

## The alluaudite-like arsenate NaCaMg<sub>3</sub>(AsO<sub>4</sub>)<sub>3</sub>

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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{As}-\text{O}) = 0.003$  Å; disorder in solvent or counterion;  $R$  factor = 0.023;  $wR$  factor = 0.061; data-to-parameter ratio = 11.5.

The title compound, sodium calcium trimagnesium tris(arsenate), an alluaudite-like arsenate, was prepared by solid-state reaction at high temperature. The structure is built up from edge-sharing MgO<sub>6</sub> octahedra in chains associated with the AsO<sub>4</sub> arsenate groups. The three-dimensional network leads to two different tunnels occupied statistically by Na<sup>+</sup> and Ca<sup>2+</sup>. One As and one Mg atom lie on twofold rotation axes; one Na and one Ca are disordered over two sites with occupancies of 0.7 and 0.3 and these sites lie on a twofold rotation axis and an inversion centre, respectively.

### Related literature

For the alluaudite structure type, see: Moore (1971); Yakubovitch *et al.* (1977); Cu<sub>1.35</sub>Fe(PO<sub>4</sub>)<sub>3</sub> (Warner *et al.*, 1993); NaFe<sub>3.67</sub>(PO<sub>4</sub>)<sub>3</sub> (Korzanski *et al.*, 1998). For related alluaudite-like arsenates, see: NaCo<sub>3</sub>(AsO<sub>4</sub>)(HAsO<sub>4</sub>)<sub>2</sub> (Kwang-Hwa & Pei-Fen, 1994); NaCaCdMg<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (Khorari *et al.*, 1997); Ag<sub>1.49</sub>Mn<sub>1.49</sub>Mn<sub>2</sub>(AsO<sub>4</sub>)<sub>3</sub> (Ayed *et al.*, 2002); Na<sub>1.72</sub>Mn<sub>3.28</sub>(AsO<sub>4</sub>)<sub>3</sub> (Brahim *et al.* 2003). For related literature, see: Leroux *et al.* (1995).

### Experimental

#### Crystal data

NaCaMg<sub>3</sub>(AsO<sub>4</sub>)<sub>3</sub>

$M_r = 552.74$

Monoclinic,  $C2/c$   
 $a = 11.880$  (1) Å  
 $b = 12.817$  (1) Å  
 $c = 6.741$  (2) Å  
 $\beta = 112.45$  (1)°  
 $V = 948.7$  (3) Å<sup>3</sup>

$Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 11.36$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.6 \times 0.2 \times 0.15$  mm

#### Data collection

Enraf–Nonius CAD-4 diffractometer  
Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.110$ ,  $T_{\max} = 0.180$   
1358 measured reflections

1154 independent reflections  
1133 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$   
2 standard reflections  
frequency: 120 min  
intensity decay: 0.4%

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$   
 $wR(F^2) = 0.060$   
 $S = 1.29$   
1154 reflections

100 parameters  
 $\Delta\rho_{\max} = 0.99$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.00$  e Å<sup>-3</sup>

Data collection: *CAD-4 EXPRESS* (Duisenberg, 1992; Macíček & Yordanov, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2069).

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**supplementary materials**

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## The alluaudite-like arsenate $\text{NaCaMg}_3(\text{AsO}_4)_3$

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### Comment

The crystal structure of  $\text{NaCaMg}_3(\text{AsO}_4)_3$  is closely related to the common structure type of the well known mineral Alluaudite with the general formula  $X(1)X(2)M(1)M(2)_2(\text{PO}_4)_3$  (Moore, 1971; Yakubovitch *et al.*, 1994). It can be described by a  $\text{Mg}_3(\text{AsO}_4)_3$  framework built up by a complex arrangement of distorted  $\text{MgO}_6$  octahedra, and  $\text{AsO}_4$  tetrahedra. The projection of the structure in a polyhedral representation is presented in Fig. 1. It consists of  $\text{Mg1O}_6$  and  $\text{Mg2O}_6$  octahedra that share edges to form staggered chains stacked parallel to the  $[10\bar{1}]$  direction. Equivalent chains are linked together through the  $\text{AsO}_4$  tetrahedra corners.  $\text{As1O}_4$  connects two chains and thus two of its O atoms belong of the same chain. The  $\text{As2O}_4$  tetrahedron shares his four oxygen summits with four different  $\text{MgO}_6$  octahedra belonging to three adjacent chains, two belong to the same chain and the two others from two different chains. The arrangement of magnesium octahedra  $\text{Mg1O}_6$  and  $\text{Mg2O}_6$  in chains present a distortion, with the mean  $\text{Mg1—O}$  and  $\text{Mg2—O}$  distances 2.135 Å and 2.079 Å respectively. The  $\text{O—Mg1—O}$  angles range from 73.28° to 112.20°, whereas the  $\text{O—Mg2—O}$  angles vary between 77.62° to 108.84°. The two crystallographic distinct As atoms are surrounded by four O atoms with the mean distance of  $\text{As1—O}$ : 1.691 Å and  $\text{As2—O}$ : 1.694 Å. This structural arrangement delimits two types of hexagonal tunnels, parallel to the  $c$  axis and located at  $(1/2, 0, z)$  and  $(0, 0, z)$  respectively. Sodium Na1, Na2 and calcium Ca1, Ca2 cations are located in those channels. The structure is closely related to the alluaudite structure type. In  $\text{NaCaMg}_3(\text{AsO}_4)_3$ , the  $X(1)$  site at  $(1/2, 0, 0)$  is empty. Whereas the  $X(2)$  site at  $(0, 0, 0)$  contains 0.30 Na2 and 0.70 Ca2. The site in the tunnel at  $(0, 0, z)$  shifted from the  $X(2)$  site by  $\pm 0.25$  along  $z$  is occupied by Na1 and Ca1 with respectively the occupation number 0.70 and 0.30. There are a number of possible models for the cationic distribution and it's not possible to decide which is the best solution. We retain the solution with same amount of sodium and calcium. First, the occupancies of Na1 and Ca1 in the site shifted from  $X(2)$  were refined. Second, for the site  $X(2)$ , the occupancies of Na2 and Ca2 were fixed to obtain the electroneutrality. For each two cations in the same site the atomic displacement parameters were maintained the same with the instruction EADP. The bond valence sum of the Na1, Na2, Ca2, Mg1, Mg2, As1 and As2 atoms are in a good agreement with their oxidation states (Brown & Altermatt, 1985). For the calcium Ca1 which occupy partialy the tunnel the bond valence sums is different (1.33).

### Experimental

Single crystals of  $\text{NaCaMg}_3(\text{AsO}_4)_3$  were prepared by a mixture of  $\text{NaNO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgN}_2\text{O}_6(\text{H}_2\text{O})_6$  and  $\text{NH}_4\text{H}_2\text{AsO}_4$  with molar ratio of (1:1:2:3). The powder was ground, then heated in a porcelain crucible progressively until 1223 K. This temperature was held for 3 days. Then the mixture was cooled slowly to room temperature at 10 K/h. The product was washed with hot water. Prismatic and colorless crystals of the title compound were extracted. Their qualitative analysis by electron microscope probe revealed that it contains sodium, calcium, oxygen, arsenic and magnesium atoms.

## Figures

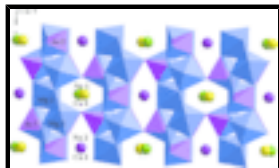


Fig. 1. Projection of the structure of  $\text{NaCaMg}_3(\text{AsO}_4)_3$  along  $[001]$  direction.

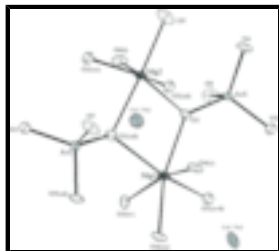


Fig. 2. A view of a sheet showing the association mode of the  $\text{MgO}_6$  in chains with  $\text{AsO}_4$  tetrahedra shown with 50% probability displacement ellipsoids.

## Sodium calcium trimagnesium tris(arsenate)

### Crystal data

$\text{NaCaMg}_3(\text{AsO}_4)_3$

$M_r = 552.74$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 11.880(1)\ \text{\AA}$

$b = 12.817(1)\ \text{\AA}$

$c = 6.741(2)\ \text{\AA}$

$\beta = 112.45(1)^\circ$

$V = 948.7(3)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1048$

$D_x = 3.870\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 2.4\text{--}28^\circ$

$\mu = 11.36\ \text{mm}^{-1}$

$T = 293(2)\ \text{K}$

Prismatic, colourless

$0.6 \times 0.2 \times 0.15\ \text{mm}$

### Data collection

Enraf-Nonius CAD-4  
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293(2)\ \text{K}$

$\omega/2\theta$  scans

Absorption correction:  $\psi$  scan  
(North *et al.*, 1968)

$T_{\min} = 0.110$ ,  $T_{\max} = 0.180$

1358 measured reflections

1154 independent reflections

1133 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 28.0^\circ$

$\theta_{\min} = 2.4^\circ$

$h = -15 \rightarrow 14$

$k = -1 \rightarrow 16$

$l = 0 \rightarrow 8$

2 standard reflections

every 120 min

intensity decay: 0.4%

*Refinement*

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0244P)^2 + 8.0874P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.060$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.29$	$\Delta\rho_{\max} = 0.99 \text{ e } \text{\AA}^{-3}$
1154 reflections	$\Delta\rho_{\min} = -1.00 \text{ e } \text{\AA}^{-3}$
100 parameters	Extinction correction: SHELXL97 (Sheldrick, 2008),
Primary atom site location: structure-invariant direct methods	$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.0071 (4)

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
As1	0.26904 (3)	0.38625 (2)	0.37969 (5)	0.00207 (13)	
As2	0.5000	0.21057 (3)	0.2500	0.00248 (14)	
Mg1	0.5000	0.23783 (13)	0.7500	0.0043 (3)	
Mg2	0.78584 (10)	0.15824 (9)	0.37643 (18)	0.0030 (2)	
Na1	0.5000	0.511 (3)	0.7500	0.019 (2)	0.70
Ca1	0.5000	0.523 (3)	0.7500	0.019 (2)	0.30
Ca2	0.5000	0.0000	0.0000	0.0132 (3)	0.70
Na2	0.5000	0.0000	0.0000	0.0132 (3)	0.30
O1	0.4635 (2)	0.28350 (19)	0.0247 (4)	0.0063 (5)	
O2	0.2837 (2)	0.31609 (19)	0.1792 (4)	0.0061 (5)	
O3	0.3415 (2)	0.32937 (19)	0.6218 (4)	0.0053 (5)	
O4	0.1175 (2)	0.39767 (19)	0.3197 (4)	0.0074 (5)	
O5	0.6086 (2)	0.1221 (2)	0.2626 (4)	0.0105 (5)	
O6	0.3381 (2)	0.50307 (19)	0.3963 (4)	0.0082 (5)	

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
As1	0.00076 (18)	0.00152 (19)	0.00403 (19)	0.00028 (10)	0.00101 (12)	0.00027 (10)
As2	0.0017 (2)	0.0013 (2)	0.0040 (2)	0.000	0.00054 (16)	0.000
Mg1	0.0020 (7)	0.0036 (7)	0.0080 (7)	0.000	0.0027 (6)	0.000
Mg2	0.0021 (5)	0.0022 (5)	0.0053 (5)	0.0000 (4)	0.0022 (4)	-0.0001 (4)
Na1	0.0091 (8)	0.035 (7)	0.0131 (8)	0.000	0.0032 (7)	0.000
Ca1	0.0091 (8)	0.035 (7)	0.0131 (8)	0.000	0.0032 (7)	0.000
Ca2	0.0161 (6)	0.0036 (5)	0.0107 (5)	-0.0026 (4)	-0.0051 (5)	-0.0003 (4)
Na2	0.0161 (6)	0.0036 (5)	0.0107 (5)	-0.0026 (4)	-0.0051 (5)	-0.0003 (4)
O1	0.0039 (11)	0.0094 (11)	0.0060 (11)	0.0020 (9)	0.0022 (9)	0.0025 (9)
O2	0.0080 (11)	0.0064 (11)	0.0045 (11)	0.0004 (9)	0.0031 (9)	-0.0010 (8)
O3	0.0050 (10)	0.0072 (11)	0.0033 (11)	0.0043 (9)	0.0010 (8)	0.0022 (8)
O4	0.0006 (10)	0.0065 (11)	0.0142 (12)	0.0005 (8)	0.0016 (9)	0.0000 (9)
O5	0.0034 (11)	0.0071 (11)	0.0169 (13)	0.0038 (9)	-0.0007 (9)	-0.0040 (9)
O6	0.0089 (11)	0.0022 (10)	0.0138 (12)	-0.0025 (9)	0.0047 (10)	-0.0007 (9)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

As1—O2	1.687 (2)	Na1—O1 <sup>ix</sup>	2.99 (3)
As1—O6	1.690 (2)	Na1—O1 <sup>viii</sup>	2.99 (3)
As1—O3	1.692 (2)	Ca1—O6	2.439 (5)
As1—O4	1.694 (2)	Ca1—O6 <sup>ii</sup>	2.439 (5)
As2—O1 <sup>i</sup>	1.693 (2)	Ca1—O6 <sup>viii</sup>	2.497 (6)
As2—O1	1.693 (2)	Ca1—O6 <sup>ix</sup>	2.497 (6)
As2—O5 <sup>i</sup>	1.695 (2)	Ca1—O1 <sup>ix</sup>	2.85 (4)
As2—O5	1.695 (2)	Ca1—O1 <sup>viii</sup>	2.85 (4)
Mg1—O3 <sup>ii</sup>	2.104 (2)	Ca1—O3	3.04 (4)
Mg1—O3	2.104 (2)	Ca1—O3 <sup>ii</sup>	3.04 (4)
Mg1—O1 <sup>iii</sup>	2.139 (2)	Ca2—O5	2.346 (3)
Mg1—O1 <sup>i</sup>	2.139 (2)	Ca2—O5 <sup>x</sup>	2.346 (3)
Mg1—O4 <sup>iv</sup>	2.164 (3)	Ca2—O4 <sup>vii</sup>	2.453 (3)
Mg1—O4 <sup>v</sup>	2.164 (3)	Ca2—O4 <sup>xi</sup>	2.453 (3)
Mg2—O5	2.001 (3)	Ca2—O4 <sup>xii</sup>	2.538 (3)
Mg2—O3 <sup>vi</sup>	2.068 (3)	Ca2—O4 <sup>vi</sup>	2.538 (3)
Mg2—O6 <sup>vii</sup>	2.072 (3)	Ca2—O5 <sup>i</sup>	2.872 (3)
Mg2—O2 <sup>v</sup>	2.077 (3)	Ca2—O5 <sup>xiii</sup>	2.872 (3)
Mg2—O1 <sup>v</sup>	2.098 (3)	Na2—O5	2.346 (3)
Mg2—O2 <sup>i</sup>	2.163 (3)	Na2—O5 <sup>x</sup>	2.346 (3)
Na1—O6	2.428 (3)	Na2—O4 <sup>vii</sup>	2.453 (3)
Na1—O6 <sup>ii</sup>	2.428 (3)	Na2—O4 <sup>xi</sup>	2.453 (3)
Na1—O6 <sup>viii</sup>	2.481 (4)	Na2—O4 <sup>xii</sup>	2.538 (3)

Na1—O6 <sup>ix</sup>	2.481 (4)	Na2—O4 <sup>vi</sup>	2.538 (3)
Na1—O3	2.91 (3)	Na2—O5 <sup>i</sup>	2.872 (3)
Na1—O3 <sup>ii</sup>	2.91 (3)	Na2—O5 <sup>xiii</sup>	2.872 (3)
O2—As1—O6	109.24 (12)	O6—Ca1—O6 <sup>ix</sup>	92.2 (3)
O2—As1—O3	111.91 (11)	O6 <sup>ii</sup> —Ca1—O6 <sup>ix</sup>	86.1 (2)
O6—As1—O3	105.22 (12)	O6—Ca1—O1 <sup>ix</sup>	121.1 (13)
O2—As1—O4	106.26 (12)	O6 <sup>ii</sup> —Ca1—O1 <sup>ix</sup>	70.7 (6)
O6—As1—O4	112.57 (12)	O6 <sup>viii</sup> —Ca1—O1 <sup>ix</sup>	83.7 (7)
O3—As1—O4	111.73 (12)	O6 <sup>ix</sup> —Ca1—O1 <sup>ix</sup>	110.2 (10)
O1 <sup>i</sup> —As2—O1	112.96 (17)	O6—Ca1—O1 <sup>viii</sup>	70.7 (6)
O1 <sup>i</sup> —As2—O5 <sup>i</sup>	110.10 (13)	O6 <sup>ii</sup> —Ca1—O1 <sup>viii</sup>	121.1 (13)
O1—As2—O5 <sup>i</sup>	113.27 (12)	O6 <sup>viii</sup> —Ca1—O1 <sup>viii</sup>	110.2 (10)
O1 <sup>i</sup> —As2—O5	113.27 (12)	O6 <sup>ix</sup> —Ca1—O1 <sup>viii</sup>	83.7 (7)
O1—As2—O5	110.10 (13)	O6 <sup>ii</sup> —Ca1—O3	111.3 (13)
O5 <sup>i</sup> —As2—O5	96.04 (18)	O6 <sup>viii</sup> —Ca1—O3	60.9 (6)
O3 <sup>ii</sup> —Mg1—O3	112.20 (15)	O6 <sup>ix</sup> —Ca1—O3	105.3 (12)
O3 <sup>ii</sup> —Mg1—O1 <sup>iii</sup>	86.41 (10)	O6—Ca1—O3 <sup>ii</sup>	111.3 (13)
O3—Mg1—O1 <sup>iii</sup>	75.96 (9)	O6 <sup>viii</sup> —Ca1—O3 <sup>ii</sup>	105.3 (12)
O3 <sup>ii</sup> —Mg1—O1 <sup>i</sup>	75.96 (9)	O6 <sup>ix</sup> —Ca1—O3 <sup>ii</sup>	60.9 (6)
O3—Mg1—O1 <sup>i</sup>	86.41 (10)	O3—Ca1—O3 <sup>ii</sup>	70.2 (9)
O3—Mg1—O4 <sup>iv</sup>	87.51 (9)	O5—Ca2—O4 <sup>vii</sup>	74.30 (9)
O1 <sup>iii</sup> —Mg1—O4 <sup>iv</sup>	94.61 (10)	O5 <sup>x</sup> —Ca2—O4 <sup>vii</sup>	105.70 (9)
O1 <sup>i</sup> —Mg1—O4 <sup>iv</sup>	111.02 (10)	O5—Ca2—O4 <sup>xi</sup>	105.70 (9)
O3 <sup>ii</sup> —Mg1—O4 <sup>v</sup>	87.51 (9)	O5 <sup>x</sup> —Ca2—O4 <sup>xi</sup>	74.30 (9)
O3—Mg1—O4 <sup>v</sup>	159.81 (11)	O5—Ca2—O4 <sup>xii</sup>	103.17 (9)
O1 <sup>iii</sup> —Mg1—O4 <sup>v</sup>	111.02 (10)	O5 <sup>x</sup> —Ca2—O4 <sup>xii</sup>	76.83 (9)
O1 <sup>i</sup> —Mg1—O4 <sup>v</sup>	94.61 (10)	O4 <sup>vii</sup> —Ca2—O4 <sup>xii</sup>	62.31 (10)
O4 <sup>iv</sup> —Mg1—O4 <sup>v</sup>	73.28 (14)	O4 <sup>xi</sup> —Ca2—O4 <sup>xii</sup>	117.69 (10)
O5—Mg2—O3 <sup>vi</sup>	108.84 (12)	O5—Ca2—O4 <sup>vi</sup>	76.83 (9)
O5—Mg2—O6 <sup>vii</sup>	92.76 (11)	O5 <sup>x</sup> —Ca2—O4 <sup>vi</sup>	103.17 (9)
O3 <sup>vi</sup> —Mg2—O6 <sup>vii</sup>	86.82 (11)	O4 <sup>vii</sup> —Ca2—O4 <sup>vi</sup>	117.69 (10)
O5—Mg2—O2 <sup>v</sup>	90.41 (11)	O4 <sup>xi</sup> —Ca2—O4 <sup>vi</sup>	62.31 (10)
O6 <sup>vii</sup> —Mg2—O2 <sup>v</sup>	101.79 (11)	O5—Ca2—O5 <sup>i</sup>	56.66 (10)
O3 <sup>vi</sup> —Mg2—O1 <sup>v</sup>	77.62 (10)	O4 <sup>vii</sup> —Ca2—O5 <sup>i</sup>	91.59 (8)
O6 <sup>vii</sup> —Mg2—O1 <sup>v</sup>	95.10 (11)	O4 <sup>xi</sup> —Ca2—O5 <sup>i</sup>	88.41 (8)
O2 <sup>v</sup> —Mg2—O1 <sup>v</sup>	82.14 (10)	O4 <sup>xii</sup> —Ca2—O5 <sup>i</sup>	64.46 (7)
O5—Mg2—O2 <sup>i</sup>	82.74 (10)	O4 <sup>vi</sup> —Ca2—O5 <sup>i</sup>	115.54 (7)
O3 <sup>vi</sup> —Mg2—O2 <sup>i</sup>	90.36 (10)	O5 <sup>x</sup> —Ca2—O5 <sup>xiii</sup>	56.66 (10)
O2 <sup>v</sup> —Mg2—O2 <sup>i</sup>	82.81 (10)	O4 <sup>vii</sup> —Ca2—O5 <sup>xiii</sup>	88.41 (8)
O1 <sup>v</sup> —Mg2—O2 <sup>i</sup>	89.86 (10)	O4 <sup>xi</sup> —Ca2—O5 <sup>xiii</sup>	91.59 (8)

## supplementary materials

O6—Na1—O6 <sup>viii</sup>	86.76 (12)	O4 <sup>xii</sup> —Ca2—O5 <sup>xiii</sup>	115.54 (7)
O6 <sup>ii</sup> —Na1—O6 <sup>viii</sup>	92.89 (13)	O4 <sup>vi</sup> —Ca2—O5 <sup>xiii</sup>	64.46 (7)
O6—Na1—O6 <sup>ix</sup>	92.89 (13)	O5—Na2—O4 <sup>vii</sup>	74.30 (9)
O6 <sup>ii</sup> —Na1—O6 <sup>ix</sup>	86.76 (12)	O5 <sup>x</sup> —Na2—O4 <sup>vii</sup>	105.70 (9)
O6—Na1—O3	59.6 (5)	O5—Na2—O4 <sup>xi</sup>	105.70 (9)
O6 <sup>ii</sup> —Na1—O3	116.0 (11)	O5 <sup>x</sup> —Na2—O4 <sup>xi</sup>	74.30 (9)
O6 <sup>viii</sup> —Na1—O3	63.1 (5)	O5—Na2—O4 <sup>xii</sup>	103.17 (9)
O6 <sup>ix</sup> —Na1—O3	109.6 (10)	O5 <sup>x</sup> —Na2—O4 <sup>xii</sup>	76.83 (9)
O6—Na1—O3 <sup>ii</sup>	116.0 (11)	O4 <sup>vii</sup> —Na2—O4 <sup>xii</sup>	62.31 (10)
O6 <sup>viii</sup> —Na1—O3 <sup>ii</sup>	109.6 (10)	O4 <sup>xi</sup> —Na2—O4 <sup>xii</sup>	117.69 (10)
O6 <sup>ix</sup> —Na1—O3 <sup>ii</sup>	63.1 (5)	O5—Na2—O4 <sup>vi</sup>	76.83 (9)
O3—Na1—O3 <sup>ii</sup>	73.7 (8)	O5 <sup>x</sup> —Na2—O4 <sup>vi</sup>	103.17 (9)
O6—Na1—O1 <sup>ix</sup>	116.3 (11)	O4 <sup>vii</sup> —Na2—O4 <sup>vi</sup>	117.69 (10)
O6 <sup>ii</sup> —Na1—O1 <sup>ix</sup>	68.4 (5)	O4 <sup>xi</sup> —Na2—O4 <sup>vi</sup>	62.31 (10)
O6 <sup>viii</sup> —Na1—O1 <sup>ix</sup>	81.2 (6)	O4 <sup>vii</sup> —Na2—O5 <sup>i</sup>	91.59 (8)
O6 <sup>ix</sup> —Na1—O1 <sup>ix</sup>	106.4 (9)	O4 <sup>xi</sup> —Na2—O5 <sup>i</sup>	88.41 (8)
O6—Na1—O1 <sup>viii</sup>	68.4 (5)	O4 <sup>xii</sup> —Na2—O5 <sup>i</sup>	64.46 (7)
O6 <sup>ii</sup> —Na1—O1 <sup>viii</sup>	116.3 (11)	O4 <sup>vi</sup> —Na2—O5 <sup>i</sup>	115.54 (7)
O6 <sup>viii</sup> —Na1—O1 <sup>viii</sup>	106.4 (9)	O4 <sup>vii</sup> —Na2—O5 <sup>xiii</sup>	88.41 (8)
O6 <sup>ix</sup> —Na1—O1 <sup>viii</sup>	81.2 (6)	O4 <sup>xi</sup> —Na2—O5 <sup>xiii</sup>	91.59 (8)
O6—Ca1—O6 <sup>viii</sup>	86.1 (2)	O4 <sup>xii</sup> —Na2—O5 <sup>xiii</sup>	115.54 (7)
O6 <sup>ii</sup> —Ca1—O6 <sup>viii</sup>	92.2 (3)	O4 <sup>vi</sup> —Na2—O5 <sup>xiii</sup>	64.46 (7)

Symmetry codes: (i)  $-x+1, y, -z+1/2$ ; (ii)  $-x+1, y, -z+3/2$ ; (iii)  $x, y, z+1$ ; (iv)  $-x+1/2, -y+1/2, -z+1$ ; (v)  $x+1/2, -y+1/2, z+1/2$ ; (vi)  $x+1/2, -y+1/2, z-1/2$ ; (vii)  $x+1/2, y-1/2, z$ ; (viii)  $x, -y+1, z+1/2$ ; (ix)  $-x+1, -y+1, -z+1$ ; (x)  $-x+1, -y, -z$ ; (xi)  $-x+1/2, -y+1/2, -z$ ; (xii)  $-x+1/2, y-1/2, -z+1/2$ ; (xiii)  $x, -y, z-1/2$ .



Fig. 1

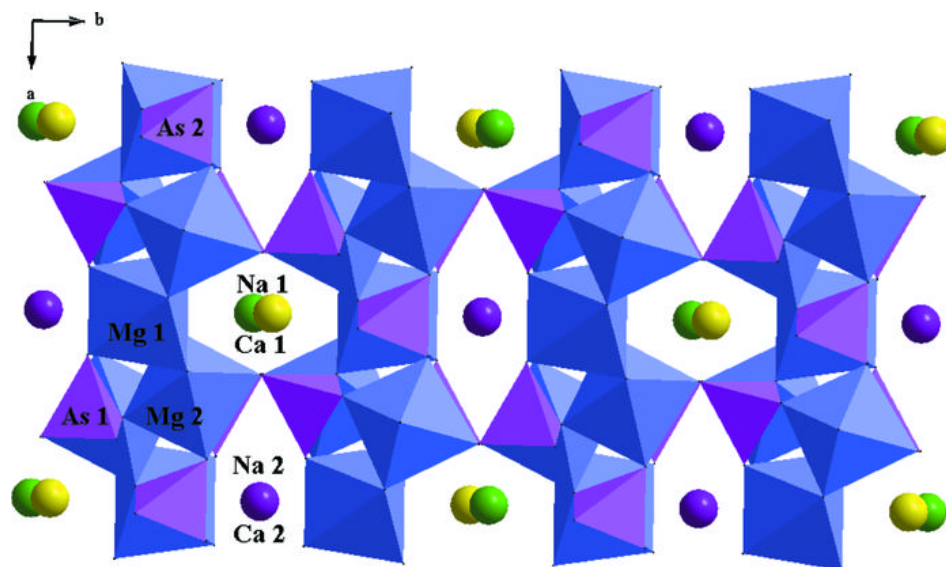


Fig. 2

