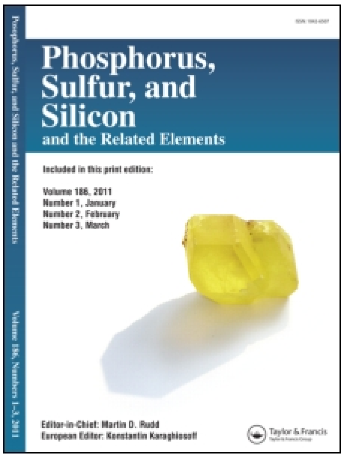

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Synthesis, Structural Characterization, and Cation Transport of Tripotassium Pentabismuth Arsenate $K_3Bi_5(AsO_4)_6$

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Synthesis, Structural Characterization, and Cation Transport of Tripotassium Pentabismuth Arsenate $K_3Bi_5(AsO_4)_6$

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During the exploration of the K_2O-Bi_2O_3-As_2O_5 system, single crystals of a new arsenate of trivalent bismuth, $K_3Bi_5(AsO_4)_6$, were isolated by solid state reaction at 600°C. The title compound crystallizes in the monoclinic system, space group C2/c (N°15) with $a = 18.257(2)$ Å, $b = 7.260(1)$ Å, $c = 20.130(4)$ Å, $\beta = 119.86(1)°$, and $Z = 4$. Its structure consists of a three-dimensional framework made up of AsO_4 tetrahedra and BiO_6 and BiO_7 polyhedra sharing edges and corners, delimiting cavities wherein K^+ ions reside. This compound exhibits a potassium ion conductivity but with rather low conductivity value.

Keywords Arsenate; bismuth; cation transport; crystal structure; potassium; synthesis

INTRODUCTION

Double monophosphates of alkali metals and divalent, trivalent or tetravalent cations are interesting compounds with various potential applications:[1–8] luminescence, ferroelectricity, and ionic conductivity. To our knowledge, in the system A-Bi-As-O (A = alkali metals) only two crystal structure investigations—on $Na_5Bi_2(AsO_4)(As_2O_7)_2$[9] and on

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$K_3Bi_2(AsO_4)_3$[10]—have previously been reported. These compounds have a three-dimensional framework made up of corner-sharing BiO_6 octahedra and AsO_4 tetrahedra, with the A^+ ions located in interstitial spaces. To our knowledge no other structural study was carried out in the A-Bi-As-O (A = alkali metal) system. In this paper, we present the synthesis and the crystal structure determination of the new $K_3Bi_5(AsO_4)_6$ phase.

EXPERIMENTAL

Synthesis

Crystals of the title compound were grown by melting a mixture of K_2CO_3, Bi_2O_3 and $(NH_4)H_2AsO_4$ in a molar ratio of $K : Bi : As = 5 : 2 : 5$ in a porcelain crucible. After grinding, the powder was successively preheated for 12 h at 300°C in free air to remove volatile species and then was heated at 600°C for 7 days and cooled down to room temperature with a rate of 5°C/h. Finally, parallelpiped-shaped colorless crystals of $K_3Bi_5(AsO_4)_6$ were obtained after washing the mixture with boiling water. The powder X-ray diffraction pattern shows that the sample is not pure. The data of the structure determination have been deposited with the ICSD database under reference 391391 chir17.

Structure Determination

A transparent single crystal of 0.018 × 0.09 × 0.108 mm was selected for the structure determination. The cell parameters reported in Table I were determined and refined by diffractometric techniques at 20°C with $10 < \theta < 15°$. The systematic absences are $h + k = 2n + 1$ for hkl and $h + l = 2n + 1$ for h0l. Thus, the structure of $K_3Bi_5(AsO_4)_6$ has been solved in the space group C2/c.

The data were collected on an Enraf-Nonius CAD4 diffractometer with the conditions reported in Table I. The reflections were corrected for the Lorentz and polarization effects. An empirical absorption correction[11] was applied. Scattering factors for neutral atoms and anomalous dispersion correction for atoms were taken from the "International Tables for X-Ray Crystallography".

The structure was solved by the Patterson method,[12] leading to the atomic positions for the As and Bi atoms. The other atoms were located by subsequent difference Fourier synthesis.

In the final Fourier-difference map, rather high electron density ranging from +6.01 to 3.16 e.Å^{-3} occurs, surrounding the Bi(1), Bi(2), and Bi(3) atoms at distances less than 1 Å. This is probably due to

TABLE I Crystal Data and Refinement Parameters for $K_3Bi_5(AsO_4)_6$

Crystal data	
$K_3Bi_5(AsO_4)_6$	MoK_α radiation
$M_r = 1995.72$	$\lambda = 0.71069$Å
Monoclinic	$\theta = 10 - 15°$(for reflexions used to refine cell)
C2/c	$\mu = 47.06\ mm^{-1}$
a = 18.257(2) Å	T = 293 (2) K
b = 7.260(1) Å	parallelpiped
c = 20.130(4) Å	0.018 × 0.09 × 0.108 mm
$\beta = 119.86(1)°$	Colorless
V = 2313.9(6) $Å^3$	$D_x = 5.729$
Z = 4	
Intensity measurement	
Diffractometer Enraf-Nonius CAD-4	$R_{int} = 0.043$
Scan mode ω-2θ	$\theta_{max} = 27°$
Absorption correction by ψ-scan	$0 \leq h \leq 23$
$T_{min} = 0.0056$ $T_{max} = 0.0358$	$0 \leq k \leq 9$
2566 measured reflections	$-25 \leq l \leq 22$
2488 Independent reflections	1812 reflections $I > 2\sigma(I)$
Refinement	
R = 0.0521	$\Delta\rho_{max} = 6.013$ e.$Å^{-3}$
wR = 0.1278	$\Delta\rho_{min} = -4.737$ e.$Å^{-3}$
Goof = 1.008	Extinction correction: SHELXL97
2488 reflections	Extinction coefficient: 0.00035(3)
174 parameters	Atomic scattering factors from International Tables for Crystallography (Vol. C)
$w = 1/[\sigma^2 F_o^2) + (0.0883P)^2 + 0.0000P]$	
$P = (F_o^2 + F_c^2)/3$	

the effect of the stereoactive $6s^2$ lone pair of electrons E as observed in compound $Na_5Bi_2(AsO_4)(As_2O_7)_2$.[9]

The atomic coordinates and the anisotropic displacement factors were refined by a full matrix least squares[13] which led to R = 0.0521 and $R_w = 0.1278$. The atomic coordinates are listed in Table II. Selected interatomic distances and angles are reported in Table III.

RESULTS AND DISCUSSION

The structure of the title compound, viewed along the **c** axis, is shown in Figure 1. The structure has a complex three-dimensional open anionic framework of corner and edge sharing BiO_n (n = 6 or 7) polyhedra

TABLE II Atomic Positions and Displacement Parameters for $K_3Bi_5(AsO_4)_6$

Atoms	x/a	y/b	z/c	U_{eq}
Bi(1)	0.41108(4)	0.15167(8)	0.52570(4)	0.0063(2)
Bi(2)	0	0.0887(1)	1/4	0.0051(3)
Bi(3)	0.17075(4)	0.14693(8)	0.70096(4)	0.0051(2)
As(1)	0.2039(1)	0.1551(2)	0.3839(1)	0.0029(4)
As(2)	0.6179(1)	0.1275(2)	0.6534(1)	0.0041(4)
As(3)	−0.0340(1)	0.1702(2)	0.5864(1)	0.0035(4)
K(1)	0.2576(3)	−0.1452(6)	0.5830(3)	0.017(1)
K(2)	1/2	0.0512(8)	1/4	0.024(2)
O(1)	0.1291(8)	0.298(2)	0.3794(7)	0.009(3)
O(2)	0.2697(8)	0.051(2)	0.4666(8)	0.012(3)
O(3)	0.2707(9)	0.290(2)	0.3677(9)	0.020(3)
O(4)	0.1482(8)	−0.006(2)	0.3143(7)	0.012(3)
O(5)	0.5785(9)	0.078(2)	0.5601(8)	0.018(3)
O(6)	0.6486(8)	−0.059(2)	0.7139(7)	0.012(3)
O(7)	0.7037(9)	0.269(2)	0.6886(9)	0.015(3)
O(8)	0.5360(8)	0.225(2)	0.6579(9)	0.016(3)
O(9)	0.0542(8)	0.173(2)	0.5771(8)	0.012(3)
O(10)	−0.1065(9)	0.013(2)	0.5335(8)	0.014(3)
O(11)	−0.0783(9)	0.382(2)	0.5821(8)	0.013(3)
O(12)	0.0141(9)	0.134(2)	0.6847(8)	0.011(3)

and AsO_4 tetrahedra. The K^+ cations are located into closed cavities (Figure 1).

The asymmetric unit can be decomposed into a unit consisting of edge sharing $As(3)O_4$ and $Bi(3)O_6$ polyhedra, connected to a $Bi(2)O_6$-$As(1)O_4$-$Bi(1)O_7$-$As(2)O_4$ chain by means of two mixed bridges Bi-O-As (Figure 2).

Taking into account the Bi-O bonds shorter than 3 Å, the two crystallographically independent bismuth atoms Bi(2) and Bi(3) have a similar environment of oxygen polyhedra, consisting of six oxygen atoms forming strongly distorted octahedra, whereas the coordination number for Bi(1) is seven. A low symmetry environment is usual for Bi^{3+} cations and is in fact to be completed by the $6s^2$ stereoactive lone-pair of electrons E. This effect is especially pronounced around Bi(2) and Bi(3). One indeed observes two shorter Bi-O distances (2.18(1)–2.21(1) Å), two intermediate distances (2.34(1)–2.44(1) Å) and two longer Bi-O distances characteristic of the triply bonded oxygen atoms: the later being shared by one PO_4 group and two BiO_n polyhedra. Bi(1) is bonded to seven oxygen atoms, O(11), O(1), O(5), O(2) and O(8) at distances ranging from 2.22(1) Å to 2.56(1) Å, and O(10) and O(9) at distances of 2.66(1) Å and

TABLE III Selected Interatomic Distances (Å) and Bond Angles (°) obtained for $K_3Bi_5(AsO_4)_6$

As(1)O$_4$tetrahedron			
As(1)—O(1)	1.68 (1)	As(1)—O(3)	1.72 (1)
As(1)—O(2)	1.69 (1)	As(1)—O(4)	1.71 (1)
O(1)—As(1)—O(2)	119.6 (6)	O(2)—As(1)—O(3)	102.8 (7)
O(1)—As(1)—O(3)	105.5 (7)	O(2)—As(1)—O(4)	110.3 (7)
O(1)—As(1)—O(4)	104.1 (6)	O(3)—As(1)—O(4)	115.0 (7)
As(2)O$_4$ tetrahedron			
As(2)—O(5)	1.68 (1)	As(2)—O(7)	1.70 (1)
As(2)—O(6)	1.72 (1)	As(2)—O(8)	1.70 (1)
O(5)—As(2)—O(6)	115.5 (7)	O(6)—As(2)—O(7)	105.8 (7)
O(5)—As(2)—O(7)	112.7 (7)	O(6)—As(2)—O(8)	106.2 (7)
O(5)—As(2)—O(8)	104.5 (7)	O(7)—As(2)—O(8)	112.1 (7)
As(3)O$_4$ tetrahedron			
As(3)—O(9)	1.71 (1)	As(3)—O(11)	1.72 (1)
As(3)—O(10)	1.66 (1)	As(3)—O(12)	1.74 (1)
O(9)—As(3)—O(10)	115.3 (7)	O(10)—As(3)—O(11)	112.3 (7)
O(9)—As(3)—O(11)	115.4 (7)	O(10)—As(3)—O(12)	114.5 (7)
O(9)—As(3)—O(12)	98.9 (7)	O(11)—As(3)—O(12)	98.6 (6)
Bi(1)O$_7$ polyhedron			
Bi(1)—O(11)$^{f)}$	2.22 (1)	Bi(1)—O(8)	2.55 (1)
Bi(1)—O(2)	2.36 (1)	Bi(1)—O(10)$^{g)}$	2.66 (1)
Bi(1)—O(1)$^{d)}$	2.39 (1)	Bi(1)—O(9)$^{d)}$	2.76 (1)
Bi(1)—O(5)$^{c)}$	2.48 (1)		
O(11)$^{f)}$-Bi(1)— O(2)	77.4 (5)	O(1)$^{d)}$-Bi(1)— O(5)$^{c)}$	145.1 (5)
O(11)$^{f)}$-Bi(1)— O(1)$^{d)}$	73.1 (5)	O(1)$^{d)}$-Bi(1)— O(8)	66.8 (4)
O(11)$^{f)}$-Bi(1)— O(5)$^{c)}$	75.3 (5)	O(1)$^{d)}$-Bi(1)— O(10)$^{g)}$	73.1 (4)
O(11)$^{f)}$-Bi(1)— O(8)	81.2 (5)	O(1)$^{d)}$-Bi(1)— O(9)$^{d)}$	143.7 (4)
O(11)$^{f)}$-Bi(1)— O(10)$^{g)}$	145.2 (5)	O(5)$^{c)}$-Bi(1)— O(8)	122.1 (5)
O(11)$^{f)}$-Bi(1)— O(9)$^{d)}$	142.7 (4)	O(5)$^{c)}$-Bi(1)— O(10)$^{g)}$	139.4 (5)
O(2)—Bi(1)— O(1)$^{d)}$	75.8 (5)	O(5)$^{c)}$-Bi(1)— O(9)$^{d)}$	70.2 (4)
O(2)—Bi(1)— O(5)$^{c)}$	83.3 (5)	O(8)—Bi(1)— O(10)$^{g)}$	78.4 (4)
O(2)—Bi(1)— O(8)	140.9 (5)	O(8)—Bi(1)— O(9)$^{d)}$	105.4 (4)
O(2)—Bi(1)— O(10)$^{g)}$	101.8 (4)	O(10)$^{g)}$-Bi(1)— O(9)$^{d)}$	70.6 (4)
O(2)—Bi(1)— O(9)$^{d)}$	111.5 (4)		
Bi(2)O$_6$ polyhedron			
Bi(2)—O(12)$^{e)}$	2.18 (1)	Bi(2)—O(4)	2.45 (1)
Bi(2)—O(12)$^{h)}$	2.18 (1)	Bi(2)—O(8)$^{d)}$	2.63 (1)
Bi(2)—O(4)$^{o)}$	2.45 (1)	Bi(2)—O(8)$^{q)}$	2.63 (1)
O(12)$^{e)}$-Bi(2)— O(12)$^{h)}$	84.0 (7)	O(12)$^{h)}$-Bi(2)— O(8)$^{q)}$	162.3 (5)
O(12)$^{e)}$-Bi(2)— O(4)$^{o)}$	84.6 (5)	O(4)$^{o)}$-Bi(2)—O(4)	147.6 (6)
O(12)$^{e)}$-Bi(2)—O(4)	71.3 (5)	O(4)$^{o)}$-Bi(2)— O(8)$^{d)}$	85.2 (4)
O(12)$^{e)}$-Bi(2)— O(8)$^{d)}$	162.3 (5)	O(4)$^{o)}$-Bi(2)— O(8)$^{q)}$	111.6 (4)
O(12)$^{e)}$-Bi(2)— O(8)$^{q)}$	79.0 (5)	O(4)—Bi(2)— O(8)$^{d)}$	111.6 (4)
O(12)$^{h)}$-Bi(2)— O(4)$^{o)}$	71.3 (5)	O(4)—Bi(2)— O(8)$^{q)}$	85.3 (4)
O(12)$^{h)}$-Bi(2)—O(4)	84.6 (5)	O(8)$^{d)}$-Bi(2)— O(8)$^{q)}$	118.3 (7)
O(12)$^{h)}$-Bi(2)— O(8)$^{d)}$	79.0 (5)		

(Continued on next page)

TABLE III Selected Interatomic Distances (Å) and Bond Angles (°) obtained for $K_3Bi_5(AsO_4)_6$ *(Continued)*

$Bi(3)O_6$ polyhedron			
Bi(3)—O(3)$^{d)}$	2.18 (1)	Bi(3)—O(7)$^{i)}$	2.43 (2)
Bi(3)—O(6)$^{b)}$	2.22 (1)	Bi(3)—O(12)	2.71 (1)
Bi(3)—O(9)	2.34 (1)	Bi(3)—O(4)$^{p)}$	2.71 (1)
O(3)$^{d)}$-Bi(3)— O(6)$^{b)}$	92.8 (5)	O(6)$^{b)}$-Bi(3)— O(4)$^{p)}$	98.9(5)
O(3)$^{d)}$-Bi(3)—O(9)	77.3 (5)	O(9)—Bi(3)— O(7)$^{i)}$	152.5(5)
O(3)$^{d)}$-Bi(3)— O(7)$^{i)}$	88.1 (5)	O(9)—Bi(3)—O(12)	62.0(4)
O(3)$^{d)}$-Bi(3)—O(12)	138.8 (5)	O(9)—Bi(3)— O(4)$^{p)}$	119.2(4)
O(3)$^{d)}$-Bi(3)— O(4)$^{p)}$	160.3 (5)	O(7)$^{i)}$-Bi(3)—O(12)	125.5(4)
O(6)$^{b)}$-Bi(3)—O(9)	85.8 (5)	O(7)$^{i)}$-Bi(3)— O(4)$^{p)}$	80.6(4)
O(6)$^{b)}$-Bi(3)— O(7)$^{i)}$	71.6 (5)	O(12)—Bi(3)— O(4)$^{p)}$	59.8(4)
O(6)$^{b)}$-Bi(3)—O(12)	78.7 (4)		
$K(1)O_8$ polyhedron			
K(1)—O(10)$^{h)}$	2.76 (1)	K(1)—O(11)$^{f)}$	3.01 (1)
K(1)—O(7)$^{a)}$	2.82 (1)	K(1)—O(2)$^{l)}$	3.07 (1)
K(1)—O(2)	2.84 (1)	K(1)—O(1)$^{d)}$	3.10 (1)
K(1)—O(3)$^{d)}$	2.90 (2)	K(1)—O(4)$^{l)}$	3.18 (1)
$K(2)O_{10}$ polyhedron			
K(2)—O(12)$^{d)}$	2.71 (1)	K(2)—O(8)$^{e)}$	3.02 (2)
K(2)—O(12)$^{k)}$	2.71 (1)	K(2)—O(1)$^{n)}$	3.10 (1)
K(2)—O(11)$^{d)}$	2.98 (1)	K(2)—O(1)$^{f)}$	3.10 (1)
K(2)—O(11)$^{k)}$	2.98 (1)	K(2)—O(6)$^{c)}$	3.14 (1)
K(2)—O(8)$^{c)}$	3.02 (2)	K(2)—O(6)$^{e)}$	3.14 (1)

Symmetry codes:

$^{a)}$ x−1/2,y−1/2,z
$^{b)}$ x−1/2,y+1/2,z
$^{c)}$ −x+1,−y,−z+1
$^{d)}$ −x+1/2,−y+1/2,−z+1
$^{e)}$ x,−y,z−1/2
$^{f)}$ x+1/2,y−1/2,z
$^{g)}$ x+1/2,y+1/2,z
$^{h)}$ −x,−y,−z+1
$^{i)}$ −x+1,y,−z+3/2
$^{j)}$ −x+1/2,y−1/2,−z+3/2
$^{k)}$ x+1/2,−y+1/2,z−1/2
$^{l)}$ −x+1/2,−y−1/2,−z+1
$^{m)}$ −x+1/2,y+1/2,−z+3/2
$^{n)}$ −x+1/2,y−1/2,−z+1/2
$^{o)}$ −x,y,−z+1/2
$^{p)}$ x,−y,z+1/2
$^{q)}$ x−1/2,−y+1/2,z−1/2

2.76(1) Å, respectively. The first five oxygen ions form a distorted trigonal prism around Bi(1). The inclusion of the two long bismuth oxygen distances results in the formation of a monocapped trigonal prism. The repulsion by the lone pair of electrons causes the lengthening of the Bi(1)-O(9) and the Bi(1)-O(10) bonds.

The environment of Bi^{3+} is also confirmed by the determination of the valence number using Brown's method,[14] which gives 2.67, 2.82, and 2.80 for Bi(1), Bi(2), and Bi(3), respectively.

The coordination sphere of bismuth should be analyzed with relation to its $6s^2$ lone pair of electrons. As a matter of fact, a close examination of the chemical bond within the polyhedra occupied by Bi^{3+} in the title compound shows that O-Bi-O angles are acute for short Bi-O distances

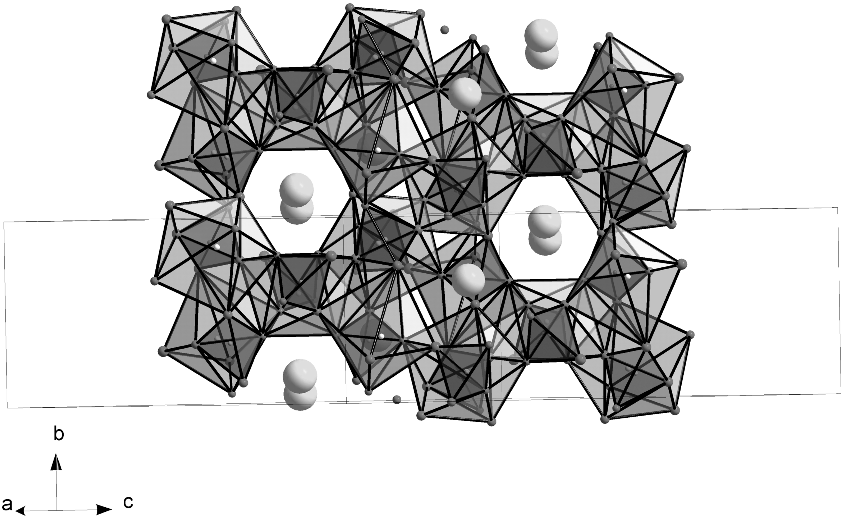

FIGURE 1 View of the structure of $K_3Bi_5(AsO_4)_6$ along [101] direction, showing closed cavities wherein the K^+ cations are located. The BiO_n (n = 6 or 7) polyhedra have not been drawn for the sake of clarity.

while angles made of longer Bi-O distances are obtuse. This geometry is compatible with the stereoactivity of the bismuth $6s^2$ lone pair of electrons which points its orbital lobe between the longest Bi-O bonds.

The $As(1)O_4$ and $As(2)O_4$ tetrahedra exhibit an almost regular tetrahedral geometry and are characterized by four close As-O distances ranging from 1.67(1) to 1.72(1) Å. Due to the corner and edge sharing, the arsenate group $As(3)O_4$ shows a distorted tetrahedral environment, with average As-O distances As(3)-O = 1.71(1) Å.

The three-dimensional structural arrangement formed by the As, Bi, and O atoms contains interstitial spaces forming closed cavities in which K^+ ions are located (Figure 1). The two crystallographically distinct potassium cations in $K_3Bi_5(AsO_4)_6$ are both irregularly coordinated. K(1) has an environment formed by eight O atoms with K-O distances ranging from 2.76(1) to 3.18(1) Å, while K(2) is ten–coordinated, with K-O distances between 2.71(1) and 3.14(1) Å (d_{av}[K(1)-O] = 2.96(1) Å; d_{av}[K(2)-O] = 2.99(1) Å). These average distances are significantly larger than the sum of the ionic radii for K^+ and O^{2-} which is ~2.78 Å.[15]

In spite of the similar sum formula, $K_3Fe_5(PO_4)_6$ (C2/c),[16] $Na_3Bi_5(PO_4)_6$ (I-43d)[5] and $K_3Bi_5(AsO_4)_6$ (C2/c) are not isotypic. The iron coordination polyhedra (FeO_5 and FeO_6) are more regular than those of the bismuth (BiO_6 and BiO_7) in the arsenate. It is well known that substitution of phosphorus by arsenic lowers the symmetry.

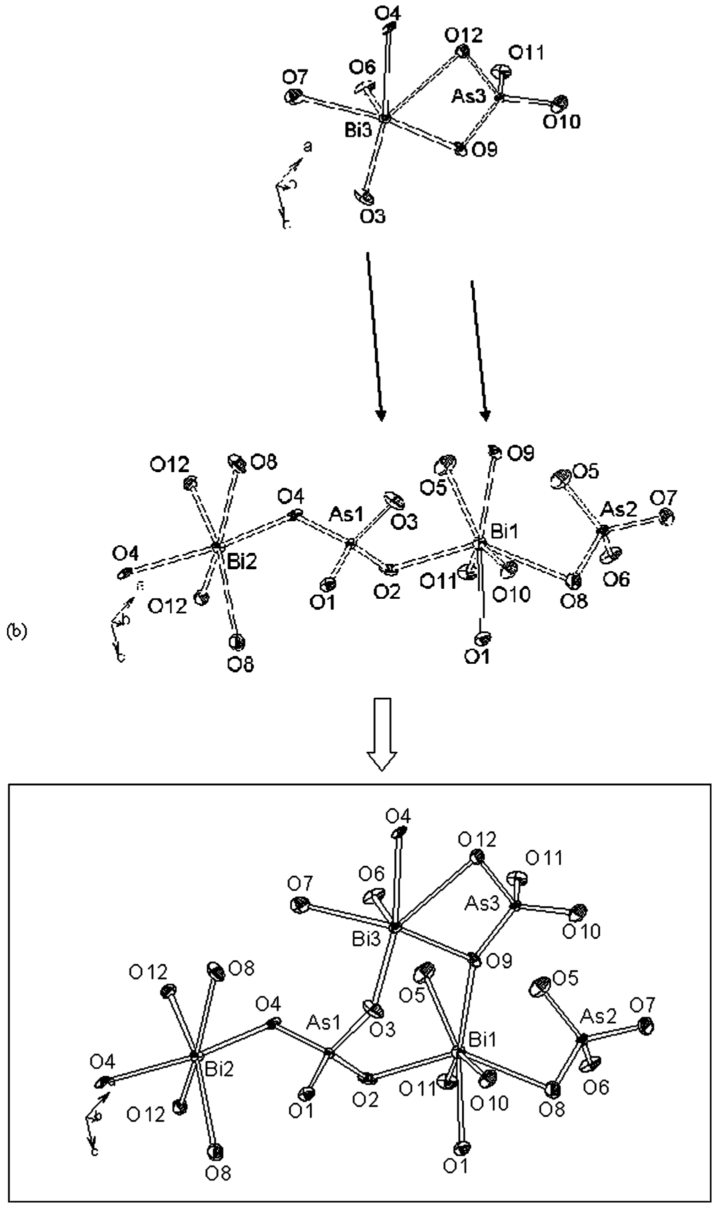

FIGURE 2 Subdivision (a) and (b) of the asymmetric unit of $K_3Bi_5(AsO_4)_6$ (c).

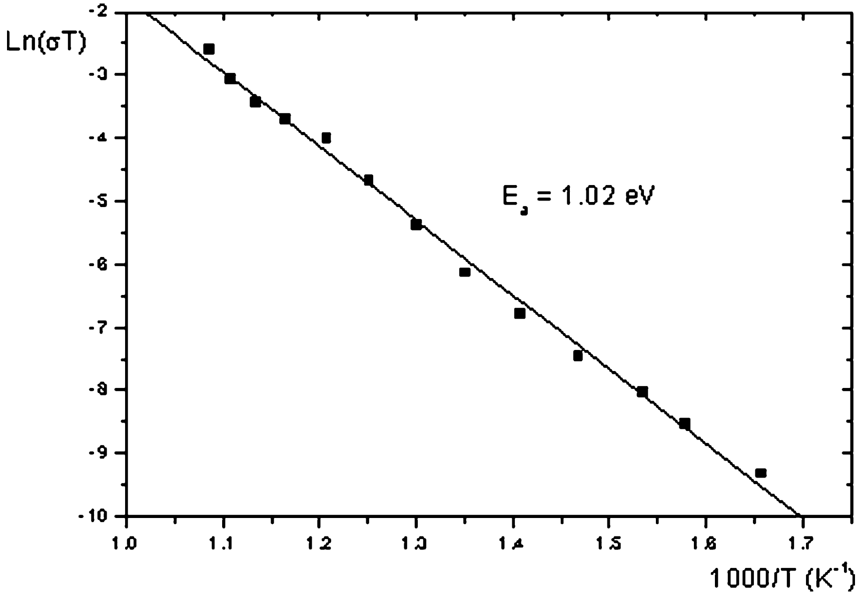

FIGURE 3 Arrhenius plot for $K_3Bi_5(AsO_4)_6$ of conductivity.

Cation Transport Properties

The frequency dependence of the impedance was measured between 603 K and 920 K in a heating cooling cycle. The ion conductivity was calculated from the intercept of the semicircular arcs obtained in complex impedance plots. The σT relationship points to an Arrhénius-like equation $\sigma T = A \exp(-E_a/RT)$. Figure 3 shows the logarithm of the conductivity log(σT) as a function of the inverse temperature 1000/T. The curve can be described rather well by a straight line, with corresponding activation energy of 1.02 eV. The activation energy is high and the ionic conductivity ($\sigma = 1.47.10^{-7}\Omega.\mathrm{cm}^{-1}$; T = 603 K) is considerably lower. This probably indicates that in $K_3Bi_5(AsO_4)_6$, the K^+ ions occupy energetically stable sites or that the bottlenecks are too narrow to allow an easy migration.

CONCLUSION

Besides the title compound, a few Bi^{III} and Fe^{III} phosphates with analogous in formulae have been synthesized, for example $Na_3Bi_5(PO_4)_6$[5] and $K_3Fe_5(PO_4)_6$.[16] We note here that the structure of these compounds, although analogous in composition, is different from the arsenate studied in the present article.

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