Solid reagent-grade calcium hydroxide (Jenneile Chemical Company, Cincinnati, Ohio) was reacted with a slight excess of approximately 0.7 *M* perbromic acid prepared using a modification of Appelman's (1972) procedure. The resulting solution was evaporated at room temperature to produce crystalline tetraaquacalcium perbromate; the experimental sample grew upon further evaporation of the saturated mother liquor decanted from the initial growth. The sample was mounted with epoxy cement and was coated with Apiezon L grease to retard potential loss or gain of water.

Data were collected using scan widths of $(1.55 + 0.35\tan\theta)^\circ$ in ω, and a background/scan time ratio of 0.5. No decay correction was applied but the data were corrected for Lorentz-polarization effects and for absorption. For the latter, ψ-scan data were obtained just prior to the conclusion of intensity-data collection; the correction method was that of North, Phillips & Mathews (1968).

The crystal system was found to be triclinic. The initial space-group choice $P\bar{1}$ (No. 2) was confirmed by structure refinement. The direct-methods program *SHELXS*86 (Sheldrick, 1985) in the *TEXSAN* structure analysis package (Molecular Structure Corporation, 1989) was used to generate an *E* map from which the initial positions of the Ca atom and the two Br atoms were assigned. Subsequently, difference Fourier maps provided initial positions of the remaining 20 atoms. The non-H atoms were refined anisotropically, the H atoms isotropically, using full-matrix least squares. An extinction coefficient (Zachariasen, 1963, 1968) was included in the least-squares refinement; the maximum effect of extinction was 5.5% of F_o for 110.

As analyzed by the program *THMA*11 (1986) based on the work of Schomaker & Trueblood (1968), the polyhedron did not conform to rigid-body behavior, but the average magnitudes of the differences in the mean-square displacement amplitudes along the interatomic vectors for the ten unique atom pairs of the Br(1) and the Br(2) perbromate ions were both $17\,(18) \times 10^{-4}$ Å. Thus, the Hirshfeld (1976) rigid-bond test, extended as described by Rosenfield, Trueblood & Dunitz (1978), is satisfied by both anions and corrections for the rigid-body motion have been made (Table 2).

In the water molecules, the O—H bond lengths ranged from 0.57 to 1.00 Å. The molecular H—O—H angles were held fixed at the X-ray determined values; the O—H distances were adjusted to the mean values as determined by neutron diffraction for the appropriate hydrate class (Chiari & Ferraris, 1982; Ferraris & Franchini-Angela, 1972). O(1) and O (3) were assigned to hydrate class H, for which the mean O—H distance is 0.972 Å; O(2) and O (4) were assigned to class D, for which the mean distance is 0.956 Å. The neutron-adjusted distances involving the water H atoms and O acceptors are taken to be the hydrogen-bond lengths (Table 3).

Lists of structure factors, anisotropic displacement parameters and material relating to the rigid-body analysis have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71101 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1042]

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A New Modification of Sr_5Sb_3

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Abstract

Single crystals of Sr_5Sb_3 in the orthorhombic form (β-Yb_5Sb_3 structure type) were obtained as a minor product of a reaction of the elements and Mn in a welded Nb container. To date only the hexagonal form (Mn_5Si_3 structure type) of Sr_5Sb_3 has been reported. The orthorhombic phase of Sr_5Sb_3 has

been synthesized in high yield by the reaction of stoichiometric amounts of the elements in an alumina crucible, sealed in a quartz tube.

Comment

The binary system composed of Sr and Sb contains a number of compounds, such as SrSb, $SrSb_3$, Sr_2Sb, Sr_3Sb_2 (Scott, 1990), $SrSb_2$ (Deller & Eisenmann, 1976), Sr_2Sb_3 (Eisenmann, 1979) and Sr_5Sb_3 (Martinez-Ripoll & Brauer, 1973). Of these only the latter three have been characterized by a single crystal structure determination and the structure of Sr_5Sb_3 (Mn_5Si_3 structure type) has been reported twice (Martinez-Ripoll & Brauer, 1973; Hurng & Corbett, 1989). During an investigation of the synthesis of a ternary intermetallic compound with Sr, Sb and a transition metal, we obtained single crystals which had lattice constants and a crystal system that were different from any binary or ternary structures previously reported for these elements. The structure refinement indicated that the compound is Sr_5Sb_3 and that it is isotypic with β-Yb_5Sb_3. Two structure types have been reported for A_5Pn_3 (A = Ca, Sr, Ba; Pn = As, Sb, Bi) (Hurng & Corbett, 1989): the hexagonal Mn_5Si_3 and the orthorhombic β-Yb_5Sb_3 structure type. Except for Ca_5Bi_3, all compounds crystallize in the Mn_5Si_3 structure type. Only Ca_5Sb_3, Ca_5Bi_3 and Sr_5Bi_3 were reported to form the orthorhombic structure type. Whether these structures are actually interstitially stabilized by impurities such as O atoms has been investigated and the compounds A_5Pn_3X (X = halogen) have been prepared (Hurng & Corbett, 1989). Our paper reports the orthorhombic structure type for Sr_5Sb_3.

The orthorhombic crystal structure (β-Yb_5Sb_3) has been described in detail previously (Brunton & Steinfink, 1971; Martinez-Ripoll & Brauer, 1974; Martinez-Ripoll, Haase & Brauer, 1974). It is described as being built up from atomic layers perpendicular to the **b** direction. The layers form distorted closest-packed sheets which contain Sb(1) and Sr(1) in one layer, alternated by a layer containing Sb(2), Sr(2), Sr(3) and Sr(4). Sr is surrounded by 12 or 13 neighbors. Sb(1) forms an $SbSr_9$ unit, and Sb(2) has only eight Sr neighbors. The average values of the Sb(1)—Sr and Sb(2)—Sr distances are 3.553 (3) and 3.393 (3) Å, respectively. Similar to the hexagonal modification [$SbSr_9$ unit, average 3.516 (6) Å] these distances are shorter than would be predicted from the sum of metallic radii given by Pauling. The short distances observed may be attributed to significant effects resulting from electron transfer or from partial ionic character of the bonds.

The structure was also refined with Sr, Sb or O in the interstitial site; this resulted in either unreasonably large U values (full occupancy) or negligible amounts [Sr 0.007 (1.4%), Sb 0.005 (1.0%), O 0.042 (8.4%); U_{iso} = 0.01]. One of the most important features is that the atom positions are fully occupied and that the interstitial hole that might be occupied in this structure is empty.

Experimental

Crystal data

Sb_3Sr_5
M_r = 803.4
Orthorhombic
Pnma
a = 13.173 (6) Å
b = 10.101 (7) Å
c = 8.734 (4) Å
V = 1162.1 (11) Å^3
Z = 4
D_x = 4.592 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 6–15.5°
μ = 29.553 mm^{-1}
T = 130 K
Cuboid
0.225 × 0.05 × 0.025 mm
Metallic

Data collection

Syntex $P2_1$ diffractometer
Absorption correction: empirical based on F_o and F_c differences (*XABS*; Moezzi, 1987)
T_{min} = 0.0125, T_{max} = 0.232
1417 measured reflections
1417 independent reflections

1010 observed reflections [$F > 4.0\sigma(F)$]
θ_{max} = 55.0°
$h = 0 \rightarrow 17$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 11$
2 standard reflections monitored every 198 reflections intensity variation: ±2.0%

Refinement

Refinement on F
Final R = 0.0373
wR = 0.0320
S = 1.17
1010 reflections
43 parameters
$w = [\sigma^2(F) + 0.0002F^2]^{-1}$

$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.95 e Å^{-3}
$\Delta\rho_{min}$ = −2.10 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement coefficients* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Sr(1)	0.0766 (1)	0.0396 (1)	0.6922 (1)	0.008 (1)
Sr(2)	0.2262 (1)	0.2500	0.3234 (2)	0.007 (1)
Sr(3)	0.2892 (1)	0.2500	0.8518 (2)	0.008 (1)
Sr(4)	0.5063 (1)	0.2500	0.4649 (2)	0.007 (1)
Sb(1)	0.1701 (1)	−0.0151 (1)	0.0686 (1)	0.006 (1)
Sb(2)	−0.0160 (1)	0.2500	0.4231 (1)	0.006 (1)

Table 2. *Interatomic distances* (Å)

Sr(1)—Sb(2)	3.195 (2)	Sr(4)—Sr(2)	3.837 (3)
Sr(1)—Sb(2)	3.395 (3)	Sr(4)—Sr(2)	3.892 (3)
Sr(1)—Sb(1)	3.516 (3)	Sr(4)—Sr(1) ×2	3.927 (3)
Sr(1)—Sb(1)	3.554 (3)	Sr(4)—Sr(3)	4.056 (3)
Sr(1)—Sb(1)	3.872 (3)	Sr(4)—Sr(3)	4.427 (4)
Sr(1)—Sr(3)	3.783 (3)		
Sr(1)—Sr(4)	3.788 (3)	Sb(1)—Sr(4)	3.443 (3)
Sr(1)—Sr(4)	3.927 (3)	Sb(1)—Sr(4)	3.451 (3)
Sr(1)—Sr(1)	3.997 (3)	Sb(1)—Sr(3)	3.469 (3)

Sr(1)—Sr(2)	4.077 (3)	Sb(1)—Sr(2)	3.476 (3)
Sr(1)—Sr(1)	4.251 (3)	Sb(1)—Sr(1)	3.516 (3)
Sr(1)—Sr(2)	4.333 (3)	Sb(1)—Sr(1)	3.554 (3)
Sr(1)—Sr(3)	4.358 (3)	Sb(1)—Sr(2)	3.559 (3)
		Sb(1)—Sr(3)	3.635 (3)
Sr(3)—Sb(2)	3.232 (3)	Sb(1)—Sr(1)	3.872 (3)
Sr(3)—Sb(1) ×2	3.469 (3)	Sb(1)—Sb(1)	4.650 (3)
Sr(3)—Sb(1) ×2	3.635 (3)	Sb(1)—Sb(1)	4.746 (3)
Sr(3)—Sr(1) ×2	3.783 (3)		
Sr(3)—Sr(4)	4.056 (3)	Sb(2)—Sr(1) ×2	3.195 (3)
Sr(3)—Sr(2)	4.202 (4)	Sb(2)—Sr(3)	3.232 (3)
Sr(3)—Sr(1) ×2	4.358 (3)	Sb(2)—Sr(2)	3.307 (3)
Sr(3)—Sr(4)	4.427 (4)	Sb(2)—Sr(1) ×2	3.395 (3)
		Sb(2)—Sr(4)	3.401 (3)
Sr(2)—Sb(2)	3.307 (3)	Sb(2)—Sr(2)	4.021 (3)
Sr(2)—Sb(1) ×2	3.476 (3)		
Sr(2)—Sb(1) ×2	3.559 (3)	Averages	
Sr(2)—Sb(2)	4.021 (3)	Sr(1)—Sb	3.506 (3)
Sr(2)—Sr(4)	3.837 (3)	Sr(1)—Sr	4.064 (3)
Sr(2)—Sr(4)	3.892 (3)	Sr(3)—Sb	3.488 (3)
Sr(2)—Sr(1) ×2	4.077 (3)	Sr(3)—Sr	4.138 (3)
Sr(2)—Sr(3)	4.202 (4)	Sb(1)—Sr	3.553 (3)
Sr(2)—Sr(1) ×2	4.333 (3)	Sr(2)—Sb	3.566 (3)
		Sr(2)—Sr	4.107 (3)
Sr(4)—Sb(2)	3.401 (3)	Sr(4)—Sb	3.438 (3)
Sr(4)—Sb(1) ×2	3.444 (3)	Sr(4)—Sr	3.955 (3)
Sr(4)—Sb(1) ×2	3.451 (3)	Sb(2)—Sr	3.393 (3)
Sr(4)—Sr(1) ×2	3.788 (3)		

Crystals of the orthorhombic Sr_5Sb_3 were initially obtained from a reaction containing Sr, Mn and Sb. The elements in the ratio 11:1:9 (Sr:Mn:Sb) were weighed in an Ar-filled drybox and placed into a niobium tube and sealed with an argon arc welder. The niobium tube was then sealed in quartz under vacuum. The reaction was heated (50 K h^{-1}) to 1273 K for 0.5 h and cooled (50 K h^{-1}) to room temperature. Crystals were obtained in addition to Nb_5Sb_4 and $NbSb_2$ and other unidentified impurities. The product was handled in a drybox. The crystals were separated and transferred to a paratone N oil for X-ray determination. Quantitative yields of the orthorhombic Sr_5Sb_3 can be obtained by the following procedure: stoichiometric amounts of Sr (Strem 99.999%) and Sb (Johnson Matthey 99.9999%) were placed in a quartz crucible under Ar (in a drybox) and sealed in a quartz ampoule under vacuum, heated (50 K h^{-1}) to 1273 K for 0.5 h and cooled (50 K h^{-1}) to room temperature. For the crystal structure determination, data were collected using a Syntex $P2_1$ diffractometer equipped with a locally modified LT-1 low-temperature apparatus. The cold-stream temperature was approximately 130 K. The system operates from a DEC VAXstation 3200 microcomputer. Structure solution and refinement were performed with *SHELXTL-Plus* (Sheldrick, 1991).

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Lists of structure factors and anisotropic displacement coefficients have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55939 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1034]

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Redetermination of the Structure of Hessite, Ag_2Te-III

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Abstract

This single-crystal study confirms the space-group symmetry reported previously [Frueh (1959). *Z. Kristallogr.* **112**, 44–52], but proves that interatomic distances were miscalculated, leading to incorrect assignment of coordination number for one Ag atom and incorrect structure description. The structure can be regarded as a strongly distorted antifluorite structure with both independent Ag atoms approximately tetrahedrally coordinated by Te. The Ag—Te distances are in the range 2.8415 (7)–3.034 (1) Å. The shortest Ag—Ag distance is 2.841 (1) Å, shorter than in metallic silver (2.89 Å).

Comment

The structure of the mineral Ag_2Te-III was determined by Frueh (1959) using single-crystal X-ray data. In the course of an extended research program on the structural and electronic properties of Ag and Au in chalcogenides (Schutte & de Boer, 1988; Van Triest, Folkerts & Haas, 1990; van der Lee, 1992), we found some inconsistencies in the paper by Frueh. Using his atomic coordinates and