Crystal structure of potassium lead bismuth oxide hydrate, $K_{1.09}(Bi_{0.93}Pb_{0.07})O_3 \cdot 1/6\,H_2O$

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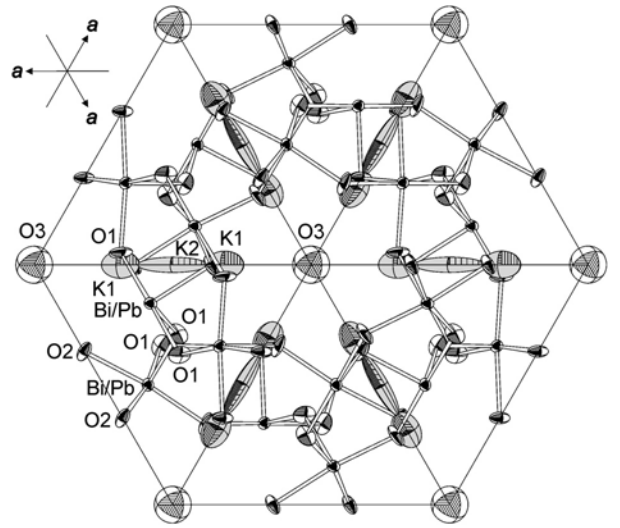

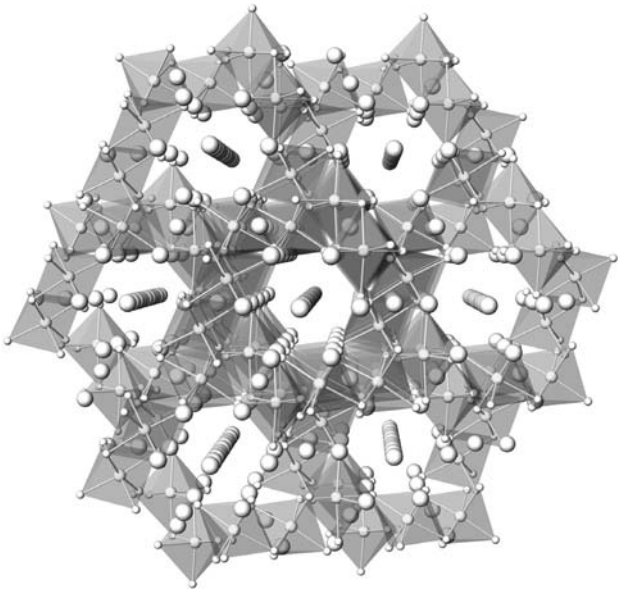

Abstract

$Bi_{0.93}H_{0.33}K_{1.09}O_{3.17}Pb_{0.07}$, cubic, $Im\bar{3}$ (no. 213), a = 10.013(1) Å, V = 1003.9 Å^3, Z = 12, $R_{gt}(F)$ = 0.010, $wR_{ref}(F^2)$ = 0.023, T = 295 K.

Source of material

The title compound was prepared by hydrothermal technique in a 5.5 ml Teflon-lined steel autoclave using 1 M aqueous solution of KOH as a mineralizer (filling degree 70 %). A small quantity of Pb-doped γ-B_2O_3 phase having the composition $12Bi_2O_3 \cdot PbO$ was prepared by solid state reaction [1] and used as starting material. After four days of heating at 200 °C, the autoclave was quenched in air to room temperature. During the synthesis most of water evaporated leaving about one tenth of the initial solution volume. As a result two kinds of crystals with similar chemical composition (EDX analysis) were obtained. The crystal structure of red cuboctahedral crystals with a Bi:Pb atomic ratio of 0.93(1)/0.07 is described here.

Discussion

The title compound adopts the $KSbO_3$ type of structure [2] and represents the first example with a partial substitution of skeletal Bi(V) ions. The structure consists of a complex Bi/Pb-O framework with metal atoms in a deformed octahedral environment (figure, top), as well as tunnels extending along <111> that host K^+ ions and H_2O molecules (figure, bottom). Pairs of Bi/Pb-octahedra share one edge making $(Bi/Pb)_2O_{10}$ building units, which are further interconnected to the four neighboring units via eight common O atoms. Since in $KSbO_3$-type structures tunnels make about 20 % of the unit cell volume, they can be filled by various species resulting in different formulae of the title and previously reported compounds with essentially the same structure as $Na_{1.29}SbO_3$ [3], $AgSbO_3$ [3], $NaSbO_3 \cdot 1/6\,NaF$ [4], $KSbO_3 \cdot 1/6\,KF$ [4], $KBiO_3$ [5], $KBiO_3 \cdot 1/6\,H_2O$ [6] and $(Ba_{0.059}K_{0.941})BiO_3 \cdot 1/6\,H_2O$ [7]. Structurally, the title compound, $K_{1.09}(Bi_{0.93}Pb_{0.07})O_3 \cdot 1/6\,H_2O$ (I) is very similar to the recently published $(Ba_{0.059}K_{0.941})BiO_3 \cdot 1/6\,H_2O$ (II) [7]. Both compounds are characterized by very elongated displacement ellipsoids of K2(Ba) atoms (figure, top), and have almost identical average Bi—O distances (2.106 for (I) and 2.102 Å for (II)). A slightly smaller unit cell volume of (I) in respect to (II) (1003.91(2) Å^3 versus 1006.13(1) Å^3) could be a consequence of high K^+ content causing a shrinkage of tunnels by electrostatic attractions.

Table 1. Data collection and handling.

Crystal:	red irregular fragment, size 0.06 × 0.07 × 0.09 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	536.96 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	57.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	452, 261
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 257
$N(param)_{refined}$:	24
Programs:	SHELXS-97 [8], SHELXL-97 [9], ATOMS [10]

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi	12*e*	0.93	½	0	0.16041(2)	0.0060(1)	0.0051(1)	0.0042(1)	0	0	0
Pb	12*e*	0.07	½	0	0.16041	0.0060	0.0051	0.0042	0	0	0
K(1)	16*f*	0.646(9)	0.8440(2)	–0.1560(2)	0.1560(2)	0.0338(9)	0.0338(9)	0.0338(9)	0.0102(7)	–0.0102(7)	–0.0102(7)
K(2)	8*c*	0.34(1)	¾	–¼	¼	0.066(5)	0.066(5)	0.066(5)	0.059(5)	–0.059(5)	–0.059(5)
O(1)	24*g*		0.6625(3)	0	0.2876(3)	0.010(1)	0.024(2)	0.005(1)	0	–0.004(1)	0
O(2)	12*d*		0.6390(4)	0	0	0.006(2)	0.018(2)	0.004(2)	0	0	0
O(3)	2*a*		0	0	0	0.047(5)	0.047(5)	0.047(5)	0	0	0

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