

Crystal structure of the orthophosphate RbBaPO_4

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Abstract

RbBaPO_4 single-crystals were prepared by the flux method. The X-ray diffraction patterns show that this compound crystallizes in the orthorhombic system with $Pnma$ space group and the following unit cell parameters: $a = 7.812(2)$ Å, $b = 5.740(1)$ Å, $c = 10.056(2)$ Å, $Z = 4$. RbBaPO_4 is isostructural with KBaPO_4 which derives from the glaserite, where potassium and sodium are substituted by rubidium and barium respectively. The structure is formed by regular PO_4^{3-} tetrahedra surrounding the Rb^+ and Ba^{2+} cations in ten-fold and nine-fold coordinations respectively.

1. Introduction

The determination of the structure of RbBaPO_4 is part of a large research programme undertaken in our laboratory on crystal chemistry and non-linear properties of orthophosphates with general formula $\text{A}^1\text{B}^{\text{II}}\text{PO}_4$ (A is a monovalent cation, B is a bivalent cation) [1, 2]. This compound exhibits a reversible phase transition at 1060°C [3]. The present investigation describes the structure of the low temperature polymorph.

2. Experimental details

The single crystals were prepared by the flux method. The best crystals were obtained by melting Rb_2MoO_4 and RbBaPO_4 with a molar ratio of product to flux of 0.5 and a cooling rate of 6°C h^{-1} . The crystals grow as sheets and are relatively stable under surrounding atmosphere. Investigation of the structure of RbBaPO_4 using X-ray diffraction was performed on single crystals with well grown faces. A three-dimensional set of intensities was obtained on an automated X-ray four-circle diffractometer. The experimental conditions for the intensity recording are summarized in Table 1. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was made using "azimuthal data" (ψ -scan). The scattering factors for neutral atoms including f' and f'' terms for anomalous

dispersion, were taken from the International Tables for X-ray Crystallography [5].

3. Description of the crystal structure

The structure of RbBaPO_4 was solved by the Patterson method and refined by the least squares method. The refinement carried out in the space group $Pnma$ gives a final R value of 0.026 for 885 independent reflections. The final refined atomic parameters and anisotropic factors are reported in Tables 2 and 3 respectively. (Lists of structure factors are available on request from the authors). The projection of this structure on the (100) plane is shown in Fig. 1. The PO_4^{3-} tetrahedra are quite regular, as can be seen from Table 4 which gives the most important interatomic distances and angles. The rubidium has ten-fold coordination whilst the barium has nine-fold coordination. The polyhedron surrounding the rubidium is formed by three edges of three tetrahedra located approximately in the same plane and by one face and one corner of two different tetrahedra located respectively below and above. The barium atoms are coordinated to nine oxygen atoms, (4O(3) + 2O(1)) placed at the vertices of an octahedron and 3O(2) localized approximately at the same level of barium atoms.

The crystal structure of RbBaPO_4 is isostructural with that of KBaPO_4 which derives from the $\beta\text{-K}_2\text{SO}_4$ structure, where one potassium atom is substituted by the barium [6, 7]. The relation between RbBaPO_4 and glaserite structures occurs through the similarity of the cell parameters. As a matter of fact, there is a close relation between their unit cells, as that of RbBaPO_4 is

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TABLE 1. Experimental conditions for data collections

Apparatus	Syntex R3
Monochromator	Graphite plate
Wavelength	Mo $K\alpha$ ($\lambda = 0.7107 \text{ \AA}$)
Scan mode	$\omega/2\theta$
Scan width (deg)	1.2
Theta range (deg)	2–30; $-18 \leq h \leq 18$, $-8 \leq k \leq 8$, $-11 \leq l \leq 0$
Number of collected reflections	4392
Number of independent reflections	1076
Number of independent reflections	885 with $I(hkl) \geq 3\sigma(I)$
Number of parameters	41
Crystal size (mm)	$0.16 \times 0.06 \times 0.03$
Weight schema	$w = [\sigma(F) + 0.00007F]^{-1}$
Extinction corrections	yes
Calculation program	SHELXTL [4]
R and (wR)	0.026 (0.024)

TABLE 2. Atomic coordinates and temperature factors

Atom	x/a	y/b	z/c	$U(\text{equivalent})$
Rb	0.1582(1)	0.7500	0.5874(1)	0.0101(1)
Ba	0.4941(1)	0.7500	0.3052(1)	0.0126(1)
P	0.2673(2)	0.2500	0.4163(1)	0.0073(3)
O(1)	0.1999(5)	0.2500	0.5617(3)	0.0102(9)
O(2)	0.4652(5)	0.2500	0.4186(5)	0.0173(11)
O(3)	0.2038(4)	0.0293(4)	0.3438(3)	0.0134(7)

TABLE 3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb	14(1)	11(1)	13(1)	0	-0(1)	0
Ba	7(1)	13(1)	10(1)	0	-0(1)	0
P	7(1)	8(1)	7(1)	0	0(1)	0
O(1)	9(2)	13(2)	9(2)	0	2(1)	0
O(2)	6(2)	24(2)	22(2)	0	-3(1)	0
O(3)	16(1)	10(1)	15(1)	-3(1)	-1(1)	-1(1)

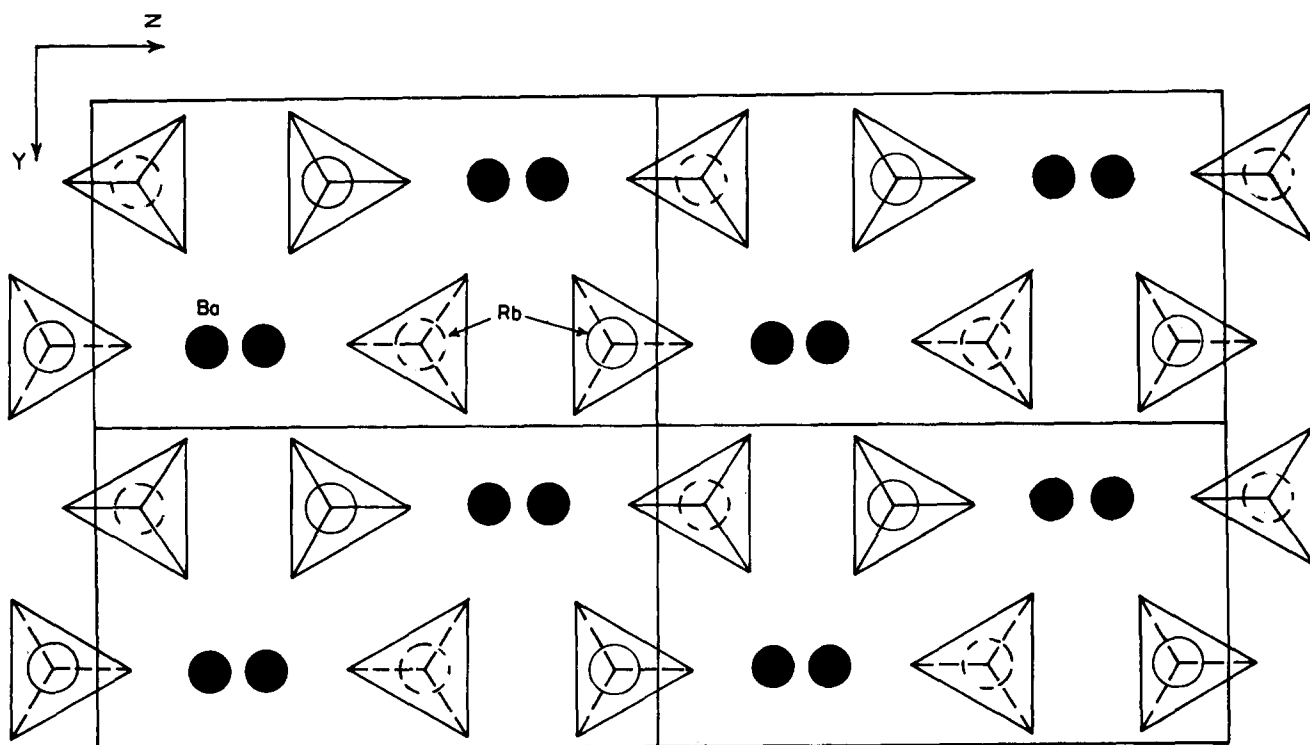
Fig. 1. Four unit cells of $RbBaPO_4$ structure projected down the a axis.

TABLE 4. Interatomic distances (Å) and angles (deg)

Rb–O(1)	2.900(1) × 2	Ba–O(1)	2.739(4)
Rb–O(1')	3.174(4)	Ba–O(1')	2.880(4)
Rb–O(2)	2.942(4)	Ba–O(2)	2.796(5)
Rb–O(3)	2.949(3) × 2	Ba–O(2')	3.096(3) × 2
Rb–O(3')	3.175(3) × 2	Ba–O(3)	2.804(3) × 2
Rb–O(3'')	3.069(3) × 2	Ba–O(3')	2.739(3) × 2
P–O(1)	1.553(4)	O(1)–P–O(2)	109.6(1) × 2
P–O(2)	1.546(4)	O(1)–P–O(3)	109.0(2)
P–O(3)	1.543(3) × 2	O(2)–P–O(3)	109.2(1) × 2
		O(2)–P–O(3')	110.3(2)

pseudo-orthohexagonal with the ratio $c/b = 1.75 \approx \sqrt{3}$. The value of $c/b = \sqrt{3}$ corresponds to the ideal orthohexagonal lattice. However, the order of large cations in the latter, is linear along the [001] direction while it is in zigzags in the case of the truly orthorhombic RbBaPO₄. This is again compatible with the fact that the zigzagging order gives rise to a smaller $a \approx c_g$ (c_g = glaserite) than in the ideal case (RbBaPO₄ with ideal glaserite $c/b = \sqrt{3}$ and $a \approx c_g$). There is also a slight difference between the coordination numbers of the large cations in RbBaPO₄ (rubidium 10, barium 9)

and those of the glaserite structure (12 and 10); this is probably induced by a small tilt of the PO₄³⁻ tetrahedra.

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