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$Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$, a quaternary oxide with mixed occupations of Ca/Y and Y/Sn

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A new quaternary oxide, calcium yttrium stannate, $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$, is isostructural with Mg_3TeO_6 (trigonal, $R\overline{3}$). The empirical formula can be expressed as $(Ca_{0.2667}Y_{0.7333})_6(Y_{0.4}Sn_{0.6})SnO_{12}$. The Ca/Y site has a distorted coordination octahedron of O atoms, with Ca/Y—O distances ranging from 2.227 (3) to 2.350 (3) Å, while the octahedra of O atoms that coordinate to the Sn and Y/Sn sites are nearly regular, with an Sn—O distance of 2.066 (2) Å and a Y/Sn—O distance of 2.147 (3) Å.

Comment

New quaternary compounds have recently been found in addition to the previously known compounds in the CaO–Y_2O_3–SiO_2 (Nagasawa *et al.*, 1998) and CaO–Y_2O_3–GeO_2 systems (Yamane *et al.*, 2006). Since no quaternary compound had been reported for the CaO–Y_2O_3–SnO_2 system, we have carried out a materials survey for this system. As a result, the new quaternary compound $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$ was prepared by solid-state reaction. The crystal structure of $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$ reveals that it has the same structure type as Mg_3TeO_6, in which Te atoms are located at the 3*a* and 3*b* special positions in the space group $R\overline{3}$, while the Mg and O atoms are at general (18*f*) positions (Newnham *et al.*, 1970; Schulz & Bayer, 1971).

In the starting model, Sn and Y atoms were placed statistically at the 3*a* and 3*b* sites and Ca and Y atoms at an 18*f* site. The occupancies at the Ca1/Y1, Sn1 and Y2/Sn2 sites were refined to values of 0.270 (3)/0.730 (3), 0.996 (3) and 0.404 (4)/0.596 (4), respectively, giving a Ca:Y:Sn molar ratio of 1:3:1. This ratio agrees with the initial molar ratio of metal elements in the mixture used in the synthesis. For the final refinement, the occupation parameters were fixed at values of 0.2667/0.7333, 1.0 and 0.40/0.60 for Ca1/Y1, Sn1 and Y2/Sn2. The structural formula of $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$ can be expressed as $(Ca_{0.2667}Y_{0.7333})_6(Y_{0.4}Sn_{0.6})SnO_{12}$.

Fig. 1 shows the O-atom coordination surrounding the Ca1/Y1 and Sn sites. The extended structure, illustrated by the Sn1- and Y2/Sn2-centered oxygen octahedra, is shown in Fig. 2. Table 1 lists selected interatomic distances and angles. The Sn1—O1 distance in the $Sn1(O1)_6$ octahedron is 2.066 (2) Å, which is in good agreement with the Sn—O distances (2.061–2.063 Å) reported for $CaSnO_3$ and $SrSnO_3$, which have the perovskite-type structure (Vegas *et al.*, 1986). The bond valence sum for atom Sn1, calculated with the bond valence parameter of Sn^{IV}—O^{II} (1.905 Å), is 3.848 (Brese & O'Keeffe, 1991). This value is close to the formal valence of Sn^{IV}. The Y2/Sn2—O2 distance in the $Y2/Sn2(O2)_6$ octahedron is 2.147 (3) Å. This value is longer than that in the $Sn1(O1)_6$ octahedron, consistent with the statistical occupation of Sn and Y atoms in the same site with an Sn:Y occupancy ratio of 0.6:0.4. The Ca1/Y1 site is surrounded by six O atoms in three

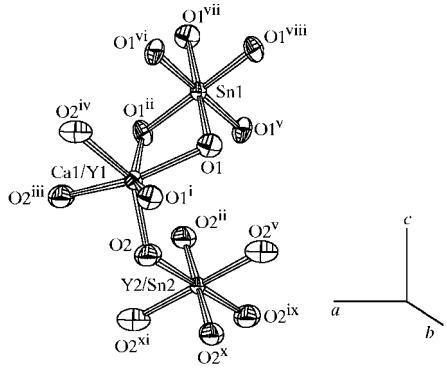

Figure 1
The arrangement of atomic positions in the structure of $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$, shown with 99% probability displacement ellipsoids. [Symmetry codes as in Table 1; additional codes: (vii) $-x, -y, -z+1$; (ix) $-x, -y, -z$; (xi) $y, -x+y, -z$.]

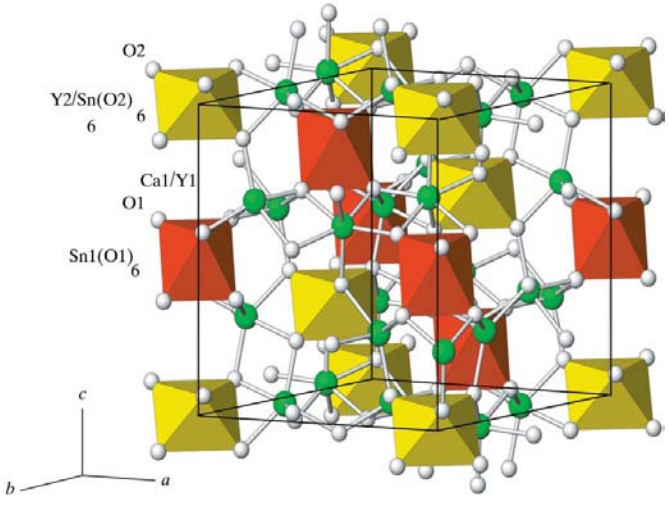

Figure 2
The crystal structure of $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$ in a representation using oxygen-centred Sn1 and Y2/Sn2 octahedra.

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O1 and three O2 sites; the Ca1/Y1—O1 and Ca1/Y1—O2 distances are in the range 2.227 (3)–2.350 (3) Å, with an average value of 2.308 Å. The bond valence sum for Ca, calculated with the bond valence parameter of $Ca^{II}—O^{II}$ (1.967 Å), is 2.409 and that of Y, calculated with the parameter of $Y^{III}—O^{II}$ (2.014 Å), is 2.735. These results agree with a mixed occupation of Ca and Y atoms in the 18*f* site, having a Ca:Y ratio of 0.2667:0.7333.

In the quaternary compounds prepared in the $CaO–Y_2O_3–SiO_2$ and $CaO–Y_2O_3–GeO_2$ systems, coordination numbers for Ca and Y range from six to eight, and Si or Ge atoms lie in tetrahedral sites. However, all cations in $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$ are in sixfold coordination sites, octahedrally surrounded by O atoms. The bond length distortion, octahedral edge length distortion and octahedral angle variance defined by Renner & Lehmann (1986) are 0%, 3.62% and 1.70°, respectively, for $Sn1(O1)_6$, 0%, 6.63% and 5.76° for $Y2/Sn2(O1)_6$, and 5.23%, 10.02% and 25.07° for $Ca1/Y1(O1,2)_6$. These values indicate that the $Ca1/Y1(O1,2)_6$ octahedron is the most distorted in the structure. This octahedron shares an edge of length 2.832 (2) Å with $Y2/Sn2(O2)_6$, another edge of length 2.815 (4) Å with $Sn1(O1)_6$, and four edges [2.972 (2)–2.987 (3) Å, average 2.973 Å] with a related $Ca1/Y1(O1,2)_6$ unit.

Experimental

The starting materials were powders of Y_2O_3 (99.99% purity; Nippon Yttrium), $CaCO_3$ (99.99% purity; Rare Metallic) and SnO_2 (99.9% purity; Sigma–Aldrich). Y_2O_3 and SnO_2 powders were heated at 1273 K for 6 h before weighing. The powders were weighed and mixed in a Ca:Y:Sn molar ratio of 1:3:1. The mixture was pressed into a pellet at 50 MPa and placed on a platinum plate. The polycrystalline sample of $Ca_{0.8}Y_{2.4}Sn_{0.8}O_6$ was prepared by reaction sintering at 1400 K with an electric furnace in air. After heating at this temperature for 12 h, the sample was cooled to room temperature in the furnace. Grain growth in the sample was observed upon heating at 1773 K for 24 h. A colorless granular single crystal with a size less than 0.08 × 0.08 × 0.07 mm was selected from the resulting grains.

Crystal data

$Ca_{0.8}O_6Sn_{0.8}Y_{2.4}$
M_r = 436.40
Trigonal, $R\overline{3}$
a = 9.509 (5) Å
c = 10.989 (8) Å
V = 860.5 (9) Å^3
Z = 6
D_x = 5.051 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 28.19 mm^{-1}
T = 296.1 K
Granule, colourless
0.08 × 0.08 × 0.07 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
T_{min} = 0.101, T_{max} = 0.123
2843 measured reflections
445 independent reflections
430 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.041
S = 1.18
445 reflections
33 parameters
$w = 1/[\sigma^2(F_o^2) + 1.9055P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.63 e Å^{-3}
$\Delta\rho_{min}$ = −0.60 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0044 (2)

Table 1
Selected geometric parameters (Å, °).

Ca1/Y1—O2	2.227 (3)	Ca1/Y1—O2^{iii}	2.335 (3)
Ca1/Y1—O1^{i}	2.280 (3)	Ca1/Y1—O2^{iv}	2.350 (3)
Ca1/Y1—O1	2.325 (2)	Sn1—O1	2.066 (2)
Ca1/Y1—O1^{ii}	2.328 (3)	Y2/Sn2—O2	2.147 (3)
O1—Ca1/Y1—O1^{ii}	74.42 (11)	O2—Ca1/Y1—O2^{iii}	80.38 (9)
O1^{ii}—Ca1/Y1—O2^{iii}	79.60 (8)	O2—Ca1/Y1—O1^{i}	92.93 (8)
O1^{i}—Ca1/Y1—O1	80.37 (8)	O2—Ca1/Y1—O1	104.50 (9)
O1^{i}—Ca1/Y1—O2^{iv}	80.27 (8)	O2—Ca1/Y1—O1^{ii}	105.40 (9)
O1^{ii}—Ca1/Y1—O2^{iv}	96.64 (9)	O1^{vi}—Sn1—O1^{viii}	85.86 (10)
O1—Ca1/Y1—O2^{iv}	110.38 (9)	O1^{vi}—Sn1—O1^{ii}	94.14 (10)
O1^{i}—Ca1/Y1—O2^{iii}	125.35 (8)	O2—Y2/Sn2—O2^{x}	82.41 (9)
O2^{iii}—Ca1/Y1—O2^{iv}	74.28 (12)	O2—Y2/Sn2—O2^{v}	97.59 (9)

Symmetry codes: (i) $-x+\frac{1}{3}, -y+\frac{2}{3}, -z+\frac{2}{3}$; (ii) $-x+y, -x, z$; (iii) $-x+\frac{2}{3}, -y+\frac{1}{3}, -z+\frac{1}{3}$; (iv) $-y+\frac{2}{3}, x-y+\frac{1}{3}, z+\frac{1}{3}$; (v) $-y, x-y, z$; (vi) $y, -x+y, -z+1$; (viii) $x-y, x, -z+1$; (x) $x-y, x, -z$.

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2005); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3014). Services for accessing these data are described at the back of the journal.

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