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A new sodium dimangnesium trivanadate, $NaMg_2V_3O_{10}$

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Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Mg–O) = 0.003 Å; R factor = 0.033; wR factor = 0.096; data-to-parameter ratio = 11.7.

A single crystal of $NaMg_2V_3O_{10}$ has been prepared by solid-state reaction at 1173 K. The $[Mg_2(V_3O_{10})]^-$ anions are built up from edge-sharing MgO_6 octahedra to form $[Mg_4O_{18}]$ units, which are linked to each other by trivanadate groups (V_3O_{10}). The Na^+ ions are located in the tunnel space.

Related literature

For related literature, see: Barbier (1988); Brown & Altermatt (1985); Gopal & Calvo (1974); Krishnamachari & Calvo (1971); Mitiaev *et al.* (2004); Murashova *et al.* (1988*a*, 1988*b*); Ng & Calvo (1972); Saux & Galy (1973).

Experimental

Crystal data

$NaMg_2V_3O_{10}$
M_r = 384.42
Triclinic, $P\overline{1}$
a = 6.7369 (1) Å
b = 6.7553 (1) Å
c = 9.6222 (1) Å
α = 104.325 (1)°
β = 100.604 (1)°
γ = 101.696 (1)°
V = 402.63 (1) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.66 mm^{-1}
T = 293 (2) K
0.4 × 0.07 × 0.03 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.871, T_{max} = 0.965
(expected range = 0.809–0.896)
3118 measured reflections
1712 independent reflections
1415 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
2 standard reflections
frequency: 120 min
intensity decay: 0.4%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.095
S = 1.06
1712 reflections
146 parameters
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −1.18 e Å^{-3}

Table 1
Selected bond lengths (Å).

V1—O4	1.672 (3)	V2—O7	1.717 (3)
V1—O6	1.688 (3)	V2—O5	1.848 (3)
V1—O2	1.704 (3)	V3—O8	1.642 (3)
V1—O1	1.806 (3)	V3—O3	1.655 (3)
V2—O9	1.643 (3)	V3—O1^{i}	1.757 (3)
V2—O10	1.694 (3)	V3—O5^{ii}	1.827 (3)

Symmetry codes: (i) $-x, -y, -z+1$; (ii) $-x, -y-1, -z$.

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: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2067).

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supplementary materials

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A new sodium dimangnesium trivanadate, $NaMg_2V_3O_{10}$

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Comment

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. In the system $MgO–V_2O_5$, a small number of compounds have been structurally characterized now, namely, $Mg_2V_2O_7$ (Gopal & Calvo, 1974), MgV_2O_6 (Ng & Calvo, 1972), $Mg_3(VO_4)_2$ (Krishnamachari & Calvo, 1971) and MgV_3O_8 (Saux & Galy, 1973). The same is true for the inclusion of alkali elements into this system, to our knowledge, only the structure of $NaMg_4(VO_4)_3$ (Murashova *et al.*, 1988*a*), $LiMg(VO_4)$ (Barbier, 1988), $K_2MgV_2O_7$ (Murashova *et al.*, 1988*b*) and $Na_6Mg_2(V_4O_{15})$(Mitiaev *et al.*, 2004) have been determined. Extending our investigation a new magnesium trivanadate, $NaMg_2V_3O_{10}$ has been prepared by a conventional solid-state reaction and characterized by single-crystal X-ray diffraction. The structure of $NaMg_2V_3O_{10}$ consists of MgO_6 octahedra and VO_4 tetrahedral sharing corners and edges to form a three-dimensional framework. The Na^+ are located in the tunnels space. A projection of the structure, showing the displacement ellipsoids, is presented in Fig 1. The Mg_2 $(V_3O_{10})]^-$ anions are built up from edge sharing MgO_6 octahedra to form $[Mg_4O_{18}]$ units, which are linked to each other by trivanadate groups (V_3O_{10}). The Mg_4O_{18} basal unit is built up by the edge linkages of four MgO_6 octahedra, Such a unit is formed by two kind of divalent-metal cations, one labeled as Mg1 share edge with another labelled Mg2 forming Mg_2O_{10} dimers, repetition of the dimers ensured by centres of symmetry on the shared edge between two $Mg1O_6$ leads to the formation of Mg_4O_{10} unit. Each trivanadate is formed by three tetrahedra, $V1O_4$, $V2O_4$ and $V3O_4$, interconnected through the corners O1 and O5. The V1, V2 and V3 tetrahedron shares the eight remaining O-atom corners with five Mg_4O_{18} units forming ribbons running along the [011] direction (Fig. 2). The projection of the structure along the [001] show that the trivanadate groups and the MgO_6 polyhedra form six side tunnels running along [001] in which Na^+ cations are located (Fig3). The geometry of the VO_4 tetrahedra is close to that generally observed. Two groups of distances can be distinguished. The V—O bonds corresponding to the two V—O—V bridges of the V_3O_{10} groups are the largest one. Consequently, the two external tetrahedra V1 and V2 present one long V—O distance and three smaller ones. Whereas the cental V3 tetrahedron has two long and two shorter. The Mg atoms are surrounded by six O atoms and the sodium cations exhibit a sixfold coordination. The bond valence sums determined using the Brown & Altermatt (1985) formulation are in the agreement with the formal charges deduced from the chemical formula: 5.088, 5.020, 5.100 from V1 to V3 respectively; 0.858 for Na; 2,188, 1.960 for Mg1 and Mg2 respectively, and ranging from 1.928 to 2.197 for the oxygen atoms.

Experimental

The starting materials for synthesizing $NaMg_2V_3O_{10}$ were $NaVO_3$, V_2O_5 and $Mg(NO_3)_2·7H2O$. The stoichiometric mixture was heated in air, in a platinum crucible, after a progressive heating to 873 K, the mixture was heated at 1173 K, cooled

to 773 K at rate of 5 K.hr-1 and then to room temperature. The parallelepiped crystals obtained after washing with hot water were brown. Quantitative analysis of these crystals, by electron microscope probe, revealed that they contain sodium, magnesium and vanadium.

Figures

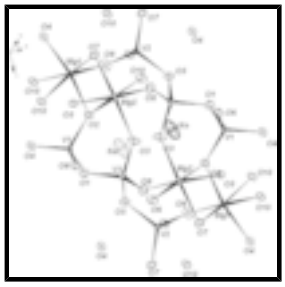

Fig. 1. A projection of $NaMg_2V_3O_{10}$, showing the displacement ellipsoids.

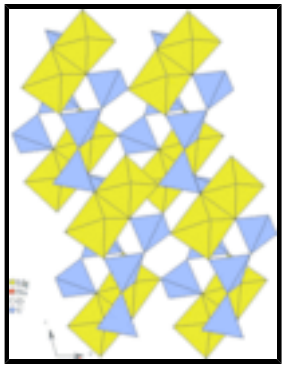

Fig. 2. View showing the ribbons running along the [011] direction.

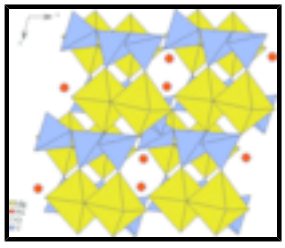

Fig. 3. Projection of the structure of $NaMg_2V_3O_{10}$ along [001] direction.

Sodium dimagnesium trivanadate

Crystal data

$NaMg_2V_3O_{10}$	$Z = 2$
$M_r = 384.42$	$F_{000} = 368$
Triclinic, $P\bar{1}$	$D_x = 3.171$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.7369$ (1) Å	Cell parameters from 25 reflections
$b = 6.7553$ (1) Å	$\theta = 1.5$–27.0º
$c = 9.6222$ (1) Å	$\mu = 3.66$ mm^{-1}
$\alpha = 104.325$ (1)º	$T = 293$ (2) K
$\beta = 100.604$ (1)º	Parallelepiped, brown
$\gamma = 101.696$ (1)º	0.4 × 0.07 × 0.03 mm

V = 402.625 (9) Å^3

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.049
Radiation source: fine-focus sealed tube	θ_{max} = 27.0º
Monochromator: graphite	θ_{min} = 2.3º
T = 293(2) K	h = −8→8
ω/2θ scans	k = −8→8
Absorption correction: ψ scan (North *et al.*, 1968)	l = −12→12
T_{min} = 0.871, T_{max} = 0.965	2 standard reflections
3118 measured reflections	every 120 min
1712 independent reflections	intensity decay: 0.4%
1415 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.4338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.033	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.095	$\Delta\rho_{max}$ = 0.73 e Å^{-3}
S = 1.06	$\Delta\rho_{min}$ = −1.18 e Å^{-3}
1712 reflections	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
146 parameters	Extinction coefficient: 0.003 (2)
Primary atom site location: structure-invariant direct methods	

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
V1	0.11192 (10)	0.04819 (10)	0.30906 (7)	0.00700 (18)
V2	0.23427 (10)	−0.33675 (10)	−0.04757 (7)	0.00795 (18)

V3	−0.22756 (10)	−0.42610 (10)	0.38667 (7)	0.00858 (19)
Mg1	−0.20718 (18)	−0.18407 (18)	−0.01815 (13)	0.0043 (3)
Mg2	−0.76019 (19)	−0.4331 (2)	0.29306 (14)	0.0098 (3)
Na	0.6408 (4)	0.0239 (3)	0.3640 (3)	0.0416 (6)
O1	0.0677 (4)	0.1930 (5)	0.4803 (3)	0.0156 (6)
O2	0.2277 (4)	0.2383 (4)	0.2402 (3)	0.0118 (6)
O3	−0.2797 (5)	−0.6006 (5)	0.4778 (3)	0.0172 (6)
O4	−0.1271 (4)	−0.0914 (5)	0.2063 (3)	0.0143 (6)
O5	0.0972 (4)	−0.4778 (4)	−0.2430 (3)	0.0118 (6)
O6	0.2690 (5)	−0.1090 (5)	0.3424 (3)	0.0163 (6)
O7	0.2151 (4)	−0.5009 (4)	0.0627 (3)	0.0130 (6)
O8	−0.4437 (4)	−0.3693 (5)	0.3187 (3)	0.0159 (6)
O9	0.4808 (5)	−0.2374 (5)	−0.0409 (3)	0.0188 (7)
O10	0.1292 (4)	−0.1322 (4)	0.0086 (3)	0.0116 (5)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0082 (3)	0.0063 (3)	0.0071 (3)	0.0016 (2)	0.0016 (2)	0.0034 (2)
V2	0.0112 (3)	0.0072 (3)	0.0066 (3)	0.0036 (2)	0.0021 (2)	0.0032 (2)
V3	0.0110 (3)	0.0083 (3)	0.0078 (3)	0.0031 (2)	0.0034 (2)	0.0033 (2)
Mg1	0.0063 (6)	0.0029 (5)	0.0037 (6)	0.0009 (4)	0.0012 (4)	0.0014 (4)
Mg2	0.0104 (7)	0.0096 (6)	0.0093 (6)	0.0022 (5)	0.0016 (5)	0.0033 (5)
Na	0.0371 (13)	0.0245 (11)	0.0622 (16)	0.0043 (9)	0.0221 (11)	0.0066 (11)
O1	0.0171 (15)	0.0156 (14)	0.0122 (14)	0.0003 (11)	0.0059 (11)	0.0020 (11)
O2	0.0143 (14)	0.0099 (13)	0.0114 (13)	0.0023 (10)	0.0029 (11)	0.0045 (11)
O3	0.0259 (16)	0.0128 (14)	0.0188 (15)	0.0092 (12)	0.0101 (13)	0.0087 (12)
O4	0.0123 (14)	0.0150 (14)	0.0136 (14)	−0.0011 (11)	0.0024 (11)	0.0053 (11)
O5	0.0140 (14)	0.0133 (14)	0.0101 (13)	0.0054 (11)	0.0050 (11)	0.0043 (11)
O6	0.0184 (15)	0.0149 (14)	0.0198 (15)	0.0075 (11)	0.0059 (12)	0.0092 (12)
O7	0.0150 (14)	0.0129 (14)	0.0124 (13)	0.0059 (11)	0.0014 (11)	0.0057 (11)
O8	0.0124 (14)	0.0175 (14)	0.0190 (15)	0.0051 (11)	0.0034 (11)	0.0069 (12)
O9	0.0173 (16)	0.0167 (15)	0.0241 (17)	0.0046 (12)	0.0073 (13)	0.0074 (13)
O10	0.0127 (13)	0.0097 (13)	0.0142 (13)	0.0038 (10)	0.0041 (11)	0.0054 (11)

Geometric parameters (Å, °)

V1—O4	1.672 (3)	Mg2—Mg1^{i}	3.1470 (17)
V1—O6	1.688 (3)	Mg2—V2^{i}	3.4044 (14)
V1—O2	1.704 (3)	Mg2—Na^{iv}	3.492 (3)
V1—O1	1.806 (3)	Mg2—Na^{ii}	3.575 (3)
V2—O9	1.643 (3)	Na—O3^{viii}	2.404 (4)
V2—O10	1.694 (3)	Na—O6	2.435 (4)
V2—O7	1.717 (3)	Na—O4^{ix}	2.477 (4)
V2—O5	1.848 (3)	Na—O8^{ix}	2.509 (4)
V2—Mg1	3.3760 (14)	Na—O6^{x}	2.665 (4)
V2—Mg2^{i}	3.4044 (14)	Na—O1^{ix}	2.771 (4)

V3—O8	1.642 (3)	Na—V1^{ix}	3.291 (2)
V3—O3	1.655 (3)	Na—V3^{ix}	3.380 (2)
V3—O1^{ii}	1.757 (3)	Na—V1^{x}	3.474 (3)
V3—O5^{iii}	1.827 (3)	Na—Mg2^{ix}	3.492 (3)
V3—Na^{iv}	3.380 (2)	Na—Na^{x}	3.543 (5)
V3—Na^{v}	3.582 (2)	O1—V3^{ii}	1.757 (3)
Mg1—O9^{iv}	2.020 (3)	O1—Na^{iv}	2.771 (4)
Mg1—O4	2.028 (3)	O2—Mg1^{vi}	2.049 (3)
Mg1—O2^{vi}	2.049 (3)	O2—Mg2^{viii}	2.132 (3)
Mg1—O7^{iii}	2.051 (3)	O3—Mg2^{vii}	2.120 (3)
Mg1—O10^{vi}	2.069 (3)	O3—Na^{v}	2.404 (4)
Mg1—O10	2.178 (3)	O4—Na^{iv}	2.477 (4)
Mg1—Mg2^{i}	3.1470 (17)	O5—V3^{iii}	1.827 (3)
Mg1—Mg1^{vi}	3.240 (2)	O5—Mg2^{i}	2.156 (3)
Mg1—V1^{vi}	3.2839 (13)	O6—Mg2^{ix}	2.082 (3)
Mg2—O8	2.043 (3)	O6—Na^{x}	2.665 (4)
Mg2—O6^{iv}	2.082 (3)	O7—Mg1^{iii}	2.051 (3)
Mg2—O7^{iv}	2.117 (3)	O7—Mg2^{ix}	2.117 (3)
Mg2—O3^{vii}	2.120 (3)	O8—Na^{iv}	2.509 (4)
Mg2—O2^{v}	2.132 (3)	O9—Mg1^{ix}	2.020 (3)
Mg2—O5^{i}	2.156 (3)	O10—Mg1^{vi}	2.069 (3)
O4—V1—O6	112.10 (15)	O10^{vi}—Mg1—O10	80.59 (12)
O4—V1—O2	113.54 (14)	O8—Mg2—O6^{iv}	88.16 (13)
O6—V1—O2	111.46 (14)	O8—Mg2—O7^{iv}	86.61 (12)
O4—V1—O1	104.42 (14)	O6^{iv}—Mg2—O7^{iv}	98.45 (12)
O6—V1—O1	110.07 (14)	O8—Mg2—O3^{vii}	90.45 (13)
O2—V1—O1	104.72 (14)	O6^{iv}—Mg2—O3^{vii}	88.10 (13)
O9—V2—O10	107.80 (14)	O7^{iv}—Mg2—O3^{vii}	172.73 (13)
O9—V2—O7	110.35 (15)	O8—Mg2—O2^{v}	88.64 (13)
O10—V2—O7	111.25 (14)	O6^{iv}—Mg2—O2^{v}	176.66 (13)
O9—V2—O5	107.91 (14)	O7^{iv}—Mg2—O2^{v}	80.40 (12)
O10—V2—O5	107.49 (13)	O3^{vii}—Mg2—O2^{v}	92.89 (12)
O7—V2—O5	111.87 (13)	O8—Mg2—O5^{i}	173.94 (13)
O8—V3—O3	109.72 (15)	O6^{iv}—Mg2—O5^{i}	95.28 (12)
O8—V3—O1^{ii}	106.39 (15)	O7^{iv}—Mg2—O5^{i}	87.95 (11)
O3—V3—O1^{ii}	106.04 (14)	O3^{vii}—Mg2—O5^{i}	94.64 (12)
O8—V3—O5^{iii}	111.97 (14)	O2^{v}—Mg2—O5^{i}	87.83 (11)
O3—V3—O5^{iii}	111.02 (14)	O3^{viii}—Na—O6	105.48 (13)
O1^{ii}—V3—O5^{iii}	111.43 (13)	O3^{viii}—Na—O4^{ix}	115.05 (13)
O9^{iv}—Mg1—O4	96.22 (13)	O6—Na—O4^{ix}	131.92 (14)

O9^{iv}—Mg1—O2^{vi}	94.40 (13)	O3^{viii}—Na—O8^{ix}	163.72 (16)
O4—Mg1—O2^{vi}	168.05 (13)	O6—Na—O8^{ix}	70.96 (12)
O9^{iv}—Mg1—O7^{iii}	93.58 (13)	O4^{ix}—Na—O8^{ix}	76.24 (12)
O4—Mg1—O7^{iii}	100.80 (12)	O3^{viii}—Na—O6^{x}	70.20 (12)
O2^{vi}—Mg1—O7^{iii}	83.95 (12)	O6—Na—O6^{x}	92.11 (12)
O9^{iv}—Mg1—O10^{vi}	100.55 (13)	O4^{ix}—Na—O6^{x}	124.66 (14)
O4—Mg1—O10^{vi}	88.02 (12)	O8^{ix}—Na—O6^{x}	93.84 (13)
O2^{vi}—Mg1—O10^{vi}	84.66 (12)	O3^{viii}—Na—O1^{ix}	69.27 (11)
O7^{iii}—Mg1—O10^{vi}	162.47 (13)	O6—Na—O1^{ix}	162.23 (15)
O9^{iv}—Mg1—O10	178.74 (12)	O4^{ix}—Na—O1^{ix}	62.91 (10)
O4—Mg1—O10	83.25 (12)	O8^{ix}—Na—O1^{ix}	109.07 (13)
O2^{vi}—Mg1—O10	86.24 (12)	O6^{x}—Na—O1^{ix}	70.12 (11)
O7^{iii}—Mg1—O10	85.40 (11)		

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

Fig. 1

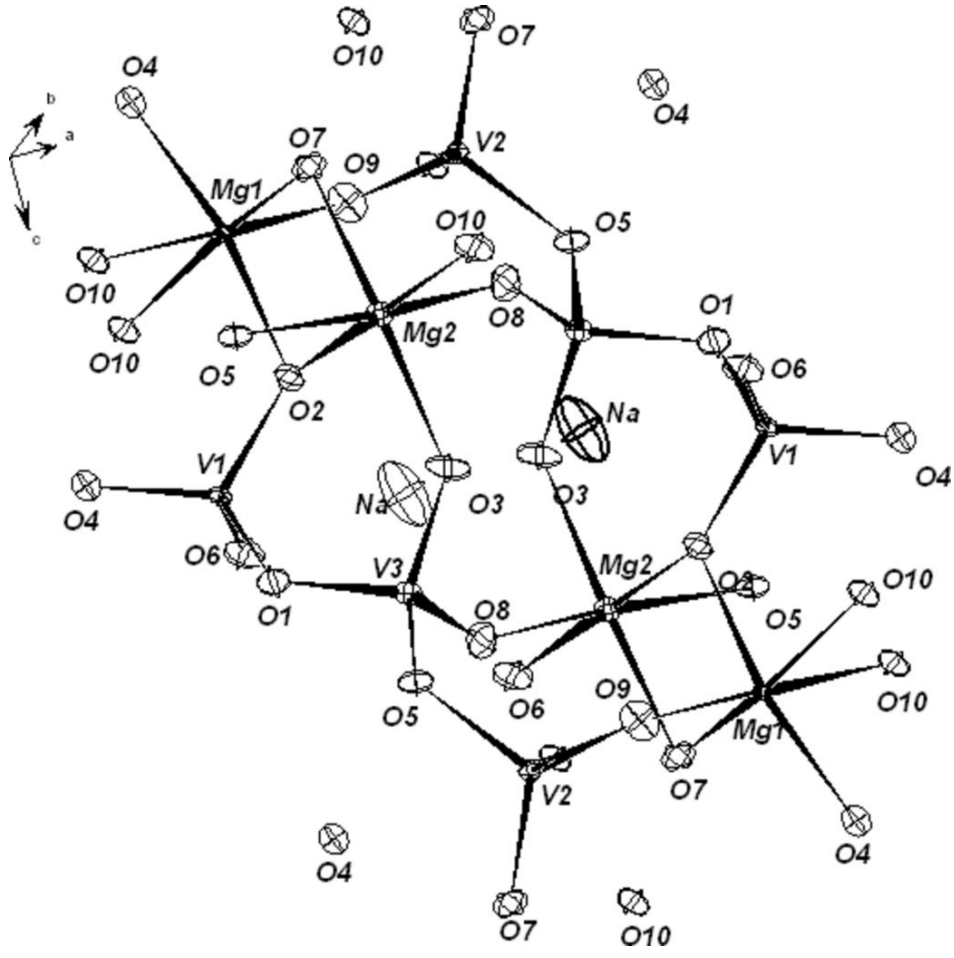
O10
O7
O4
O4
b
a
c
O7
O9
V2
Mg1
O10
O5
O10
O8
O1
O10
Mg2
O6
O5
O2
Na
V1
O4
V1
O4
Na
O3
O3
O6
V3
Mg2
O10
O1
O8
O5
O5
O6
O9
O10
Mg1
V2
O7
O4
O4
O7
O10

Fig. 2

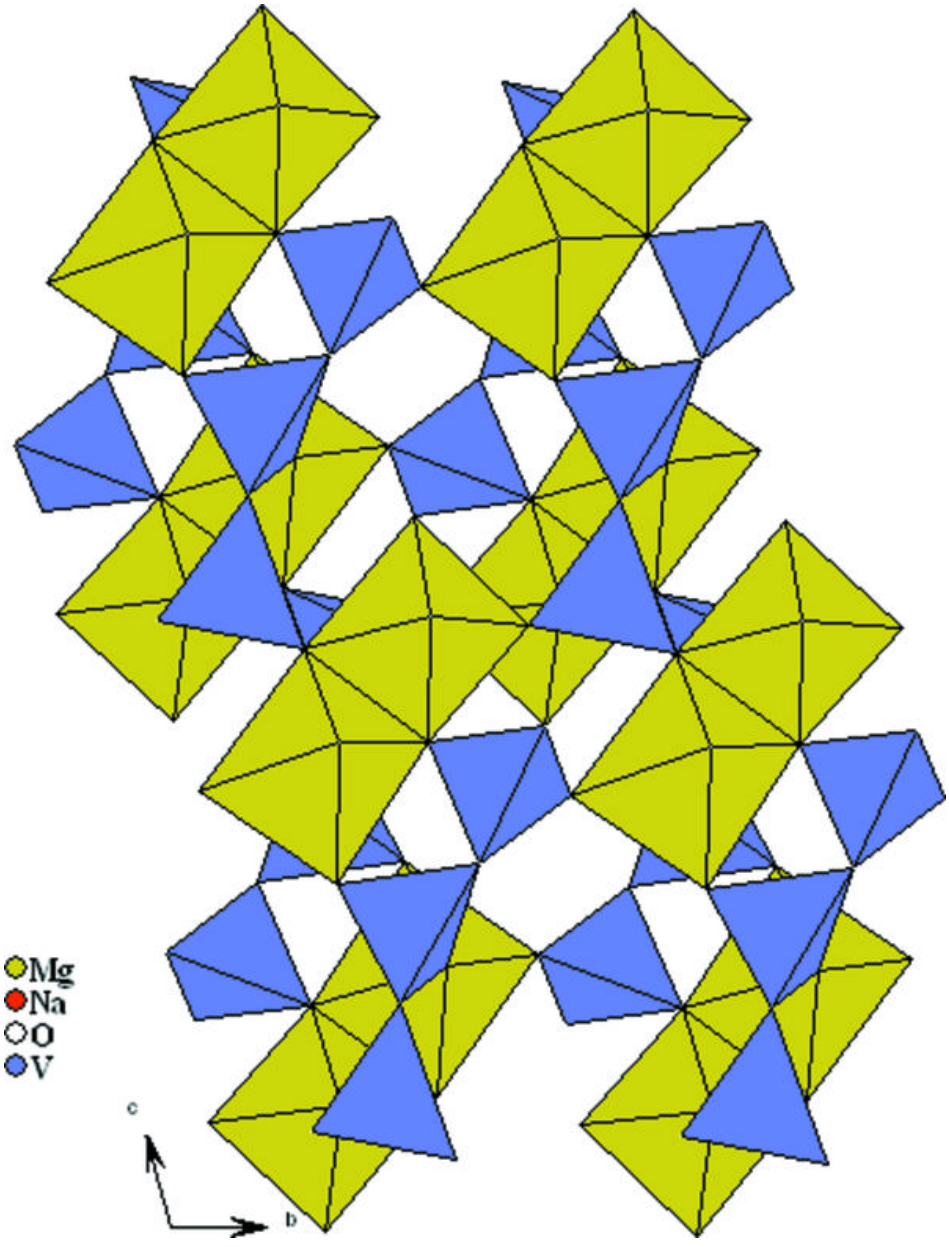

Fig. 3