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Tripotassium trichromium (III) tetraarsenate $K_3Cr_3(ASO_4)_4$: synthesis, structural study, IR spectroscopy characterization and ionic behavior

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Abstract

The potassium chromium (III) arsenate $K_3Cr_3(AsO_4)_4$ is prepared by solid state reaction at 900°C from a mixture of K_2CO_3, As_2O_3 and $(NH_4)_2Cr_2O_7$. It is structurally characterized by single-crystal X-ray diffraction. It crystallizes in the *Cmca* (no. 64) space group with $a = 10.671(1)$ Å, $b = 20.911(5)$ Å, $c = 6.500(3)$ Å, $V = 1450.4(8)$ Å^3, $Z = 4$, $R(F^2) = 0.0424$ and $R\omega(F^2) = 0.1199$ for 846 reflections with $F^2 > 2\sigma(F^2)$. The structure consists of CrO_6 octahedra and AsO_4 tetrahedra sharing corners and edges to form a two-dimensional framework. The $K^+(2)$ cations are located in the interlayer space. Conductivity measurement ($\sigma_{703\,K} = 4.61 \times 10^{-5}$) shows that $K_3Cr_3(AsO_4)_4$ is a poor ionic conductor.

Keywords: Two-dimensional framework; Interlayer space; Six-member windows; Conductivity

1. Introduction

The synthesis and structural characterization of new materials characterized by mixed open frameworks of MO_6 octahedra and XO_4 tetrahedra sharing edges and/or corners delimiting tunnels where cations are located and study of their properties are an active area of research in solid state chemistry, due to their interest in the fields of catalysis, ion exchange and ion conduction. But compounds of the formula $(A^I)_3(M^{III})_3(XO_4)_4$ (A^I: alkaline, M^{III}: transition metal, X=P, As) are rare. To our knowledge, there is only one reported phosphate $K_3Fe_3(PO_4)_4 \cdot H_2O$ [1] structural determination. Extending our investigation to K_2O–Cr_2O_3–As_2O_5 system, we prepared two compounds: $K_3Cr_3(AsO_4)_4$ and $K_2Cr_2O(AsO_4)_2$. In the present paper, chemical synthesis and single-crystal X-ray investigation of the former is reported. $K_2Cr_2O(AsO_4)_2$ has been shown to be isostructural to $Rb_2Cr_2O(AsO_4)_2$ [2] by Rietveld method.

2. Experimental

2.1. Synthesis

Using the method adopted by Schwarz and Schmidt to $Na_3M_2^{III}(AsO_4)_3$ arsenates synthesis [3], the crystals of the title compound were prepared from mixture of K_2CO_3, As_2O_3 and $(NH_4)_2Cr_2O_7$ in a stoichiometric molar ratio K/Cr/As = 3/4/3. After grinding, the mixture was held in the platinum curcible and first heated at 500°C for 6 h to decompose the ammonium salt. It was then heated at 900°C for 60 h. The product was cooled at room temperature and washed with water and rinsed with HCl acid. Two phases were obtained. The major one forms regular hexagonal green crystals of $K_3Cr_3(AsO_4)_4$. The second phase forms very small hexagonal brown crystals consisting of $K_2Cr_2O(AsO_4)_2$; the structure of this compound has been determined by X-ray powder diffraction using the Rietveld method, starting from the isostructural phase $Rb_2Cr_2O(AsO_4)_2$ [2].

2.2. Structure determination

A single crystal with a plate-like shape $0.4 \times 0.4 \times 0.1$ mm^3 was mounted on an Enarf–Nonius

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CAD4 automatic four-circle diffractometer. Crystallographic data for the title compound are summarized in Table 1. The unit-cell parameters were refined using 25 reflections with $10.03 \leqslant \theta \leqslant 14.47$. The intensity data were corrected for Lorentz, polarization and absorption using empirical ψ-scan correction [4]. The systematic absences in the reduced data ($hkl, h+k=2n; hk0, h=2n; h0l, h+l=2n$) uniquely indicated the space group *Cmca* no. 64 (International tables for crystallography, 1983, vol. A). The crystal structure of $K_3Cr_3(AsO_4)_4$ was solved by direct methods using SHELXS-86 program [5]. The metal and arsenate atoms were first located and then all the oxygen atoms were found by successive Fourier difference synthesis. At this stage the atomic coordinates and isotropic temperature factors were refined to $R=0.0721$ and $R_W=0.1885$. When all the atoms were anisotropically refined, the agreement factors R and R_W converged, respectively, to 0.0424 and 0.1199. Table 2 presents the final atomic coordinates and thermal parameters. In Table 1, the rather high value $\Delta\rho_{max} = 2.63\,e\text{Å}^{-3}$ occurs at 0.68 Å from a heavy atom: As(2). This is due to the effects of Fourier series termination.

Table 1
Crystal, measurement, and refinement parameters for $K_3Cr_3(AsO_4)_4$

Crystal data	
Formula	$K_3Cr_3(AsO_4)_4$
Formula weight ($g\,mol^{-1}$)	$829.0\,g\,mol^{-1}$
Crystal system	Orthorhombic
Space group	*Cmca* (no. 64)
Cell dimensions	
a (Å)	10.741(3)
b (Å)	21.179(6)
c (Å)	6.548(1)
V (Å^3)	1489.63(0)
Z	4
ρ_{cal} ($g\,cm^{-3}$)	3.70
Crystal shape, color	Hexagonal, green
Crystal size (mm)	$0.1 \times 0.4 \times 0.1$
Data collection	
Radiation	Mo$K\alpha$ ($\lambda = 0.71073$ Å)
Scan type	$\omega - 2\theta$
Scan angle (deg)	$\Delta w = 1.1 + 0.35 tg\theta$
Theta range (deg)	$3.66 \leqslant \theta \leqslant 27.97$
hkl range	($0 \leqslant h \leqslant 14$; $0 \leqslant k \leqslant 27$; $-1 \leqslant l \leqslant 8$)
Number of measured reflections	1109
Number of unique reflections	952
Number of observed reflections	846
R_{int}	0.0424
μ	$11.893\,mm^{-1}$
Structure solution and refinement	
Agreement factor	$R(I > 2\sigma(I)) = 0.0424/wR(F^2) = 0.1199$
Parameter refined	88
W	$\sigma^2(F_o^2) + (0.0820P)^2 + 15.9172P$
S	1.095
$\Delta\rho_{max}$ ($e\text{Å}^{-3}$)	2.630
$\Delta\rho_{min}$ ($e\text{Å}^{-3}$)	−1.497

2.3. Infrared spectroscopy

The IR absorption spectrum was carried out on the PARAGOM 1000 PC, Perkin-Elmer FT-IR spectrometer in the range 200–4000 cm^{-1} of wave numbers using a dry KBr pellet containing 2% sample.

2.4. Conductivity measurements

The sample under study was a cylindrical pellet (13 mm in diameter and 1 mm thick) obtained by

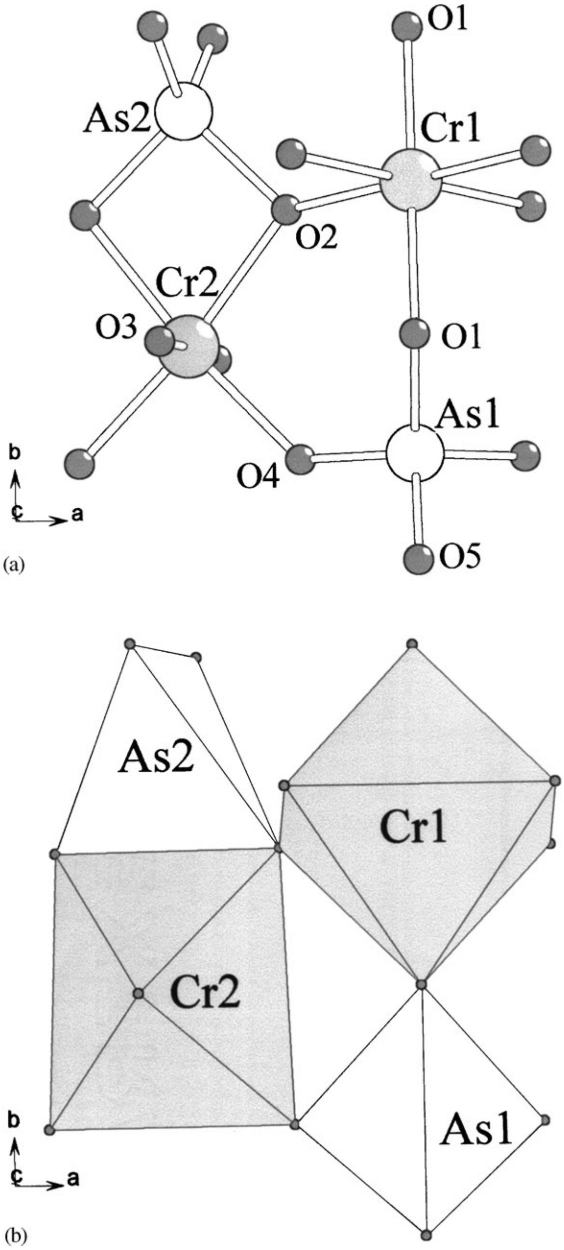

Fig. 1. Detail of asymmetric unit of $K_3Cr_3(AsO_4)_4$.

Table 2

Atom	x/a	y/b	z/c	$*U_{eq}$ (Å^2)^a	Occupation
(a) Fraction atomic coordinates and thermal parameters for $K_3Cr_3(AsO_4)_4$					
As1	0	0.15408(4)	1.06647(12)	0.0102(3)	1
As2	1/4	−0.04534(4)	1.2500	0.0069(3)	1
Cr1	0	0	1	0.0065(4)	1
Cr2	1/4	0.08809(6)	1.2500	0.0072(3)	1
K1	0	0.1620(2)	−0.4329(6)	0.024(2)	0.56(2)
K2	−0.219 (1)	0.22280(4)	−0.376(2)	0.109(5)	0.380(8)
K3	−0.079(5)	0.182(1)	−0.420(4)	0.055(2)	0.08(1)
O1	0	0.0885(3)	0.9188(8)	0.011(1)	1
O2	0.1373(3)	0.0120(2)	1.2062(5)	0.0084(7)	1
O3	0.2865(4)	0.0902(2)	0.9501(6)	0.0112(8)	1
O4	0.1263(4)	0.1534(2)	1.2220(6)	0.0150(8)	1
O5	0	0.2171(3)	0.914(1)	0.023(2)	1

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
(b) Anisotropic thermal parameters for the atoms of $K_3Cr_3(AsO_4)_4$						
As1	0.0038(4)	0.0116(4)	0.0152(4)	0.0022(3)	0	0
As2	0.0038(4)	0.0123(5)	0.0045(4)	0	0.0006(2)	0
Cr1	0.0025(7)	0.0116(8)	0.0055(7)	0.0009(6)	0	0
Cr2	0.0035(6)	0.0121(6)	0.0059(6)	0	0.0006(4)	0
K1	0.025(3)	0.036(3)	0.0113(18)	0.0019(14)	0	0
K2	0.116(8)	0.074(6)	0.136(9)	0.024(5)	−0.060(7)	−0.064(6)
K3	0.09(3)	0.03(2)	0.04(2)	0.006(1)	−0.03(2)	−0.03(2)
O1	0.012(3)	0.013(3)	0.010(3)	0.002(2)	0	0
O2	0.002(2)	0.014(2)	0.008(2)	0.001(2)	0.002(1)	0.001(1)
O3	0.011(2)	0.015(2)	0.006(2)	-0.002(2)	0.001(1)	−0.003(2)
O4	0.005(2)	0.020(2)	0.019(2)	-0.001(15	−0.004(2)	0.01(2)
O5	0.024(3)	0.018(4)	0.028(4)	0.013(3)	0	0

^{a} $*U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

pressing the crystal powder at 10 tons and heated at 873 K for 24 h. The sample is placed between two blocking electrodes in tubular furnace, submitted to temperature regulator. The conductivity was measured in the temperature range 483–773 K with 20–30°C steps and in the frequency range from 10 Hz to 13 kHz.

3. Results and discussion

3.1. Structure description

The structure of $K_3Cr_3(AsO_4)_4$ consists of CrO_6 octahedra and AsO_4 tetrahedra sharing corners and edges to form a two-dimensional framework. The K^+ cations are located in the interlayer space.

The asymmetric unit (Fig. 1) is formed by triangular units constituted by two CrO_6 octahedra and one AsO_4 tetrahedron sharing corners, the $Cr(2)O_6$ octahedra sharing one O2–O2(g) edge with a second $As(2)O_4$ tetrahedron. These are connected via mixed Cr–O–As bridges to form layers parallel to the [010] direction. There are two layers within the repeat distance b. Each layer lies on a c-glide plane perpendicular to the b-axis at $y = 0$ and 1/2 (Fig. 2). Within the layer there are six-member windows, each of which is formed by the edges of three CrO_6 octahedra and three AsO_4 tetrahedra (Fig. 3). Two adjacent layers are shifted so as to form puckered tunnels.

3.1.1. $As(1)O_4$ tetrahedron

The As(1) atom has a rather regular coordination tetrahedron with average As–O distance of 1.688(5) Å. The As–O distances are consistent with other arsenate structures [6–9]. The As1–O5 bond is considerably shorter than the other three As1–O bonds, as reported in Table 3, because O5 is not coordinated to any Cr atoms, it points to the interlayer space.

3.1.2. $As(2)O_4$ tetrahedron

This tetrahedron is strongly distorted because the four As2–O bonds are of two types: two long distances (1.739(4) Å) and two short distances (1.666(4) Å). The long As2–O bonds involve the oxygen atoms forming the shared edge. In this tetrahedron, the average As–O distance of 1.702(4) Å is consistent with that reported for other arsenate compounds [7,10–12].

3.1.3. $Cr(2)O_6$ octahedron

The $Cr(2)O_6$ octahedron is also strongly distorted. This is likely due to the cation–cation repulsion of highly charged cations, As^{5+} and Cr^{3+}, so the O2–Cr2–

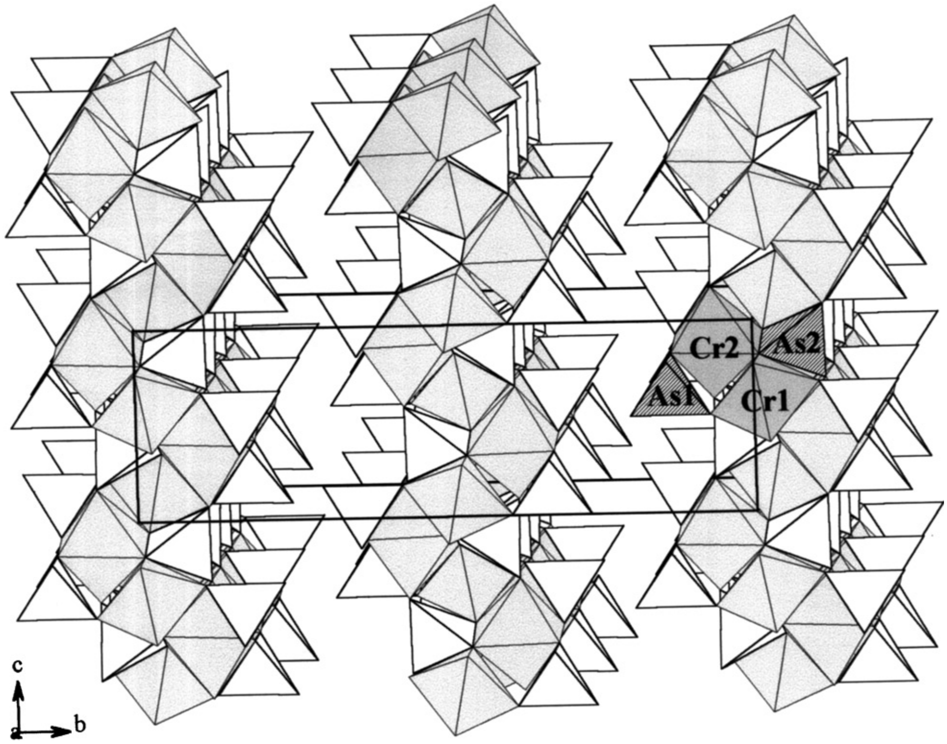

Fig. 2. Representation of the $K_3Cr_3(AsO_4)_4$ structure along the [100] direction showing the asymmetric unit.

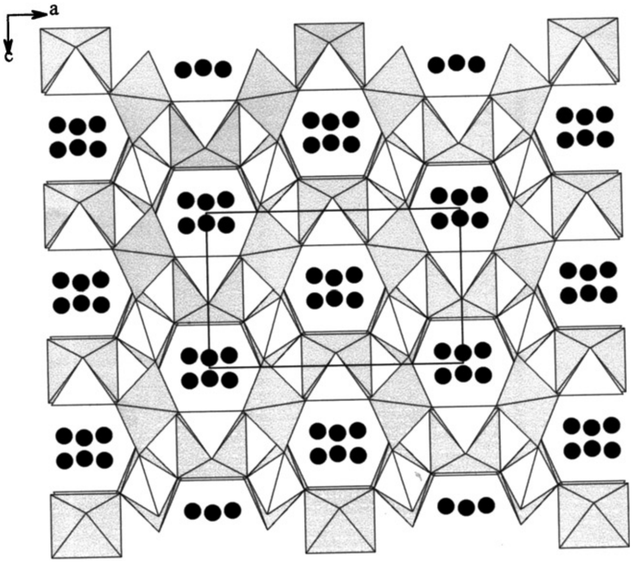

Fig. 3. Layer of the $K_3Cr_3(AsO_4)_4$ structure viewed along [010] showing the six-membered windows. Solid circles are K(1) and K(3).

O2(g)(=75.4°) and O2–As2–O2(g)(=91.4°) angles are more acute than those corresponding to an ideal octahedron and tetrahedron, respectively, and as a consequence, the common edge of $As(2)O_4$ and $Cr(2)O_6$ (O2–O2(g) = 2.488(8) Å) is markedly shorter than usual. Similar strong deformation of the XO_6 octahedron (X = Fe) is observed in $K_3Fe_3(PO_4)_4 \cdot H_2O$ compound [1].

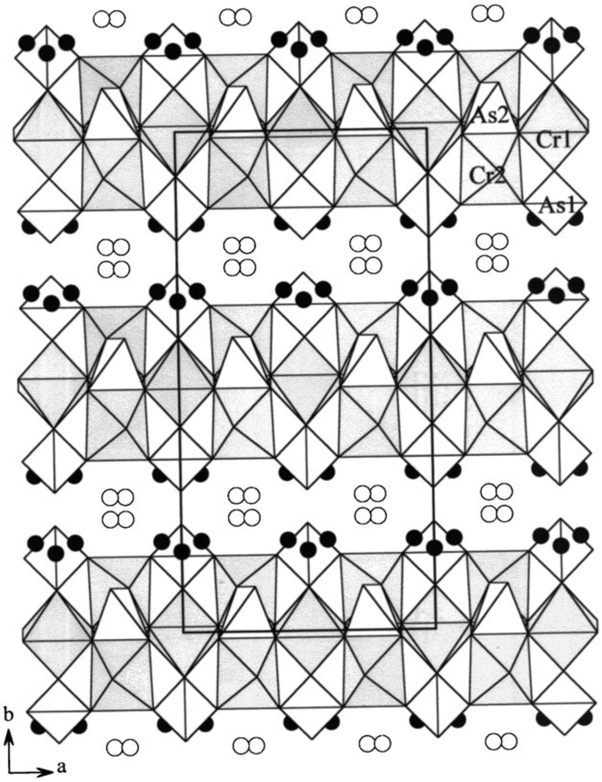

Fig. 4. Representation of the $K_3Cr_3(AsO_4)_4$ structure along [001]. Open circles, K(2); solid circles, K(1) and K(3).

Table 3
Selected bond lengths (Å) and bond angles (deg) for $K_3Cr_3(AsO_4)_4$

As1	O5	O1	O4	O4(j)
The As1O_4 tetrahedron				
O5	*1.667(7)*	2.725(9)	2.779(9)	2.779(9)
O1	108.4(3)	*1.693(6)*	2.771(6)	2.771(6)
O4	111.4(2)	109.7(2)	*1.697(4)*	2.714(8)
O4(j)	111.4(2)	109.7(2)	106.2(3)	*1.697(4)*
〈As1–O〉 = 1.688(5) Å				

As2	O3(b)	O3(e)	O2(g)	O2
The As2O_4 tetrahedron				
O3(b)	*1.666(4)*	2.736(7)	2.882(6)	2.813(5)
O3(e)	110.4(3)	*1.666(4)*	2.813(5)	2.882(6)
O2(g)	115.7(2)	111.4(2)	*1.739(4)*	2.488(8)
O2	111.4(2)	115.7(2)	91.4(2)	*1.739(4)*
〈As2–O〉 = 1.702(4) Å				

Cr1	O1	O1(h)	O2	O2(h)	O2(b)	O2(j)
The Cr1O_6 octahedron						
O1	*1.948(6)*	3.89(2)	2.897(6)	2.715(6)	2.887(6)	2.715(6)
O1(h)	180	*1.948(6)*	2.715(6)	2.887(6)	2.715(6)	2.887(6)
O2	93.5(2)	86.5(2)	*2.015(4)*	4.030(7)	2.949(7)	2.747(7)
O2(h)	86.5(2)	93.5(2)	180	*2.015(4)*	2.747(7)	2.949(7)
O2(b)	86.5(2)	93.5(2)	85.9(2)	94.1(2)	*2.015(4)*	4.030(7)
O2(j)	93.5(2)	86.5(2)	94.1(2)	85.9(2)	180	*2.015(4)*
〈Cr1–O〉 = 1.992(5) Å						

Cr2	O4(g)	O4	O3(g)	O3	O2	O2(g)
The Cr2O_6 octahedron						
O4(g)	*1.928(4)*	2.682(8)	2.814(6)	2.698(6)	3.955(5)	2.999(6)
O4	88.2(2)	*1.928(4)*	2.698(6)	2.814(6)	2.999(6)	3.995(5)
O3(g)	91.4(2)	86.7(2)	*2.003(4)*	4.005(7)	2.912(5)	2.850(5)
O3	86.7(2)	91.4(2)	117.4(2)	*2.003(4)*	2.850(5)	2.912(5)
O2	172.7(2)	98.3(2)	92.3(2)	89.8(1)	*2.036(4)*	2.488(8)
O2(g)	98.3(2)	172.7(2)	89.8(1)	92.3(2)	75.4(2)	*2.036(4)*
〈Cr2–O〉 = 1.989(4) Å						

K1O_7 polyhedron		K2O_6 polyhedron		K3O_6 polyhedron	
K1–O5	2.555(8)	K2–O4(a)	2.780(9)	K3–O3(m)	2.44(2)
–O4(j)	2.642(5)	–O3(m)	2.95(2)	–O5	2.46(2)
–O4	2.642(5)	–O5(a)	2.96(2)	–O4(j)	2.48(3)
–O5(a)	2.750(9)	–O5(m)	3.02(2)	–O5(a)	2.53(3)
–O3(m)	2.753(5)	–O5	3.04(1)	–O1	3.10(3)
–O3(g)	2.753(5)	–O4(f)	3.1(2)	–O4	3.28(5)
–O1	2.779(7)				
〈K1–O〉 = 2.699(7) Å		〈K2–O〉 = 2.975(3) Å		〈K3–O〉 = 2.715(3) Å	

Symmetry code: (a) $-x, -y+\frac{1}{2}, z+\frac{1}{2}$; (b) $x, -y, -z$; (c) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$; (d) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (e) $-x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (f) $x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (g) $-x+\frac{1}{2}, y+1, -z+\frac{1}{2}$; (h): $-x, -y, -z$; (i) $x, y-\frac{1}{2}, -z-\frac{1}{2}$; (j): $-x, y, z$; (k) $x, -y-\frac{1}{2}, z-\frac{1}{2}$; (l) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (m) $x+\frac{1}{2}, y, -z-\frac{1}{2}$; (n) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (o) $x+\frac{1}{2}, -y, z-\frac{1}{2}$.

3.1.4. Cr(1)O_6 octahedron

The octahedron around Cr(1) is rather regular, because the Cr(1) atom occupies a special position. Four oxygen atoms can be considered as forming the equatorial plane with long Cr–O distances 2.015(4) Å, while the two axial O1 atoms have short distance (1.948(6) Å).

3.1.5. Potassium atoms

K(1) and K(3) atoms are seven- and six-coordinated, respectively. The K(1)O_7 and K(3)O_6 polyhedra are located in front of six-member windows (Fig. 3). But K(2) is located in the interlayer space, it lies on a plane perpendicular to the *b*-axis at $y = 1/4$ and $3/4$ (Fig. 4), which is equidistant to adjacent layers, it is six-coordinated. The bond valence sum of K–O, using Brown and Alternalt's data [13], are 1.59, 0.68 and 1.66 for K(1), K(2) and K(3), respectively. The bond strength sums for K(1) and K(3) are higher than the expected value +1, suggesting that the KO_7 and KO_6 polyhedra appear too small for these ions. On the contrary, the value 0.68 for K(2) suggests that this is in KO_6 polyhedron and is too big in accordance with the K–O distance values in Table 3.

3.1.6. Comparison between $K_3Cr_3(AsO_4)_4$ and $K_3Fe_3(PO_4)_4 \cdot H_2O$

The comparison of the title compound (space group *Cmca*) with that of $K_3Fe_3(PO_4)_4 \cdot H_2O$ (space group *Pnna*) shows that these two compounds have structures formed by similar layers characterized by the same organization of MO_6 (M = Cr, Fe) octahedra and XO_4 (X = As, P) tetrahedra. They differ by the presence of a water molecule in the interlayer space. In addition, in $K_3Fe_3(PO_4)_4 \cdot H_2O$ two successive layers are crystallographically equivalent by the *n*-glide plane perpendicular to the *b*-axis (Fig. 5), whereas in the arsenate two successive layers are equivalent by the *c*-glide plane perpendicular to the *b*-axis.

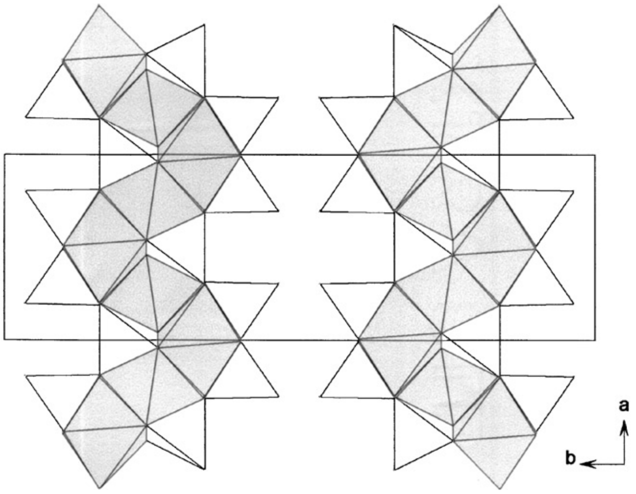

Fig. 5. Representation of the $K_3Fe_3(PO_4)_4 \cdot H_2O$ structure along the [100] direction.

3.2. Infrared spectroscopy

The IR spectrum of $K_3Cr_3(AsO_4)_4$ compound is shown in Fig. 6. The frequencies corresponding to asymmetric (ν_{as}) and symmetric (ν_s) As–O–As vibrational modes concerning the AsO_4 tetrahedra are centered at 876 and 810 cm^{-1}, respectively, in good agreement with the literature [14]. The bands centered at 700 and 522 cm^{-1} are typical of the symmetric (ν_s) Cr–O–Cr vibration. The bands centered at 414, 376 and 394 cm^{-1} are due to the ($\delta_{as} + \delta_s$) [(As–O–As) + (Cr–O–Cr)] vibrations.

3.3. Thermal analysis

The thermal stability of the compound was investigated by DTA analysis using a SETARAM TGDTA 92 equipment. The DTA curve shows only one sharp endotherm at 1356 K assigned to the compound melting.

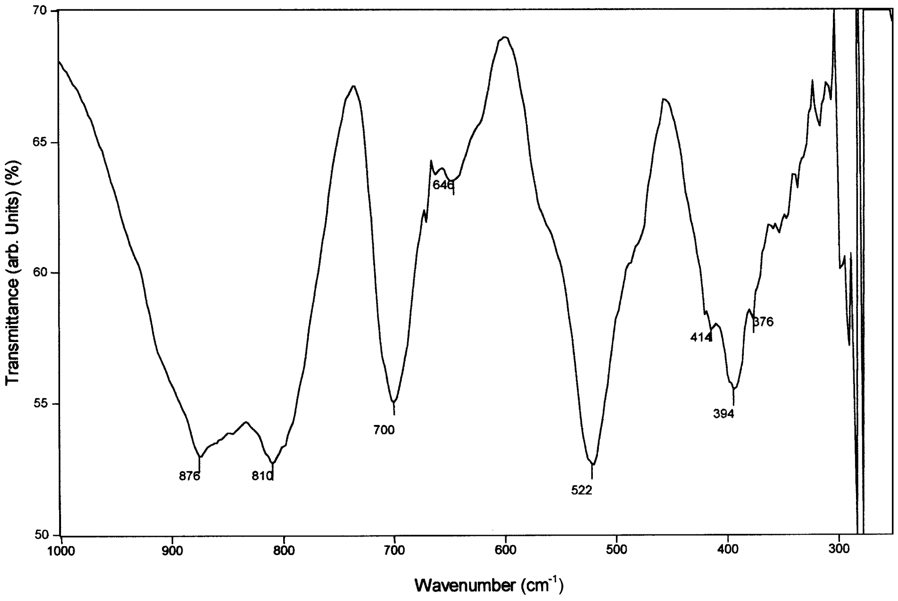

Fig. 6. The infrared spectrum of the $K_3Cr_3(AsO_4)_4$.

Table 4
Activation energy and conductivity values

Polyarsenates	Temperature range (K)	E_a (eV)	σ (Ω^{-1} cm^{-1})
$K_3Cr_3(AsO_4)_4$	563–773	1.21	$\sigma_{703\ K} = 4.61 \times 10^{-5}$
$Na_3Bi_2(PO_4)_3$ [15]	500–700	0.882	8.21×10^{-5}
$Na_3Sc_2(AsO_4)_3$ [16]	400–600	0.46	$\sigma_{600\ K} = 1.7 \times 10^{-3}$
$K^+\beta$ alumine [17]	573	0.29	$\sigma_{573\ K} = 6.5 \times 10^{-4}$

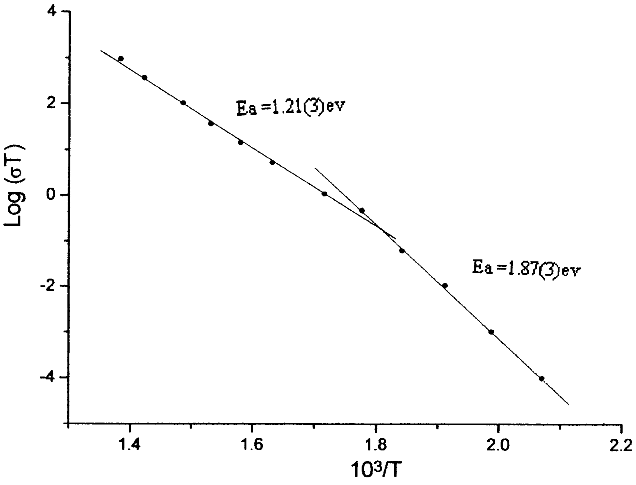

Fig. 7. Temperature dependence of the conductivity Log(σT)(Ω^{-1} cm^{-1} K) $=f(T^{-1})$ (K) of the $K_3Cr_3(AsO_4)_4$.

3.4. *Conductivity study*

Some structural features of the title compound are in favor of potential conductivity properties: open framework, $K^+(2)$ ions lying in the interplanar spaces with partial occupation site and high thermal motion along the [100] and [001] directions. So conductivity measurements have been made. The activation energy and conductivity values deduced from the Fig. 7 are: $E_a = 1.87$ eV for 483–563 K; $E_a = 1.21$ eV for 563–773 K and $\sigma_{703\ K} = 4.61 \times 10^{-5}\ \Omega^{-1}$ cm^{-1}, and compared with that of similar compounds in Table 4.

This material shows low conductivity performances. This probably can be explained by other unfavorable structural features: $K^+(1)$ and $K^+(3)$ lies in too small polyhedra as mentioned in the discussion above. So ionic conduction in solids is a much too complex phenomenon to be simply interpreted.

4. Conclusion

$K_3Cr_3(AsO_4)_4$ has a layer structure, built up from CrO_6 and AsO_4 polyhedra units, linked by corner- and edge-sharing. Adjacent Cr/As/O layers are held together by seven- or six-coordinated K bonding. Conductivity measurements show that $K_3Cr_3(AsO_4)_4$ compound is a poor ionic conductor.

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