Contribution to the Crystal Chemistry of $M^I M^{II} PO_4$ Monophosphates (M^I = K, Rb, Cs; M^{II} = Be)

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Single-crystal growth experiments and crystal structures of $KBePO_4$, $RbBePO_4$, and $CsBePO_4$ are reported. $KBePO_4$ is orthorhombic, $Pc2_1n$, with $a = 8.506(4)$, $b = 4.937(4)$, $c = 8.344(5)$ Å, and $Z = 4$. $RbBePO_4$ is orthorhombic, $Pcmn$ or $Pc2_1n$, with $a = 8.636(3)$, $b = 5.012(2)$, $c = 8.587(3)$ Å, and $Z = 4$. $CsBePO_4$ is orthorhombic, $Pnam$ with $a = 8.713(4)$, $b = 8.836(5)$, $c = 5.147(4)$ Å, and $Z = 4$. The crystal structures of $KBePO_4$ and $CsBePO_4$ have been solved with respective final R values of 0.043 (472 reflections) and 0.027 (717 reflections). They are closely related to that of β-tridymite. © 1988 Academic Press, Inc.

Introduction

The crystal chemistry of $M^I M^{II} PO_4$ monophosphates with $M^I = NH_4^+$, Ag^+, and alkali metals is far from being extensively known. Many of these compounds are polymorphic, one of the forms being frequently noncentric leading to possible applications in the fields of ferroelectrics or nonlinear optics.

Various classical methods have been used for their preparation:

—direct synthesis of material in the form of crystalline powder, melting, and slow cooling;
—direct synthesis with the addition of a compound lowering the melting point;
  —flux method;
  —hydrothermal synthesis.

The main difficulty for preparation rests on the high melting points of these compounds. In the present work we describe an exchange reaction which lowers significantly the preparation temperatures. The general scheme is:

$$M_3^I PO_4 + M^{II} F_2 \rightarrow M^I M^{II} PO_4 + 2M^I F.$$
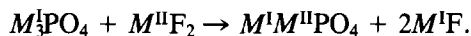
By carrying out this reaction at temperatures ranging from 600 to 750°C we obtained single crystals of $KBePO_4$, $RbBePO_4$, and $CsBePO_4$.

Chemical Preparations

All the title compounds have been prepared by using the following method: for $KBePO_4$, stoichiometric amounts of K_3PO_4 and BeF_2 are mixed and melted at 750°C in a platinum crucible. The temperature is slowly lowered to 400°C and then the sample is quenched. The insoluble prismatic crystals are isolated by washing with water. The same process is used for $RbBePO_4$ and

	$KBePO_4$				$RbBePO_4$		
hkl	d_{obs}	d_{calc}	I_{obs}	hkl	d_{obs}	d_{calc}	I_{obs}
101	5.90	5.94	31	101	6.09	6.09	35
002	4.15	4.16	17	200	4.32	4.32	35
111	3.79	3.79	33	111	3.87	3.87	29
201	3.78	3.78	49	012	3.26	3.26	5
012	3.17	3.17	7	112	3.05	3.06	100
211	3.00	3.00	100	301	2.727	2.729	56
112	2.973	2.976	86	020	2.508	2.506	65
301	2.678	2.679	8	310	2.496	2.496	65
103	2.637	2.636	11	220	2.168	2.167	65
212	2.545	2.544	2	400	2.160	2.159	53
020	2.465	2.464	24	004	2.149	2.147	44
310	2.455	2.454	48	303	2.029	2.029	18
302	2.339	2.339	5	222	1.933	1.935	20
121	2.276	2.276	2	114	1.924	1.924	20
220	2.134	2.131	14	321	1.847	1.846	12
400	2.122	2.122	28	123	1.841	1.842	12
022	2.117	2.120	19				
004	2.083	2.080	18				

Note. System orthorhombic; formula units, 4. Space group $Pc2_1n$: $KBePO_4$, 8.489(5), 4.929(3), 8.318(5) Å. Space groups $Pcmn$ or $Pc2_1n$: $RbBePO_4$, 8.636(3), 5.012(2), 8.587(3) Å.

$CsBePO_4$ preparations by mixing, respectively, Rb_3PO_4 and Cs_3PO_4 with BeF_2. All crystals have a prismatic habit.

Crystal Data

Approximate unit cells and possible space groups for these compounds have been determined by single-crystal film techniques. The cell parameters were refined by using the θ angle of 25 reflections collected with an automatic four-circles X-ray diffractometer. $KBePO_4$: $a = 8.506(4)$, $b = 4.937(4)$, $c = 8.344(5)$ Å; space group, $Pc2_1n$ or $Pcmn$; $Z = 4$; $d_x = 2.712$. $Cs BePO_4$: $a = 8.713(4)$, $b = 8.836(5)$, $c = 5.147(4)$ Å; space group, $Pnam$ or $Pna2_1$; $Z = 4$; $d_x = 3.971$. Two other refinements for $KBePO_4$ and $RbBePO_4$ have been made

starting from X-ray powder diffractometer data. The results are mentioned in Table I.

Crystal Structure Determination

The parameters used for the X-ray diffraction data collections are reported in Table II. Lorentz and polarization corrections were made. No absorption correction was applied. The $KBePO_4$ and $CsBePO_4$ crystal structures were solved using the Patterson method and comparison with the structure of the $CsMgPO_4$ monophosphate (*1*). The extinction correction was applied using the formula $(F_c) \cdot (1 + gI_c)^{-1}$ in the various refinements (*2*) (g = extinction parameter).

$$g = 0.15 \times 10^{-5} \quad \text{for } KBePO_4$$

$$g = 2.02 \times 10^{-6} \quad \text{for } CsBePO_4$$

A unit weighting scheme was used throughout the least-squares refinements (*3*).

(*1*) $KBePO_4$. Two crystalline forms of $KBePO_4$ were found by Jaulmes and Durif (*4*). The first parameter cell determination of the low-temperature form was made by Schultz (*5*). The high-temperature form can be obtained by following the preparation

TABLE II

Parameters Used for the X-Ray Diffraction
Data Collection

	$KBePO_4$	$CsBePO_4$
Apparatus	Enraf–Nonius CAD4	Philips PW1100
Monochromator	Graphite plate	Graphite plate
Wavelength (Å)	$MoK\alpha$ (0.71073)	$AgK\alpha$ (0.56083)
Scan mode	ω	$\omega/2\theta$
Scan speed (°/sec)	0.018 to 0.042	0.02
Total background measurement (sec)	14 to 33	
Scan width (°)	1.2	1.0
θ range (°)	3–30	3–30
Intensity reference reflections	132, 1$\bar{3}$2	323, $\bar{3}$23
Number of collected reflections	632 (h,k,l)	978 (h,k,l)
Observed independent reflections	477	883
Crystal size (mm)	$0.13 \times 0.16 \times 0.16$	$0.13 \times 0.16 \times 0.19$
μ (cm^{-1})	18	50.3

Atom	x (σ)	y (σ)	z (σ)	B_{eq} (σ) Å^2
K	0.2092(2)	0.2500(0)	−0.0020(2)	1.92(3)
P	0.4185(2)	0.7361(7)	0.1910(2)	1.04(3)
O1	0.4589(5)	0.023(1)	0.2519(6)	1.4(1)
O2	0.4528(5)	1.039(1)	0.7516(6)	1.3(1)
O3	0.4072(5)	0.736(2)	0.0090(5)	1.7(1)
O4	0.2614(6)	0.645(1)	0.2600(6)	1.5(1)
Be	0.0891(8)	0.756(2)	0.3169(7)	0.9(1)

previously described. The investigation of Patterson, Fourier, and difference Fourier syntheses allowed us to locate all the atoms. The space group $Pc2_1n$ was imposed by the structure refinement and confirmed by a piezoelectricity test. The final R value for 472 independent reflections is 0.043. One hundred fifty-five reflections such that $F_o^2 < 2\sigma(F_o^2)$ were eliminated. Strong reflections badly corrected because of the attenuator were rejected. Tables III and IV give the atomic parameters, B_{eq}, and anisotropic temperature factors.

(2) *CsBePO$_4$*. The same procedure was followed for this compound. The space group used in the refinement was *Pnam*. The final R value is 0.027 for 717 reflections. One hundred sixty-six reflections having $F_o^2 < 4\sigma(F_o^2)$ were eliminated. The positional parameters, the B_{eq} values, and the anisotropic temperature factors are reported in Tables V and VI.[1]

Structure Descriptions

(1) *KBePO$_4$*. The structure of KBePO$_4$ is related to that of β-tridymite (6). In this structure, the SiO$_4$ tetrahedra are arranged

alternatively with a vertex up and a vertex down in order to form a hexagonal framework. In the KBePO$_4$ monophosphate, the SiO$_4$ tetrahedra are replaced by BeO$_4$ and PO$_4$ tetrahedra: three tetrahedra with three vertices up alternate with three tetrahedra having their three vertices down; a pseudohexagonal framework (Fig. 1) is obtained in this case. The Be and P atoms occupy adjacent tetrahedral sites in an ordered way. A double sheet of corners sharing BeO$_4$ and PO$_4$ tetrahedra generates cages inside of which the K atoms are located. This structure is similar to RbCoPO$_4$ (1) or NH$_4$LiSO$_4$ (7). Table VII summarizes the interatomic distances and bond angles. The PO$_4$ tetrahedron is regular with an average distance $\langle$P–O$\rangle$ = 1.532 Å. The BeO$_4$ tetrahedron is slightly distorted $\langle$Be–O$\rangle$ = 1.620 Å. The same situation is true for the CoO$_4$ tetrahe-
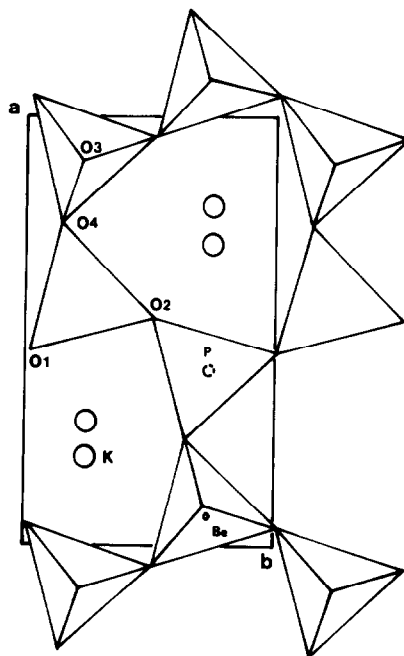

FIG. 1. Projection along the c axis of the partial atomic arrangement of KBePO$_4$. Only one tetrahedral layer is shown.

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

TABLE IV

REFINED TEMPERATURE FACTOR EXPRESSIONS (β's) FOR KBePO$_4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
K	0.0079(1)	0.0214(4)	0.0050(1)	−0.0049(8)	0.0003(3)	0.002(1)
P	0.0038(1)	0.0126(4)	0.0028(1)	0.000(1)	0.0002(3)	0.001(1)
01	0.0059(6)	0.015(2)	0.0038(5)	0.001(2)	0.0013(9)	−0.005(2)
02	0.0051(5)	0.013(2)	0.0044(5)	−0.002(2)	−0.0022(9)	0.002(2)
03	0.0083(5)	0.018(1)	0.0038(4)	−0.002(3)	−0.0006(10)	−0.010(4)
04	0.0034(5)	0.014(1)	0.0081(6)	−0.004(2)	0.0035(10)	0.000(2)
Be	0.0043(7)	0.007(2)	0.0028(6)	0.000(4)	0.000(1)	−0.005(4)

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

dra in RbCoPO$_4$ (*1*). A complete structural study of the three forms of CsZnPO$_4$ (*8*) and their ferroic properties (*9*) suggest that KBePO$_4$ and CsZnPO$_4$ (form II) are isostructural and KBePO$_4$ may reveal ferroelectric properties.

(*2*) *CsBePO*$_4$ (*Fig. 2*). The CsBePO$_4$ framework is also related to that of β-tridymite (*6*) and can be compared to KBePO$_4$ (Fig. 1). The CsBePO$_4$ structure is more symmetrical than that of KBePO$_4$ and isostructural with CsMgPO$_4$ (*1*). The interatomic distances and bond angles show that the PO$_4$ tetrahedron is regular with an average $\langle P-O \rangle$ distance of 1.521 Å (Table VIII). The BeO$_4$ tetrahedron is more regular than in KBePO$_4$. $\langle Be-O \rangle$ = 1.627 Å.

(*3*) *RbBePO*$_4$. This compound is probably isostructural with KBePO$_4$ as suggested by the similarity of the X-ray powder diagrams, cell parameters, and space groups. No piezoelectrical signal was detected. The

refinement of the structure should give the solution with regard to the space group, either *Pcmn* or *Pc2$_1$n*.

These compounds belong to the large family of $M^IM^{II}PO_4$ monophosphates. About 20% of these materials have a noncentrosymmetrical structure. They belong
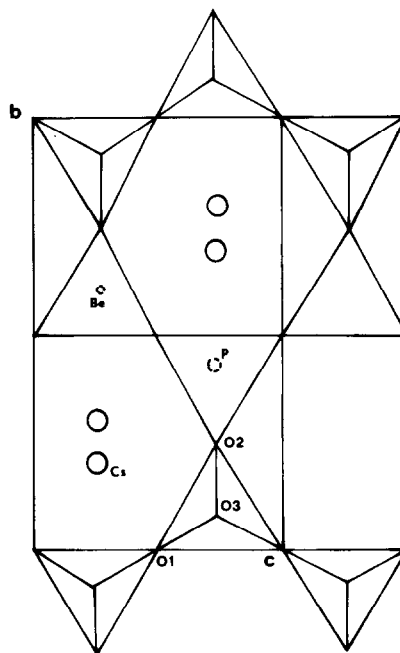

FIG. 2. Projection along the *a* axis of the partial atomic arrangement of CsBePO$_4$. Only one tetrahedral layer is shown. *a*, *b*, and *c* are cell parameters in *Pnam* representation of space group D_{2h}^{16}.

TABLE V

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR CsBePO$_4$

Atom	x (σ)	y (σ)	z (σ)	B_{eq} (σ) Å^2
Cs	−0.00637(8)	0.19614(8)	0.250	0.961(7)
P1	0.1829(3)	0.4161(3)	0.750	0.37(3)
01	0.7633(5)	0.4978(9)	0.009(1)	0.99(6)
02	0.257(1)	0.261(1)	0.750	1.4(1)
03	0.0105(9)	0.4000(9)	0.750	1.3(1)
Be	0.326(2)	0.090(2)	0.750	1.0(2)

TABLE VI

REFINED TEMPERATURE FACTOR EXPRESSIONS (β's) FOR $CsBePO_4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs	0.00320(4)	0.00320(4)	0.0086(1)	−0.0001(2)	0	0
P1	0.0015(2)	0.0010(2)	0.0031(6)	0.0005(4)	0	0
01	0.0030(4)	0.0045(5)	0.006(1)	0.000(1)	−0.000(2)	−0.006(1)
02	0.00431(8)	0.0015(7)	0.023(3)	0.002(1)	0	0
03	0.0015(6)	0.0057(8)	0.015(2)	0.000(2)	0	0
Be	0.003(1)	0.004(1)	0.010(3)	−0.001(2)	0	0

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

TABLE VII

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN $KBePO_4$

K–0(1)	2.742(5) Å	K–0(3)	2.933(6)	K–0(1)	3.203(5)
K–0(2)	3.099(11)	K–0(4)	2.964(5)	K–0(1)	3.271(5)
K–0(2)	2.731(14)	K–0(4)	2.796(5)	K–0(2)	3.336(11)
K–0(3)	3.047(6)			K–0(3)	3.264(6)

PO_4 tetrahedron

P	0(1)	0(2)	0(3)	0(4)
0(1)	1.542(8)	2.503(7)	2.512(8)	2.509(7)
0(2)	108.5(9)	1.541(10)	2.520(7)	2.488(6)
0(3)	110.1(4)	110.8(6)	1.521(5)	2.475(6)
0(4)	109.9(3)	108.7(9)	108.8(3)	1.522(5)

BeO_4 tetrahedron

Be	0(1)	0(2)	0(3)	0(4)
0(1)	1.697(9)	2.658(7)	2.673(7)	2.646(7)
0(2)	110.1(6)	1.542(10)	2.646(8)	2.666(7)
0(3)	108.0(5)	114.4(6)	1.606(6)	2.564(6)
0(4)	105.1(5)	114.0(5)	104.6(4)	1.635(8)

TABLE VIII

MAIN INTERATOMIC DISTANCES AND BOND ANGLES IN $CsBePO_4$

Cs–0(1)	3.599(4) Å	(×2)	Cs–0(2)	3.318(2) Å	(×2)
Cs–0(1)	3.140(3)	(×2)	Cs–0(3)	3.145(2)	(×2)
Cs–0(1)	3.161(3)	(×2)	Cs–0(3)	3.568(4)	(×2)
Cs–0(2)	3.497(3)	(×2)			

PO_4 tetrahedron

P	0(1)	0(1)	0(2)	0(3)
0(1)	1.529(4)	2.481(10)	2.473(10)	2.498(9)
0(1)	108.5(3)	1.529(4)	2.473(10)	2.498(9)
0(2)	108.6(2)	108.6(2)	1.517(5)	2.477(11)
0(3)	110.6(1)	110.6(1)	109.9(3)	1.509(4)

BeO_4 tetrahedron

Be	0(1)	0(1)	0(2)	0(3)
0(1)	1.638(6)	2.666(10)	2.647(10)	2.676(9)
0(1)	108.9(6)	1.628(6)	2.647(10)	2.676(9)
0(2)	108.4(4)	108.4(4)	1.625(10)	2.625(11)
0(3)	111.2(3)	111.2(3)	108.6(5)	1.606(8)

to the space groups $P2_1$, $Pna2_1$, or $P6_3$. Piezoelectric and ferroelectric properties may be found. The noncentrosymmetrical $M^IM^{II}XO_4$ (X = S, P, As) phases, already investigated, are known as "light ferroelectrics." The study of ferroic transitions in the M^IBePO_4 family should be promising.

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