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Crystal Structure and Electrical Properties of $K_3Bi_2(VO_4)_3$, a New Potassium Bismuth Vanadate

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$K_3Bi_2(VO_4)_3$ crystallizes in the space group $C2/c$, $a = 13.957(4)$, $b = 13.858(4)$, $c = 7.095(2)$ Å, $\beta = 112.80(3)°$, $Z = 4$. The crystal structure was determined from single-crystal intensity data obtained by means of an automated four-circle diffractometer and refined to the conventional values $R = 0.050$ and $R_w = 0.059$ for 1498 observed reflections. The structure is characterized by a three-dimensional network of Bi_2O_{10} units and VO_4 tetrahedra. A Bi_2O_{10} unit is formed by two BiO_6 octahedra sharing an edge. K^+ ions occupy three different crystallographic sites. One of them has a high thermal vibration which could reflect ionic mobility. The ionic conductivity highly increases at 790 K. DSC measurements show a reversible transition at this temperature. One K atom, and only one, can be substituted by one Na atom to give $NaK_2Bi_2(VO_4)_3$; this substitution improves the conductivity.

Introduction

Several compounds of the general formula $A_3^{\mathrm{I}}M_2^{\mathrm{III}}(PO_4)_3$ have been reported in the literature. For M = Ti, V, Cr, Fe and A = Li, Na, the compounds adopt, at ambient temperature, structures related to that of Nasicon and undergo several reversible transitions (*1*). For M = Cr, Fe, they are solid electrolytes (*2–4*). For A = K, only one compound is known today, $K_3Fe_2(PO_4)_3$, which has a structure with a three-dimensional network of linked PO_4, FeO_6, and FeO_5 polyhedra (*5*).

In the system K_2O–$BiPO_4$, we have recently isolated an oxyphosphate $K_2Bi_3(PO_4)_3O$ which exhibits an order–disorder transition (*6*). Attempts to prepare isotypic oxyvanadate failed, but a vanadate of formula $K_3Bi_2(VO_4)_3$ was isolated.

Because of the lone-pair $6s^2$ electrons, the Bi^{3+} ion generally leads to unique structural features. The present paper reports the structure determination of this vanadate which exhibits a phase transition at 790 K. This transition is accompanied by a great increase in conductivity.

Experimental

Preparation

All starting materials were Specpure Grade Chemicals from Johnson Matthey and were used without further purification.

In the aim of preparing a compound

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isotypic with $K_2Bi_3(PO_4)_3O$, we started with a mixture of the same composition as that used in (*6*): Bi_2O_3 (1.406 g), V_2O_5 (0.549 g), and K_2CO_3 (0.278 g) were mixed together. The reaction was first carried out at 775 K for 15 hr; after regrinding of the prereaction products, a second firing was carried out at 1025 K overnight, followed by slow cooling (3.6 K/hr) to 475 K and quenching to room temperature. Reaction was carried out in a pure gold container in air at ambient pressure.

The product thus obtained was not homogeneous; it contained several distinguishable phases. The compound chosen for this study was present chiefly as needle-shaped single crystals. Because it was difficult and tedious to separate out enough of this compound for chemical analyses, single-crystal X-ray diffraction was used to identify the phase and led to the formula $K_3Bi_2(VO_4)_3$. Pure $K_3Bi_2(VO_4)_3$ was obtained by reaction of the appropriate amounts of K_2CO_3, Bi_2O_3, and V_2O_5 at 775 K for 16 hr before calcination at 995 K for 72 hr in air, with an intermediate regrinding. The unit cell constants (Table I) were least squares refined from a Guinier powder spectrum. The X-ray powder pattern is given in Table II.

X-ray Data Collection

A single crystal was mounted with greatest dimension of the needle as the rotation axis. Preliminary oscillation and Weissenberg photographs indicated 2/*m* Laüe symmetry. Systematic absences (hkl: $h + k = 2n + 1$ and $h0l$: $l = 2n + 1$) were consistent with space groups *Cc* or *C*2/*c*. The intensity data were collected with a Philips PW 1100 automated diffractometer using Mo$K\alpha$ radiation and a graphite monochromator. Conditions for data collection are given in Table III. The intensity of each reflection was corrected for background and for Lorentz and polarization effects.

TABLE I

UNIT CELL PARAMETERS

Crystal symmetry	Monoclinic
a (Å)	13.957(4)
b (Å)	13.858(4)
c (Å)	7.095(2)
β (°)	112.80(3)
V (Å^3)	1265.1(1)
Z	4
Space group	*C*2/*c*
μ (cm^{-1}) (for $\lambda K\alpha$ = 0.7107 Å)	297

TABLE II

$K_3Bi_2(VO_4)_3$ X-RAY POWDER DIFFRACTION DATA

$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)	$h\ k\ l$	d_{obs} (Å)	d_{calc} (Å)
0 2 0	6.943	6.929	$\bar{1}$ 3 2	2.797	2.795
2 0 0	6.430	6.434	$\bar{4}$ 2 2	2.699	2.699
$\bar{1}$ 1 1	6.279	6.273	$\bar{3}$ 3 2	2.677	2.677
0 2 1	4.753	4.756	$\bar{1}$ 5 1	2.579	2.579
$\bar{2}$ 2 1	4.475	4.474	4 0 1	2.525	2.525
0 4 0	3.462	3.465	1 3 2	2.466	2.463
$\bar{1}$ 1 2	3.399	3.403	1 5 1	2.433	2.434
0 0 2	3.267	3.270	4 4 0	2.357	2.357
$\bar{3}$ 3 1	3.213	3.211	$\bar{3}$ 1 3	2.311	2.312
$\bar{4}$ 2 1	3.101	3.101	$\bar{1}$ 1 3	2.272	2.270
2 4 0	3.046	3.050	$\bar{5}$ 3 2	2.241	2.240
3 1 1	3.010	3.007	$\bar{6}$ 2 1	2.200	2.201
$\bar{2}$ 4 1	2.985	2.982	0 6 1	2.178	2.178
$\bar{4}$ 0 2	2.931	2.930	5 1 1	2.105	2.105
1 1 2	2.850	2.850	$\bar{1}$ 3 3	2.059	2.060

Structure of $K_3Bi_2(VO_4)_3$

Structure Determination

The structure was solved by the heavy atom method. A second harmonic generation measurement did not give any significant signal, thus strongly suggesting a centrosymmetric space group: therefore, the structural determination was carried out in the space group *C*2/*c*.

From a three-dimensional Patterson synthesis tentative coordinates for one Bi atom were found in point set 8(*f*). The discrepancy index R was at this stage 0.29. From a three-dimensional ($F_{obs} - F_{Bi}$) synthesis with approximate signs given by the refined

TABLE III

DATA COLLECTION AND REFINEMENT CONDITIONS

Data collection	
Equipment	Philips PW 1100 diffractometer
Radiation (Å)	Mo$K\bar{\alpha}$, graphite monochromator, $\lambda = 0.7107$
Scan mode	$\omega - 2\theta$
Scan angle (°)	$\Delta\omega = 1.2$
Recording angular range (°)	2–30
Recording reciprocal space	$-19 \leq h \leq 19, -19 \leq k \leq 19, 0 \leq l \leq 9$
Number of measured reflections	3685
Number of reflections $I > 3\sigma(I)$	2901
Number of independent reflections (used in refinement)	1498
Refinement	
Number of variables	64
$R = \Sigma[\lvert F_o\rvert - \lvert F_c\rvert]/\Sigma\lvert F_o\rvert$	0.050
$R_w = [\Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma F_o^2]^{1/2}$ with $w = 1$	0.059

Bi position, V atoms were located in point sets 8(*f*) and 4(*e*), which explained the more prominent peaks observed, and K atoms were located in two 4(*e*) point sets and one 4(*b*) point set, which explained the lowest peaks. Refinement of these positions yielded a conventional R value of 0.15. It was not possible, in a next difference synthesis, to locate the oxygen atoms. Therefore, absorption corrections were applied assuming the formula $K_3Bi_2(VO_4)_3$, according to site multiplicities and electrical neutrality, and using the method of De Meulenaer and Tompa (*7*). The crystal used for data collection was bounded by pairs of planes {001}, {010}, and {110} equidistant by 0.270, 0.059, and 0.059 mm, respectively. The transmission factor ranged from 0.17 to 0.49. Finally, the difference synthesis allowed location of all oxygen atoms in six 8(*f*) point sets and confirmed the formula $K_3Bi_2(VO_4)_3$. Anisotropic thermal factors were introduced for metal atoms. Omission of a few reflections, for which $\lvert F_{obs} - F_{cal}\rvert > 3\sigma$, led to the final results. Atomic scattering factors were taken from (*8*). A final three-dimensional difference Fourier synthesis was computed, and the residual peak showed a maximum height of less than 25% of the smallest oxygen peak in the corresponding ($F_{obs} - F_{Bi+V+K}$) synthesis. Anomalous dispersion corrections were made in accordance with the data of Cromer and Liberman (*9*). A weight of unity was attributed to all reflections. Refined atomic and thermal parameters are listed in Tables IV and V. Table VI gives the most significant distances and angles. A table of the observed and calculated struc-

TABLE IV

ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS

Atom	Site	x	y	z	B or B_{eq} (Å^2)[a]
Bi	8*f*	0.23314(4)	0.14628(4)	0.15221(8)	0.66
V(1)	8*f*	0.7417(2)	0.3878(2)	0.1394(4)	0.59
V(2)	4*e*	0	0.7610(3)	$\frac{1}{4}$	0.72
K(1)	4*e*	0	0.2763(4)	$\frac{1}{4}$	1.27
K(2)	4*e*	0	0.0209(4)	$\frac{1}{4}$	1.56
K(3)	4*b*	0	$\frac{1}{2}$	0	5.07
O(1)	8*f*	0.4290(9)	0.3373(8)	0.0459(17)	1.2(2)
O(2)	8*f*	0.8252(9)	0.1662(8)	0.0991(17)	1.1(2)
O(3)	8*f*	0.8156(10)	0.4372(9)	0.1427(19)	1.6(2)
O(4)	8*f*	0.5737(10)	0.1878(10)	0.1696(20)	1.7(2)
O(5)	8*f*	0.6661(10)	0.4769(10)	0.1658(19)	1.4(2)
O(6)	8*f*	0.2310(9)	0.3059(8)	0.1504(17)	1.0(2)

[a] For atoms refined anisotropically, isotropic equivalent parameters defined by $B_{eq} = \frac{4}{3} \Sigma \beta_{ij} a_i a_j$ are given.

TABLE V

ANISOTROPIC TEMPERATURE FACTORS (× 10^5)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi	58(3)	132(3)	288(11)	1(2)	20(4)	7(4)
V(1)	74(11)	118(10)	284(44)	−12(9)	89(18)	−15(18)
V(2)	29(16)	166(17)	302(64)	0	−16(26)	0
K(1)	101(23)	247(25)	613(94)	0	38(37)	0
K(2)	113(23)	301(27)	1020(111)	0	184(41)	0
K(3)	279(36)	619(54)	2282(196)	−121(35)	90(67)	606(84)

Note. The form of the anisotropic thermal parameters is $\exp(-\Sigma\, \beta_{ij} h_i h_j)$.

ture factors has been deposited with the National Auxiliary Publications Service.[1]

Description of Structure

The structure can be described as a three-dimensional framework of VO_4 tetrahedra and distorted BiO_6 octahedra linked by edges and vertices. The K^+ ions occupy interstitial sites (Figs. 1 and 2).

BiO_6 octahedra are linked together by an O(6)–O(6) edge to form dimeric units Bi_2O_{10}. A $V(1)O_4$ tetrahedron connects three Bi_2O_{10} units; it shares with these three different units either an O(6) oxygen atom of the common edge or an O(2) or an O(5)

TABLE VI

SIGNIFICANT DISTANCES (Å) AND ANGLES (°) IN $K_3Bi_2(VO_4)_3$

		Bi environment			
Bi–Bi	3.733(1)				
Bi–O(1)	2.16(1)	O(1)–O(2)	2.92(2)	O(2)–O(6)	2.93(2)
Bi–O(2)	2.22(1)	O(1)–O(5)	3.02(2)	O(4)–O(5)	4.45(2)
Bi–O(4)	2.56(1)	O(1)–O(6)	2.91(2)	O(4)–O(6)	3.01(2)
Bi–O(5)	2.54(1)	O(1)–O(6)	3.15(2)	O(4)–O(6)	3.26(1)
Bi–O(6)	2.22(1)	O(2)–O(4)	3.74(2)	O(5)–O(6)	4.32(2)
Bi–O(6)	2.47(1)	O(2)–O(5)	3.09(2)	O(6)–O(6)	2.85(2)
Average	2.36(18)				

K(1) environment		K(2) environment		K(3) environment	
K(1)–O(2)	2.72(1)(2×)	K(2)–O(1)	2.92(1)(2×)	K(3)–O(3)	2.77(1)(2×)
K(1)–O(3)	2.94(1)(2×)	K(2)–O(2)	3.02(1)(2×)	K(3)–O(3)	2.71(1)(2×)
K(1)–O(4)	2.78(1)(2×)	K(2)–O(5)	2.68(1)(2×)	K(3)–O(4)	2.89(1)(2×)
K(1)–O(1)	3.08(1)(2×)	K(2)–O(5)	2.95(1)(2×)		
Average	2.88(15)	Average	2.89(14)	Average	2.79(8)

	V(1) tetrahedron		
V(1)–O(2)	1.75(1)	O(2)–V(1)–O(3)	109(2)
V(1)–O(3)	1.67(1)	O(2)–V(1)–O(5)	107(2)
V(1)–O(5)	1.68(1)	O(2)–V(1)–O(6)	113(1)
V(1)–O(6)	1.79(1)	O(3)–V(1)–O(5)	108(2)
Average	1.72(6)	O(3)–V(1)–O(6)	110(2)
		O(5)–V(1)–O(6)	108(2)
		Average	109(2)

	V(2) tetrahedron		
V(2)–O(1)	1.75(1)(2×)	O(1)–V(2)–O(1)	106(2)(2×)
V(2)–O(4)	1.69(2)(2×)	O(1)–V(2)–O(4)	108(2)(2×)
Average	1.72(4)	O(1)–V(2)–O(4)	115(2)(2×)
		Average	110(4)

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[1] See NAPS Document 04515 for 10 pages of supplementary material. Order from NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10163. Remit in advance in U.S. funds only \$7.75 for photocopies and \$4.00 for microfiche. Outside the U.S. and Canada, add postage of \$4.50 for the first 20 pages and \$1.00 for each of 10 pages of material; thereafter \$1.50 for microfiche postage.

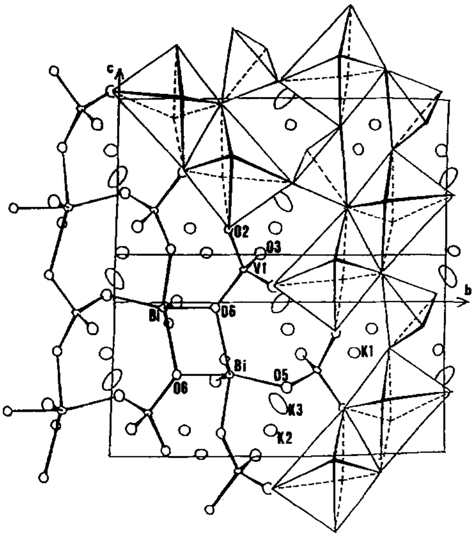

FIG. 1. $K_3Bi_2(VO_4)_3$ structure projected on {100}.

atom of the vertices (Fig. 1). Thus, three oxygen atoms of the $V(1)O_4$ are common with Bi_2O_{10} units when the fourth O(3) oxygen atom is not shared with any Bi_2O_{10} group. It belongs to the environment of the K(1) and K(3) ions.

Bi_2O_{10} groups and $V(1)O_4$ tetrahedra form two-dimensional sheets parallel to {100} planes (Fig. 1). $V(2)O_4$ tetrahedra link these sheets (Fig. 2). A $V(2)O_4$ tetrahedron connects two Bi_2O_{10} units related by a twofold axis by two O(1)–O(4) edges.

The bismuth atom has an irregular octahedral arrangement of six oxygen atoms at distances ranging from 2.16 to 2.56 Å. The coordination around Bi atoms is asymmetric: three bond lengths are appreciably shorter (2.16–2.22 Å) than the other three (2.47–2.56 Å). This arrangement is typical of the lone-pair effect of Bi^{3+} ion. The two bismuth atoms of one Bi_2O_{10} unit are 3.733(1) Å apart.

The potassium ions occupy three sites: K(1) and K(2) atoms are on twofold axes and are surrounded by eight atoms at distances ranging from 2.72 to 3.08 Å for K(1) and 2.68 to 3.02 Å for K(2); the K(3) atom is on an inversion center, and it has six oxygen neighbors at distances ranging from 2.71 to 2.89 Å, forming a distorted octahedron.

$V(1)O_4$ and $V(2)O_4$ tetrahedra have different symmetries, $C1$ and $C2$ respectively, but are similarly distorted: two short V–O distances and two longer ones. These different distances may result from the competition between V–O and Bi–O bonds: the oxygen atoms involved in short Bi–O distances give the largest V–O distances and vice versa.

Ionic Conductivity and Phase Transitions

The electrical conductivities were measured by the complex impedance method using a sample obtained by cold-pressing and sintering at 760 K. The relative density of the pellets is low (about 80%); thus, the measured conductivity is only the lower limit of the true conductivity but the trend is certainly representative of the true behavior. Figure 3 shows that the conductivity increases greatly at about 790 K; the activation energy is 0.87(3) and 0.76(1) eV on both sides of this temperature. DT analysis, obtained with a 1090 B Dupont thermal analyzer, revealed a transition at 790 K; the compound melts at 980 K.

The high thermal vibration of the K(3)

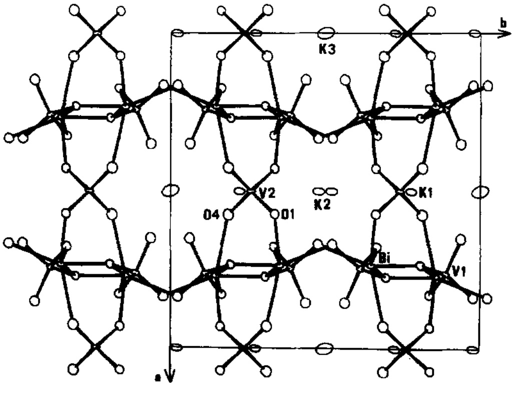

FIG. 2. $K_3Bi_2(VO_4)_3$ structure projected down [001].

atom could reflect mobility of this cation, which is perhaps responsible for the conductivity. To confirm this hypothesis, we attempted cationic exchange in fused $NaNO_3$, but the compound was destroyed and a new unidentified phase was formed. One K atom, and only one, however, can be substituted by a Na atom by solid-state reaction of Na_2CO_3 with K_2CO_3, Bi_2O_3, and V_2O_5 in the ratio 1 : 2 : 3 : 3 to form $NaK_2Bi_2(VO_4)_3$. The unit cell parameters of this compound are $a = 13.821(5)$, $b = 13.786(5)$, $c = 7.065(3)$ Å, and $\beta = 113.04(3)°$. From DT analysis, transition occurs near 770 K and melting at 910 K. This substitution improves the conductivity (Fig. 3) even though the activation energy increases above the transition [0.72(1) and 1.59(9) eV on both sides]. These results indicate that the conductivity is very likely ionic and due to the K(3) (or Na) atoms. This result must be confirmed by a structural study of $NaK_2Bi_2(VO_4)_3$ but, as yet, no single crystal suitable for X-ray study has been prepared. A high-temperature X-ray structure determination could probably explain the surprising behavior of the $NaK_2Bi_2(VO_4)_3$ sample, which exhibits a high activation energy above the phase transition.

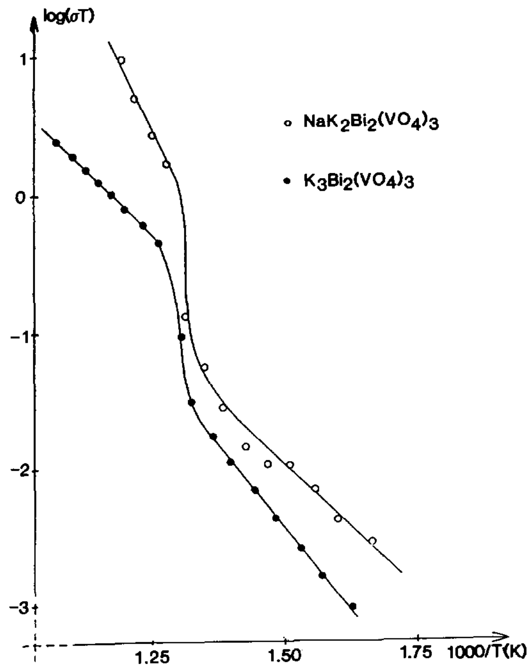

FIG. 3. Arrhenius plots for $K_3Bi_2(VO_4)_3$ and $NaK_2Bi_2(VO_4)_3$ samples.

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