

Barium antimonide oxide, Ba<sub>3</sub>Sb<sub>2</sub>OMichael Boss, Frank Pickhard, Markus Zumdick and  
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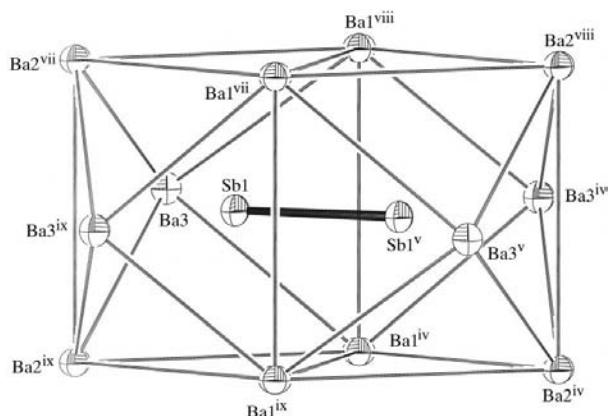
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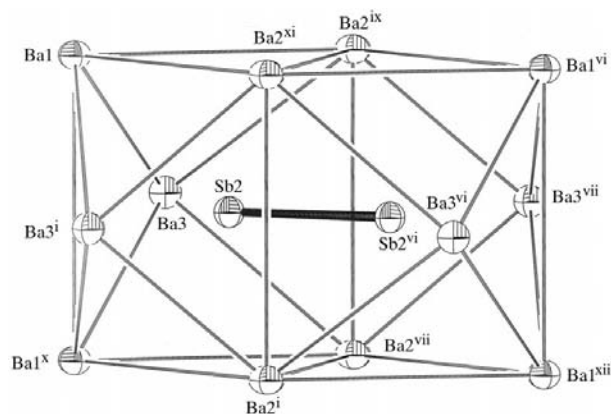
The antimonide oxide Ba<sub>3</sub>Sb<sub>2</sub>O consists of discrete [Sb<sub>2</sub>]<sup>4-</sup> and O<sup>2-</sup> anions, and crystallizes with a new structure type. The Sb—Sb distances are comparable to those known from electron-precise zintl phases and the tetrahedral coordination of the O<sup>2-</sup> anion is also observed in some other Ba-rich metallide oxides.

## Comment

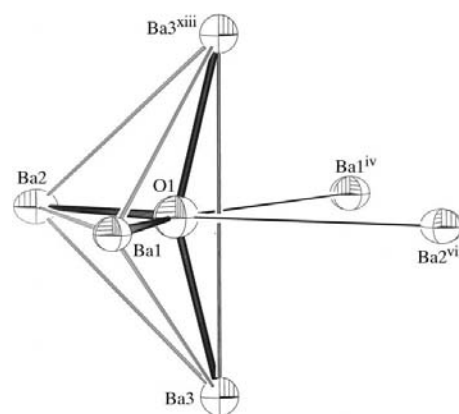
Besides Ba<sub>4</sub>Sb<sub>2</sub>O, with isolated Sb<sup>3-</sup> and O<sup>2-</sup> anions (George & Röhr, 1996), Ba<sub>3</sub>Sb<sub>2</sub>O is the second ternary antimonide oxide to be reported. It crystallizes in the orthorhombic space group *Pbam* with a new structure type. The crystal structure contains [Sb<sub>2</sub>]<sup>4-</sup> and O<sup>2-</sup> anions separated by charge-compensating Ba<sup>2+</sup> cations. The Sb—Sb distances in the two crystallographically independent dumb-bells are 2.837 (2) (Sb1—Sb1) and 2.857 (2) Å (Sb2—Sb2), and are comparable to those observed in Ba<sub>5</sub>Sb<sub>4</sub> [*d*(Sb—Sb) = 2.886 Å; Brechtel *et al.*, 1981; Derrien *et al.*, 1999], in the mixed antimonide K<sub>2</sub>Ba<sub>3</sub>Sb<sub>4</sub> [*d*(Sb—Sb) = 2.856 and 2.899 Å; Eisenmann *et al.*, 1999] or in KBa<sub>4</sub>Sb<sub>3</sub>O [*d*(Sb—Sb) = 2.898 Å; Eisenmann *et al.*, 1999]. In the only known binary alkaline phase with Sb dumb-bells, Cs<sub>4</sub>Sb<sub>2</sub> (Hirschle & Röhr, 2000), the Sb—Sb bond is



**Figure 1**  
ORTEP view (Johnson, 1968) of the [Sb1—Sb1]<sup>4-</sup> dumb-bell together with the coordinating Ba atoms (75% probability ellipsoids). [Symmetry codes: as in Table 1 plus (viii)  $\frac{1}{2} + x, \frac{1}{2} - y, 1 + z$ ; (ix)  $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$ .]



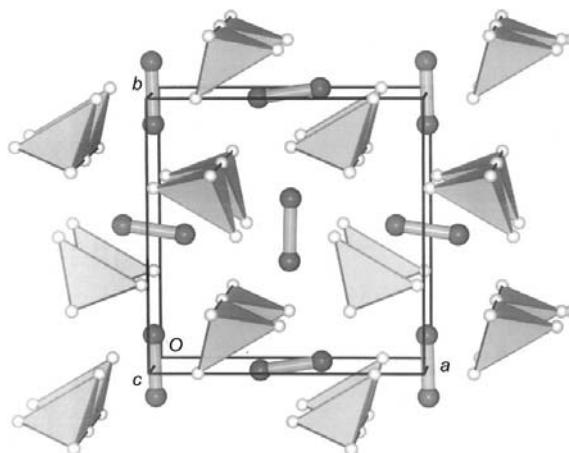
**Figure 2**  
ORTEP view (Johnson, 1968) of the [Sb2—Sb2]<sup>4-</sup> dumb-bell together with the coordinating Ba atoms (75% probability ellipsoids). [Symmetry codes: as in Table 1 and Fig. 1 plus (x)  $x, y, 1 + z$ ; (xi)  $x - \frac{1}{2}, \frac{1}{2} - y, 1 + z$ ; (xii)  $-x, -y, -z$ .]



**Figure 3**  
ORTEP view (Johnson, 1968) of the bicapped [OBa<sub>4</sub>] tetrahedron (75% probability ellipsoids). [Symmetry codes: as in Table 1 plus (xiii)  $x, y, z - 1$ .]

slightly longer (2.923 Å), showing that the distance is somewhat influenced by the crystal packing. The Sb atoms of the [Sb<sub>2</sub>]<sup>4-</sup> dumb-bells in all these compounds have a tricapped trigonal prismatic environment composed of six Ba atoms (Ba1 and Ba2, trigonal prism), two Ba atoms (Ba3) and their Sb partner, shown in Figs. 1 and 2 for the title compound.

The oxide ions are coordinated by four barium cations (Fig. 3) in a distorted tetrahedral geometry, with O—Ba distances ranging from 2.528 (9) to 2.630 (3) Å. Two additional Ba cations, with much longer O—Ba distances of 4.04 (1) (Ba1) and 4.06 (1) Å (Ba2), extend the coordination to an octahedron. A similar coordination and comparable O—Ba distances are known from other oxygen-poor Ba metallide oxides and are observed, for example, in KBa<sub>4</sub>Sb<sub>3</sub>O [*d*(O—Ba) = 2.5436 Å; Eisenmann *et al.*, 1999] and Ba<sub>10</sub>Ge<sub>7</sub>O<sub>3</sub> [*d*(O—Ba) = 2.57–2.79 Å; von Schnering *et al.*, 1997]. The O-centered Ba tetrahedra (center at  $z = 0$ ) are connected *via* corners to form chains running along [001]. In the unit cell (Fig. 4), the Sb—Sb anions (all Sb at  $z = \frac{1}{2}$ ) are located between these chains. The Sb<sub>2</sub>—Sb<sub>2</sub> dumb-bells at the unit-cell origin and the center of the cell are oriented along [010], whereas the Sb1—Sb1 dumb-bells at the faces of the unit cell are oriented



**Figure 4**  
View of the unit cell (projection down [001]) of the crystal structure of  $\text{Ba}_3\text{Sb}_2\text{O}$  (light-gray balls represent Ba, light-gray tetrahedra represent  $[\text{OBa}_4]$  and dark-gray balls represent Sb).

along [100]. The coordination spheres of the Ba cations are composed of one O and six Sb (Ba1 and Ba2) or two O and four Sb (Ba3) anions.

## Experimental

Single crystals of  $\text{Ba}_3\text{Sb}_2\text{O}$  were first obtained from melts of stoichiometric mixtures of Ba (99%, Alkali-Metallhandels-gesellschaft mbH, Bonn), Sb (99%, ABCR, Karlsruhe) and  $\text{Sb}_2\text{O}_3$  (99.999%, ABCR, Karlsruhe). Ba (2.455 g, 17.88 mmol), Sb (0.967 g, 7.943 mmol) and  $\text{Sb}_2\text{O}_3$  (0.578 g, 1.98 mmol) were heated in corundum crucibles under an argon atmosphere to 1170 K over a period of 3 h and then cooled to room temperature at a rate of  $20 \text{ K h}^{-1}$ . The X-ray powder patterns of these samples can be indexed on the basis of the reported single-crystal data but show additional reflections for  $\text{BaSb}_2$  (Pickhard & Röhr, 2000) and BaO. Single-phase products were obtained by simultaneous decomposition of  $\text{BaH}_2$  and the use of steel autoclaves as containers for the corundum crucibles. Ba (2.0531 g, 14.95 mmol) and  $\text{BaH}_2$  (0.6943 g, 4.98 mmol) were reacted with Sb (1.0112 g, 8.31 mmol) and  $\text{Sb}_2\text{O}_3$  (0.2414 g, 0.83 mmol) using the same temperature program mentioned above. The title compound forms dark hygroscopic crystals with a metallic lustre, which were handled in a dry-box and prepared in capillaries filled with dried oil.

### Crystal data

$\text{Ba}_3\text{Sb}_2\text{O}$	Mo $K\alpha$ radiation
$M_r = 671.52$	Cell parameters from 848 reflections
Orthorhombic, <i>Pbam</i>	$\theta = 6.45\text{--}56.55^\circ$
$a = 12.4228 (11) \text{ \AA}$	$\mu = 21.10 \text{ mm}^{-1}$
$b = 12.630 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 5.101 (3) \text{ \AA}$	Irregular, metallic dark black
$V = 800.4 (4) \text{ \AA}^3$	$0.14 \times 0.12 \times 0.10 \text{ mm}$
$Z = 4$	
$D_x = 5.573 \text{ Mg m}^{-3}$	

### Data collection

Bruker AXS CCD diffractometer	925 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.035$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 27.48^\circ$
$T_{\text{min}} = 0.068$ , $T_{\text{max}} = 0.121$	$h = -15 \rightarrow 16$
4726 measured reflections	$k = -7 \rightarrow 16$
1026 independent reflections	$l = -6 \rightarrow 6$
	Intensity decay: none

**Table 1**  
Selected geometric parameters ( $\text{Å}$ ).

Ba1—O1	2.528 (9)	Ba3—Sb1	3.4487 (12)
Ba1—Sb1 <sup>i</sup>	3.6592 (12)	Ba3—Sb2	3.5584 (11)
Ba1—Sb1 <sup>ii</sup>	3.6770 (13)	Ba3—Sb2 <sup>iv</sup>	3.5618 (11)
Ba1—Sb2	3.7174 (13)	Ba3—Sb1 <sup>ii</sup>	3.7294 (13)
Ba2—O1	2.563 (9)	Sb1—Sb1 <sup>v</sup>	2.8369 (16)
Ba2—Sb1 <sup>ii</sup>	3.6446 (12)	Sb2—Sb2 <sup>vi</sup>	2.8571 (17)
Ba2—Sb2 <sup>ii</sup>	3.6795 (12)	O1—Ba1 <sup>iv</sup>	4.041 (10)
Ba2—Sb2 <sup>iii</sup>	3.6996 (12)	O1—Ba2 <sup>vii</sup>	4.055 (10)
Ba3—O1	2.630 (3)		

Symmetry codes: (i)  $x - \frac{1}{2}, \frac{1}{2} - y, z$ ; (ii)  $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$ ; (iii)  $\frac{1}{2} + x, \frac{1}{2} - y, z - 1$ ; (iv)  $\frac{1}{2} + x, \frac{1}{2} - y, z$ ; (v)  $1 - x, -y, 1 - z$ ; (vi)  $-x, -y, 1 - z$ ; (vii)  $\frac{1}{2} - x, y - \frac{1}{2}, -z$ .

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2 + 10.2529P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.228$	$\Delta\rho_{\text{max}} = 1.81 \text{ e \AA}^{-3}$
1026 reflections	$\Delta\rho_{\text{min}} = -2.44 \text{ e \AA}^{-3}$
37 parameters	

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1968) and *DRAWxtl* (Finger & Kroeker, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1006). Services for accessing these data are described at the back of the journal.

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