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Chemical Preparation and Crystal Structure Refinement of $KBaPO_4$ Monophosphate

R. MASSE AND A. DURIF

Laboratoire de Cristallographie, Centre National de la Recherche Scientifique, Laboratoire associé à l'USTMG, 166X 38042 Grenoble Cédex, France

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Single-crystal preparation of $KBaPO_4$ is reported. $KBaPO_4$ is orthorhombic, *Pnma*, with $a = 7.709(4)$, $b = 5.663(4)$, $c = 9.972(5)$ Å and $Z = 4$. The β-K_2SO_4-like model previously proposed for this salt from X-ray powder data is confirmed by the present single-crystal study. $R = 0.016$ for 970 reflections.

Introduction

The crystal chemistry of $M^IM^{II}PO_4$ monophosphates yields numerous polymorphic phases belonging to at least eight different structure types, such as olivine, arcanite, glaserite, tridymite, α-K_2SO_4, β-Na_2SO_4, γ-Na_2SO_4. A complete updated review of all $M^IM^{II}PO_4$ compounds, for both high- and low-temperature forms, has been made recently by Blum (*1*). Many phases have ferroic properties. The main difficulty rests in the preparation of crystals. Until now, two $KBaPO_4$ forms have been known: glaserite and arcanite (*2*, *3*). The $KBaPO_4$ arcanite form was studied by

TABLE I

PARAMETERS USED FOR THE X-RAY DIFFRACTION DATA COLLECTION, $KBaPO_4$

Apparatus	Enraf–Nonius CAD4
Monochromator	Graphite plate
Wavelength (Å)	Ag$K\alpha$ (0.56083)
Scan mode	ω
Scan speed (°/sec)	0.014–0.042
Total background measurement (sec)	14–42
Scan width (°)	1.30
θ range (°)	3–30
Intensity reference reflections	113, 213
Number of collected reflections	1556 (h, k, l)
Observed independent reflections	1267
Crystal size	0.13 × 0.14 × 0.18
μ (cm−1)	54.4

TABLE II

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x (σ)	y (σ)	z (σ)	B_{eq} (σ)Å^2
Ba	−0.00928(2)	0.250	0.19501(2)	0.695(2)
P	0.2361(1)	0.250	0.91761(9)	0.57(1)
K	0.1619(1)	0.250	0.58597(9)	1.27(1)
O1	0.1976(2)	−0.0268(3)	0.3460(2)	1.10(3)
O2	0.0358(3)	0.250	0.9164(3)	1.17(4)
O3	0.3015(3)	0.250	0.0643(3)	0.94(4)

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TABLE III

REFINED TEMPERATURE FACTOR EXPRESSIONS: β VALUES FOR $KBaPO_4$[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba	0.00257(2)	0.00612(3)	0.00174(1)	0	0.00005(3)	0
P	0.00267(8)	0.0039(2)	0.00145(6)	0	0.0002(1)	0
K	0.0068(1)	0.0072(2)	0.00324(6)	0	0.0011(1)	0
O1	0.0060(2)	0.0054(4)	0.0030(1)	0.0013(5)	−0.0015(3)	0.0029(4)
O2	0.0029(3)	0.0119(7)	0.0032(2)	0	−0.0007(4)	0
O3	0.0042(3)	0.0092(6)	0.0018(2)	0	−0.0012(4)	0

[a] $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Struck and White (*3*). A reliability factor of 17.6% had been obtained with data collected from X-ray powder diffractograms; the space group had not been confirmed. Arcanite-type $KBaPO_4$ single crystals may be obtained by either of the following chemical reactions, at 650°C:

$$K_3PO_4 + BaF_2 \rightarrow KBaPO_4 + 2KF$$

$$K_4P_2O_7 + BaF_2 \rightarrow KBaPO_4 + KPO_3 + 2KF$$

Stoichiometric amounts of K_3PO_4 and BaF_2 or of $K_4P_2O_7$ and BaF_2 (0.01 mole) are mixed and heated at 350°C in a platinum crucible. The temperature is increased to 650°C. After 4 hr at 650°C, the mixture is slowly cooled to 400°C and quenched. Crystals are isolated after water washing of the mixture.

Crystal Data and Structure Determination

Approximate unit cell and possible space groups have been determined by single-crystal film techniques. The cell parameters were refined using 2θ ($9 < \theta° < 11$) reflections collected with an automatic X-ray four-circle diffractometer: a = 7.709(4), b

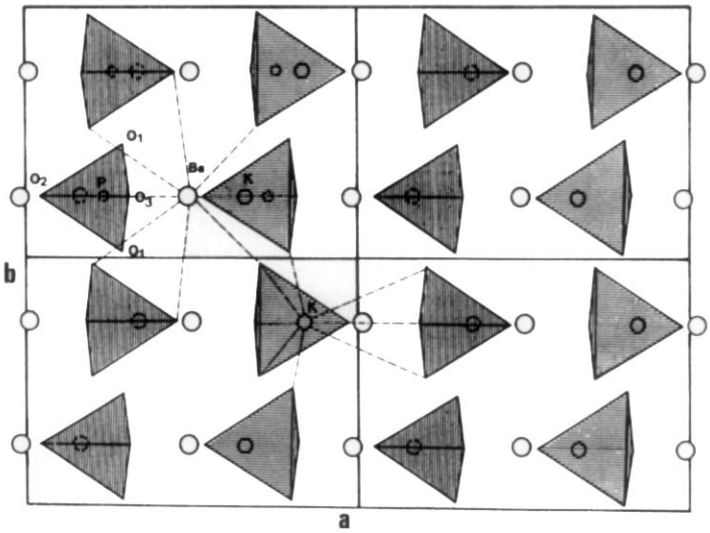

FIG. 1. Simplified (a, b) projection of $KBaPO_4$.

TABLE IV

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN $BaKPO_4$

K–O(1)	2.874(2)Å × 2	Ba–O(1)	2.695(2) × 2
K–O(1)	3.121(2) × 2	Ba–O(1)	2.780(2) × 2
K–O(1)	3.081(2) × 2	Ba–O(2)	2.800(3)
K–O(2)	2.882(3)	Ba–O(2)	3.048(1) × 2
K–O(3)	3.157(3)	Ba–O(3)	2.727(3)
K–O(3)	2.854(2)	Ba–O(3)	2.808(3)

PO_4 tetrahedron

P	O(1)	O(1)	O(2)	O(3)
O(1)	1.539(2)	2.528(4)	2.513(3)	2.518(3)
O(1)	110.4(1)	1.539(2)	2.513(3)	2.518(3)
O(2)	109.2(1)	109.2(1)	1.544(3)	2.524(4)
O(3)	109.3(1)	109.3(1)	109.5(1)	1.547(3)

= 5.663(4) and c = 9.972(5) Å; space group *Pnma* or $Pn2_1a$; Z = 4; dX = 4.141 g cm^{-3}.

The parameters used for the X-ray diffraction data collection are reported in Table I. Lorentz and polarization corrections have been made. No absorption correction was applied. The crystal structure solved by the Patterson method confirms the model given by Struck and White (*3*). A unit weighting scheme throughout the least-squares refinements (*4*) was applied. The refinement carried out in the space group *Pnma* gives a final R value of 0.016 for 970 reflections; 297 reflections with $F^2 < 4\sigma(F^2)$ were eliminated. The final refined parameters are reported in Tables II and III.[1]

Description

A simplified (a, b) projection of $KBaPO_4$ is represented in Fig. 1. The framework is built with successive arrays of K atoms and PO_4 tetrahedra at the same height. The barium and potassium atoms are surrounded by PO_4 tetrahedra in a very compact arrangement. No distortion is observed in the PO_4 tetrahedron which is very regular with ⟨P–O⟩ averaging 1.542 Å. The pseudohexagonal character of the network is revealed by the value of the ratio b/c = 0.568 in the pseudo-orthohexagonal cell (0.577 is the value for the ideal orthohexagonal cell). The parameters a = 7.709 Å and b = 5.663 Å are close to those of the glaserite structure: c = 7.33 Å and a = 5.66 Å (*5*). The similarity with the structure of β-K_2SO_4 arcanite (*6*, *7*) is well established by the same space group and framework in which one site of K atoms is replaced by Ba atoms. The relation between $KBaPO_4$ and glaserite occurs through the similarity of the cell parameters.

[1] Lists of structure factors are available on request to the authors.

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