

## Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub>, a rock-salt superstructure phase with a fully ordered cation arrangement

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The title quaternary oxide, trisodium dicalcium tantalum hexaoxide, is isostructural with Li<sub>3</sub>Ni<sub>2</sub>TaO<sub>6</sub>, a partially ordered rock-salt phase. The Na, Ca and Ta atoms occupy octahedral sites in an orderly manner and form a cation-ordered superstructure.

### Comment

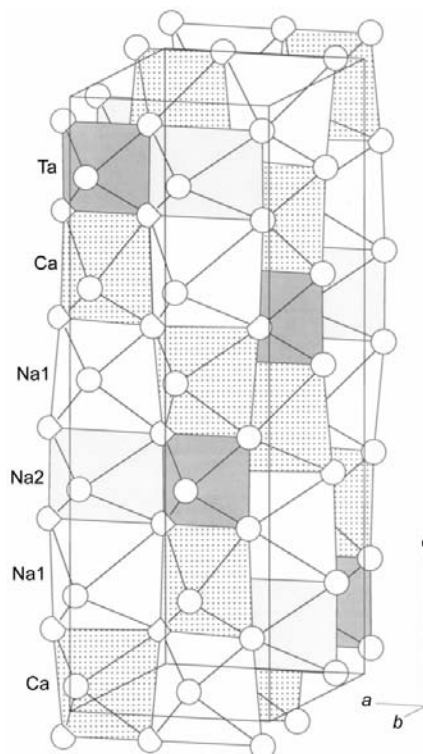
The crystal structures of a series of quaternary compounds containing lithium, *i.e.* Li<sub>3</sub>M<sub>2</sub>XO<sub>6</sub> (*M* = Mg, Co, Ni; *X* = Nb, Ta), were analyzed by X-ray and/or neutron powder diffraction (Fletcher *et al.*, 1994; Mather *et al.*, 1995). These compounds have a rock-salt superstructure with partial cation order. There are four fully occupied octahedral cation sites in the structure; three of these are occupied statistically by Li and *M* atoms with different occupancies. The title compound, Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub>, has the same crystal structure and is the first compound with a fully ordered cation arrangement (Table 1).

Bond-valence sums were calculated with the bond distances listed in Table 1, using the bond-valence parameters presented by Brese & O'Keeffe (1991). The values of 1.00 for the Na1 site, 1.03 for the Na2 site and 2.18 for the Ca site support the full occupation of the Na and Ca atoms at each octahedral site in Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub>. The bond-valence sums calculated with an Ni<sup>II</sup>–O parameter for the three partially ordered octahedral sites in Li<sub>3</sub>Ni<sub>2</sub>TaO<sub>6</sub>, for example, were in the range 1.6–1.8. These values suggest partial substitution of Li<sup>II</sup> for Ni<sup>II</sup>.

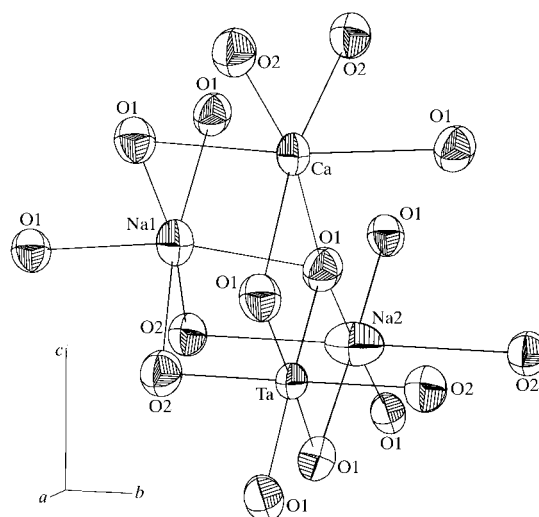
As shown in Fig. 1, the ordering sequence of cations along the *c* axis is –Ca–Na1–Na2–Na1–Ca–Ta–. The CaO<sub>6</sub> octahedron is elongated along the *c* axis (Fig. 2). The lengths of the six Ca–O bonds in the octahedron are in a narrow range [2.3142 (10)–2.353 (3) Å]. The oxygen octahedron of the Na2 site, adjacent to the Ta site along the *a* axis, is most distorted. The Na2–O distance along the *b* axis is 2.735 (4) Å, while the others are 2.366 (3) Å. The displacement ellipsoid of the Na2 atom is also elongated along the *b* axis. On the other hand, the Ta–O bond distances in the TaO<sub>6</sub> octahedron are

almost the same [2.012 (4)–2.027 (3) Å] and the O–Ta–O angles are close to the ideal value for a regular octahedron. The Ta–O bond distances are consistent with those observed in Li<sub>3</sub>Ni<sub>2</sub>TaO<sub>6</sub> [1.989 (2)–2.015 (2) Å; Mather *et al.*, 1995].

The polycrystalline sintered sample of Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub> was an insulator at room temperature and conductive at high temperatures. Evidence of electrode-polarization effects was seen in impedance plots above 700 K. The conductivity was 1.65 × 10<sup>−6</sup> S cm<sup>−1</sup> at 573 K and 7.54 × 10<sup>−5</sup> S cm<sup>−1</sup> at 670 K. The activation energy, *E<sub>a</sub>*, was 130 kJ mol<sup>−1</sup> in the tempera-



**Figure 1**  
The structure of Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub> showing the oxygen octahedra.



**Figure 2**  
The structure of the octahedral coordinations in Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub>, showing 99% probability displacement ellipsoids.

ture region from 570 to 670 K. Above 700 K,  $E_a$  changed to about 40 kJ mol<sup>-1</sup>. The conductivity was 8.13 × 10<sup>-4</sup> S cm<sup>-1</sup> at 773 K and 1.53 × 10<sup>-3</sup> S cm<sup>-1</sup> at 873 K. The two-probe dc (direct current) measurement with the Au ion-blocking electrodes at 673 K, also showed a polarization effect. These data suggested ionic conduction of Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub>. Ionic conduction was not detected for Li<sub>3</sub>Ni<sub>2</sub>TaO<sub>6</sub> with partial cation ordering (Fletcher *et al.*, 1994).

## Experimental

Na<sub>2</sub>CO<sub>3</sub> (extra pure grade, Wako Pure Chemical Industries Ltd), CaCO<sub>3</sub> (99.99% purity, Rare Metallic Co. Ltd) and Ta<sub>2</sub>O<sub>5</sub> (99.99% purity, Rare Metallic Co. Ltd) were weighed to give a 6:3:1 atomic ratio of Na:Ca:Ta. The powders were mixed in an agate mortar and then pressed into a pellet. The pellet was heated at 1273 K for 1 h in air on a Pt plate. After heating, the sample was cooled to 1073 K at a rate of 3 K h<sup>-1</sup>. Below this temperature, the sample was cooled in a furnace by shutting off the electric power. Grain growth was observed in the obtained pellet sample. A colourless transparent granule of Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub> with a size of about 100 μm was picked from the crushed sample and used for the single-crystal X-ray diffraction analysis. Semi-quantitative energy dispersive X-ray analysis (EDAX KeveX) was carried out for the granule on a scanning electron microscope (Hitachi X-60). The Na:Ca:Ta atomic ratio obtained was 3.0:1.9:0.7, which was close to the ideal ratio of 3:2:1. EDAX analysis did not detect any other impurity elements. For conductivity measurements, a sintered polycrystalline pellet of Na<sub>3</sub>Ca<sub>2</sub>TaO<sub>6</sub> was prepared at 1137 K over a period of 12 h from a mixture of starting materials with the stoichiometric composition. The electric impedance at ambient temperature was sensitive to moisture in air. Thus, the measurements were made under an argon atmosphere with Au electrodes, using an impedance analyzer (HP 4194-A).

### Crystal data

Na <sub>3</sub> Ca <sub>2</sub> TaO <sub>6</sub>	Mo Kα radiation
$M_r = 426.08$	Cell parameters from 1501 reflections
Orthorhombic, <i>Fddd</i>	$\theta = 3.89\text{--}27.46^\circ$
$a = 6.5948$ (17) Å	$\mu = 19.730$ mm <sup>-1</sup>
$b = 9.493$ (3) Å	$T = 298$ (2) K
$c = 19.640$ (5) Å	Granule, colourless
$V = 1229.5$ (6) Å <sup>3</sup>	0.10 × 0.09 × 0.05 mm
$Z = 8$	
$D_x = 4.604$ Mg m <sup>-3</sup>	

### Data collection

CCD area-detector diffractometer	305 reflections with $I > 2\sigma(I)$
$\varphi$ and $\omega$ scans	$R_{\text{int}} = 0.024$
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)	$\theta_{\text{max}} = 27.46^\circ$
$T_{\text{min}} = 0.197$ , $T_{\text{max}} = 0.295$	$h = -8 \rightarrow 8$
1891 measured reflections	$k = -12 \rightarrow 6$
361 independent reflections	$l = -24 \rightarrow 25$
	Intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0195P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.015$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.035$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.130$	$\Delta\rho_{\text{max}} = 0.93$ e Å <sup>-3</sup>
361 reflections	$\Delta\rho_{\text{min}} = -1.51$ e Å <sup>-3</sup>
32 parameters	

**Table 1**

Selected geometric parameters (Å, °).

Na1—O2 <sup>i</sup>	2.3986 (16)	Ca—O2 <sup>ii</sup>	2.3142 (10)
Na1—O2 <sup>ii</sup>	2.3986 (16)	Ca—O2 <sup>i</sup>	2.3142 (10)
Na1—O1 <sup>iii</sup>	2.433 (3)	Ca—O1 <sup>xi</sup>	2.353 (3)
Na1—O1 <sup>iv</sup>	2.433 (3)	Ca—O1 <sup>xiii</sup>	2.353 (3)
Na1—O1 <sup>v</sup>	2.573 (3)	Ca—O1 <sup>xiii</sup>	2.361 (3)
Na1—O1 <sup>vi</sup>	2.573 (3)	Ca—O1 <sup>xiv</sup>	2.361 (3)
Na2—O1 <sup>vii</sup>	2.366 (3)	Ta—O2 <sup>xv</sup>	2.012 (4)
Na2—O1 <sup>vi</sup>	2.366 (3)	Ta—O2	2.012 (4)
Na2—O1 <sup>viii</sup>	2.366 (3)	Ta—O1 <sup>xv</sup>	2.027 (3)
Na2—O1 <sup>v</sup>	2.366 (3)	Ta—O1 <sup>xiv</sup>	2.027 (3)
Na2—O2 <sup>ix</sup>	2.735 (4)	Ta—O1 <sup>xiii</sup>	2.027 (3)
Na2—O2 <sup>x</sup>	2.735 (4)	Ta—O1	2.027 (3)
O2 <sup>i</sup> —Na1—O2 <sup>ii</sup>	89.45 (8)	O2 <sup>ii</sup> —Ca—O2 <sup>i</sup>	93.66 (5)
O2 <sup>i</sup> —Na1—O1 <sup>iii</sup>	97.86 (12)	O2 <sup>ii</sup> —Ca—O1 <sup>xi</sup>	100.53 (12)
O2 <sup>ii</sup> —Na1—O1 <sup>iii</sup>	73.18 (13)	O2 <sup>i</sup> —Ca—O1 <sup>xi</sup>	74.67 (13)
O1 <sup>iii</sup> —Na1—O1 <sup>iv</sup>	167.67 (16)	O1 <sup>xi</sup> —Ca—O1 <sup>xiii</sup>	173.16 (14)
O2 <sup>i</sup> —Na1—O1 <sup>v</sup>	171.67 (11)	O2 <sup>ii</sup> —Ca—O1 <sup>xiii</sup>	167.83 (10)
O2 <sup>ii</sup> —Na1—O1 <sup>v</sup>	89.08 (6)	O2 <sup>i</sup> —Ca—O1 <sup>xiii</sup>	96.56 (7)
O1 <sup>iii</sup> —Na1—O1 <sup>v</sup>	89.57 (10)	O1 <sup>xi</sup> —Ca—O1 <sup>xiii</sup>	88.56 (10)
O1 <sup>iv</sup> —Na1—O1 <sup>v</sup>	98.90 (9)	O1 <sup>xiii</sup> —Ca—O1 <sup>xiii</sup>	96.90 (11)
O1 <sup>v</sup> —Na1—O1 <sup>vi</sup>	93.53 (14)	O1 <sup>xiii</sup> —Ca—O1 <sup>xiv</sup>	74.14 (14)
O1 <sup>vii</sup> —Na2—O1 <sup>vi</sup>	178.30 (15)	O2 <sup>xv</sup> —Ta—O2	180
O1 <sup>viii</sup> —Na2—O1 <sup>viii</sup>	104.84 (14)	O2 <sup>xv</sup> —Ta—O1 <sup>xv</sup>	89.01 (9)
O1 <sup>vi</sup> —Na2—O1 <sup>viii</sup>	75.19 (14)	O2—Ta—O1 <sup>xv</sup>	90.99 (9)
O1 <sup>vii</sup> —Na2—O2 <sup>ix</sup>	89.15 (7)	O1 <sup>xv</sup> —Ta—O1 <sup>xiv</sup>	178.01 (17)
O1 <sup>viii</sup> —Na2—O2 <sup>ix</sup>	90.85 (7)	O1 <sup>xv</sup> —Ta—O1 <sup>xiii</sup>	90.82 (15)
O2 <sup>ix</sup> —Na2—O2 <sup>x</sup>	180	O1 <sup>xiv</sup> —Ta—O1 <sup>xiii</sup>	89.21 (15)

Symmetry codes: (i)  $-x, \frac{1}{2} - y, \frac{1}{2} - z$ ; (ii)  $\frac{1}{4} + x, y - \frac{1}{4}, \frac{1}{2} - z$ ; (iii)  $\frac{1}{2} - x, -y, \frac{1}{2} - z$ ; (iv)  $x - \frac{1}{4}, \frac{1}{4} + y, \frac{1}{2} - z$ ; (v)  $\frac{3}{4} - x, \frac{1}{4} - y, \frac{1}{2} + z$ ; (vi)  $x - \frac{1}{2}, y, \frac{1}{2} + z$ ; (vii)  $\frac{3}{4} - x, y, \frac{3}{4} - z$ ; (viii)  $x - \frac{1}{2}, \frac{1}{4} - y, \frac{3}{4} - z$ ; (ix)  $\frac{1}{4} - x, \frac{3}{4} - y, \frac{1}{2} + z$ ; (x)  $x, y - \frac{1}{4}, \frac{1}{2} + z$ ; (xi)  $x - \frac{1}{4}, \frac{1}{2} - y, \frac{1}{4} + z$ ; (xii)  $\frac{1}{2} - x, y - \frac{1}{4}, \frac{1}{4} + z$ ; (xiii)  $\frac{1}{4} - x, y, \frac{1}{4} - z$ ; (xiv)  $x, \frac{1}{4} - y, \frac{1}{4} - z$ ; (xv)  $\frac{1}{4} - x, \frac{1}{4} - y, z$ .

Data collection: *SMART* and *SAINT* (Bruker, 1997); cell refinement: *SMART* and *SAINT*; data reduction: *EXPREP* (Bruker, 1997); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1102). Services for accessing these data are described at the back of the journal.

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