

**Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub>: a calcium europium tin oxide with a novel structure**

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A new quaternary compound in the Ca–Eu–Sn–O system, namely calcium europium tin heptaoxide, Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub>, was prepared by solid-state reaction at 2073 K. All atoms in the structure are on 4*i* special positions (on mirrors) in space group *C2/m*. Ca/Eu sites are situated within two O octahedra and within two sevenfold coordination sites surrounded by O-capped trigonal prisms. A Ca/Eu/Sn site is coordinated by five O atoms. The structural formula can be represented as (Ca<sub>0.28</sub>Eu<sub>0.72</sub>)(Ca<sub>0.16</sub>Eu<sub>0.84</sub>)(Ca<sub>0.46</sub>Eu<sub>0.54</sub>)(Ca<sub>0.28</sub>Eu<sub>0.72</sub>)(Ca<sub>0.32</sub>Eu<sub>0.18</sub>Sn<sub>0.50</sub>)O<sub>7</sub>. The crystal structure is a new type and is related to the structure of B-form Eu<sub>2</sub>O<sub>3</sub>.

**Comment**

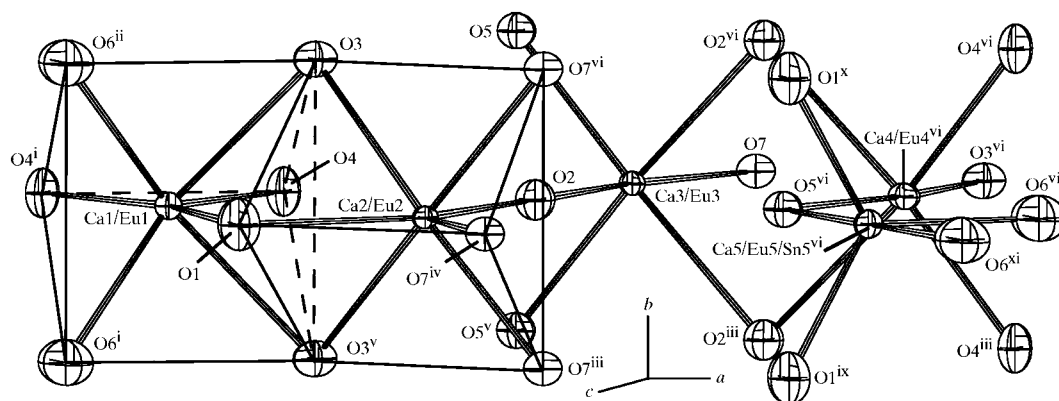
Recently, a new quaternary oxide, Ca<sub>0.8</sub>Y<sub>2.4</sub>Sn<sub>0.8</sub>O<sub>6</sub>, isostructural with Mg<sub>3</sub>TeO<sub>6</sub> and a member of the Ca–Y–Sn–O system, was prepared by solid-state reaction (Kaminaga *et al.*, 2006). In an attempt to substitute Eu atoms for all Y atoms in the compound, a mixture of the compound, with the Mg<sub>3</sub>TeO<sub>6</sub>-type structure, and CaSnO<sub>3</sub>, with a perovskite-type structure, was prepared at 1673 K. In order to form single crystals, we

heated the sample to 2073 K and in fact obtained the title new quaternary compound with a new structure in the Ca–Eu–Sn–O system, and present its structure here.

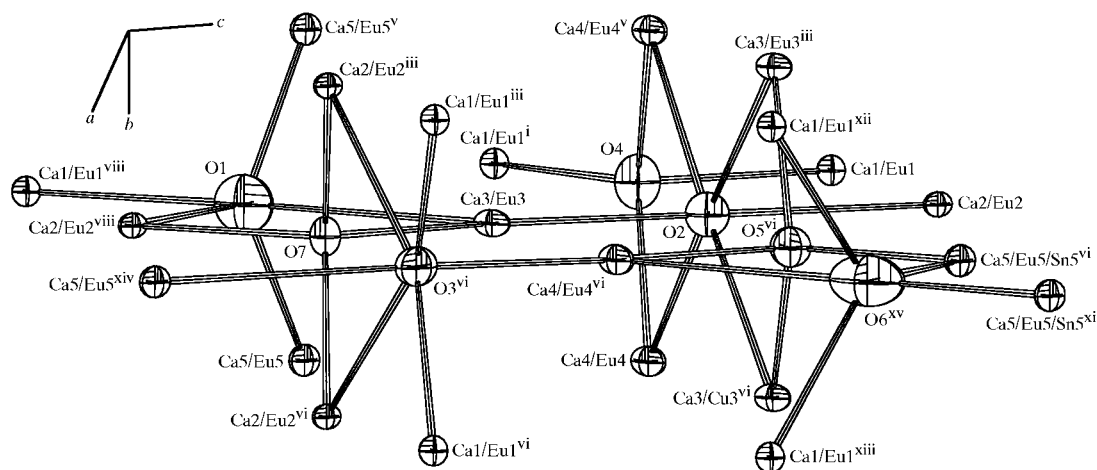
A Ca:Eu:Sn molar ratio of 3:6:1 was measured for the single crystals obtained using an energy-dispersive X-ray (EDX) analyser on a scanning electron microscope. The proportions of Eu and Sn in the crystals were lower than those in the starting materials (Ca:Eu:Sn = 1:3:1).

All metal (*M*) and O atoms are located on mirrors (4*i* special positions) with *y* = 0 and  $\frac{1}{2}$ . After obtaining a starting model using *SIR2004* (Burla *et al.*, 2005), Eu atoms were tentatively placed at all *M* sites for the first step and their positions were refined. The bond-valence sums for the *M* sites, calculated with the bond lengths of *M*–O and the bond-valence parameter of Eu<sup>III</sup>–O<sup>II</sup> = 2.076 (Bresle & O'Keefe, 1991), were 2.771, 2.943, 2.694, 2.947 and 3.785, respectively. Based on this information, we set four mixed sites of Ca and Eu atoms (Ca/Eu), where the bond-valence sums were below 3, and a Ca/Eu/Sn site with the bond valence above 3. In accordance with the composition analysed by EDX, the occupancy parameter of Sn at the Ca/Eu/Sn site was fixed at 0.5. The occupancy parameters of the Ca and Eu atoms at the sites Ca1/Eu1, Ca2/Eu2, Ca3/Eu3, Ca4/Eu4 and Ca5/Eu5/Sn5 were refined to 0.278 (3)/0.722 (3), 0.165 (3)/0.835 (3), 0.458 (3)/0.542 (3), 0.281 (3)/0.719 (3) and 0.32 (19)/0.18 (5), respectively. The overall Ca:Eu:Sn molar ratio, calculated with these values, was in good agreement with the ratio from the EDX analysis (Ca:Eu:Sn = 3:6:1).

Fig. 1 shows the atomic arrangement around the *M* sites with Ca1/Eu1- and Ca2/Eu2-centred oxygen trigonal prisms. The Ca1/Eu1 and Ca2/Eu2 sites are surrounded by six nearest O atoms which form trigonal prisms. The *M*–O bond lengths in the Ca1/Eu1- and Ca2/Eu2-centred prisms are 2.272 (6)–2.528 (4) and 2.288 (3)–2.488 (4) Å, respectively. The second-nearest neighbour O atoms, capping the widest rectangular plane of each trigonal prism, are located 2.606 (7) Å from Ca1/Eu1 and 2.716 (5) Å from Ca2/Eu2. Consequently, the corresponding metal atom sites are best described as seven-coordinated. The O atoms surrounding the Ca3/Eu3 and Ca4/Eu4 sites form distorted octahedra. The *M*–O bond lengths are

**Figure 1**

The O-atom coordination around five *M* sites in the structure of Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub>, showing Ca1/Eu1- and Ca2/Eu2-centred oxygen trigonal prisms. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes as in Table 1; additionally: (x)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z$ ; (xi)  $x + \frac{1}{2}, y - \frac{1}{2}, z + 1$ .]



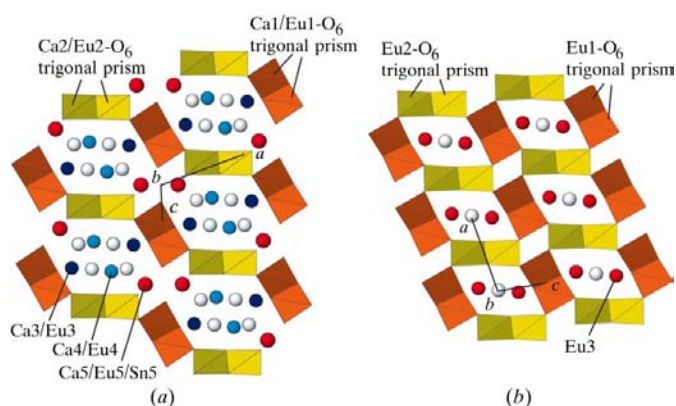
**Figure 2**

The *M*-atom coordination around O sites. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes as in Table 1; additionally: (xi)  $x + \frac{1}{2}, y - \frac{1}{2}, z + 1$ ; (xii)  $x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (xiii)  $x + \frac{1}{2}, y + \frac{1}{2}, z$ ; (xiv)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$ ; (xv)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .]

2.213 (5)–2.541 (4) (Ca3/Eu3–O) and 2.250 (3)–2.580 (4) Å (Ca4/Eu4–O). Second-nearest neighbour O atoms are located at distances of 3.204 (7) (Ca3/Eu3–O1) and 3.311 (9) Å (Ca4/Eu4–O6) Å. The Ca5/Eu5/Sn5 site is coordinated by five O atoms, with bond lengths ranging from 2.118 (3) to 2.386 (9) Å. The second-nearest neighbour O atom is 3.236 (5) Å from the Ca5/Eu5/Sn5 site.

The arrangement of *M* atoms around O atoms is shown in Fig. 2. Atoms O4, O5, O6 and O7 are surrounded by four *M* atoms, atom O1 by five *M* atoms, and atoms O2 and O3 by six *M* atoms. The equivalent isotropic displacement parameter of atom O6 is almost twice those of the other O atoms. This may result from the difference in the coordination environment around O6 compared with the others. Each O atom, except O6 is located inside an *M* polyhedron, while atom O6<sup>xv</sup> lies in a plane formed by Ca1/Eu1<sup>xii</sup>, Ca1/Eu1<sup>xiii</sup> and Ca5/Eu5/Sn5<sup>vi</sup> (symmetry codes as in Fig. 2 and Table 1). These three sites are parts of a distorted tetrahedron which is completed by Ca5/Eu5/Sn5<sup>xi</sup>. The direction of the ellipsoid long axis is toward the Ca4/Eu4<sup>vi</sup> and Ca5/Eu5/Sn5<sup>xi</sup> sites, with distances of 3.311 (9) and 2.386 (9) Å, respectively.

We could not find any isotopic compound in the Inorganic Crystal Structure Database (ICSD, 2005). However, the crystal structure of Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub> can be related to the structure of the B-form of Eu<sub>2</sub>O<sub>3</sub>. This form is a mid-temperature monoclinic phase which is stable from 1423 to 2273 K, between the high-temperature A-form hexagonal phase and the low-temperature C-form cubic phase (Yakel, 1979). The space group of the B-form of Eu<sub>2</sub>O<sub>3</sub> is the same (*C2/m*) as that of Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub>. The refined unit-cell parameters of B-form Eu<sub>2</sub>O<sub>3</sub> are  $a = 14.1105$  (2) Å,  $b = 3.6021$  (1) Å,  $c = 8.8080$  (2) Å and  $\beta = 100.037$  (1)°, and the unit-cell volume is 440.84 (3) Å<sup>3</sup>. In the structure of B-form Eu<sub>2</sub>O<sub>3</sub>, there are three Eu sites and five O sites, all of which are also on 4*i* special positions with  $y = 0$  and  $\frac{1}{2}$ . The *b* axis lengths of B-form Eu<sub>2</sub>O<sub>3</sub> and Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub> [3.6294 (2) Å] are similar. The coordination environments of Eu1 and Eu2 are similar to those of Ca1/Eu1 and Ca2/Eu2 in

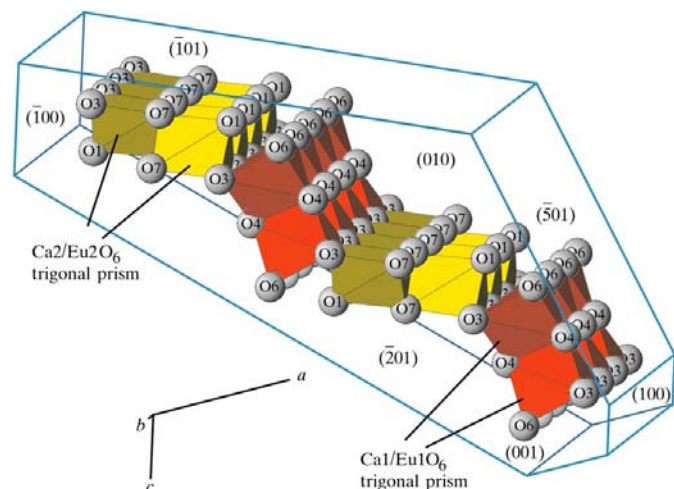


**Figure 3**

(a) The extended structure of Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub>, illustrated with Ca1/Eu1- and Ca2/Eu2-centred oxygen trigonal prisms. (b) The structure of B-form Eu<sub>2</sub>O<sub>3</sub>, illustrated with Eu1- and Eu2-centred oxygen trigonal prisms.

Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub>. The Eu1–O bond lengths are 2.290 (2)–2.537 (2) (prism) and 2.656 (4) Å (cap), and the Eu2–O bond lengths are 2.288 (2)–2.462 (2) (prism) and 2.7394 (2) Å (cap). As with the Ca3/Eu3 and Ca4/Eu4 sites of the present structure of Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub>, in B-form Eu<sub>2</sub>O<sub>3</sub>, the Eu3 atoms are in a distorted O octahedron, with *M*–O bond lengths ranging from 2.239 (2) to 2.544 (1) Å. The second-nearest neighbour O atom is 3.133 (4) Å from Eu3.

The extended structure of Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub> is illustrated in Fig. 3(a), with Ca1/Eu1- and Ca2/Eu2-centred oxygen trigonal prisms. The structure of B-form Eu<sub>2</sub>O<sub>3</sub> is shown in Fig. 3(b), with Eu1- and Eu2-centred oxygen trigonal prisms. As shown in Fig. 4, pairs of Ca1/Eu1-centred prisms in Ca<sub>1.5</sub>Eu<sub>3</sub>Sn<sub>0.5</sub>O<sub>7</sub>, sharing O4–O4<sup>i</sup> edges lying in the plane ( $\bar{5}01$ ), stack parallel to the *b*-axis direction by sharing O3–O6<sup>ii</sup> edges. Pairs of Ca2/Eu2-centred prisms, which share O7<sup>iii</sup>–O7<sup>iv</sup> and O7<sup>v</sup>–O7<sup>vi</sup> edges lying in the ( $\bar{1}01$ ) plane, stack parallel to the *b*-axis direction by sharing O3–O7<sup>vi</sup> edges. Ca1/Eu1- and Ca2/Eu2-centred trigonal prism pairs share O3–O3<sup>v</sup> edges and form trigonal prism layers in the (20 $\bar{1}$ ) plane. Ca3/Eu3, Ca4/Eu4 and



**Figure 4**  
The arrangement of Ca1/Eu1-centred and Ca2/Eu2-centred oxygen trigonal prisms in  $\text{Ca}_{1.5}\text{Eu}_3\text{Sn}_{0.5}\text{O}_7$ .

Ca5/Eu5/Sn5 atoms are located between the trigonal prism layers (Fig. 3a). A similar arrangement of prism pairs is seen in the structure of B-form  $\text{Eu}_2\text{O}_3$ , where the layers of Eu1- and Eu2-centred prism pairs share vertices and form tunnels parallel to the *b*-axis direction. Eu3 atoms are located in sevenfold coordination sites in the tunnels.

### Experimental

The starting materials were powders of  $\text{Eu}_2\text{O}_3$  (99.99% purity; Rare Metallic),  $\text{CaCO}_3$  (99.99% purity; Rare Metallic) and  $\text{SnO}_2$  (99.9% purity; Sigma–Aldrich).  $\text{Eu}_2\text{O}_3$  and  $\text{SnO}_2$  powders were heated at 1273 K for 6 h before weighing. The powders were weighed and mixed in a Ca:Eu:Sn molar ratio of 1.3:1. The mixture was pressed into a pellet at 50 MPa and placed on a platinum–rhodium plate. The polycrystalline sample of  $\text{Ca}_{1.5}\text{Eu}_3\text{Sn}_{0.5}\text{O}_7$  was prepared by reaction sintering at 2073 K using an electric furnace in air. After heating at this temperature for 12 h, the sample was cooled to room temperature in the furnace. The growth of grains was observed in the sample. A colourless translucent single-crystal platelet was selected from the grains. The compositions of Ca, Eu and Sn in the single-crystal were measured using a scanning electron microscope (SEM, Hitachi, S3500N) with an energy dispersive X-ray spectrometer (EDX, HORIBA, EMAX-500).

#### Crystal data

$\text{Ca}_{1.5}\text{Eu}_3\text{O}_7\text{Sn}_{0.5}$   
 $M_r = 687.35$   
Monoclinic,  $C2/m$   
 $a = 22.8628$  (11) Å  
 $b = 3.6294$  (2) Å  
 $c = 9.0610$  (4) Å  
 $\beta = 107.9150$  (14)°  
 $V = 715.41$  (6) Å<sup>3</sup>

$Z = 4$   
 $D_x = 6.384$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
 $\mu = 28.75$  mm<sup>-1</sup>  
 $T = 296.1$  K  
Platelet, colourless  
 $0.07 \times 0.05 \times 0.03$  mm

#### Data collection

Rigaku R-AXIS RAPID diffractometer  
 $\omega$  scans  
Absorption correction: numerical (NUMABS; Higashi, 1999)  
 $T_{\min} = 0.276$ ,  $T_{\max} = 0.719$   
3610 measured reflections  
945 independent reflections  
858 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.059$   
 $\theta_{\text{max}} = 27.4^\circ$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.061$   
 $S = 1.06$   
945 reflections  
73 parameters

$w = 1/[\sigma^2(F_o^2) + 4.2873P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 1.52 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.42 \text{ e \AA}^{-3}$

**Table 1**

Selected bond lengths (Å).

Ca1/Eu1—O4 <sup>i</sup>	2.272 (6)	Ca3/Eu3—O2	2.513 (5)
Ca1/Eu1—O6 <sup>ii</sup>	2.367 (4)	Ca3/Eu3—O2 <sup>iii</sup>	2.541 (4)
Ca1/Eu1—O4	2.395 (5)	Ca4/Eu4—O4	2.250 (3)
Ca1/Eu1—O3	2.528 (4)	Ca4/Eu4—O5	2.264 (5)
Ca1/Eu1—O1	2.606 (7)	Ca4/Eu4—O3	2.291 (5)
Ca2/Eu2—O7 <sup>iii</sup>	2.288 (3)	Ca4/Eu4—O2	2.580 (4)
Ca2/Eu2—O7 <sup>iv</sup>	2.293 (5)	Ca4/Eu4—O6	3.311 (9)
Ca2/Eu2—O1	2.402 (6)	Ca5/Eu5/Sn5—O1 <sup>v</sup>	2.118 (3)
Ca2/Eu2—O3	2.488 (4)	Ca5/Eu5/Sn5—O6	2.160 (7)
Ca2/Eu2—O2	2.716 (5)	Ca5/Eu5/Sn5—O5	2.202 (5)
Ca3/Eu3—O7	2.213 (5)	Ca5/Eu5/Sn5—O6 <sup>vi</sup>	2.386 (9)
Ca3/Eu3—O5	2.293 (4)		

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

The highest peak and deepest hole in the final electron-density difference map were observed at (0.1437, 0.0000, 0.0666), 0.87 Å from atom O1, and at (0.3523, 0.0000, 0.4679), 0.63 Å from atom Eu4, respectively.

Data collection: *PROCESS-AUTO* (Rigaku/MSC, 2005); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2005); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 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: FA3035). Services for accessing these data are described at the back of the journal.

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