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Preparation and Crystal Structure of $K_2Ag_{12}Te_7$

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Summary. Single crystals of $K_2Ag_{12}Te_7$ ($a = 11.460(2)$, $c = 4.660(1)$ Å; $V = 530.01$ Å^3; space group: $P6_3/m$; $Z = 1$) were synthesized under hydrothermal conditions at 250°C in concentrated aqueous KOH solution from elementary silver and tellurium. The crystal structure is characterized by trigonal prismatic KTe_6 polyhedra, connected *via* two common faces to KTe_3 rods parallel to [001]. These rods are combined by two crystallographically independent Ag atoms, each coordinated to four Te and three Ag atoms (Ag–Te and Ag–Ag < 3.1 Å) to a framework of the formula $(K_2Ag_{12}Te_6)^{2+}$ and with channels parallel to the sixfold axis. These channels are statistically occupied by one further Te atom per unit cell, distributed over two independent positions.

Keywords. $K_2Ag_{12}Te_7$; Single crystals; Crystal structure; Crystal chemistry.

Introduction

Occurrence, analysis, and synthesis of tellurium minerals as well as the investigation of the geochemical and crystal chemical behaviour of the element tellurium are general scientific topics [1]. Reports about structure determinations of naturally occuring silver tellurides [2–4], their syntheses under hydrothermal conditions [5, 6], and the crystal chemistry of these tellurides [7] have been published within the last two decades.

Synthesis experiments in the system Ag–Te (aqueous solutions of sodium or potassium hydroxide, various *pH* values) have revealed *e.g.* crystals of $Ag_{10,5}Te_7$ [5, 6] and crystals of the phase $K_2Ag_{12}Te_7$. The latter compound is a further representative of the type $A_2B_{12}C_7$ with the prototype structure $Zr_2Fe_{12}P_7$ [8]; approximately twenty further isotypic phosphorus and arsenic compounds are known [9–12].

From the chemical point of view, KAg_3Te_2 [13], a layer type structure, and $CsAg_5Te_3$ [14], a tunnel structure, are comparable to $K_2Ag_{12}Te_7$. However, only the coordination polyhedra, but not the interconnection of the individual polyhedra are comparable within these three different structures.

Although the solar system abundance of Te with *ca.* 3.1 c.a.u. (cosmic abundance units, *i.e.* atoms per 10^6 Si atoms) is very low [15], the ionic radius of tellurium and its physico-chemical properties are so different from the other

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chalcogen atoms that there is only a very limited diadochy to be expected. Therefore, it is not surprising that the mineral group of tellurites (including tellurates) includes about two dozens of approved representatives, the groups of tellurides (including sulfosalts) about three dozens.

Results and Discussion

The final atomic parameters and selected interatomic distances determined for the title compound $K_2Ag_{12}Te_7$ are compiled in Tables 1 and 2; in Fig. 1, the atomic arrangement is given in a projection onto (00.1).

Not affected by the occupation statistics of position Te(2), the potassium atom exhibits a clear-cut six coordination by Te(1) atoms in the form of a trigonal prism.

Table 1. Atomic coordinates, number of positions, individual *Wyckoff* notation, and anisotropic (split Te-positions with occupation factors 0.15(5) for Te(2) and 0.20(5) for Te(3) isotropic) displacement parameters defined as $\exp(-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_j\mathbf{a}_i^*\mathbf{a}_j^*)$ Å^2 $\times$ 10^4; e.s.d. values in parentheses

	Atom	x	y	z	
	K on 2(d)	2/3	1/3	1/4	
	Ag(1) on 6(h)	0.0638(2)	0.4076(3)	1/4	
	Ag(2) on 6(h)	0.2782(3)	0.1536(3)	1/4	
	Te(1) on 6(h)	0.3159(2)	0.4228(1)	1/4	
	Te(2) on 4(e)	0	0	0.181(2)	
	Te(3) on 2(b)	0	0	0	
Atom	U_{11}/U_{iso}	U_{22}	U_{33}	$U_{23} = U_{13}$	U_{12}
K	313(28)	U_{11}	249(47)	0	$1/2U_{11}$
Ag(1)	339(12)	528(14)	409(14)	0	185(10)
Ag(2)	512(15)	368(13)	758(20)	0	210(11)
Te(1)	240(8)	223(8)	218(8)	0	124(6)
Te(2)	275(24)				
Te(3)	342(63)				

Table 2. Selected interatomic bond distances (Å) for $K_2Ag_{12}Te_7$; e.s.d. values in parentheses; due to statistics in the occupations of the two atomic positions Te(2) and Te(3), only one interatomic distance is realized; the e.s.d. values for these distances are not significant and therefore omitted

Ag(1)−Te(1) = 2.806(3)	Ag(2)−Te(1) = 2.894(3)
Ag(1)−Te(1) = 2.882(2); 2x	Ag(2)−Te(1) = 3.057(2); 2x
Ag(1)−Te(1) = 2.953(3)	Ag(2)−Ag(1) = 2.939(3)
Ag(1)−Ag(2) = 2.939(3)	Ag(2)−Ag(1) = 3.025(2); 2x
Ag(1)−Ag(2) = 3.025(2); 2x	Ag(2)−Te(2) = 2.784(−)
	Ag(2)−Te(3) = 3.001(−)
Te(1)−Ag(1) = 2.806(3)	Te(2)−Ag(2) = 2.784(−)
Te(1)−Ag(1) = 2.882(2); 2x	Te(3)−Ag(2) = 3.001(−)
Te(1)−Ag(1) = 2.953(3)	
Te(1)−Ag(2) = 2.894(3)	
Te(1)−Ag(2) = 3.057(2); 2x	K−Te(1) = 3.566(1); 6x
Te(1)−K = 3.566(1); 2x	

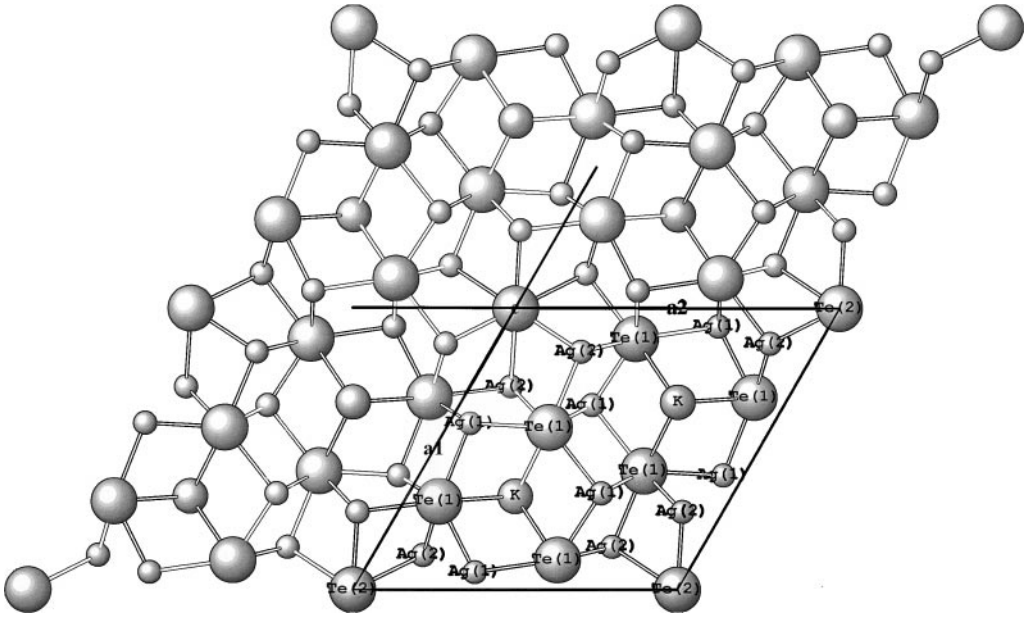

Fig. 1. Atomic arrangement of $K_2Ag_{12}Te_7$ in a projection onto (00.1)

These prisms are combined *via* two common faces (representing their basis) to rods parallel to [001]. The numerical values of the K–Te distances, six times 3.566 Å, are comparable to values determined in the following potassium tellurides: KAg_3Te_2 [15] and the isotypic compound KCu_3Te_2 [16], K_2Te [17], KLiTe [18], K_3BiTe_3 [19], $KSmTe_2$ [20], KAuTe [21], KCuTe [22], and $KInTe_2$ [23]. All these compounds with more or less regular coordination polyhedra exhibit K–Te distances ranging from 3.50 to 3.80 Å. It is remarkable that within these KTe_x polyhedra neither the number of neighbours nor the interconnection of the polyhedra show great influence on the individual K–Te distance.

The two crystallographically independent Ag atoms are coordinated to Ag as well as to Te atoms. The Ag–Ag distances between 2.939 and 3.025 Å are comparable to the Ag–Ag distances in elementary silver (2.889 Å), but metallic interactions between the Ag atoms are unlikely. An argument might be the strong covalent character of the short Ag–Te bonds in the silver polyhedra (from 2.806 to 3.057 Å). They are within the range of Ag–Te bonds from ~2.74 to ~3.30 Å (without clear upper limit), recalculated from the crystal structures of ten compounds with individual Ag–Te bonds [7].

The coordination polyhedron around the atom Ag(1) exhibits an ordered arrangement, the polyhedron around atom Ag(2) splits up into two arrangements caused by a statistic occupation of two independent Te atom positions. The distances Ag(2) to Te(2) and Te(3), the split positions, differ by 0.22 Å (cf. Table 2).

Each of the Te(1) atoms involved in the polyhedra of the K and Ag atoms exhibits a coordination in which two K atoms and seven Ag atoms are arranged in opposite positions. In the broadest sense, this polyhedra may be described as trigonal prisms with three further atoms located at the centres of the rectangular faces.

Structure determinations for the ternary compounds $A_2B_{12}C_7$ and the title compound yielded the same motive for the framework. Some differences exist in

the location of atoms, statistically distributed and arranged parallel to the six-fold axis. In $Zr_2Fe_{12}P_7$, one P atom is located at (0,0,0) [8, 9]; in the family $M_2Rh_{12}As_7$, the As atom is located at (0,0,$z \sim 0.10$) [10]. In both cases the thermal displacement parameters for these atoms parallel to [001] are by twenty to forty times larger than orthogonal to this direction. These parameters indicate a very strong one-dimensional disorder. Within the determined size of lattice parameter c, only one fully occupied Te atom may be situated at the six fold axis, with interatomic distances to the identic atom of 4.66 Å. In the present structure model the shortest distances between the positions Te(2) and Te(3) with 0.846 Å or Te(2) and Te(2) with 0.638 Å prevent full occupancy of one position as well as an ordered arrangement of the two different positions. A nonstatistic arrangement of the Te atoms, achievable by a change of symmetry ore lattice parameters, was excluded by careful investigation of the *Weissenberg* photographs.

Experimental

Syntheses were started from the elements Ag (Silberkolloid reinst, Merck, Darmstadt) and Te (tellurium metal, pure powder, Riedel-De Haen AG., Seelze-Hannover) in a molar ratio of Ag:Te ≈ 2:1. The powders of the elements were ground together. A suspension of 1 g of this mixture in concentrated aqueous KOH solution (KOH *p.a.* Austranal Präparate) was used in each experiment. The experiments were performed in a teflon-lined steel vessel (volume $\sim 5\,cm^3$). The vessel was filled to 80% of its capacity and heated to 250°C for two days, followed by cooling to room temperature in one day. Variations in the Ag:Te ratio at constant conditions and milieu resulted in crystals of the title compound and aggregates of elementary Ag or well-developed prismatic Te crystals depending on the excess of the individual element. It is worth mentioning that the described experiments performed in NaOH solution result in crystals of a phase $Ag_{10,5}Te_7$, related to the mineral stützite [6, 7]. The quality of the single crystals suitable for X-ray work was investigated by classical film methods. These photographs provided evidence for isotypism between the title compound and compounds of the structure type $A_2B_{12}C_7$.

For this structure type, on the basis of single-crystal *Weissenberg* photographs taken for the prototype structure of $Zr_2Fe_{12}P_7$, the *Laue* symmetry 6/m without any extinctions for the individual reflections was derived [9], and space group P-6 (Nr.174) was postulated. Contrary to this fact, for the family of compounds with formula $M_2Rh_{12}X_7$ (M = Y, Zr, rare earths; X = P, As) a systematic

Table 3. Summary of crystal data, X-ray data collection, and data of structure refinement of $K_2Ag_{12}Te_7$

$a = 11.460(2)$ Å	Crystal size: 0.20 × 0.20 × 0.40 mm^3
$c = 4.660(1)$ Å	μ: 206.3 cm^{-1}
$c/a = 0.407$	2 ϑ/ω – scan mode, scan width 1.50^0 + (α_1−α_2 dispersion)
$V = 530.01$ Å^3	3 standard reflections, interval 120 min
$Z = 1$	Range of data: $2^0 < 2\vartheta < 57^0$
F (000) ≈ 966	Measured reflections: 1667 (±h,±k,±l)
$\rho_{(calc)} = 7.099$ g · cm^{-3}	Unique reflections: 471; $R_{int} = 0.013$
Space group: $P6_3$/m (No 176)	Reflections with $F_o > 2\sigma(F_o)$: 471
R(F), $F_o > 2\sigma(F_o) = 0.035$	Empirical absorption correction: ψ−scan data
$R_w = 0.030$; $w = (\sigma(F_o))^{-2}$	Final difference *Fourier* summation: 2.90 to −3.09 e/Å^3
Variable parameters: 27	Stoe AED 2 four circle diffractometer
Max $\Delta/\sigma < 0.001$	Mo X-ray tube, graphite monochromator

extinction of reflections 001 with $l = 2n + 1$ was observed, indicating either space group $P6_3/m$ (Nr.176) or $P6_3$ (Nr.173) [12, 13].

Conscious of this discrepancy in symmetry, careful investigations of the title compound by *Weissenberg* photographs were performed. These investigations as well as the internal *R*-value of the 3-dimensional data set ($R = 0.013$, cf. Table 3) and the determined extinctions confirmed the *Laue* class and condensed space group $P6_3/^*$.

A difference *Fourier* summation starting from the framework $[K_2Ag_{12}Te_6]^{2+}$ revealed two maxima in channels parallel to [001]. The positional as well as the occupation parameters of the two maxima labelled Te(2) and Te(3) were refined by the least squares technique. The anisotropic refinement failed. The two maxima show an unusual elongation parallel to [001], indicating a great mobility of these atoms in this direction.

The crystal data, parameters for X-ray data collection, and results of structure refinement by full-matrix least-squares techniques are compiled in Table 3. Refinement of the atomic parameters was performed using complex neutral atomic scattering functions [24, 25].

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