

Crystal Structure of Ag_2TeS_3 and $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$) and the Geometry of $\text{Te}(\text{IV})\text{S}_3$ Polyhedra

F. Pertlik

Institut für Mineralogie und Kristallographie, Universität Wien, A-1090 Wien, Austria

Summary. Structural data determined by single crystal X-ray experiments ($T = 300 \text{ K}$) are reported for Ag_2TeS_3 (monoclinic, $Cc-C_3^4$; $a = 6.783(1)$, $b = 11.567(2)$, $c = 7.693(1) \text{ \AA}$; $\beta = 114.44(1)^\circ$; $Z = 4$; $R = 0.044$) and for $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$; monoclinic, $P2_1/c-C_{2h}^5$; $a = 5.761(9)$, $b = 12.171(8)$, $c = 8.342(4) \text{ \AA}$; $\beta = 92.26(6)^\circ$; $Z = 4$; $R = 0.030$). In both compounds the atomic arrangements are characterized by isolated trigonal pyramidal TeS_3 polyhedra, irregularly coordinated Ag and Na atoms forming AgS_4 and $(\text{Na}, \text{Ag})\text{S}_4$ polyhedra, and slightly distorted NaS_6 octahedra. Crystals of both compounds were synthesized under moderate hydrothermal conditions from an equimolar mixture of the elements in concentrated aqueous ammonia and 5 N NaOH solution, respectively.

Keywords. Ag_2TeS_3 ; $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$); Hydrothermal syntheses; Crystal structure; Crystal chemistry.

Kristallstruktur von Ag_2TeS_3 und $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$) nebst einem Vergleich der Geometrie von TeS_3 -Gruppen

Zusammenfassung. Es wird über die mittels Röntgenbeugungsexperimenten an Einkristallen bei 300 K bestimmten Strukturen von Ag_2TeS_3 (monoklin $Cc-C_3^4$; $a = 6.783(1)$, $b = 11.567(2)$, $c = 7.693(1) \text{ \AA}$; $\beta = 114.44(1)^\circ$; $Z = 4$; $R = 0.044$) und $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$; monoklin, $P2_1/c-C_{2h}^5$; $a = 5.761(9)$, $b = 12.171(8)$, $c = 8.342(4) \text{ \AA}$; $\beta = 92.26(6)^\circ$; $Z = 4$; $R = 0.030$) berichtet. In beiden Verbindungen ist die Atomanordnung durch isolierte trigonal-pyramidale TeS_3 -Polyeder, unregelmäßig koordinierte Ag- und Na-Atome, AgS_4 - und $(\text{Na}, \text{Ag})\text{S}_4$ -Polyeder bildend, sowie leicht verzerrte NaS_6 -Oktaeder charakterisiert. Kristalle der beiden Verbindungen wurden unter moderaten Hydrothermalbedingungen aus einem equimolaren Gemenge der Elemente und konzentrierter wässriger Ammoniaklösung bzw. 5 N NaOH-Lösung gezüchtet.

Introduction

The coordination chemistry of Ag(I) atoms and sulfur atoms is characterized by tendencies to form collinear bonds (sp -hybridization) or more or less distorted tetrahedral bonds (sp^3 -hybridization). Intermediates between these two coordination types are also common. An appreciable covalent character of these Ag–S bonds is indicated by some physical properties (e.g. colour, electric conductivity).

Crystals suitable for X-ray investigations have been synthesized under hydrothermal conditions in silver-chalcogen-atom systems and characterized by their physical and chemical properties [1–3].

The two title compounds are members of a group of thiotellurites of which only four structures have been described in the literature: $\text{BaTeS}_3 \cdot 2\text{H}_2\text{O}$ [4, 5], $(\text{NH}_4)_2\text{TeS}_3$ [5], BaTeS_3 [6], and $\text{K}_3(\text{SH})\text{TeS}_3$ [7]. In all these structures, isolated TeS_3 polyhedra occur; no aggregation to larger units like groups, chains, or rings *via* common S atom corners is observed. TeS_3 polyhedra can also be found in structures of minerals of the tetrahedrite group (especially goldfieldite) [8].

Results and Discussion

The values of some geometric parameters for the two crystallographically independent Ag polyhedra in Ag_2TeS_3 and the (Na, Ag) position in $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$), for which the occupation was more or less postulated by semi-quantitative analyses in combination with cell volume and cell content (four formula units per unit cell) and later confirmed by electron density values in structure factor calculations, are given in Table 2. Whereas the values for the two first mentioned polyhedra are of common crystal chemical experience, the (Na, Ag) S_4 polyhedron is, to the best knowledge of the author, unique in crystal chemistry. There is a clear cut four coordination by sulfur atoms for this position, and the mean $\langle(\text{Na, Ag})\text{-S}\rangle$ value of 2.80 Å is close to the sum of the effective radii of formal Na^{1+} and S^{2-} atoms (ca. 2.72 Å, [10]). The relatively high values for the anisotropic displacement parameters of the (Na, Ag) position (cf. Table 1) can be interpreted as great thermal vibrations or as split atom positions. Comparable parameters for Ag atom positions without any substitution by other atoms have been determined in the structure of xanthokonite for one Ag atom [11], and splittings of Ag atom positions up to distances of approximately 2.0 Å in the structure of $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ for two Ag atom positions [3]. These disorder phenomena (static or dynamic effects; postulated or definitely determined) in crystal structures are responsible for a more one sided coordination of the Ag atoms with shorter Ag–S and $\langle\text{Ag-S}\rangle$ distances, respectively. The mean $\langle(\text{Na, Ag})\text{-S}\rangle$ distance is in accordance with values found for NaS_4 polyhedra. Therefore, no severe contradiction occurs for such an Ag–Na substitution of this position, and the height and shape of electron density function for position (Na, Ag) is the mean value for two atoms, statistically distributed over this position.

It is worth mentioning that the crystal chemistry of AgS_x polyhedra is very complex with regard to the coordination number of the Ag atoms, the mean Ag–S distances, and the volumes of the space filling AgS_x polyhedra. A compilation of the geometric parameters in clear cut AgS_4 polyhedra concerning Ag–S and S–S distances as well as S–Ag–S angles and distortion parameters reveals a range from 2.57 Å to 2.71 Å for the mean Ag–S distance [9]. This variability could also be found for the calculated volumes of space-filling polyhedra for AgS_4 tetrahedra (18.97 Å³ to 23.33 Å³, [2]).

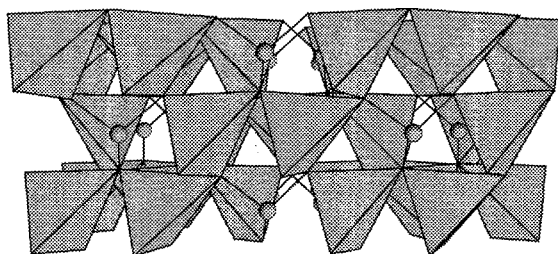


Fig. 1. Perspective projection of the atomic arrangement in Ag_2TeS_3 onto (100); in a mixed technique, the connection of AgS_4 tetrahedra (dashed) *via* common corners (S atoms arranged parallel to (001)) as well as the Te atoms with their shortest bonds (balls and sticks) are drawn [18]

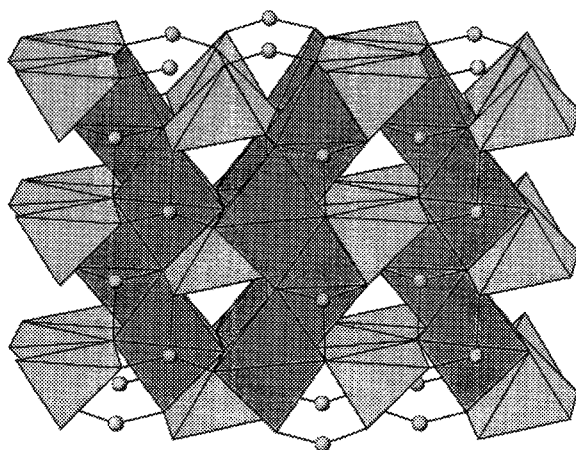


Fig. 2. Perspective projection of $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$) onto (001) showing the interconnection of NaS_6 octahedra and $(\text{Na}, \text{Ag})\text{S}_4$ tetrahedra (dashed) with the pyramidal TeS_3 groups; direction b from left to right [18]

In both title compounds the TeS_3 polyhedra can be described as trigonal pyramids with the Te atom at the apex at a distance of *ca.* 1.0 Å away from the plane defined by the three S atoms.

The connection of the AgS_4 and TeS_3 polyhedra in the structure of Ag_2TeS_3 is such that the S atoms are arranged in layers parallel to (001), whereas Ag and Te atoms are located in between (Fig. 1). The AgS_4 polyhedra themselves are combined *via* common S atom corners to a network. The topological description of this arrangement of atoms doesn't correspond with the strength of the chemical bonds, and a pronounced cleavage parallel to these layers was not observed. The structure of $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ consists of a complex three dimensional connection of tetrahedra and octahedra as shown in Fig. 2. Especially the NaS_6 octahedra form rows parallel to the direction (100).

The Geometry of Te(IV)S₃ Polyhedra

A one-sided coordination of tetravalent tellurium against oxygen atoms is common experience in crystal structures of this element. Usually, this coordination occurs as a three, three plus one, or two plus two, occasionally also as an approximately ideal one-sided five coordination [12–15]. Summarizing the crystal chemistry of tetravalent tellurium against oxygen, the following crystal chemical axiom has been worked out by *Zemann* [13]: in TeO_x polyhedra, the short bonded O atom neighbours together with the long bonded O atom neighbours are arranged in a way that can be described as distorted octahedra in which, depending on the coordination number, some corners remain unoccupied.

The crystal structures containing TeS₃ polyhedra mentioned in Refs. [4–7] are somewhat different with respect to this feature. There is a clear gap in the sequence of distances: three Te–S distances are below 2.5 Å, whereas the next S atom neighbours are more than 3.1 Å apart [16]. The problem of transitions from coordination number three to four or even five without any gap as well as that concerning a condensation of TeS₃ units over common S atom corners remain still unsolved.

Experimental

Crystals of the title compounds were synthesized under hydrothermal conditions in teflon-lined steel vessels at 300 K. Reaction time: one week; Ag₂TeS₃: system Ag–Te–S, concentrated aqueous ammonia solution; Na(Na_{1-x})TeS₃ (*x* ≈ 0.5): same system, 5 N NaOH solution; equimolar ratios of elements. Small variations of the stoichiometric ratio yielded no further crystalline compounds up to now.

Table 1. Atomic coordinates and anisotropic displacement parameters (pm²) defined as $\exp(-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j a_i^* a_j^*)$ in Ag₂TeS₃ and Na(Na_{1-x}Ag_x)TeS₃ (*x* ≈ 0.5), respectively; e.s.d. in parentheses; (*) fixes the origin

	<i>x</i>	<i>y</i>	<i>z</i>	U11	U22	U33	U23	U13	U12
Ag₂TeS₃									
Te	0.2(*)	0.4013(1)	0.6(*)	200(2)	186(2)	177(2)	-9(1)	45(1)	6(2)
Ag(1)	0.7095(2)	0.7749(1)	0.1308(2)	360(5)	386(5)	374(8)	-38(2)	82(5)	-52(3)
Ag(2)	0.7133(2)	0.4373(1)	0.0940(2)	345(6)	368(6)	421(6)	-19(2)	96(3)	-72(4)
S(1)	0.4587(4)	0.0449(2)	0.4028(4)	238(10)	193(10)	237(10)	5(3)	59(6)	17(5)
S(2)	0.4827(5)	0.2622(2)	0.9691(4)	221(11)	212(11)	264(11)	14(3)	34(6)	9(6)
S(3)	0.9370(4)	0.8801(2)	0.4443(4)	217(10)	215(9)	265(10)	-6(3)	76(6)	-6(5)
Na(Na_{1-x}Ag_x)TeS₃ (<i>x</i> ≈ 0.5)									
Te	0.21208(6)	0.08967(3)	0.18276(4)	189(1)	214(1)	240(1)	-2(1)	17(1)	3(1)
Na	0.2549(4)	0.0811(2)	0.6369(3)	248(11)	264(12)	341(12)	3(4)	18(7)	-1(8)
(Na, Ag)	0.7436(2)	0.2687(1)	0.3731(2)	331(7)	332(7)	332(7)	-24(2)	33(4)	-45(4)
S(1)	0.2462(3)	0.9360(1)	0.3532(2)	254(6)	223(7)	300(7)	6(2)	15(4)	7(4)
S(2)	0.8059(2)	0.0981(2)	0.1389(2)	216(6)	364(6)	343(7)	19(3)	6(4)	7(5)
S(3)	0.2671(3)	0.2346(1)	0.3692(2)	307(7)	225(6)	277(7)	-6(2)	22(4)	-5(4)

Table 2. Interatomic distances (\AA), corresponding mean values $\langle \rangle$ (\AA), and bond angles ($^\circ$) within the Ag, Na, and (Na, Ag) polyhedra; e.s.d. in parentheses

Ag_2TeS_3				
Ag(1)	S(3)	S(3')	S(2)	S(1)
S(3)	2.548(3)	4.956(4)	3.982(3)	3.898(4)
S(3')	151.16(9)	2.569(3)	4.031(4)	4.177(9)
S(2)	100.55(8)	101.72(8)	2.629(2)	4.045(3)
S(1)	93.43(9)	102.05(9)	96.31(8)	2.801(3)
$\langle \text{Ag}(1)\text{-S} = 2.64 \rangle$				
Ag(2)	S(2)	S(1)	S(1')	S(3)
S(2)	2.495(3)	4.832(4)	4.124(2)	4.146(4)
S(1)	143.78(9)	2.587(3)	3.984(4)	3.923(4)
S(1')	106.70(9)	99.16(8)	2.646(2)	4.150(4)
S(3)	104.67(9)	94.77(9)	100.62(9)	2.741(3)
$\langle \text{Ag}(2)\text{-S} = 2.62 \rangle$				
$\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$)				
(Na, Ag)	S(2)	S(3)	S(1)	S(2')
S(2)	2.758(2)	4.277(2)	4.125(2)	5.574(3)
S(3)	101.22(6)	2.776(2)	4.210(2)	4.070(2)
S(1)	96.31(7)	98.58(6)	2.779(2)	4.125(2)
S(2')	162.20(7)	91.93(6)	93.49(6)	2.884(2)
$\langle (\text{Na, Ag})\text{-S} = 2.80 \rangle$				
$\text{Na} - \text{S}(1) = 2.880(3)$		$\text{Na} - \text{S}(3) = 2.914(3)$		
$-\text{S}(1') = 2.899(3)$		$-\text{S}(1'') = 2.952(3)$		
$-\text{S}(2) = 2.903(3)$		$-\text{S}(3') = 2.963(3)$		
$\langle \text{Na} - \text{S} = 2.91 \rangle$				
S - Na - S from 76.66(7) to 98.49(9) and 167.54(9) to 171.09(9) respectively.				

The crystals used for structure investigations were checked by *Weissenberg* type film methods. Details on cell metrics, data collection, structure solutions, and refinements are given in Table 3. The atomic coordinates of the Ag and Te atom positions were found by direct method strategy, those of the other atoms by subsequent *Fourier* and difference *Fourier* summations. During the final stage of refinement, anisotropic displacement factors were allowed to vary. The structure parameters are given in Table 1, some relevant interatomic distances in Table 2. In both structure calculations, complex neutral scattering functions [17] were used, and the *Lorentz* and polarization effects were corrected in usual ways. ($|F_o| - |F_c|$) lists were deposited at the Institute for Mineralogy and Crystallography of the University of Vienna, Austria.

Crystals of Ag_2TeS_3 decomposes during X-ray exposure, therefore only one set of data was measured. For $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$), two set of data were collected ($R_{\text{int}} = 0.023$).

Table 3. Unit cell parameters as well as data for X-ray intensity measurements and structure refinements for Ag_2TeS_3 and $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$); Stoe four-circle diffractometer AED2, Mo X-ray tube graphite monochromator

$a(\text{\AA})$	6.783(1)	5.761(9)
$b(\text{\AA})$	11.567(2)	12.171(8)
$c(\text{\AA})$	7.693(1)	8.342(4)
$\beta(^{\circ})$	114.44(1)	92.26(6)
$V(\text{\AA}^3)$	549.5	584.5
Z	4	4
Space group	Cc	$\text{P2}_1/\text{c}$
Crystal dimensions (mm)	$0.20 \times 0.15 \times 0.20$	$0.30 \times 0.15 \times 0.15$
Colour	dark red	redish-yellow
2θ max for data collection ($^{\circ}$)	70	70
Measured reflections	2522	5370
Unique reflections	2328	2519
Reflections with $F_o > 4\sigma(F_o)$	1669	1759
Absorption correction	ψ scan data	ψ scan data
$R/R_w; w = [\sigma(F_o)]^{-2}$	0.047/0.044	0.030/0.030
$\max \Delta/\sigma$	$< 10^{-3}$	$< 10^{-3}$
Variable parameters	54	56
Final difference <i>Fourier</i> map ($\text{e}\text{\AA}^{-3}$)	2.5 to -3.6	1.2 to -1.0

The chemical composition of the title compounds was determined semiquantitatively by EDX analyses. Ordering phenomena for position (Na, Ag) within the structure of $\text{Na}(\text{Na}_{1-x}\text{Ag}_x)\text{TeS}_3$ ($x \approx 0.5$) could not be detected, even on long exposure *Weissenberg* type film photographs.

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