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$K_3Al_2As_3O_{12}$

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Key indicators: single-crystal X-ray study; T = 100 K; mean σ(Al–O) = 0.001 Å; R factor = 0.018; wR factor = 0.039; data-to-parameter ratio = 53.2.

Single crystals of $K_3Al_2As_3O_{12}$, tripotassium dialuminotriarsenate(V), were obtained unintentionally by the reaction of $KAsO_3$ with a corundum crucible at 973 K. The asymmetric unit contains three K, two Al, three As and 12 O atoms. The structure of the title compound is isotypic with those of other $K_3M'_2X_3O_{12}$ (M' = Al, Ga; X = P, As) structures and is made up of a three-dimensional network of corner-sharing [AlO_4] and [AsO_4] tetrahedra. The three K^+ cations are located in channels running along the [100], [001], [101] and [$10\overline{1}$] directions, exhibiting different coordination numbers of 9, 8 and 6, respectively. All corresponding [KO_x] polyhedra are considerably distorted.

Related literature

For a recent review on NASICON-type materials, see: Anantharamulu *et al.* (2011). For isotypic $K_3M'_2X_3O_{12}$ structures, see: Beaurain *et al.* (2008) and Yakubovich *et al.* (2008) for $K_3Ga_2P_3O_{12}$; Boughzala *et al.* (1997) for the solid solution $K_3Al_2(As_{1.92}P_{1.08})O_{12}$; Devi & Vidyasagar (2000) for $K_3Al_2P_3O_{12}$. For the isopointal structure of $Tl_3Al_2P_3O_{12}$, see: Devi & Vidyasagar (2000). For background to the bond-valence method, see: Brown & Altermatt (1985).

Experimental

Crystal data

$K_3Al_2As_3O_{12}$
M_r = 588
Orthorhombic, $Pna2_1$
a = 8.7943 (2) Å
b = 17.4400 (2) Å
c = 8.6610 (3) Å
V = 1328.36 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 8.63 mm^{-1}
T = 100 K
0.10 × 0.06 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008) T_{min} = 0.49, T_{max} = 0.92
52293 measured reflections
9623 independent reflections
8606 reflections with $I > 3\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 3\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.039
S = 0.80
9623 reflections
181 parameters
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 3882 Friedel pairs
Flack parameter: 0.008 (3)

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus*; method used to solve structure: coordinates taken from an isotypic structure; program(s) used to refine structure: *JANA2006* (Petříček *et al.*, 2006); molecular graphics: *ATOMS* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GW2112).

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supplementary materials

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$K_3Al_2As_3O_{12}$

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Comment

During crystal growth studies of $KAsO_3$, we inadvertently obtained single crystals with composition $K_3Al_2As_3O_{12}$ from an attacked corundum crucible. Many oxides with general formula $M_xM'_2X_3O_{12}$ crystallize with three-dimensional framework structures (Devi & Vidyasagar, 2000) and are of technological interest. Most notably, compounds crystallizing in the NASICON ($Na_3Zr_2Si_2PO_{12}$) structure type are excellent ion conductors and have been intensely studied. A recent review on compounds with the NASICON structure has been given by Anantharamulu *et al.* (2011).

The structure of $K_3Al_2As_3O_{12}$ is isotypic with the phosphate analogue $K_3Al_2P_3O_{12}$ (Devi & Vidyasagar, 2000), the mixed arsenate/phosphate solid solution $K_3Al_2As_{1.92}P_{1.08}O_{12}$ (Boughzala *et al.*, 1997) and $K_3Ga_2P_3O_{12}$ (Beaurain *et al.*, 2008; Yakubovich *et al.*, 2008). Trithallium dialuminotriphosphate, $Tl_3Al_2P_3O_{12}$ (Devi & Vidyasagar, 2000), can be considered as isopointal to the title compound, because it features distinctly different coordinations of the Al sites and the cationic network due to the electron lone pairs of the Tl^+ ions.

Whereas in the NASICON structure type the M' site is octahedrally and the X site tetrahedrally coordinated, in the title compound both sites exhibit a tetrahedral coordination. Two crystallographically different [AlO_4] and three [AlO_4] tetrahedra, all on general positions, are linked *via* their corners to a complex three-dimensional network, whereby [AlO_4] units connect only to [AsO_4] units and *vice-versa*. This network can be decomposed into undulating sheets normal to [010] (Al1, Al2, As1, As2) which are connected by [AsO_4] units (As3) (Fig. 1).

The three different K^+ cations are located in channels running along the [100] and [001] (K1, K2) (Fig. 1) as well as the [101] and [$10\bar{1}$] (K3) (Fig. 2) directions. Considering K–O distances up to 3.5 Å as relevant for first coordination spheres, the K^+ cations are coordinated by 9 (K1), 8 (K1) and 6 (K3) O atoms, respectively, all in the form of irregular [KO_x] polyhedra. The total bond valence sums (parameters: $R_0 = 2.132$ Å, $b = 0.37$ (Brown & Altermatt, 1985)), 1.08 (K1), 1.04 (K2) and 0.90 (K3) valence units (v.u.) are close to the expected value of 1 v.u. and point to a slight undersaturation of K3. The coordination of the K^+ cations is very similar in all isotypic structures. The main difference in these structures pertains to the bond lengths of the XO_4 tetrahedra. Corresponding mean bond lengths are 1.746 Å for AlO_4 and 1.680 Å for AsO_4 tetrahedra in the title compound; 1.737 Å for AlO_4 and 1.527 Å for PO_4 tetrahedra in $K_3Al_2P_3O_{12}$; 1.730 Å for AlO_4 and 1.615 Å for $(As/P)O_4$ tetrahedra in $K_3Al_2As_{1.92}P_{1.08}O_{12}$; 1.816 Å for GaO_4 and 1.535 Å for PO_4 tetrahedra in $K_3Ga_2P_3O_{12}$.

Experimental

K_2CO_3 and H_3AsO_4 were obtained commercially and used without purification. 10 g $80\%_{wt}$ H_3AsO_4 were titrated against an aqueous K_2CO_3 solution using methyl red as indicator. The water was evaporated and the residue recrystallized from water to obtain KH_2AsO_4. This solid was then heated in a corundum crucible at 973 K, cooled to 633 K over 24 h and quenched. Few colourless crystals of the title compound were isolated from the reaction mixture.

Refinement

The first refinement cycle was performed using the published atomic coordinates of $K_3Al_2As_{1.92}P_{1.08}O_{12}$ (Boughzala *et al.*, 1997) as starting parameters.

Figures

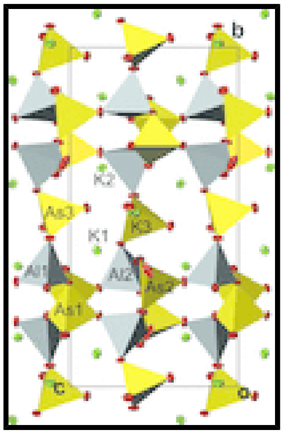

Fig. 1. The crystal structure of $K_3Al_2As_3O_{12}$ viewed down [100], showing sheets of corner-sharing $[AsO_4]$ and $[AlO_4]$ tetrahedra extending parallel to (010). Displacement ellipsoids are drawn at the 90% probability level.

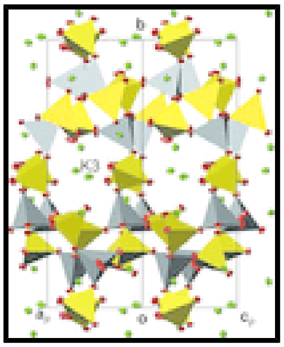

Fig. 2. The crystal structure of $K_3Al_2As_3O_{12}$ viewed down [101]. Displacement ellipsoids are drawn at the 90% probability level.

tripotassium dialuminotriarsenate(V)

Crystal data

$K_3Al_2As_3O_{12}$

$M_r = 588$

Orthorhombic, $Pna2_1$

Hall symbol: P 2c -2n

$a = 8.7943$ (2) Å

$b = 17.4400$ (2) Å

$c = 8.6610$ (3) Å

$V = 1328.36$ (6) Å^3

$Z = 4$

$F(000) = 1112$

$D_x = 2.939$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 54411 reflections

$\theta = 3.3$–44.8°

$\mu = 8.63$ mm^{-1}

$T = 100$ K

Plate, colourless

0.10 × 0.06 × 0.01 mm

Data collection

Bruker APEXII CCD diffractometer	9623 independent reflections
Radiation source: X-ray tube	8606 reflections with $I > 3\sigma(I)$
graphite	$R_{\text{int}} = 0.038$
ω and φ scans	$\theta_{\text{max}} = 45.1°$, $\theta_{\text{min}} = 2.6°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$h = -17 \rightarrow 17$
$T_{\text{min}} = 0.49$, $T_{\text{max}} = 0.92$	$k = -34 \rightarrow 34$
52293 measured reflections	$l = -15 \rightarrow 17$

Refinement

Refinement on F^2	Primary atom site location: isomorphous structure methods
$R[F^2 > 2\sigma(F^2)] = 0.018$	Weighting scheme based on measured s.u.'s $w = 1/(\sigma^2(I) + 0.0004I^2)$
$wR(F^2) = 0.039$	$(\Delta/\sigma)_{\text{max}} = 0.003$
$S = 0.80$	$\Delta\rho_{\text{max}} = 0.33$ e Å^{-3}
9623 reflections	$\Delta\rho_{\text{min}} = -0.31$ e Å^{-3}
181 parameters	Absolute structure: Flack (1983), 3882 Friedel pairs
0 restraints	Flack parameter: 0.008 (3)
1 constraint	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
As1	0.156896 (11)	0.215743 (6)	0.0009	0.004155 (18)
As2	0.293241 (12)	0.313601 (6)	0.511929 (16)	0.004909 (19)
As3	0.236068 (12)	0.502941 (6)	0.085202 (18)	0.005355 (19)
K1	0.01017 (3)	0.402188 (14)	0.84037 (3)	0.00837 (4)
K2	0.95033 (3)	0.354962 (14)	0.30906 (3)	0.00818 (4)
K3	0.68161 (3)	0.488891 (15)	0.11580 (3)	0.01179 (5)
Al1	0.34851 (4)	0.34012 (2)	0.14668 (4)	0.00492 (7)
Al2	0.13204 (4)	0.16767 (2)	0.65562 (4)	0.00520 (7)
O1	0.29089 (10)	0.15184 (5)	0.03110 (9)	0.00824 (17)
O2	0.02014 (10)	0.20900 (5)	0.13689 (9)	0.00746 (16)
O3	0.21755 (9)	0.30785 (4)	0.00781 (10)	0.00643 (14)
O4	0.06929 (10)	0.20939 (5)	0.82779 (9)	0.00730 (16)
O5	0.17013 (13)	0.37287 (6)	0.58794 (12)	0.0139 (2)
O6	0.47459 (12)	0.34183 (7)	0.53518 (11)	0.0168 (2)
O7	0.27956 (11)	0.22138 (5)	0.57055 (11)	0.01044 (18)
O8	0.26654 (10)	0.30933 (6)	0.31927 (9)	0.00936 (18)
O9	0.07409 (11)	0.46866 (6)	0.15273 (11)	0.01076 (18)
O10	0.29028 (11)	0.57855 (5)	0.19818 (10)	0.00894 (17)
O11	0.23407 (11)	0.52699 (6)	0.90078 (10)	0.01074 (19)
O12	0.37999 (10)	0.43772 (5)	0.12022 (10)	0.00883 (16)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As1	0.00437 (3)	0.00356 (3)	0.00453 (3)	0.00007 (3)	−0.00035 (3)	−0.00027 (3)
As2	0.00554 (3)	0.00472 (4)	0.00447 (3)	−0.00042 (3)	0.00028 (3)	0.00036 (3)
As3	0.00642 (4)	0.00336 (3)	0.00628 (3)	−0.00018 (3)	−0.00018 (3)	−0.00019 (3)
K1	0.00698 (7)	0.01015 (8)	0.00797 (6)	−0.00039 (6)	0.00040 (5)	0.00102 (6)
K2	0.00765 (8)	0.00734 (8)	0.00955 (7)	0.00014 (6)	0.00017 (6)	0.00078 (6)
K3	0.01516 (10)	0.00792 (9)	0.01230 (8)	−0.00147 (7)	−0.00295 (7)	−0.00020 (6)
Al1	0.00487 (12)	0.00439 (12)	0.00550 (10)	−0.00023 (9)	−0.00019 (9)	−0.00024 (9)
Al2	0.00592 (12)	0.00438 (12)	0.00532 (10)	0.00071 (10)	−0.00068 (9)	−0.00031 (9)
O1	0.0078 (3)	0.0069 (3)	0.0101 (3)	0.0029 (2)	−0.0011 (2)	−0.0004 (2)
O2	0.0062 (3)	0.0094 (3)	0.0067 (2)	−0.0020 (2)	0.0017 (2)	−0.0006 (2)
O3	0.0075 (2)	0.0046 (2)	0.0072 (2)	−0.0014 (2)	−0.0019 (2)	0.0005 (2)
O4	0.0078 (3)	0.0089 (3)	0.0052 (2)	0.0016 (2)	−0.0019 (2)	−0.0019 (2)
O5	0.0193 (4)	0.0088 (3)	0.0138 (3)	0.0037 (3)	0.0083 (3)	−0.0016 (3)
O6	0.0101 (3)	0.0274 (5)	0.0130 (3)	−0.0102 (3)	−0.0069 (3)	0.0108 (3)
O7	0.0121 (3)	0.0056 (3)	0.0136 (3)	0.0006 (2)	0.0041 (2)	0.0026 (2)
O8	0.0094 (3)	0.0144 (4)	0.0043 (2)	−0.0031 (3)	−0.0001 (2)	0.0002 (2)
O9	0.0084 (3)	0.0083 (3)	0.0155 (3)	−0.0023 (2)	0.0031 (2)	0.0001 (3)
O10	0.0131 (3)	0.0043 (3)	0.0094 (3)	−0.0018 (2)	0.0003 (2)	−0.0010 (2)
O11	0.0138 (3)	0.0121 (4)	0.0063 (3)	0.0010 (3)	−0.0004 (2)	0.0016 (2)
O12	0.0085 (3)	0.0044 (3)	0.0136 (3)	0.0006 (2)	−0.0019 (2)	0.0002 (2)

Geometric parameters (Å, °)

K1—O1^{i}	2.7084 (9)	Al1—O8	1.7443 (9)
K1—O3^{ii}	2.8524 (8)	Al1—O12	1.7396 (9)
K1—O5	2.6496 (11)	Al2—O4	1.7485 (9)
K1—O9^{ii}	2.9964 (10)	Al2—O6^{vii}	1.7415 (11)
K1—O9^{iii}	2.8747 (10)	Al2—O7	1.7616 (10)
K1—O10^{iii}	2.9344 (10)	Al2—O10^{viii}	1.7373 (10)
K1—O11	2.9814 (10)	As1—O1	1.6429 (9)
K2—O1^{iv}	2.7885 (9)	As1—O2	1.6875 (8)
K2—O2^{v}	3.0134 (9)	As1—O3	1.6936 (8)
K2—O7^{iv}	3.0260 (10)	As1—O4^{ix}	1.6893 (8)
K2—O8^{v}	2.8939 (10)	As2—O5	1.6352 (10)
K2—O9^{v}	2.6362 (10)	As2—O6	1.6812 (11)
K2—O11^{vi}	2.7384 (10)	As2—O7	1.6909 (9)
K3—O1^{iv}	2.7360 (9)	As2—O8	1.6867 (8)
K3—O5^{vi}	2.7515 (10)	As3—O9	1.6519 (9)
K3—O11^{vi}	2.5921 (9)	As3—O10	1.7098 (9)
K3—O12	2.7989 (10)	As3—O11^{ix}	1.6515 (9)
Al1—O2^{iv}	1.7376 (9)	As3—O12	1.7285 (9)
Al1—O3	1.7578 (9)		

O1^{i}—K1—O3^{ii}	86.82 (3)	O1^{iv}—K3—O5^{vi}	126.59 (3)
O1^{i}—K1—O5	144.51 (3)	O1^{iv}—K3—O11^{vi}	93.38 (3)
O1^{i}—K1—O9^{ii}	73.59 (3)	O1^{iv}—K3—O12	92.90 (3)
O1^{i}—K1—O9^{iii}	115.72 (3)	O5^{vi}—K3—O11^{vi}	92.38 (3)
O1^{i}—K1—O10^{iii}	69.80 (3)	O5^{vi}—K3—O12	136.86 (3)
O1^{i}—K1—O11	128.11 (3)	O11^{vi}—K3—O12	102.95 (3)
O3^{ii}—K1—O5	88.21 (3)	O2^{iv}—Al1—O3	112.21 (4)
O3^{ii}—K1—O9^{ii}	69.16 (3)	O2^{iv}—Al1—O8	104.42 (4)
O3^{ii}—K1—O9^{iii}	154.71 (3)	O2^{iv}—Al1—O12	109.74 (5)
O3^{ii}—K1—O10^{iii}	148.77 (2)	O3—Al1—O8	102.53 (4)
O3^{ii}—K1—O11	84.81 (2)	O3—Al1—O12	109.11 (4)
O5—K1—O9^{ii}	136.06 (3)	O8—Al1—O12	118.68 (5)
O5—K1—O9^{iii}	79.72 (3)	O4—Al2—O6^{vii}	107.43 (5)
O5—K1—O10^{iii}	98.85 (3)	O4—Al2—O7	111.59 (4)
O5—K1—O11	86.28 (3)	O4—Al2—O10^{viii}	108.39 (4)
O9^{ii}—K1—O9^{iii}	104.81 (3)	O6^{vii}—Al2—O7	112.68 (5)
O9^{ii}—K1—O10^{iii}	120.24 (3)	O6^{vii}—Al2—O10^{viii}	110.77 (6)
O9^{ii}—K1—O11	55.61 (2)	O7—Al2—O10^{viii}	105.95 (5)
O9^{iii}—K1—O10^{iii}	56.01 (3)	O1—As1—O2	110.66 (4)
O9^{iii}—K1—O11	72.39 (3)	O1—As1—O3	114.32 (4)
O10^{iii}—K1—O11	125.79 (3)	O1—As1—O4^{ix}	115.08 (4)
O1^{iv}—K2—O2^{v}	68.86 (2)	O2—As1—O3	105.42 (4)
O1^{iv}—K2—O7^{iv}	112.20 (3)	O2—As1—O4^{ix}	106.85 (4)
O1^{iv}—K2—O8^{v}	119.86 (2)	O3—As1—O4^{ix}	103.72 (4)
O1^{iv}—K2—O9^{v}	78.24 (3)	O5—As2—O6	113.25 (6)
O1^{iv}—K2—O11^{vi}	89.12 (3)	O5—As2—O7	115.67 (5)
O2^{v}—K2—O7^{iv}	95.73 (2)	O5—As2—O8	109.52 (5)
O2^{v}—K2—O8^{v}	65.61 (2)	O6—As2—O7	108.07 (5)
O2^{v}—K2—O9^{v}	107.28 (3)	O6—As2—O8	105.28 (4)
O2^{v}—K2—O11^{vi}	154.06 (3)	O7—As2—O8	104.19 (5)
O7^{iv}—K2—O8^{v}	109.45 (3)	O9—As3—O10	108.48 (5)
O7^{iv}—K2—O9^{v}	156.96 (3)	O9—As3—O11^{ix}	115.16 (5)
O7^{iv}—K2—O11^{vi}	79.62 (3)	O9—As3—O12	109.34 (4)
O8^{v}—K2—O9^{v}	79.97 (3)	O10—As3—O11^{ix}	111.13 (5)
O8^{v}—K2—O11^{vi}	140.08 (3)	O10—As3—O12	101.71 (4)
O9^{v}—K2—O11^{vi}	80.10 (3)	O11^{ix}—As3—O12	110.16 (5)

Symmetry codes: (i) *x*−1/2, −*y*+1/2, *z*+1; (ii) *x*, *y*, *z*+1; (iii) −*x*, −*y*+1, *z*+1/2; (iv) *x*+1/2, −*y*+1/2, *z*; (v) *x*+1, *y*, *z*; (vi) −*x*+1, −*y*+1, *z*−1/2; (vii) *x*−1/2, −*y*+1/2, *z*; (viii) −*x*+1/2, *y*−1/2, *z*+1/2; (ix) *x*, *y*, *z*−1.

Fig. 1

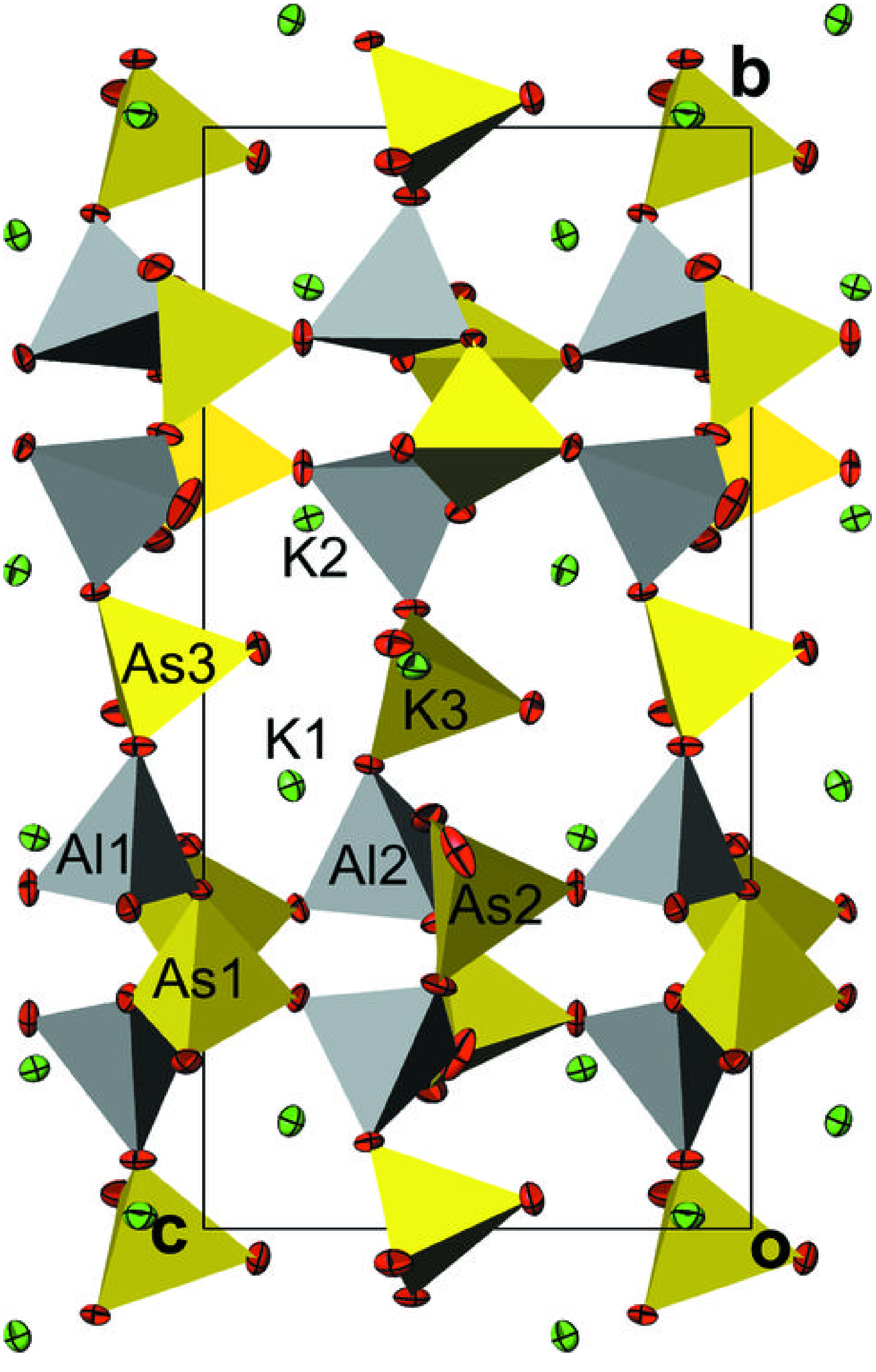

Fig. 2