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Potassium barium bismuth oxide

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KBa_4Bi_3O crystallizes in the centrosymmetric tetragonal space group *I*4/*mcm*. In this compound, bismuth is present as two anionic species, *i.e.* Bi_2^{4-} dumbbells [Bi—Bi 3.113 (3) Å] and isolated Bi^{3-}. Atom Bi1 (Bi^{3-}) lies inside a bicapped square antiprism (2 × K and 8 × Ba). Atom Bi2, which forms the Bi_2^{4-} dumbbell, sits inside a bicapped distorted trigonal prism (2 × K and 6 × Ba). O atoms occupy tetrahedral voids between Ba atoms.

Comment

KBa_4Bi_3O has been determined in the centrosymmetric space group *I*4/*mcm* (No. 140) and can be described as a packing of two types of Bi-centered Ba/K polyhedra. It is isostructural with KBa_4Sb_3O (Eisenmann *et al.*, 1999). The bicapped square antiprism Ba_8K_2 is centered by Bi1. The bicapped trigonal prism Ba_6K_2 centered by Bi2 forms twinned units by sharing a rectangular face. Tetrahedral voids between these coordination polyhedra are centered by O atoms. In the Bi_2^{4-} dumbbell, the Bi—Bi length is 3.113 (3) Å, similar to that of single Bi—Bi lengths in other compounds. In $Ca_{11}Bi_{10}$ (Deller & Eisenmann, 1976) and $Ba_{11}Bi_{10}$ (Derrien *et al.*, 2000), the structure is composed of Bi_2 dumbbells (3.15 and 3.16 Å), four-membered Bi rings (3.20 and 3.28 Å) and isolated Bi atoms. Shorter distances of 2.94 Å have been reported for Bi_4^{2-} (Cisar & Corbett, 1977) in which the Bi—Bi bonds display some double-bond character. More recently, a double Bi═Bi bond of 2.84 Å has been observed in $(K\text{-crypt})_2Bi_2$ (Xu *et al.*, 2000).

Experimental

With the aim of obtaining a ternary compound, amounts of K, Ba and Bi (in a 2:3:4 ratio) were inserted in a tantalum reactor weld-sealed under argon. The tantalum reactor was protected in a stainless container welded under argon. Single crystals of KBa_4Bi_3O were serendipitously obtained by heating at 1025 K for 10 h and then cooling the mixture at the rate of 10 K h^{-1}. Probably owing to some diffusion of oxygen through the container, the non-homogeneous product contained some crystals of KBa_4Bi_3O. Elemental analyses (SEM) confirmed the presence of potassium, barium and bismuth nearly in the ratio 1:4:3. The air-sensitive crystals were inserted into Lindemann glass capillaries for X-ray data investigations. Parameters and crystallographic space group were initially determined by oscillation and Weissenberg techniques. The best diffracting crystal was used for accurate determination of cell parameters.

Crystal data

KBa_4Bi_3O
M_r = 1231.40
Tetragonal, *I*4/*mcm*
a = 8.960 (1) Å
c = 16.617 (4) Å
V = 1334.0 (4) Å^3
Z = 4
D_x = 6.131 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 9.1–18.5°
μ = 51.298 mm^{-1}
T = 293 (2) K
Triangular wedge, metallic light grey
0.20 × 0.040 × 0.015 mm

Data collection

Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: numerical (*SHELX*76; Sheldrick, 1976)
T_{min} = 0.102, T_{max} = 0.436
830 measured reflections
495 independent reflections
381 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 29.95°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 22$
3 standard reflections
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.112
S = 1.064
495 reflections
18 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.87 e Å^{-3}
$\Delta\rho_{min}$ = −2.42 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 3.1 (6) × 10^{-4}

Table 1
Selected geometric parameters (Å).

Bi1—Ba^{i}	3.7358 (9)	Bi2—K^{iii}	3.5541 (7)
Bi1—K	4.1543 (10)	Ba—O^{iv}	2.5325 (15)
Bi2—Bi2^{ii}	3.113 (3)	Ba—K^{v}	4.2506 (11)

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

The highest residual density peak was 0.7 Å from Bi2 and the deepest hole was 1.5 Å from the O atom.

Data collection and cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989); data reduction: local program; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997).

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