inorganic compounds

A ramsayite-type oxide, $Ca_2Sn_2Al_2O_9$

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The title compound, dicalcium nonaoxidodistannate(IV)-dialuminate, is the second example which crystallizes in the isotypic structure of a pyroxene silicate, $Na_2Ti_2Si_2O_9$ (ramsayite). $^1_\infty[Sn_2O_8]$ chains and pyroxene-type $^1_\infty[Al_2O_6]$ chains are formed along the b axis by sharing O atoms. The Ca atoms are situated in the resulting channels and exhibit a coordination number of 7.

Related literature

For the structure of ramsayite, $Na_2Ti_2Si_2O_9$, see: Sundberg *et al.* (1987). For the synthesis of $Ca_8Sn_7Al_{10}O_{37}$, see: Barbanyagre & Kotlyarov (2001). For the structure of a related stannate silicate, $Ca_2SnSi_2O_9$, see: Blasse *et al.* (1995). For bond-valence parameters, see: Brese & O'Keeffe (1991). For the $CaO–Al_2O_3$ system, see: Jerebtsov & Mikhailov (2001). For the Inorganic Crystal Structure Database, see: ICSD (2009).

Experimental

Crystal data

$Ca_2Sn_2Al_2O_9$	V = 735.18 (18) Å^3
M_r = 515.50	Z = 4
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
a = 8.9866 (6) Å	μ = 8.46 mm^{-1}
b = 5.4894 (11) Å	T = 293 K
c = 14.9030 (18) Å	$0.17 \times 0.15 \times 0.07$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	Absorption correction: numerical (*NUMABS*; Higashi, 1999) T_{min} = 0.427, T_{max} = 0.717
	6534 measured reflections

845 independent reflections	R_{int} = 0.051
788 reflections with $I > 2\sigma(I)$	

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018	69 parameters
$wR(F^2)$ = 0.043	$\Delta\rho_{max}$ = 0.72 e Å^{-3}
S = 1.08	$\Delta\rho_{min}$ = −0.72 e Å^{-3}
845 reflections	

Table 1
Selected bond lengths (Å).

Ca1—O3[i]	2.303 (2)	Al1—O2	1.763 (2)
Ca1—O2	2.391 (2)	Al1—O1[iv]	1.777 (3)
Ca1—O1[ii]	2.404 (2)	Sn1—O4[v]	2.002 (2)
Ca1—O4[i]	2.412 (2)	Sn1—O3	2.032 (2)
Ca1—O2[i]	2.463 (2)	Sn1—O3[i]	2.053 (2)
Ca1—O5	2.486 (2)	Sn1—O5[vi]	2.0682 (13)
Ca1—O3[iii]	2.624 (2)	Sn1—O1[i]	2.106 (2)
Al1—O2[i]	1.735 (2)	Sn1—O1	2.207 (2)
Al1—O4	1.745 (2)		

Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, z$; (ii) $-x, y, -z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $-x+1, y, -z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2005); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *VESTA* (Momma & Izumi, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2147).

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supplementary materials

A ramsayite-type oxide, Ca$_2$Sn$_2$Al$_2$O$_9$

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Comment

Barbanyagre and Kotlyarov (2001) reported a quaternary oxide Ca$_8$Al$_{10}$Sn$_7$O$_{37}$ with a powder X-ray diffraction (PXRD) pattern, but they did not clarify the crystal structure. We have prepared single crystals of Ca$_2$Sn$_2$Al$_2$O$_9$ by slow cooling of a Ca—Al—Sn—O melt. The PXRD pattern of Ca$_8$Al$_{10}$Sn$_7$O$_{37}$ was similar to that calculated with the crystal structure parameters of Ca$_2$Sn$_2$Al$_2$O$_9$ analyzed by the present study.

Ca$_2$Sn$_2$Al$_2$O$_9$ is isostructural with ramsayite (lorenzenite) Na$_2$Ti$_2$Si$_2$O$_9$ (*a* = 8.7128 (10), *b* = 5.2327 (5), *c* = 14.487 (2) Å) (Sundberg, *et al.*, 1987). Other compounds crystallizing in the isotypic structure were not found in the Inorganic Crystal Structure Database (ICSD, 2009).

The selected bond distances in Ca$_2$Sn$_2$Al$_2$O$_9$ are summarized in Table 1. The coordination environments of Ca, Sn and Al are drawn with displacement ellipsoids in Fig. 1. The Sn site is in a distorted oxygen octhahedron with the Sn—O distances varying from 2.002 (2) to 2.207 (2) Å, (average 2.08 (8) Å). The bond valence sum (BVS) calculated for Sn atoms with the bond valence parameter of *R* (Sn—O) = 1.905 Å (Brese & O'Keeffe, 1991) was 3.815, a little smaller than the IV valence of Sn. These Sn—O bond lengths and the BVS are consistent with those reported for Ca$_3$SnSi$_2$O$_9$ (2.007–2.134 Å, avg. 2.08 (4) Å, BVS 3.803) (Blasse *et al.*, 1995).

Each SnO$_6$ octahedron shares O1—O3 edges with both adjacent sides of SnO$_6$ octahedra and a one-dimensional chain $_\infty^1$[Sn$_2$O$_8$] is formed along the *b* axis. Al atoms are tetrahedrally coordinated by O atoms and the AlO$_4$ tetrahedra form pyroxene-type $_\infty^1$[Ali$_2$O$_6$] chains along the *b* axis by sharing O2. The Al—O bond lengths are from 1.735 to 1.777 (3) Å (avg. 1.755 (19) Å) and the BVS of 3.02 is consistent with trivalent of Al(III). The chains of $_\infty^1$[Ali$_2$O$_6$] and $_\infty^1$[Sn$_2$O$_8$] are bridged by sharing O4, and the $_\infty^1$[Sn$_2$O$_8$] chains are linked each other by sharing O5 on a two-fold axis, forming rectangular channels along the *b* axis (Fig. 2). Ca sites are situated in the channels and surrounded by 7 oxygen atoms with the distances from 2.303 (2) to 2.624 (2) Å. The BVS of Ca atoms is 2.01 and well agrees with the valence number of Ca(II).

A permittivity of 48 and a tanδ of 0.02 were measured at room temperature with an impedance analyzer (Solartron 1260 and 1296) for the polycrystalline sample which was mainly composed of Ca$_2$Sn$_2$Al$_2$O$_9$ with a small amount of CaSnO$_3$ which crystallized at the initial stage of solid state reaction.

Experimental

The starting materials used were CaCO$_3$ (Rare Metallic, 99.99% purity), SnO$_2$ (Rare Metallic, 99.99% purity) and Al$_2$O$_3$ (Rare Metallic, 99.99% purity). The powders were weighed, mixed in an agate mortar with a pestle, and pressed into pellets, which were placed on a platinum plate and heated in an electric furnace in air. Single crystals of Ca$_2$Sn$_2$Al$_2$O$_9$ were prepared from a starting mixture with an atomic ratio Ca: Sn: Al = 5:1:4. The pellet of the mixture was heated to 1823 K at a heating

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rate of 200 K/h, and then cooled to 1773 K at a cooling rate of 5 K/h. The single crystals were probably grown in a flux with a composition close to a $Ca_3Al_2O_6$—$CaAl_2O_4$ mixture which has the eutectic point of 1644 K (Jerebtsov & Mikhailov, 2001). The samples were then cooled in the furnace by shutting off the electric power. The obtained sample was crushed into fragments and colorless transparent single crystals of about 0.06–0.14 mm were picked up under an optical microscope. A polycrystalline sample was prepared by heating the pellets of the starting mixtures with stoichiometric metal ratios Ca:Sn:Al = 1:1:1 at around 1600 K for 24 h.

Refinement

The highest peak in the difference electron density map is 0.94 Å from Sn1 while the deepest hole is 1.08 Å from the same atom.
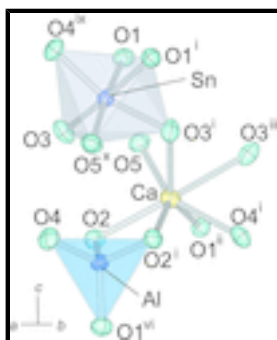
Figures

Fig. 1. O-atom coordination around Ca, Al, and Sn atoms in the structure of $Ca_2Sn_2Al_2O_9$. Displacement ellipsoids are drawn at 99% probability level. [Symmetry codes as in Table 1.]
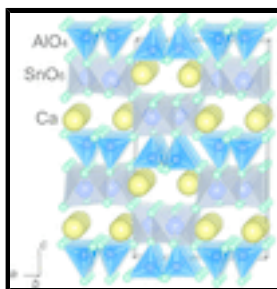
Fig. 2. Crystal structure of $Ca_2Sn_2Al_2O_9$ illustrated with distorted Sn-centered oxygen octahedra and Al-centered oxygen tetrahedra.

dicalcium nonaoxydistanate(IV) dialuminate

Crystal data

$Ca_2Sn_2Al_2O_9$	$F(000) = 952$
$M_r = 515.50$	$D_x = 4.657$ Mg m^{-3}
Orthorhombic, *Pbcn*	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Hall symbol: -P 2n 2ab	Cell parameters from 5414 reflections
$a = 8.9866$ (6) Å	$\theta = 3.6–27.8°$
$b = 5.4894$ (11) Å	$\mu = 8.46$ mm^{-1}
$c = 14.9030$ (18) Å	$T = 293$ K
$V = 735.18$ (18) Å^3	Platelet, colourless
$Z = 4$	$0.17 \times 0.15 \times 0.07$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	845 independent reflections
Radiation source: fine-focus sealed tube	788 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.051$
Detector resolution: 10.00 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.6°$
ω scans	$h = -11 \rightarrow 11$
Absorption correction: numerical (*NUMABS*; Higashi, 1999)	$k = -7 \rightarrow 7$
$T_{min} = 0.427$, $T_{max} = 0.717$	$l = -19 \rightarrow 19$
6534 measured reflections	

Refinement

Refinement on F^2	0 restraints
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.018$	Secondary atom site location: difference Fourier map
$wR(F^2) = 0.043$	$w = 1/[\sigma^2(F_o^2) + (0.002P)^2 + 2.2176P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
845 reflections	$\Delta\rho_{max} = 0.72$ e Å^{-3}
69 parameters	$\Delta\rho_{min} = -0.72$ e Å^{-3}

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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
Ca1	0.06714 (7)	0.36160 (11)	0.14603 (5)	0.00676 (14)
Al1	0.34369 (10)	0.31037 (18)	0.02817 (7)	0.0055 (2)
Sn1	0.34459 (2)	0.36611 (4)	0.333981 (15)	0.00525 (9)
O1	0.1618 (2)	0.1912 (4)	0.40897 (16)	0.0070 (5)
O2	0.2277 (2)	0.0795 (4)	0.07144 (15)	0.0071 (4)
O3	0.3314 (2)	0.0365 (4)	0.27250 (16)	0.0079 (5)
O4	0.5156 (2)	0.2310 (4)	0.07402 (16)	0.0078 (4)

O5	0.0000	0.0250 (6)	0.2500	0.0077 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0069 (3)	0.0071 (3)	0.0062 (3)	−0.0007 (2)	0.0006 (2)	−0.0003 (2)
Al1	0.0057 (5)	0.0058 (5)	0.0050 (5)	−0.0001 (3)	−0.0004 (3)	0.0001 (4)
Sn1	0.00529 (13)	0.00501 (14)	0.00544 (14)	0.00004 (7)	−0.00022 (7)	−0.00022 (8)
O1	0.0080 (11)	0.0067 (11)	0.0064 (12)	−0.0008 (8)	−0.0004 (8)	−0.0002 (9)
O2	0.0089 (11)	0.0054 (10)	0.0070 (11)	−0.0007 (8)	−0.0005 (9)	−0.0003 (9)
O3	0.0077 (11)	0.0064 (11)	0.0096 (13)	−0.0008 (8)	0.0026 (9)	−0.0019 (9)
O4	0.0059 (10)	0.0088 (11)	0.0087 (11)	−0.0003 (8)	−0.0024 (9)	−0.0011 (9)
O5	0.0086 (15)	0.0078 (15)	0.0066 (16)	0.000	−0.0014 (13)	0.000

Geometric parameters (Å, °)

Ca1—O3^i	2.303 (2)	Sn1—O1^i	2.106 (2)
Ca1—O2	2.391 (2)	Sn1—O1	2.207 (2)
Ca1—O1^{ii}	2.404 (2)	O1—Al1^{vii}	1.777 (3)
Ca1—O4^i	2.412 (2)	O1—Sn1^{viii}	2.106 (2)
Ca1—O2^i	2.463 (2)	O1—Ca1^{ii}	2.404 (2)
Ca1—O5	2.486 (2)	O2—Al1^{viii}	1.735 (2)
Ca1—O3^{iii}	2.624 (2)	O2—Ca1^{viii}	2.463 (2)
Al1—O2^i	1.735 (2)	O3—Sn1^{viii}	2.053 (2)
Al1—O4	1.745 (2)	O3—Ca1^{viii}	2.303 (2)
Al1—O2	1.763 (2)	O3—Ca1^{ix}	2.624 (2)
Al1—O1^{iv}	1.777 (3)	O4—Sn1^v	2.002 (2)
Sn1—O4^v	2.002 (2)	O4—Ca1^{viii}	2.412 (2)
Sn1—O3	2.032 (2)	O5—Sn1^x	2.0682 (13)
Sn1—O3^i	2.053 (2)	O5—Sn1^{viii}	2.0682 (13)
Sn1—O5^{vi}	2.0682 (13)	O5—Ca1^{ii}	2.486 (2)
O3^i—Ca1—O2	114.30 (8)	O3^i—Sn1—O1^i	80.21 (9)
O3^i—Ca1—O1^{ii}	141.26 (8)	O5^{vi}—Sn1—O1^i	88.98 (9)
O2—Ca1—O1^{ii}	96.08 (8)	O4^v—Sn1—O1	87.66 (9)
O3^i—Ca1—O4^i	97.80 (8)	O3—Sn1—O1	78.32 (9)
O2—Ca1—O4^i	121.59 (8)	O3^i—Sn1—O1	81.41 (9)
O1^{ii}—Ca1—O4^i	84.93 (8)	O5^{vi}—Sn1—O1	173.05 (6)
O3^i—Ca1—O2^i	82.57 (8)	O1^i—Sn1—O1	94.57 (9)
O2—Ca1—O2^i	69.69 (4)	Al1^{vii}—O1—Sn1^{viii}	121.70 (13)
O1^{ii}—Ca1—O2^i	132.50 (8)	Al1^{vii}—O1—Sn1	121.93 (11)
O4^i—Ca1—O2^i	67.76 (7)	Sn1^{viii}—O1—Sn1	96.90 (9)
O3^i—Ca1—O5	84.02 (7)	Al1^{vii}—O1—Ca1^{ii}	108.61 (10)
O2—Ca1—O5	87.41 (7)	Sn1^{viii}—O1—Ca1^{ii}	97.21 (9)

O1^{ii}—Ca1—O5	73.48 (6)	Sn1—O1—Ca1^{ii}	107.17 (10)
O4^{i}—Ca1—O5	145.85 (7)	Al1^{viii}—O2—Al1	134.02 (15)
O2^{i}—Ca1—O5	145.50 (6)	Al1^{viii}—O2—Ca1	120.07 (11)
O3^{i}—Ca1—O3^{iii}	77.78 (9)	Al1—O2—Ca1	93.51 (9)
O2—Ca1—O3^{iii}	159.97 (8)	Al1^{viii}—O2—Ca1^{viii}	91.78 (9)
O1^{ii}—Ca1—O3^{iii}	67.00 (8)	Al1—O2—Ca1^{viii}	94.11 (10)
O4^{i}—Ca1—O3^{iii}	69.47 (7)	Ca1—O2—Ca1^{viii}	123.82 (10)
O2^{i}—Ca1—O3^{iii}	129.46 (7)	Sn1—O3—Sn1^{viii}	104.43 (10)
O5—Ca1—O3^{iii}	77.73 (6)	Sn1—O3—Ca1^{viii}	135.82 (11)
O2^{i}—Al1—O4	113.24 (12)	Sn1^{viii}—O3—Ca1^{viii}	118.71 (10)
O2^{i}—Al1—O2	104.92 (9)	Sn1—O3—Ca1^{ix}	94.02 (9)
O4—Al1—O2	101.59 (11)	Sn1^{viii}—O3—Ca1^{ix}	104.41 (10)
O2^{i}—Al1—O1^{iv}	111.43 (12)	Ca1^{viii}—O3—Ca1^{ix}	84.64 (7)
O4—Al1—O1^{iv}	114.50 (11)	Al1—O4—Sn1^{v}	137.01 (13)
O2—Al1—O1^{iv}	110.23 (11)	Al1—O4—Ca1^{viii}	96.38 (10)
O4^{v}—Sn1—O3	90.89 (9)	Sn1^{v}—O4—Ca1^{viii}	101.55 (9)
O4^{v}—Sn1—O3^{i}	163.28 (9)	Sn1^{x}—O5—Sn1^{viii}	130.13 (15)
O3—Sn1—O3^{i}	99.18 (9)	Sn1^{x}—O5—Ca1^{ii}	121.78 (5)
O4^{v}—Sn1—O5^{vi}	98.44 (7)	Sn1^{viii}—O5—Ca1^{ii}	95.75 (4)
O3—Sn1—O5^{vi}	98.16 (9)	Sn1^{x}—O5—Ca1	95.75 (4)
O3^{i}—Sn1—O5^{vi}	93.33 (8)	Sn1^{viii}—O5—Ca1	121.78 (5)
O4^{v}—Sn1—O1^{i}	88.14 (9)	Ca1^{ii}—O5—Ca1	83.96 (10)
O3—Sn1—O1^{i}	172.86 (9)		

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

Fig. 1

Fig. 2