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

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cell dimensions, some of the Ag coordination details and Ag—Te distances reported could not be reproduced. A remarkable point, not reported by Frueh, is that there are Ag—Ag distances as short as 2.84 Å and 2.93 Å; this distance in metallic Ag is 2.89 Å (*International Tables for X-ray Crystallography*, Vol. IV, 1974). In order to obtain reliable and accurate interatomic distances as needed in, for instance, band-structure calculations, and for reference in multinary compounds containing Ag and Te, we have redetermined the structure of hessite, Ag_2Te-III.

The present study on an approximately cylindrically shaped fragment from a larger crystal of natural hessite from the ARAMA vein at Botes, near Bucium in Romania, confirms the space-group symmetry of the room-temperature stable polymorph of hessite, Ag_2Te-III, reported by Frueh (1959). Fig. 1 shows a projection of the structure along the *b* axis. Ag(1) atoms and coordinating Te atoms form a sheet of tetrahedra parallel to (100), sharing four edges with other $Ag(1)Te_4$ tetrahedra. $Ag(2)Te_4$ tetrahedra are linked to two other $Ag(2)Te_4$ tetrahedra *via* common edges and to four $Ag(2)Te_4$ tetrahedra *via* common vertices in another sheet parallel to (100). The two different sheets are linked to each other *via* shared tetrahedron edges.

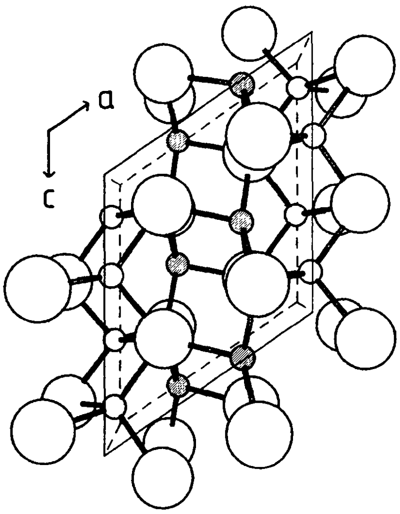

Fig. 1. Perpective projection along the *b* axis of the structure of Ag_2Te-III. Small open circles denote Ag(1), small grey circles Ag(2) and large open circles Te.

The two independent Ag atoms are fourfold coordinated. Both tetrahedra are strongly distorted although the bond distances are in the rather narrow range 2.8415 (7)–3.034 (1) Å (Table 2). The bond angles show a much larger variation, *viz*. 94.85 (2)–155.79 (3)° although the averages [109.11 (1) and 109.65 (11)° for the $Ag(1)Te_4$ and the $Ag(2)Te_4$ tetrahedra, respectively] are close to the ideal value.

The average Ag—Te bond distances [2.9381 (4) and 2.9480 (4) Å for Ag(1)—Te and Ag(2)—Te, respectively] are close to the values reported by Frueh (1959). The Ag—Ag distances range from 2.841 (1) to 3.133 (1) Å, all shorter than the van der Waals diameter of 3.40 Å; the shortest distance is even shorter than that in metallic silver (2.89 Å) and is also shorter than in the low-temperature modifications of Ag_2S (3.04–3.71 Å; Frueh, 1958) and Ag_2Se (2.93–3.68 Å; Wiegers, 1971).

Experimental

Crystal data

Ag_2Te
$M_r = 343.34$
Monoclinic
$P2_1/c$
$a = 8.164$ (1) Å
$b = 4.468$ (1) Å
$c = 8.977$ (1) Å
$\beta = 124.16$ (1)°
$V = 271.0$ (1) Å^3
$Z = 4$
$D_x = 8.395$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 30.50$–$33.19°$
$\mu = 24.56$ mm^{-1}
$T = 295$ K
Cylinder
0.055 (radius) × 0.15 mm
Grey

Data collection

Enraf-Nonius CAD-4F diffractometer
$\theta/2\theta$ scans
Absorption correction: by integration from crystal shape (Spek, 1983)
$T_{min} = 4.95$, $T_{max} = 7.95$
6332 measured reflections
3060 independent reflections
2266 observed reflections [$I > 2.5\sigma(I)$]

$R_{int} = 0.061$
$\theta_{max} = 49.99°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 9$
$l = -19 \rightarrow 19$
3 standard reflections frequency: 120 min intensity variations: 0.25,0.20, 0.29%

Refinement

Refinement on *F*
Final $R = 0.057$
$wR = 0.042$
$S = 6.979$
2266 reflections
29 parameters
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} < 10^{-5}$

$\Delta\rho_{max} = 5.7$ e Å^{-3}
$\Delta\rho_{min} = -5.8$ e Å^{-3}
Extinction correction: Zachariasen (Gaussian)
Extinction coefficient: 0.37 (1) × 10^4
Atomic scattering factors from Cromer & Mann (1968)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
Ag(1)	0.01880 (9)	0.1507 (2)	0.37099 (7)	2.04 (1)
Ag(2)	0.3327 (1)	0.8383 (2)	0.99566 (9)	2.88 (1)
Te	0.27179 (6)	0.1584 (1)	0.24247 (5)	1.277 (7)

Table 2. *Geometric parameters* (Å, °)

Ag(1)—Te	2.8765 (7)	Ag(2)—Te^{ix}	2.8415 (7)
Ag(1)—Te^{i}	2.8947 (7)	Ag(2)—Te^{x}	2.9050 (8)
Ag(1)—Te^{ii}	2.9648 (8)	Ag(2)—Te^{i}	3.0114 (9)
Ag(1)—Te^{iii}	3.0163 (8)	Ag(2)—Te^{xi}	3.034 (1)
Ag(1)—Ag(1^{iv})	2.841 (1)	Te—Te^{xii}	4.2331 (8)
Ag(1)—Ag(1^{ii})	3.0091 (7)	Te—Te^{xiii}	4.2811 (7)
Ag(1)—Ag(2^{v})	2.9093 (8)	Te—Te^{xiv}	4.3534 (8)
Ag(1)—Ag(2^{vi})	3.061 (1)		
Ag(1)—Ag(2^{vii})	3.133 (1)		
Ag(2)—Ag(2^{viii})	3.053 (2)		
Te—Ag(1)—Te^{ii}	119.17 (3)	Te^{i}—Ag(2)—Te^{x}	155.79 (3)
Te—Ag(1)—Te^{iii}	117.47 (3)	Te^{i}—Ag(2)—Te^{ix}	92.60 (2)
Te—Ag(1)—Te^{i}	104.48 (2)	Te^{i}—Ag(2)—Te^{xi}	95.32 (2)
Te^{ii}—Ag(1)—Te^{iii}	96.66 (2)	Te^{x}—Ag(2)—Te^{ix}	96.31 (2)
Te^{ii}—Ag(1)—Te^{i}	122.01 (2)	Te^{x}—Ag(2)—Te^{xi}	100.38 (2)
Te^{iii}—Ag(1)—Te^{i}	94.85 (2)	Te^{ix}—Ag(2)—Te^{xi}	117.49 (3)

Symmetry code: (i) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (iv) $-x, -y, 1 - z$; (v) $-x, 1 - y, 1 - z$; (vi) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (vii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (viii) $1 - x, 2 - y, 2 - z$; (ix) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (x) $x, 1 + y, 1 + z$; (xi) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (xii) $1 - x, -y, 1 - z$; (xiii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (xiv) $-x, -y, -z$.

The unit-cell dimensions and their e.s.d.'s were determined according to de Boer & Duisenberg (1984). We wanted to choose the same unit cell as Frueh (1959) in order to compare the atomic coordinates. The parameters a, c and β are very similar in the two alternative settings (both with space group $P2_1/c$) for this crystal. Frueh reported values (without e.s.d.'s) of a = 8.09, b = 4.46, c = 8.97 Å and β = 123.33° which can be transformed ($a' = -a-c$, $b' = -b$, $c' = c$) to a = 8.13, b = 4.46, c = 8.97 Å, β = 123.74°. Our unit cell corresponds to the former setting, despite appearing to be the latter; this became unambiguously clear on initiating refinements in both settings using Frueh's atomic coordinates as starting values. Examination of the final atomic coordinates of the structure did not yield extra metric symmetry elements (Le Page, 1987, 1988).

All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

The material used in this investigation was kindly placed at our disposal by Dr R. O. Felius (Instituut voor Aardwetenschappen, University of Utrecht, The Netherlands). We thank the Romanian Embassy in the Hague for help in tracing the exact finding place of the mineral.

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71038 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1058]

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Structure of $Na_3[VMo_{12}O_{40}].19H_2O$

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Abstract

The crystal structure of $Na_3[VMo_{12}O_{40}].19H_2O$, trisodium tetracontaoxo(dodecamolybdo)vanadate nonadecahydrate, has been determined by X-ray structure analysis. The polyanion centre sits on a special position with $\bar{4}3m$ symmetry. The VO_4 tetrahedron is at the centre, with three MoO_6 octahedra linking together, through shared edges, to form an Mo_3O_{13} unit. The O(1) atom common to these three octahedra is coordinated to the central V atom and four Mo_3O_{13} groups share O atoms to form the structure known as the Keggin anion. The V—O distance is 1.628 (15) Å, V—Mo is 3.501 (1) Å, and the Mo—O distances range from 1.665 (9) to 2.318 (8) Å.

Comment

Crystallization experiments yielded a number of different compounds containing discrete molybdovanadate anions, of which $[Mo_{57}V_6O_{183}(NO)_6(H_2O)_{18}]^{6-}$ is the largest polymetalate and shows the largest degree of aggregation of molybdate (Zhang, Huang, Shao & Tang, 1993). In solutions containing P^{v} or Si^{iv}, as well as Mo and W, Keggin-type anions are readily formed (Weakley, 1974). Owing to the similarity in behaviour between P^{v} and V^{v} in aqueous solution, a Keggin anion (Keggin, 1934) with V^{v} as the central atom was considered as a species likely to be found in the solution investigated. Crystal structures have been reported for two other Keggin-type $XM_{12}O_{40}$ anions with V^{v} at the centre,

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