Crystal Chemistry of Oxide–Chalcogenide.
I. The Crystal Structure of Sarabauite CaSb$_{10}$O$_{10}$S$_6$*

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Sarabauite, a new oxide–sulfide mineral, is monoclinic, space group $C2/c$, with $a = 25 \cdot 37$ (2), $b = 5 \cdot 654$ (1), $c = 16 \cdot 87$ (1) Å, $\beta = 117 \cdot 58$ (4)°, $Z = 4$. The structure was refined to $R = 0 \cdot 057$ for 2039 reflections. The Sb atoms are coordinated by three O and/or S atoms to form Sb(O,S)$_3$ pyramids. CaO$_8$ polyhedra link zigzag chains formed by corner or edge sharing of SbO$_3$ pyramids to form a slab parallel to (100), while SbS$_2$O and SbS$_3$ pyramids form an eight-membered Sb–S ring. The ring links to the slab through an O atom.

Introduction

Sarabauite, CaSb$_{10}$O$_{10}$S$_6$, a new mineral (Nakai *et al.*, 1978), is classified as an oxide–sulfide compound. These substances are defined as having a composition intermediate between oxides and sulfides, and are quite rare in nature, kermesite, Sb$_2$S$_2$O, being the only mineral known. Even among the synthetic compounds, the oxide–sulfides are very limited in number compared with oxides and sulfides, although some lanthanoid oxide–sulfides Ln$_2$O$_2$S are well known as phosphors.

A synthetic study of the M–Sb–O–S system (where M stands for alkali-earth metals) has been carried out and has revealed the presence of more than three new oxide–sulfides in this system (Nagashima, Ogino & Nakai, 1978). From these results, we anticipate that the M–Sb–O–S system forms a new group of inorganic compounds. The present work has been done as a part of the study of crystal chemistry of the oxide–sulfide compounds.

Experimental

A single crystal for the structural determination was taken from the original specimen of sarabauite. The ideal chemical formula CaSb$_{10}$O$_{10}$S$_6$ (Nakai *et al.*, 1978) has been used in this investigation. Monoclinic symmetry and possible space groups Cc and $C2/c$ are indicated by the Weissenberg and precession photographs. The centrosymmetric space group $C2/c$ was

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adopted from the $N(z)$ test (Howells, Phillips & Rogers, 1950) and has been confirmed in the subsequent structure refinements.

The unit-cell dimensions were determined from a least-squares refinement using the 2θ values of 26 reflections measured on a Rigaku four-circle diffractometer with Mo $K\alpha_1$ radiation (0·709258 Å). The intensity measurement was carried out with a crystal of approximately 0·09 × 0·1 × 0·12 mm. The intensities were collected on the four-circle diffractometer using the 2θ–ω scan technique with Zr-filtered Mo $K\alpha$ radiation (a scan rate of 2° min^{-1} and background counts of 10 s at each scan limit). The intensities of two standard reflections were measured every 30 reflections. No significant fluctuation of the intensity of standard reflections was observed. 2474 symmetry-independent reflections were measured within the limit of $2\theta \le 55°$. The intensities were corrected for Lorentz and polarization factors. No absorption correction was applied [μ(Mo $K\alpha$) = 125 cm^{-1}]. 2039 reflections with $|F_o| \ge 3\sigma(|F_o|)$ were regarded as observed.

Crystal data

CaSb$_{10}$O$_{10}$S$_6$, FW = 1609·9, $a = 25·37$ (2), $b = 5·654$ (1), $c = 16·87$ (1) Å, $\beta = 117·58$ (4)°, $V = 2145$ (2) Å^3, $Z = 4$, $D_m = 4·8$, $D_c = 4·98$ g cm^{-3}, space group $C2/c$.

Structure determination and refinement

The structure was solved with the aid of the Patterson method. The coordinates of an Sb atom were obtained from a three-dimensional Patterson synthesis. A

minimum function method was applied to reveal all the remaining Sb atoms. Subsequent Fourier and difference syntheses revealed the positions of Ca, S and O atoms. A full-matrix least-squares refinement was carried out with isotropic temperature factors. At this stage $R = \sum ||F_o| - |F_c||/\sum |F_o|$ was 0·105 for all reflections.

Full-matrix least-squares refinement with anisotropic temperature factors converged to $R = 0\cdot057$ for all observed reflections. The maximum shift in atomic parameters in the last cycle was less than 0·02 times the corresponding standard deviation. Since the anisotropic temperature factors of O(3) and O(4) became negative during refinement, they were calculated from the isotropic factors and were not varied in the above refinement. A secondary-extinction correction was applied (Zachariasen, 1963). However, this did not improve the R value. A difference synthesis using the final atomic parameters showed no significant residual.

The final positional and thermal parameters are given in Table 1.* The atomic scattering factors for neutral atoms and the anomalous-dispersion correction factors were taken from *International Tables for X-ray Crystallography* (1974). The full-matrix least-squares program *ORFLS* of Busing, Martin & Levy (1962), modified by Sakurai (1967) to the *UNICS* System, was used in the refinement. All the computations were carried out at the Computing Centers of the University of Tokyo and Osaka University using the *UNICS* System (Sakurai, 1967).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33859 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

Description of the structure

The principal structural features of sarabauite are eight-membered Sb–S rings and slabs composed of SbO_3 pyramids and CaO_8 polyhedra (Fig. 1). The SbO_3 pyramids of Sb(1) and Sb(3) share corner O atoms to form eight-membered Sb–O rings, while the pyramids of Sb(2) form four-membered Sb–O rings by edge-sharing O atoms. The eight-membered and four-membered Sb–O rings link through O(3) to form zigzag chains parallel to the c axis (Fig. 2). The CaO_8 polyhedra link the chains in the b direction to make the slab parallel to (100). On the other hand, $Sb(S,O)_3$ pyramids of Sb(4) and Sb(5) form eight-membered Sb–S rings. Fig. 3 shows the linkage between the slab structure and the ring structure. The Sb–S rings link to the slab through O(2) atoms. In addition, Figs. 1 and 3
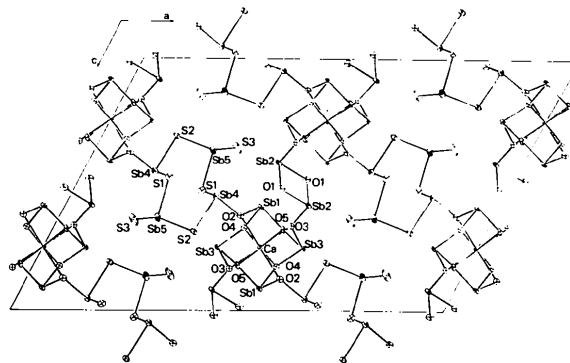

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the structure of $CaSb_{10}O_{10}S_6$, viewed along **b**. The thermal ellipsoids are at 50% probability.

Table 1. *Atomic coordinates and isotropic thermal parameters with estimated standard deviations in parentheses*

The isotropic thermal parameters are calculated from anisotropic thermal parameters according to the expression: $B = 4(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{13}ac \cos \beta)/3$.

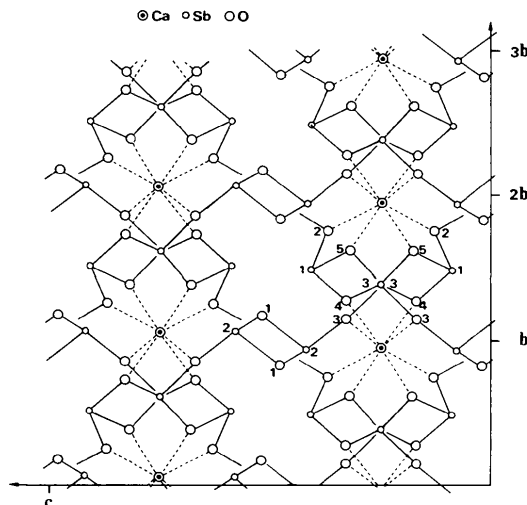|	x	y	z	B (Å^2)
Sb(1)	0·45169 (5)	0·4908 (2)	0·08811 (8)	0·93
Sb(2)	0·06051 (5)	0·4397 (2)	0·08433 (8)	1·08
Sb(3)	0·40195 (5)	0·3904 (2)	0·24784 (8)	0·88
Sb(4)	0·16446 (5)	0·3859 (2)	0·45181 (8)	1·13
Sb(5)	0·22746 (6)	0·1010 (2)	0·13422 (9)	1·75
Ca	0	0·4469 (8)	0·25	0·89
S(1)	0·29545 (21)	0·4799 (8)	0·02610 (32)	1·43
S(2)	0·17228 (21)	0·4282 (9)	0·31099 (31)	1·46
S(3)	0·32441 (32)	0·2627 (13)	0·35632 (49)	3·89
O(1)	0·02416 (61)	0·3294 (24)	0·48238 (88)	1·53
O(2)	0·08414 (58)	0·2501 (22)	0·37423 (85)	1·24
O(3)	0·45493 (56)	0·1469 (23)	0·33428 (85)	1·23
O(4)	0·43880 (54)	0·2796 (24)	0·17364 (83)	1·16
O(5)	0·03093 (55)	0·1150 (24)	0·17919 (86)	1·27

Fig. 2. A view of the slab structure, showing the bondings between the Ca atoms and the zigzag chains of Sb–O rings. The view is projected down a onto the (100) plane.

also show that the linkages of the eight-membered Sb—O rings and the Sb—S rings through O(2) form zigzag chains parallel to [101]. As a whole, the linkage of these ring structures gives rise to a two-dimensional network parallel to (010).

A stereoscopic pair of the structure is shown in Fig. 4. The cations drawn in the figure are inside the unit cell. This figure shows that within the unit cell the rings (Sb—S rings and four-membered Sb—O rings) are, in fact, not continuous. These rings are completed by linkage made between atoms in adjacent unit cells.

Selected interatomic distances and angles are listed in Table 2. Basically the Sb atom is coordinated by three O and/or S atoms. In the SbO_3 pyramids, the average Sb—O distance is 2·00 Å. This value is in good

agreement with 2·00 Å in orthorhombic Sb_2O_3 (Buerger & Hendricks, 1938). In the case of the Sb(1) atom, it has another O atom at a distance 2·476 Å. No other Sb—O bond length is less than 2·5 Å. The Sb—S bond distances range from 2·369 to 2·531 Å (average 2·465 Å) and these values show no significant difference from those of the pyramidal Sb—S bonds in stibnite: 2·455–2·678 Å (Bayliss & Nowacki, 1972), and in kermesite: 2·35–2·75 Å (Kupčik, 1967).

Ca atoms are coordinated by eight O atoms. The Ca—O bonds range from 2·399 to 2·536 Å, with an average distance of 2·467 Å. The coordination number and these bond distances are common in oxides and silicates.

One of the characteristic features of the bonding in sarabauite is the presence of S having a coordination number of one. As may be seen in Table 2, S(3) is coordinated by only an Sb atom, which gives the shortest Sb—S bond distance, 2·369 Å, and no other shorter than 3 Å. Since the other three Sb atoms are at distances 3·187 [Sb(2)], 3·328 [Sb(3)] and 3·227 Å [Sb(4)], S(3) can be considered to form weak bonds with these Sb atoms. This unusual coordination of the S atom is reflected in the large value of the temperature factor (Table 1). The nature of the thermal motion is seen in the thermal ellipsoids shown in Fig. 1.

Comparison of the structure with kermesite

Fig. 5 is a projection of a part of the structure of kermesite: this figure was illustrated by the authors using the original atomic coordinates (Kupčik, 1967).

The four Sb atoms have two different coordinations. Sb(1) and Sb(2) are coordinated by one S and three O
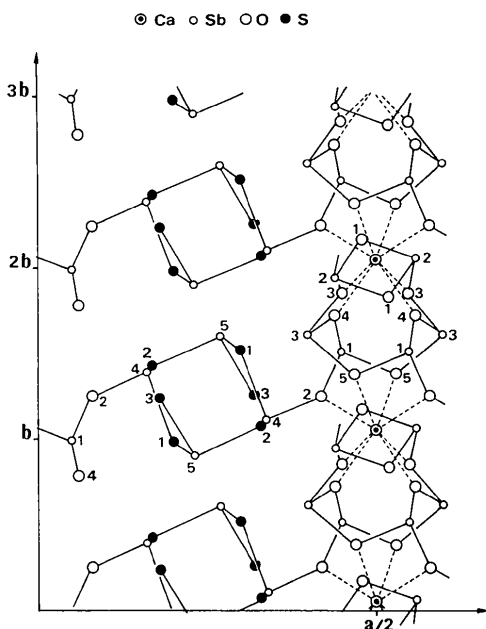
⊚ Ca ○ Sb ○○ ● S

Fig. 3. A view of the ring structures, showing the four-membered Sb—O rings, eight-membered Sb—O and Sb—S rings and their linkages. The view is projected down c onto the (001) plane.
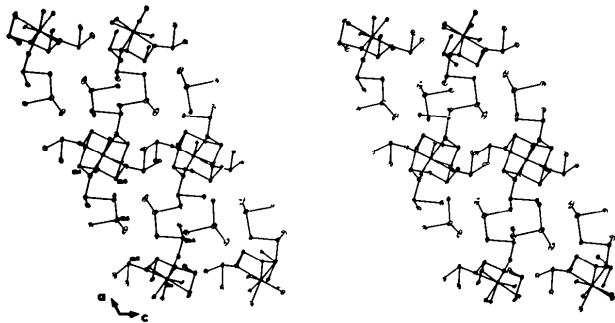

Fig. 4. A stereoscopic view of the unit cell (Johnson, 1965). The Sb-atom numbering is the same as that used in Table 1.

Table 2. Bond lengths (Å) and angles (°) for sarabauite with estimated standard deviations in parentheses

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Sb(1)—O(1)	2·476 (16)	O(2)—Sb(1)—O(4)	87·6 (6)
Sb(1)—O(2)	1·979 (15)	O(2)—Sb(1)—O(5)	86·6 (6)
Sb(1)—O(4)	2·013 (15)	O(4)—Sb(1)—O(5)	95·5 (5)
Sb(1)—O(5)	2·009 (11)		
Sb(2)—O(1)	2·011 (13)	O(1)—Sb(2)—O(1')	77·0 (6)
Sb(2)—O(1')	2·008 (13)	O(1)—Sb(2)—O(3)	92·8 (6)
Sb(2)—O(3)	1·977 (16)	O(1')—Sb(2)—O(3)	93·9 (6)
Sb(3)—O(3)	2·003 (12)		
Sb(3)—O(4)	1·979 (17)	O(3)—Sb(3)—O(4)	83·6 (6)
Sb(3)—O(5)	2·022 (12)	O(3)—Sb(3)—O(5)	84·0 (5)
Sb(4)—O(2)	1·996 (12)	O(4)—Sb(3)—O(5)	94·2 (6)
Sb(4)—S(1)	2·468 (5)		
Sb(4)—S(2)	2·486 (6)	S(1)—Sb(4)—S(2)	91·4 (2)
Sb(5)—S(1)	2·531 (6)	S(1)—Sb(4)—O(2)	88·0 (4)
Sb(5)—S(2)	2·470 (5)	S(2)—Sb(4)—O(2)	85·4 (5)
Sb(5)—S(3)	2·369 (8)		
Ca—O(2)	2·459 (11) ×2	S(1)—Sb(5)—S(2)	90·9 (2)
Ca—O(3)	2·473 (17) ×2	S(1)—Sb(5)—S(3)	93·8 (2)
Ca—O(4)	2·399 (13) ×2	S(2)—Sb(5)—S(3)	99·4 (2)
Ca—O(5)	2·536 (16) ×2		

○ Sb ● S ○ O
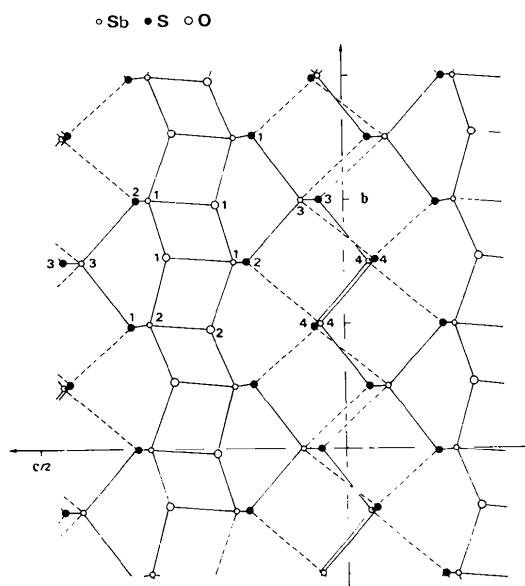
Fig. 5. A view of the structure of kermesite, Sb_2S_2O, showing a sheet parallel to (100). The view is projected down a onto the (100) plane.

atoms. These coordinated polyhedra are linked through the sharing of an O–O edge.

The other Sb atoms, Sb(3) and Sb(4), have a coordination similar to that found in stibnite (Bayliss & Nowacki, 1972; Sb–S bond distances greater than 2·9 Å are drawn as dashed lines in Fig. 5).

As a whole these linkages form a sheet structure as shown in Fig. 5. The sheets are stacked in the **a** direction by weak Sb–O and Sb–S bonds.

The structural similarity between sarabauite and kermesite is that in both compounds Sb–S and Sb–O are clearly separated into two regions. However, the two parts are linked through the $Sb–S_2O$ pyramids, in the case of sarabauite, and through the $Sb–SO_3$ polyhedra in that of kermesite (Figs. 1 and 5).

The fundamental difference between the two is that sarabauite has a distinctly three-dimensional structure while for kermesite it appears to be two-dimensional.

The difference is considered to arise from the presence of the Ca atom in sarabauite, which links the network to form a three-dimensional structure.

In this way, sarabauite has been found to have a unique structure as is expected from its composition. The structural analyses of the other synthetic oxide–sulfides in the M–Sb–O–S system are now in progress. Their crystal data are given in the literature (Nagashima, Ogino & Nakai, 1978). The results to date seem to indicate that they are not simple alkali-earth analogues of sarabauite.

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