(1)e- <i>Ta</i> -O(1)f	97.6(2)	97.3(2)

a: -x, -y+1, -z+1; b: x, y+1, -z+1/2; c: -x, y, z-1/2; d: -x+1/2, -y+1/2, z; e: -x+1, y, z+1/2; f: x-1/2, y+1/2, z+1/2

CRYSTAL STRUCTURE

For the same two crystals, [Bi] and [Bi,Sb], used for precession photography, single-crystal intensity data were collected ($4 \rightarrow 60^\circ 2\theta$; $2 \leq h \leq 7$, $1\bar{6} \leq k \leq 2$, $7 \leq l \leq 7$) using a Siemens P4 instrument. Data were corrected for absorption using a thin-plate {[Bi] = (010); [Bi,Sb] = (340)} empirical absorption correction. Systematic absences are consistent with the space group *Pcnn*, and the structures were refined using the transformed parameters for α -BiNbO₄ (Subramanian & Calabrese 1993). Ionized scattering factors were used at all sites. The scattering at the *Bi* and *Ta* sites was modeled by refining [Bi,Sb] and [Ta,Nb] coupled occupancies, respectively. The site populations (Table 4) fall within the range of compositions for each phase as determined by electron-microprobe analysis (Table 2). We can simplify the formulae for these two crystals: [Bi] = Bi(Ta_{0.8}Nb_{0.2})O₄ and [Bi,Sb] = (Bi_{0.6}Sb_{0.4})(Ta_{0.9}Nb_{0.1})O₄. Atom coordinates and displacement factors are listed in Table 5, selected interatomic distances and

angles are given in Table 6. Structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. For the two refinements, individual bond-lengths are within 0.036 Å, average bond-lengths, within 0.011 Å, and polyhedron angles, within 1.1%. Galy *et al.* (1975) gave a slightly smaller radius for Sb³⁺ relative to that for Bi³⁺, in agreement with the slightly smaller <Bi-O> distance observed for the [Bi,Sb] phase. The cell volume for the [Bi,Sb] phase (326.8 Å³) is also slightly smaller than that of the [Bi] phase (330.3 Å³).

CRYSTAL CHEMISTRY OF THE STIBIOTANTALITE GROUP

Bismutotantalite (BiTaO₄) and the low-temperature α -form of BiNbO₄ have space-group symmetry *Pcnn*, and at $\sim 1020^\circ\text{C}$, α -BiNbO₄ undergoes an irreversible phase-transition to the triclinic β -form (Keve & Skapski 1973, Roth & Waring 1963). Ponomarev *et al.* (1981) showed that the structure of SbNbO₄ is polar (*Pc2_{1n}*) at low temperature and is centrosymmetric (*Pcnn*) above

683 K; this phase transition is reversible. A structure is reported for stibiotantalite, SbTaO_4 , with the polar space-group $Pc2_1n$ (Dihlström 1938).

To summarize, at low temperature, the solid-solution series between BiTaO_4 and BiNbO_4 has $Pcnn$ symmetry, and the solid-solution series between SbTaO_4 and SbNbO_4 has $Pc2_1n$ symmetry. Thus a particular $\text{Sb}/(\text{Sb} + \text{Bi})$ ratio [for a specific $\text{Nb}/(\text{Nb} + \text{Ta})$ ratio] must mark the compositional boundary at which the centrosymmetric $Pcnn$ structure transforms to the polar $Pc2_1n$ structure. Our results show that up to ~40% replacement of Bi^{3+} by Sb^{3+} (Table 4) can be accommodated within the $Pcnn$ structure. A related study reported the existence of two solid-solutions for $\text{Bi}_{2-x}\text{Sb}_x\text{WO}_6$ (Castro *et al.* 1995). For compositions with $0 \leq x \leq 1.25$, an orthorhombic phase forms; at high Sb content ($1.5 \leq x \leq 2$), a triclinic phase forms. The authors attributed the compositionally driven phase-transition to the different stereochemical activities of the lone pairs of electrons associated with Bi^{3+} and Sb^{3+} (Galy *et al.* 1975). Although the structures of $\text{Bi}_{2-x}\text{Sb}_x\text{WO}_6$ and $(\text{Bi,Sb})(\text{Ta,Nb})\text{O}_4$ differ, it would be interesting to compare the critical 75% Sb content required in the former, with that needed in the latter, to induce structural transition. In practice, one could follow the structural change ($Pc2_1n$ to $Pcnn$) as a function of both composition and temperature within the $(\text{Bi,Sb})(\text{Ta,Nb})\text{O}_4$ system.

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