Crystal structure of tripotassium dibismuth phosphate, $K_3Bi_2(PO_4)_3$

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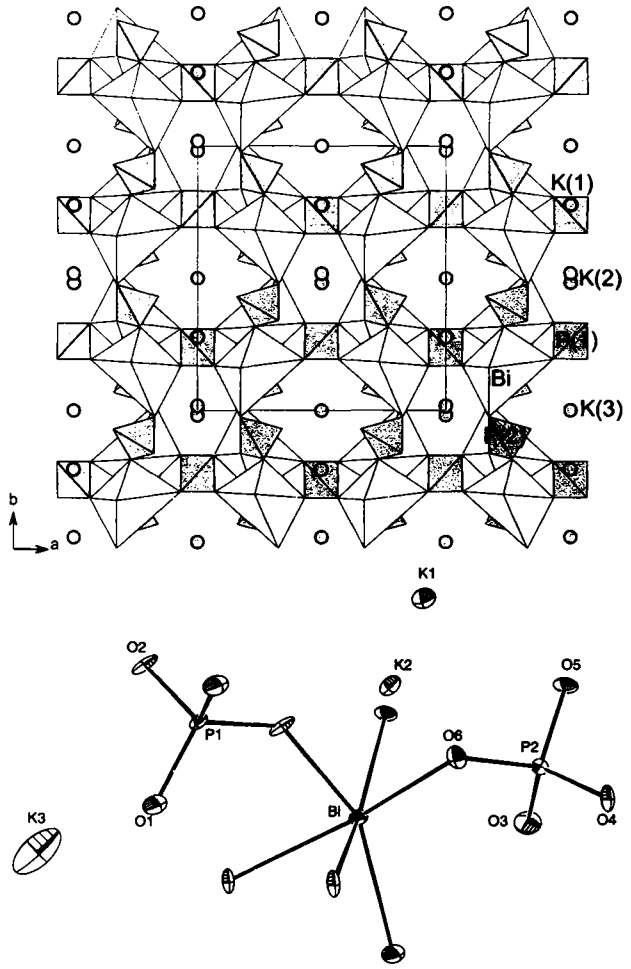
Received June 28, 2001, CSD-No. 409582



Abstract

$Bi_2K_3O_{12}P_3$, monoclinic, $C12/c1$ (No. 15), a = 13.828(7) Å, b = 13.482(5) Å, c = 6.808(3) Å, β = 114.94(4)°, V = 1150.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.028, $wR_{ref}(F^2)$ = 0.090, T = 293 K.

Source of material

The title compound was prepared by the reaction of K_2CO_3, Bi_2O_3 and $NH_4H_2PO_4$ in the molar ratio K: Bi: P = 3: 2: 3. The mixture was first heated at 573 K until decomposition, and then kept for 20 days at 823 K. A slow cooling to room temperature led to colourless plate crystals of $BiPO_4$ (high temperature form [1]) together with colourless parallelepiped crystals of $K_3Bi_2(PO_4)_3$.

Discussion

Double orthophosphates of bivalent, trivalent or quadrivalent cations with alkali metals are promising materials in the field of inorganic material technology. Several phosphates such as $M^I{}_3M^{III}{}_2(PO_4)_3$ (M^I = Li, Na; M^{III} = Cr, Fe, Sc) have been extensively investigated: they are known to be fairly good ionic conductors structurally related to Nasicon ($Na_3Zr_2Si_2PO_{12}$). Furthermore, it is well established that ions such as Bi^{3+} often generate distorted structures due to the electrostatic effect of the lone pair of electrons. In the system K–Bi–P–O, several well-characterized phases have been reported: $Bi(PO_3)_3$ [2], $Bi_2P_4O_{13}$ [3], $BiPO_4$ [1], K_3BiO_3 [4], $K_4Bi_2O_5$ [5], $KBiO_2$ [6], $K_2Bi_3O(PO_4)_3$ [7], $KBi(PO_3)_4$ [8], $KBi_4O_5(PO_4)$ [9] and $K_3Bi_2(PO_4)_3$ [9]. To our knowledge, three structural works of double phosphates of bismuth and alkali metals have been published $K_2Bi_3O(PO_4)_3$ [7], $Na_5Bi(P_2O_7)_2$ [10] and $Na_3Bi_5(PO_4)_6$ [11]. We have identified two compounds: the title compound $K_3Bi_2(PO_4)_3$ and an interesting non-centrosymmetric structure of $K_6Bi_2(P_2O_7)_3$ [12].

The structure of the title compound is built up from BiO_6 octahedra and PO_4 tetrahedra sharing corners to form a three-dimensional framework enclosing two types of tunnels where K^+ cations reside. The crystal structure consists of infinite chains of dimers of edge-sharing BiO_6 octahedra to form a Bi_2O_{10} unit. These infinite chains are linked together by $P(1)O_4$ and $P(2)O_4$ tetrahedra to form layers parallel to the (010) plane. The ten vertices of the dimer are shared with eight PO_4 tetrahedra. Two of the eight phosphates form bridges between two Bi atoms in a dimer. The BiO_6 octahedra appear to be highly distorted, the angle subtended by two of the axial oxygens is 151.3(3)°. This distortion probably occurs as a result of the need to accommodate to the connectivity of the PO_4 tetrahedra, which are rather rigid entities. This framework defines large tunnels running along the c direction (see figure). The structure is closely related to the alluaudite structure type [13,14], but there are two important differences: one site is empty and the coordination number of the K atoms. The X(1) site (1/2,0,0) is occupied by K(3), whereas the X(2) site (0,0,0) is empty. The maximum bond distance for K—O determined by using the procedure in [15] with the revised radii in [16] is 3.35 Å. Accordingly, K(1), K(2) and K(3) ions are coordinated to eight, ten and six oxygen atoms, respectively, ranging from 2.684(7) Å to 3.313(7) Å, forming irregular coordination polyhedra. In contrast to $Na_3In_2(PO_4)_3$ [17], where the coordination numbers of Na(1), Na(2) and Na(3) are six, eight and six oxygen atoms, respectively. The bond valence sum of K—O bonds using the formula in [18] is 1.18, 1.32 and 1.01 for K(1), K(2) and K(3), respectively.

In contrast to the analogous formula compound $Na_3Sc_2(PO_4)_3$ that has the well-known Nasicon structure [19], the title compound is isotypic to $Na_3In_2(PO_4)_3$.

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Table 1. Data collection and handling.

Crystal:	colourless parallelipipedic, size 0.07 × 0.07 × 0.09 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	321.05 cm^{-1}
Diffractometer, scan mode:	CAD4, ω/2θ
$2\theta_{max}$:	53.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1363, 1257
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1062
$N(param)_{refined}$:	95
Programs:	SHELXS-90 [20], SHELXL-97 [21]

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}
Bi(1)	8*f*	0.26291(2)	0.35556(2)	0.33079(5)	0.0067(2)	0.0106(2)	0.0106(2)	–0.0006(1)	0.0029(2)	0.0007(1)
P(1)	4*e*	1/2	0.2582(2)	3/4	0.005(1)	0.011(2)	0.008(1)	0	0.000(1)	0
P(2)	8*f*	0.2589(2)	0.3916(2)	–0.1393(3)	0.009(1)	0.009(1)	0.009(1)	–0.0010(9)	0.0040(8)	0.0004(9)
K(1)	4*e*	1/2	0.4817(2)	1/4	0.011(1)	0.019(2)	0.016(1)	0	0.005(1)	0
K(2)	4*e*	1/2	0.2226(2)	1/4	0.008(1)	0.009(1)	0.010(1)	0	0.000(1)	0
K(3)	4*b*	1/2	0	0	0.026(2)	0.039(2)	0.041(2)	0.010(2)	–0.003(2)	–0.018(2)
O(1)	8*f*	0.4307(5)	0.1927(5)	0.822(1)	0.010(3)	0.021(4)	0.017(3)	–0.003(3)	0.002(3)	0.004(3)
O(2)	8*f*	0.5669(5)	0.3309(5)	0.944(1)	0.007(3)	0.015(3)	0.014(3)	–0.002(3)	–0.002(3)	–0.006(3)
O(3)	8*f*	0.1571(5)	0.4312(6)	–0.129(1)	0.011(3)	0.032(4)	0.023(4)	0.001(3)	0.010(3)	–0.003(3)
O(4)	8*f*	0.2310(5)	0.3169(6)	–0.3302(9)	0.018(4)	0.015(4)	0.006(3)	0.003(3)	0.004(3)	0.004(3)
O(5)	8*f*	0.3273(5)	0.4759(5)	–0.171(1)	0.012(3)	0.009(3)	0.019(3)	–0.003(3)	0.006(3)	0.004(3)
O(6)	8*f*	0.3265(6)	0.3386(5)	0.080(1)	0.020(3)	0.006(3)	0.012(3)	–0.002(3)	0.008(3)	0.000(2)

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