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The Crystal Structure, Phase Transition, and Dielectric Properties of $K_2Bi_3(PO_4)_3O$, a New Oxyphosphate

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The title compound exhibits a transition at about 745 K detectable by DSC and dielectric measurements. The structure was determined at ambient temperature and above the transition. In both cases, the cell is orthorhombic with a = 13.139(4), b = 10.413(6), c = 9.239(6) Å at 295 K and a = 13.302(4), b = 10.506(7), c = 9.240(5) Å at 795 K, Z = 4. The structures were refined in space group *Pnma* to *R* values of 0.048 and 0.058 using 1472 and 1154 unique single-crystal reflections, respectively. The two structures are very similar and can be described as a three-dimensional network of distorted BiO_6 octahedra and PO_4 tetrahedra. At high temperature, one of the PO_4 tetrahedra is statistically disordered over two positions related by the mirror. Below the transition temperature, ordering of this ion leads to doubling of the c parameter and formation of satellite reflections (h, k, $l + \frac{1}{2}$). Extinction rules indicate $P2_1ca$ as a possible supercell space group.

Introduction

Double orthophosphates of bivalent, trivalent, or quadrivalent cations with alkali metals are promising materials in the field of inorganic material technology. For instance, (i) compounds of formula $A_3Ln(PO_4)_2$ [Ln = rare earth; A = Na, K, Rb, Cs with structures related to the β-K_2SO_4 type (*1–3*)] have possible applications as hosts for laser materials, (ii) compounds of formula $A_3M_2(PO_4)_3$ (M = Cr, Fe; A = Li, Na, Ag) (*4*) and $Na_{1+x}Zn_{2-x}L_x(PO_4)_3$ (L = Cr, In, Yb) (*5*) having the Nasicon structure are solid electrolytes, and (iii) $ABPO_4$ phases (A = Na, K; B = Ca, Zn, Sr, Cd, Ba, Pb) are ferroelectric materials (*6*). All these compounds exhibit one or more phase transitions before melting.

Furthermore, it is well established that ions such as Bi^{3+} and Pb^{2+} often generate distorted structures due to the electrostatic effect of the lone pair of electrons. The compounds formed by combination of such ions with tetrahedral anions (VO_4 or PO_4) present interesting properties, for instance, ferroelasticity in $BiVO_4$ (*7–9*) and $Pb_3(P_xV_{1-x}O_4)_2$ ($0 \leq x \leq 1$) (*10–15*). Astonishingly enough, no result on double phosphates of bismuth and alkali metals has yet been published, to our knowledge. During the investigation of the $BiPO_4$–K_3PO_4 system in air (*16*), single phases for ratios 1:1 and 4:1 were characterized by X-ray diffraction. Quenched $K_3Bi(PO_4)_2$ has a hexagonal cell [a = 5.677(3), c = 7.432(7) Å] of glaserite

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type similar to the high-temperature form of $Na_3Ln(PO_4)_2$ (*3*). Slow cooling (5 K/hr) yields monoclinic $K_3Bi(PO_4)_2$ with a = 9.560(4), b = 5.650(2), c = 7.457(3) Å, and β = 90.91(3)° which is related to the hexagonal form by $a_m = a_h \times 3$, $b_m = b_h$, $c_m = c_h$. This monoclinic form is similar to the majority of arsenates and vanadates (*17*) and some phosphates (*1*, *2*) of the rare earth elements and potassium. On heating, the transition between low- and high-temperature forms occurs at about 845 K. The X-ray powder pattern of the compound with a ratio of 4 : 1 can be indexed in a primitive cubic unit cell with a = 10.215(3) Å but its exact composition is not yet known.

In some experiments, extra X-ray diffraction lines appeared on the powder patterns for composition between 1 and 4. Microscopic examination of the material shows some transparent single crystals apparently suitable for X-ray studies and it was decided to solve the structure and so establish the composition of this phase. Furthermore, this compound exhibits a transition at about 745 K and the structure was also determined above this transition.

Experimental

Preparation. Phosphate powder samples were prepared from Bi_2O_3 (Johnson Matthey), KH_2PO_4 (Prolabo R.P.), $(NH_4)_2HPO_4$ (Fluka Puriss), and K_2CO_3 (Johnson Matthey) according to the stoichiometries

$$\begin{aligned}(x/2)Bi_2O_3 + 3KH_2PO_4 \\ + (x - 2)(NH_4)_2HPO_4 \rightarrow \\ K_3Bi_x(PO_4)_{1+x} + 2(x - 2)NH_3 \\ + (3x/2)H_2O \qquad \text{for } x \geq 2 \quad (1)\end{aligned}$$

and

$$\begin{aligned}(x/2)Bi_2O_3 + (1 + x)KH_2PO_4 \\ + ((2 - x)/2)K_2CO_3 \rightarrow \\ K_3Bi_x(PO_4)_{1+x} + ((2 - x)/2)CO_2 \\ + (1 + x)H_2O \qquad \text{for } x \leq 2. \quad (2)\end{aligned}$$

Oxyphosphate powder samples were prepared according to the stoichiometry (PbO was purchased from Johnson Matthey)

$$\begin{aligned}2xPbO + ((3 - x)/2)Bi_2O_3 \\ + ((2 - x)/2)K_2CO_3 + 3(NH_4)_2HPO_4 \rightarrow \\ K_{2-x}Bi_{3-x}Pb_{2x}(PO_4)_3O + ((2 - x)/2)CO_2 \\ + 6NH_3 + (9/2)H_2O. \quad (3)\end{aligned}$$

Mixtures of the components were preheated in gold crucibles at 575 K for 2 hr, fired at 1125 K in air overnight, and quenched.

Powder examination. Powder diffraction patterns were obtained with a Guinier camera. The radiation was monochromatic Cu$K\alpha$ (λ = 1.5418 Å), and KCl (a = 6.2931 Å) was used as an internal standard.

Transition study. DSC and DTA analyses were done with a 910 Differential Scanning Calorimeter and a 1090B Thermal Analyzer (Dupont Instruments). Dielectric measurements were performed with a 2110 LRC Video Bridge (Electro Scientific Industries).

Single-crystal measurements. The first isolated single crystals had no preferred orientation, so a nearly spherical crystal (R = 0.0087 cm) was directly examined on a Philips PW1100 diffractometer with Mo$K\alpha$ graphite monochromated radiation (λ = 0.7107 Å). The automatic peak hunting and autoindexing procedures revealed an orthorhombic unit cell. Equality of hkl, $\bar{h}kl$, $h\bar{k}l$, and $hk\bar{l}$ intensities showed $2/mmm$ Laue symmetry. The lattice parameters were refined from 25 well-centered reflections: a = 13.139(4), b = 10.413(6), c = 9.239(6) Å. A total of 4093 reflections with $2° \leq \theta \leq 30°$ were collected ($-18 \leq h \leq 18$; $0 \leq k \leq 14$; $0 \leq l \leq 12$), and corrected for background, Lorentz, and polarization effects. Absorption corrections were applied assuming a spherical crystal (R_{mean} = 0.0087 cm). Of the 4093 reflections measured, 2758 were considered significant from the criterion $I > 3\sigma(I)$ where $\sigma(I)$ is the standard deviation of the measured intensity. Averaging of the equivalent reflections led to 1472 independent data which were used in the structure determination. Since we suspected the presence of a double cell from doubling of the c parameter, the superstructure intensities (corresponding to l half integer) were also measured up to $\theta = 30°$. A total of 1583 independent superstructure reflections satisfied the criterion $I > 3\sigma(I)$; however, these are all very weak.

Since further experiments suggested a phase transition, high-temperature single-crystal measurements were considered. The crystal was enclosed in a slightly narrowed quartz capillary. The temperature was slowly increased by using a heating device consisting of a gas blower which supplies a temperature-regulated flow of air on the crystal (AET, Grenoble, France). The intensity of the highest superstructure reflection ($\bar{12}$ 1 3) was monitored during the heating. At the transition, its diffracted intensity suddenly dropped to zero. The temperature of the air flow was then regulated at about 50 K above the transition (745 K) to prevent a return to the low-temperature form during the intensity measurements. The unit cell lengths are $a = 13.302(4)$, $b = 10.506(7)$, $c = 9.240(5)$ Å.

The data collection parameters were the same as those of the ambient temperature experiments. Of the 4174 reflections measured, 2105 obeyed $I > 3\sigma(I)$ and, after averaging equivalent reflections, 1154 independent data were obtained.

In all experiments, the intensities of three standard reflections measured after every 2 hr showed no significant variation during data collections.

Results and Discussion

Low-Temperature Subcell Structure Determination

The systematic absences ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) indicated *Pnma* or *Pn2₁a* as possible space groups. Structure solution and refinement were successful in the centrosymmetric space group *Pnma*. In this space group, the Patterson map was readily interpreted by assuming that Bi atoms occupy one general position and a 4c position on a mirror plane. K and P coordinates were deduced from subsequent refinements and difference synthesis. However, at this stage, K and P atoms could not be distinguished and mean scattering factors were attributed to the positions. Absorption corrections were applied assuming a spherical crystal (R = 0.0087 cm) and $K_3Bi_3(PO_4)_4$ (Z = 4) formula according to site multiplicities and electric neutrality ($\mu = 412$ cm^{-1}). The following difference synthesis revealed five oxygen atoms, four at about 1.5 Å from P(1) and the fifth at a distance of 2.3–2.7 Å from the Bi atom. Refinement with correct scattering factors for K and P and a subsequent difference synthesis allowed location of eight maxima around the P(2) atom; they were attributed to oxygen atoms with half occupancy factors. Finally, a last difference synthesis showed symmetric peaks on both sides of the mirror in the vicinity of the P(2) atom; splitting the corresponding position led to the final results, $R = 0.048$ $R_w = 0.054$. Anisotropic thermal vibrations were assigned to Bi atoms and isotropic vibrations to other atoms. A secondary extinction correction was introduced in the form $F^2_{\mathrm{corr}} = F^2_{\mathrm{calc}}(1 + SF^2_{\mathrm{obs}})$, the final value of S being $213(9) \times 10^{-9}$. Refinement the space group $Pn2_1a$ does not give a significant improvement ($R = 0.044$; $R_w = 0.050$) since the number of refined parameters greatly increases (100 instead of 66) (*18*). Scattering factors were taken from Ref. (*19*). The anomalous dispersion corrections were made according to Cromer and Liberman (*20*). The full matrix least-squares refinements were peformed with a local modification of ORFLS (*21*). A weight

TABLE I

ATOMIC COORDINATES AND (EQUIVALENT) ISOTROPIC THERMAL PARAMETERS

Atom	Site	Occup. factor	x	y	z	B or $\langle B\rangle_{eq}$ (Å)^2
Bi(1)	8*d*	1	0.0834(1)[a]	0.0524(1)	0.1933(1)	1.8
			0.0823(1)	0.0595(1)	0.1927(1)	2.8
Bi(2)	4*c*	1	0.0256(1)	$\frac{1}{4}$	0.5143(1)	1.4
			0.0230(1)	$\frac{1}{4}$	0.5209(2)	2.5
K(1)	4*c*	1	0.7673(3)	$\frac{3}{4}$	0.2036(5)	1.2(1)
			0.7608(7)	$\frac{3}{4}$	0.2010(10))	3.1(1)
K(2)	4*c*	1	0.7997(5)	$\frac{1}{4}$	0.1549(7)	2.4(1)
			0.7961(8)	$\frac{1}{4}$	0.1547(12)	4.5(2)
P(1)	8*d*	1	0.3429(3)	0.0274(4)	0.0569(4)	1.2(1)
			0.3445(5)	0.0242(6)	0.0627(7)	2.5(1)
P(2)	8*d*	0.5	0.0096(5)	0.7313(8)	0.0804(7)	1.3(14)
			0.0109(8)	0.7422(41)	0.0733(12)	3.0(3)
O(1)	8*d*	1	0.346(1)	−0.120(1)	0.069(2)	3.1(2)
			0.353(2)	−0.120(2)	0.077(3)	4.6(5)
O(2)	8*d*	1	0.352(1)	0.067(1)	−0.102(1)	2.8(2)
			0.357(2)	0.063(3)	−0.095(3)	6.2(6)
O(3)	8*d*	1	0.244(1)	0.081(1)	0.120(2)	3.0(2)
			0.248(2)	0.073(2)	0.129(2)	4.7(5)
O(4)	8*d*	1	0.431(1)	0.086(1)	0.139(1)	2.6(2)
			0.429(2)	0.092(2)	0.143(3)	5.0(5)
O(5)	4*c*	1	0.602(1)	$\frac{1}{4}$	0.197(2)	1.9(3)
			0.598(2)	$\frac{1}{4}$	0.205(3)	3.0(5)
O(6)	8*d*	0.5	0.031(2)	0.832(3)	−0.039(3)	2.7(4)
			0.042(4)	0.855(5)	−0.013(5)	4.9(10)
O(7)	8*d*	0.5	−0.075(2)	0.631(3)	0.038(3)	2.5(4)
			−0.080(5)	0.665(7)	0.016(8)	9.5(19)
O(8)	8*d*	0.5	0.112(2)	0.656(3)	0.101(3)	2.6(4)
			0.103(5)	0.649(7)	0.081(7)	8.1(16)
O(9)	8*d*	0.5	−0.022(2)	0.800(2)	0.219(2)	1.8(4)
			−0.021(4)	0.792(5)	0.222(5)	6.2(13)

[a] First line = low-temperature results; second line = high-temperature results.

of unity was attributed to all reflections.[1]

Atomic coordinates and isotropic temperature factors are reported in Table I. Anisotropic thermal parameters of Bi atoms are listed in Table II.

The X-ray results show the compound is an oxyphosphate formulated as $K_2Bi_3(PO_4)_3O$ or $K_2O \cdot 3BiPO_4$. The unit cell parameters refined by means of powder reflections confirm those found in single-crystal study.

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[1] Lists of the observed and calculated structure factors are available on request from the authors.

TABLE II

REFINED ANISOTROPIC THERMAL COEFFICIENTS FOR Bi ATOMS (× 10^4 Å^2)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	262(3)	186(3)	214(3)	−13(2)	−84(2)	18(2)
	370(5)	348(4)	349(5)	17(5)	−60(4)	−26(4)
Bi(2)	112(3)	203(3)	173(3)	0	4(3)	0
	278(6)	323(7)	354(7)	0	6(6)	0

[a] The anisotropic temperature factor is defined by $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^*)]$.

Description and Discussion of Low-Temperature Structure

The low-temperature structure of $K_2Bi_3(PO_4)_3O$ can be described as a three-dimensional network formed by distorted BiO_6 octahedra and PO_4 tetrahedra (Figs. 1 and 2). Potassium ions occupy vacant tunnels created by this network.

The two PO_4 tetrahedra are dissimilar: $P(1)O_4$ is nearly regular with P(1)–O distances ranging from 1.50 to 1.53 Å (Table III), while the $P(2)O_4$ tetrahedron is disordered over two equivalent positions on both sides of the mirror, the P(2)–O distances ranging from 1.52 to 1.59 Å. Bi(2) is surrounded by six oxygen atoms forming a distorted octahedron characteristic of the $6s^2$ lone pair effect with three shorter distances (2.20 and 2.23 (2×) Å) on one side and three longer distances (2.53 and 2.54 (2×) Å) on the other side.

The coordination around Bi(1) is dependent on the $P(2)O_4$ tetrahedron chosen and four different geometries can be obtained; in each case, Bi(1)–O distances are compat-

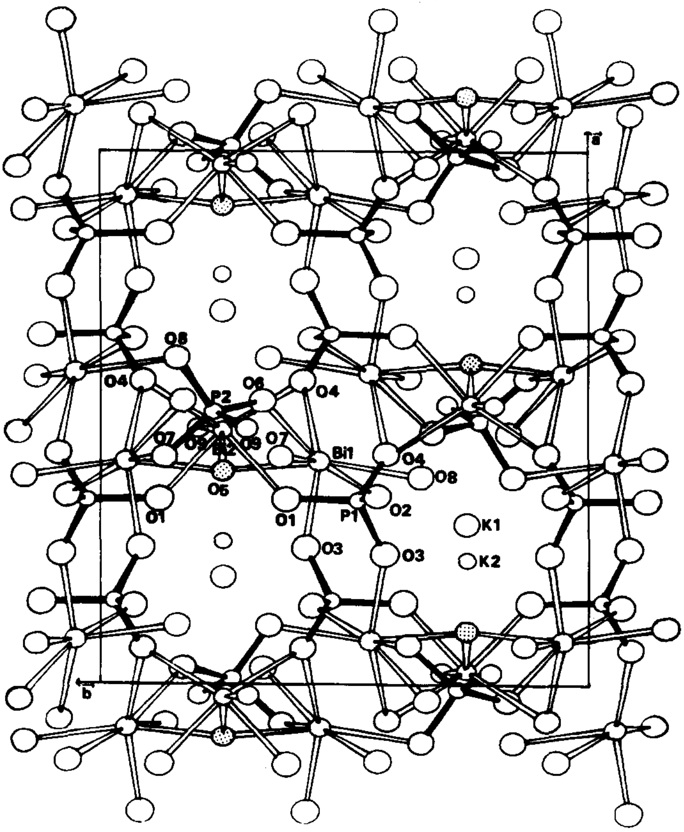

FIG. 1. $K_2Bi_3(PO_4)_3O$ structure projected on (001).

ible with the values generally accepted; consequently complete disorder and perfect long-distance ordering of the P(2)O_4 tetrahedra are equally possible.

The K(1) atom is surrounded by seven oxygen atoms at distances ranging from 2.69 to 2.91 Å with an average value of 2.77 Å; five oxygen atoms are around K(2) at distances between 2.56 and 2.81 Å (average 2.73 Å); the coordination sphere is completed by four additional oxygen atoms at 3.08 (2×) and 3.12 (2×) Å.

The oxygen, O(5), not involved in a phosphate group participates in the coordination of both Bi(1) and Bi(2).

TABLE III

PRINCIPAL DISTANCES (Å) AND ANGLES (°) IN $K_2Bi_3(PO_4)_3O$[a,b]

Bi(1) Environment		Bi(2) Environment	
Bi(1)–O(2)^{vii}	2.42(1)	Bi(2)–O(1)^{iv}	2.22(1)
	2.48(3)	Bi(2)–O(1)^{vii}	2.10(2)
Bi(1)–O(3)^{i}	2.24(1)		
	2.29(3)	Bi(2)–O(4)$^{iii}_{100}$	2.54(1)
Bi(1)–O(4)$^{viii}_{100}$	2.56(1)	Bi(2)–O(4)$^{viii}_{100}$	2.57(2)
	2.57(3)		
Bi(1)–O(5)$^{iii}_{100}$	2.31(1)	Bi(2)–O(5)$^{iii}_{100}$	2.20(2)
	2.22(1)		2.31(3)
Bi(1)–O(6)$^{ii}_{010}$	2.40(3)	Bi(2)–O(9)$^{v}_{0\bar{1}1}$	2.52(2)
	2.51(5)		2.42(5)
Bi(1)–O(7)$^{v}_{0\bar{1}0}$	2.29(3)		
	2.22(7)		
Bi(1)–O(8)^{vi}	2.36(3)		
	2.44(7)		
K(1) Environment		**K(2) Environment**	
K(1)–O(1)^{iii}	2.70(2)	K(2)–O(3)^{iii}	2.82(2)
K(1)–O(1)$^{viii}_{010}$	2.75(3)	K(2)–O(3)^{viii}	2.80(2)
K(1)–O(2)$^{ii}_{110}$	2.64(1)	K(2)–O(5)^{i}	2.63(1)
K(1)–O(2)$^{v}_{100}$	2.70(3)		2.68(3)
		K(2)–O(6)$^{ii}_{110}$	2.61(3)
K(1)–O(7)$^{i}_{100}$	2.86(3)	(K(2)–O(6)$^{v}_{1\bar{1}0}$)	2.75(5)
K(1)–O(7)$^{vi}_{110}$	2.86(7)		
		K(2)–O(8)$^{ii}_{110}$	2.81(3)
K(1)–O(8)$^{iii}_{0\bar{1}0}$	2.89(3)	(K(2)–O(8)$^{v}_{1\bar{1}0}$)	2.77(7)
K(1)–O(8)^{viii}	3.10(7)		
		K(2)–O(1)$^{ii}_{100}$	3.13(2)
K(1)–O(9)$^{i}_{100}$	2.82(3)	K(2)–O(1)$^{v}_{100}$	3.22(3)
K(1)–O(9)$^{vi}_{110}$	2.94(5)		
		K(2)–O(4)^{iii}	3.09(2)
		K(2)–O(4)^{viii}	3.06(3)

TABLE III—*Continued*

Phosphate ions		Phosphate ions	
P(1)–O(1)	1.54(1)	P(2)–O(6)	1.55(3)
	1.52(2)		1.49(6)
P(1)–O(2)	1.53(1)	P(2)–O(7)	1.57(3)
	1.52(3)		1.55(7)
P(1)–O(3)	1.53(1)	P(2)–O(8)	1.57(3)
	1.51(3)		1.57(7)
P(1)–O(4)	1.51(1)	P(2)–O(9)	1.52(2)
	1.52(3)		1.53(5)
Average	1.53 ± 0.01	Average	1.55 ± 0.02
	1.52 ± 0.01		1.53 ± 0.04
O(1)–P(1)–O(2)	110(1)	O(6)–P(2)–O(7)	114(4)
	110(3)		117(8)
O(1)–P(1)–O(3)	111(2)	O(6)–P(2)–O(8)	106(3)
	111(3)		108(7)
O(1)–P(1)–O(4)	110(1)	O(6)–P(2)–O(9)	109(3)
	112(3)		107(6)
O(2)–P(1)–O(3)	109(2)	O(7)–P(2)–O(8)	108(3)
	113(3)		107(8)
O(2)–P(1)–O(4)	108(1)	O(7)–P(2)–O(9)	109(3)
	105(3)		106(7)
O(3)–P(1)–O(4)	108(2)	O(8)–P(2)–O(9)	112(3)
	106(3)		113(8)
Average	109 ± 1	Average	110 ± 3
	110 ± 3		110 ± 4

O(5) Environment

O(5)–Bi(1)^{iii}	2.31(1)	Bi(1)^{iii}–O(5)–Bi(1)^{viii}	126(1)
O(5)–Bi(1)^{viii}	2.22(2)		128(1)
		Bi(1)^{iii}–O(5)–Bi(2)^{iii}	110(1)
O(5)–Bi(2)^{iii}	2.20(2)		110(1)
	2.31(3)	Bi(1)^{iii}–O(5)–K(2)^{i}	100(1)
O(5)–K(2)^{i}	2.63(2)		100(1)
	2.68(3)	Bi(2)^{iii}–O(5)–K(2)^{i}	109(1)
			106(1)

[a] The high-temperature distances are indicated below the low-temperature values.

[b] $A(n)^{x}_{pqr}$ represents atom $A(n)$ to which the symmetry x has been applied, followed by a translation $pa + qb + rc$. Symmetry code: (i) x, y, z; (ii) $\bar{x}, \bar{y}, \bar{z}$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (v) $\bar{x}, \frac{1}{2} + y, \bar{z}$; (vi) $x, \frac{1}{2} - y, z$; (vii) $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$; (viii) $\frac{1}{2} + x, y, \frac{1}{2} - z$.

To decide between ordering or disordering of P(2)O_4 ions, we have attempted syntheses of larger single crystals by melting $K_2Bi_3(PO_4)_3O$ at 1225 K and slow cooling (5 K/hr). Oscillation and Weissenberg photographs of the well-formed crystals display very weak supplementary reflections involving *c* parameter doubling. Unfortunately these single crystals were not good enough for diffractometer measurements (the profiles of the reflections were systematically very bad). Measurements of the superstructure reflections were carried out using the former single crystal; unfortunately, a structure refinement in the supercell was not possible (some temperature factors become negative); this failure can

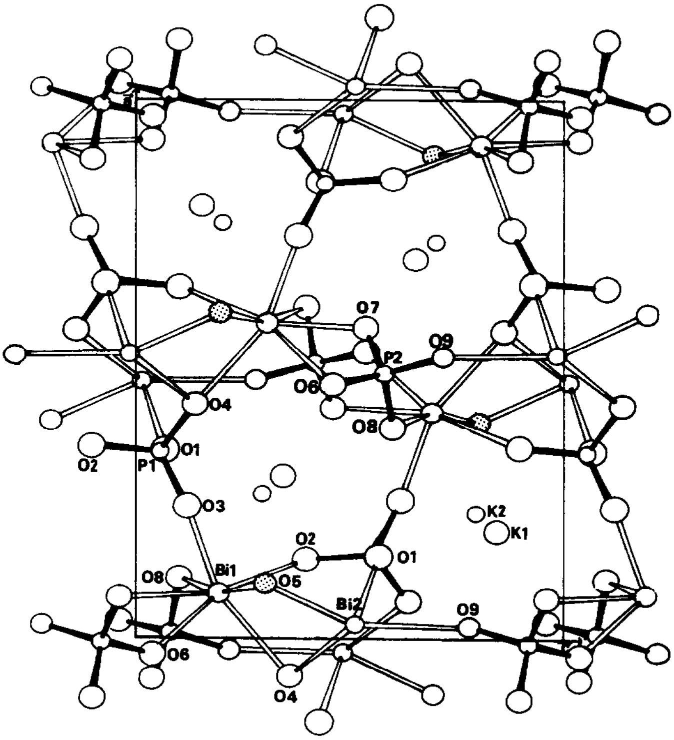

FIG. 2. $K_2Bi_3(PO_4)_3O$ structure projected on (010).

be attributed to stacking faults. However, extinction conditions seem to indicate space group $P2_1ca$.

The structure of $K_2Bi_3(PO_4)_3O$ is similar to that of $Pb_4Bi(PO_4)_3O$ (*22*) but, in the latter compound, $P(2)O_4$ anions occupy only one position: P(2) and two oxygen atoms are on the mirror and the other two are related by the mirror.

In the case of $K_2Bi_3(PO_4)_3O$ a transition to such a situation is expected. Effectively, DSC measurements exhibited a double peak (Fig. 3); the transition proceeds in two steps and begins at about 745 K. To study the character of this transition, the single-crystal structure determination above was undertaken.

High-Temperature Structure

Extinction conditions indicated space groups *Pnma* and *Pn*2_1*a*. The high-temperature determination was carried in space group *Pnma* by the same procedure as at low temperature. The P(2) and oxygen atoms around P(2) are also distributed over two positions with half occupancy factors. Refinement results are reported in Tables I and II. The reliability factors are $R = 0.058$ and $R_w = 0.063$; $S = 55(9) \times 10^{-9}$.

There are no drastic differences between low- and high-temperature atomic coordinates. The P(2) atom is nearer the mirror

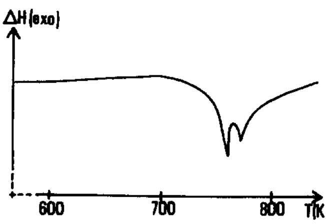

FIG. 3. DSC of $K_2Bi_3(PO_4)_3O$ (ΔH scale in arbitrary units).

plane. Higher thermal motions are due to the higher temperature of measurement.

There is no longer a supercell in the high-temperature form, so it is necessary to assume complete disorder of the $P(2)O_4$ tetrahedra. The transition is therefore of an order–disorder type. Such a transition has been observed in NH_4Br (*23*): above 235 K the structure is centrosymmetric with a disorder of NH_4^+ tetrahedra; below 235 K, NH_4^+ tetrahedra are oriented in an antiparallel manner in adjoining cells and the unit cell parameters must be doubled in two directions.

It is also interesting to compare this compound with $[N(CH_3)_4]_2CuBr_4$ of the β-K_2SO_4 type with isolated copper halide tetrahedra: at high temperature ($T > 272$ K) the space group is *Pnma* and the tetrahedra are probably disordered (*24*); between 237 and 242 K the compound is ferroelectric, satellite reflections are observed at (h, k, $l + \frac{1}{2}$), and from observed extinctions space group $Pca2_1$ can be assigned (*25*); finally between these two forms, incommensurable reflections are observed at (h, k, $l \pm \gamma$). Such an incommensurable phase is perhaps present between the two peaks observed by DSC for the oxyphosphate.

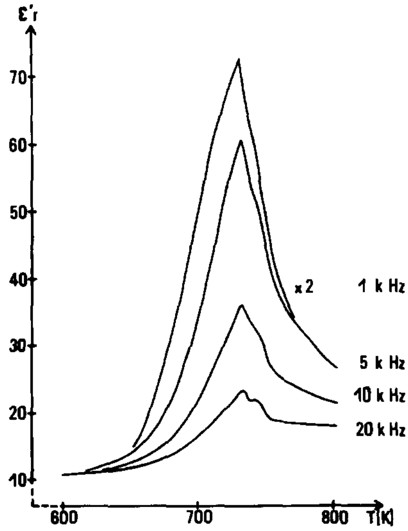

FIG. 4. Thermal variation of ε_r' for a ceramic of $K_2Bi_3(PO_4)_3O$ at different frequencies.

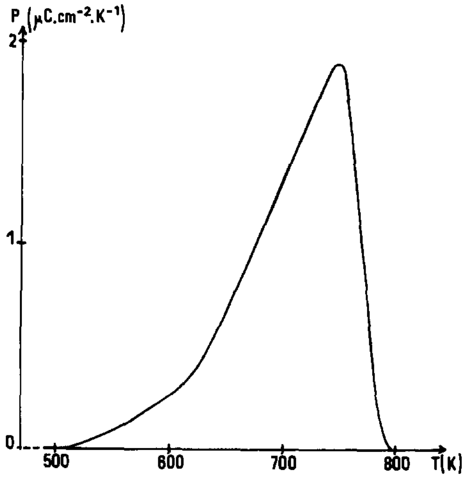

FIG. 5. Thermal variation of the pyroelectric coefficient for a ceramic of $K_2Bi_3(PO_4)_3O$.

Dielectric Properties

In view of these results, experiments were undertaken to demonstrate ferroelectric properties. Dielectric measurements between 1 and 20 kHz showed two anomalies in the dielectric constant (ε_r'): a first peak at about 735 K and a second which appears at highest frequency at about 745 K (Fig. 4) corresponding to the phase transitions. A pyroelectric study was performed by measurements of the depolarizing current vs temperature of a ceramic previously polarized by application of a 0.15-kV/cm direct electric field near 730 K and cooled to 295 K. After short-circuiting at 295 K during 15 hr, the sample was heated at 10 K/min and the current was measured vs temperature with a Keithley electrometer. A pyroelectric current passed through a maximum near 750 K (Fig. 5). Reversing the sense of the pyroelectric current results in reverse polarization sense, so spontaneous polarization is reversible. Unfortunately, no hysteresis loop $P = f(E)$ was observed.

To lower the transition temperatures, intermediate phases between $Pb_4Bi(PO_4)_3O$

TABLE IV

INTERMEDIATE $K_{2-x}Pb_{2x}Bi_{3-x}(PO_4)_3O$ PHASES

x	a (Å)	b (Å)	c (Å)	m (K)
0	13.139(4)	10.413(6)	9.239(6)	1264
0.5	13.183(4)	10.390(3)	9.265(3)	1231
1.	13.226(4)	10.385(3)	9.251(2)	1254
1.5	13.272(3)	10.336(3)	9.251(2)	1284
2.	13.313(5)	10.284(3)	9.219(4)	1294[a]

[a] From Ref. (*22*).

and $K_2Bi_3(PO_4)_3O$ which can be formulated $K_{2-x}Pb_{2x}Bi_{3-x}(PO_4)_3O$ were synthesized (Table IV). In this table melting points are also reported. For $x = 0$ and $x = 2$ there is another transition before melting at 1216 and 1182 K, respectively. For intermediate values of x only a melting peak was observed by DTA. Unfortunately, DSC experiments and dielectric measurements did not reveal any transition.

The other two phases of the $BiPO_4$–K_3PO_4 system obtained for the ratios 1 : 1 and 4 : 1 are presently under further investigation at low and high temperatures.

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