Crystal structure of potassium tetrabarium tribismutide oxide, KBa_4Bi_3O

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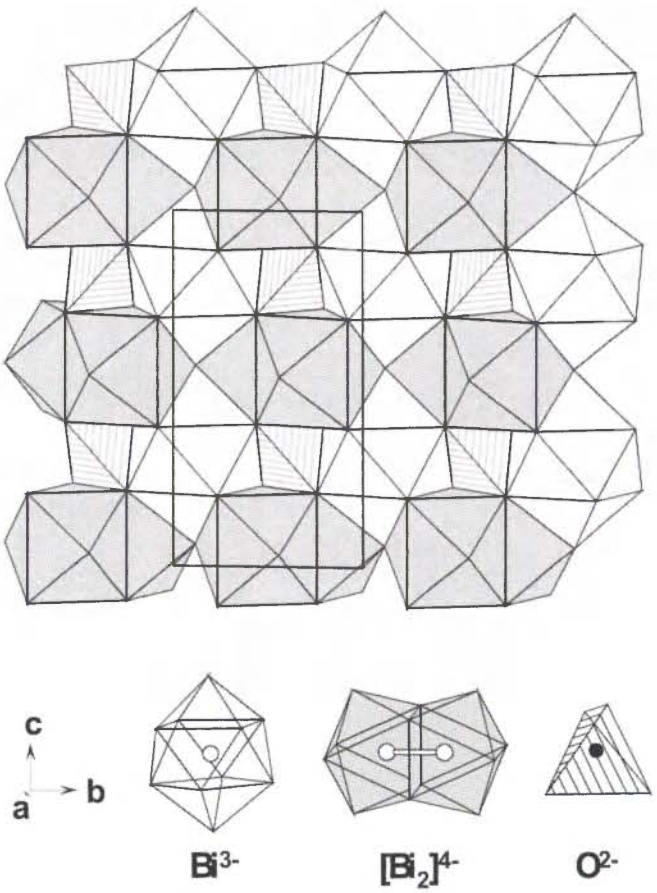

Abstract

Ba_4Bi_3KO, tetragonal, *I4/mcm* (No. 140), $a = 8.968(1)$ Å, $c = 16.664(3)$ Å, $V = 1340.1$ Å^3, $Z = 4$, $R_{gt}(F) = 0.036$, $wR_{ref}(F^2) = 0.089$, $T = 293$ K.

Source of material

All procedures of synthesis were carried out under argon atmosphere. Mixtures of the elements in stoichiometric amounts were heated in corundum crucibles enclosed in steel containers to 1023 K, tempered for one hour and slowly cooled down to room temperature. The compound crystallizing in dark metallic plates is very sensitive against moist air.

Discussion

KBa_4Bi_3O crystallizes isotypic to KBa_4Sb_3O [1]. The anionic part of the structure is characterized by dinuclear $[Bi_2]^{4-}$ units (bond length Bi—Bi: 3.113(1) Å), being the first example for such moieties in the solid state at all, and isolated Bi^{3-} and O^{2-} anions as well. The structure represents a stuffed Cr_5B_3 type structure with additionally filled tetrahedral voids. The Cr_5B_3 type itself is found for several alkaline earth metal tetrelides $(E_2)_5(E_{14})_3$ (E_2 = Ca, Sr, Ba; E_{14} = Si, Ge, Sn, Pb). The structural findings here can be understood on the basis of a segment $[KBa_4Bi_3]^{2+}$ isosteric and isostructural to Ba_5Sn_3 [2] and additional O^{2-} necessary for compensation of charge being localized in tetrahedral voids in the KBa_4Bi_3O structure (O—Ba: 2.5373(8) Å) which remain empty in the Cr_5B_3 type itself. Each atom of the anion $[Bi_2]^{4-}$ is surrounded by six Ba^{2+} (4× 3.6025(8) Å, 2× 3.810(1) Å) and two K^+ (3.5577(7) Å) building a twice capped trigonal prism which is condensed with another one via the remaining square face. The isolated anions Bi^{3-} center square antiprisms of Ba^{2+} (3.7414(6) Å) twice capped with K^+ (4.1660(6) Å).

Table 1. Data collection and handling.

Crystal:	dark metallic plate, size 0.09 × 0.09 × 0.09 mm
Wavelength:	Mo K_α radiation (0.71070 Å)
μ:	510.67 cm^{-1}
Diffractometer, scan mode:	Siemens P4, ω
$2\theta_{max}$:	60°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1297, 550
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 504
$N(param)_{refined}$:	17
Programs:	SHELXL-97 [3], DIAMOND [4]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	16*l*	0.15599(6)	*x*+1/2	0.15465(4)	0.0027(3)	U_{11}	0.0014(3)	–0.0016(2)	–0.0003(2)	U_{13}
K(1)	4*c*	0	0	0	0.002(2)	U_{11}	0.039(4)	0	0	0
Bi(1)	8*h*	0.62273(5)	*x*+1/2	0	0.0021(2)	U_{11}	0.0009(3)	–0.0018(2)	0	0
Bi(2)	4*a*	0	0	1/4	0.0008(3)	U_{11}	0.0079(4)	0	0	0
O(1)	4*b*	0	1/2	1/4	0.002(5)	U_{11}	0.000(7)	0	0	0

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