Crystal Structures and Preparation of K_2AgVS_4 and Rb_2AgVS_4 by Using the Molten Flux Method: Low-Dimensional Materials with Infinite Metal-Ion-Centered Tetrahedra Chains

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Received February 12, 1996

Key Words: Low-temperature synthesis / Reactive flux method / Quaternary vanadium sulfide / Low-dimensional materials

The quaternary sulfides K_2AgVS_4 and Rb_2AgVS_4 crystallize as dark violet needle-like crystals with a metallic lustre. Infinite Ag- and V-centered tetrahedra sharing common edges are running parallel to the crystallographic *a* axis. The chains are separated by K^+ or Rb^+ ions which are in an eightfold environment. The tetrahedra are occupied in an ordered fashion. The Ag−V interatomic distances amount to 2.904(1) and 2.910(1) Å, respectively, which is significantly larger than the sum of the ionic radii of Ag^+ and V^{5+}. Whereas the V−S distances are in the normal range, the average ⟨Ag−S⟩ distances are the shortest reported so far indicating strong covalent bonding between monovalent Ag^+ and S^{2-}. In addition, the title compounds represent very rare examples of AgS_4 polyhedra with equidistant Ag−S bonds. The geometrical parameters within the tetrahedra chains are only slightly affected when K^+ is replaced by the larger Rb^+ demonstrating the rigidity of the bonding properties within the tetrahedra. The compounds are isotypic with the quaternary copper sulfide K_2CuVS_4 and the selenides K_2CuMSe_4 (M = Nb, Ta).

Since the so-called reactive flux method has been established as a new method in preparative inorganic chemistry the synthesis of ternary and multinary metal (poly)chalcogenides in molten polychalcogenide salt solutions has been successfully applied.

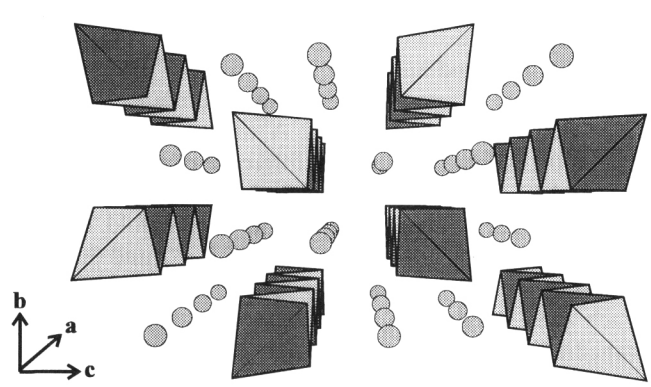
A large number of new transition metal chalcogenides were prepared[1]. These new compounds exhibit in part highly interesting new crystal features and also interesting physical properties. Many of the compounds synthesized in this way consist of one- and two-dimensional structures with polychalcogenides as ligands of the metal centers ($K_4Ti_3S_{14}$[2], $K_4Zr_3Te_{17}$[3], $K_3CuNb_2Se_{12}$[4], α-$KCuS_4$[5], $CsSbS_6$[6], $K_2Sn_2S_8$[7]). Despite the increasing number of new compounds prepared by the molten salt technique, a close look at the literature reveals a number of "white dots" in the periodic table. This means that up to now many transition metal chalcogenide compounds that would potentially be prepared by the reactive flux method are not yet known.

In this paper we report on the synthesis and structural characterization of new quaternary silver vanadium sulfides prepared by the reactive flux method.

Results and Discussion

The crystal structure of A_2AgVS_4 (A = K, Rb) is displayed in Figure 1. The transition metal ions are in a tetrahedral environment of four S^{2-} anions. These metal-centered tetrahedra share two of their outer edges. The resulting chains are running parallel to the crystallographic *a* axis. The tetrahedra are occupied in an ordered fashion. All refinements of the crystal structures with interchanged cations resulted in high reliability factors as well as physically senseless anisotropic displacement parameters (see Experimental). The fact that the equivalent isotropic displacement factor U_{eq} for Ag is twice as large as the value for V is not uncommon. The inspection of the ADPs of about 150 Ag-containing compounds in the ICSD data base revealed that in the overwhelming cases Ag exhibits larger ADPs than the other metal atoms in these compounds, regardless of the nature of the other metal atoms in the compounds and of the actual environment of Ag.

Figure 1. Structure of A_2AgVS_4 (A = K, Rb) with chains of alternating edge-sharing AgS_4 and VS_4 tetrahedra (view parallel to the crystallograpic *a* axis). Cations are represented by circles



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The V–S distance of 2.178(1) Å is identical in both compounds and comparable to those reported for K_3VS_4[8] and $(NH_4)_3VS_4$[9]. Monovalent Ag atoms coordinated to four S atoms occur in a large number of compounds (see examples given in ref.[11]). The Ag–S bond lengths for monovalent Ag reported in the literature show a large variation, and values ranging from 2.3 to 3.0 Å are common. The average ⟨Ag–S⟩ values scatter between 2.57 and 2.70 Å. But examples with silver in an equidistant tetrahedral coordination are very rare. To the best of our knowledge the only known compounds are $AgFeS_2$[10] and $(NH_4)Ag_2AsS_4$[11]. Recently, Auernhammer et al. compiled the Ag–S distances, S–Ag–S angles, and S–S distances of about 20 AgS_4 polyhedra reported in the literature[11]. When these values are used the Ag–S distances observed in the title compounds of 2.515(1) Å (A = K) and 2.513(1) Å (A = Rb) are the shortest average distances reported so far. If we assume an ionic radius of 1.00 Å for Ag^+ and of 1.84 Å for S^{2-}[12] the observed Ag–S distances are about 0.33 Å shorter than the sum of the ionic radii indicative of strong covalent bonding interactions.

The V–Ag distances of 2.904(1) and 2.910(1) Å for the K and Rb compound, respectively, are too long for interatomic bonding interactions.

As expected, the tetrahedral environment of the V^{5+} ions with angles ranging from about 106 to 114° is less distorted than the tetrahedral coordination about the Ag^+ ions (S–Ag–S: 93–119°). This is also evidenced by the distortion parameter DP_a(S–V–S) of 0.0296 and 0.0280, respectively [DP_a(S–Ag–S) = 0.0993 and 0.101; compare Table 3]. In the isotypic compound K_2CuVS_4 the tetrahedral coordination sphere about the V^{5+} ion is much less distorted (⟨S–V–S⟩ = 109.47°, DP_a = 0.0053)[13]. This observation indicates that the distortion of the VS_4 tetrahedra in the title compounds is due to the constraints exerted by the large Ag^+ ion. As noted in the abstract the title compounds are isostructural to the quaternary sulfide K_2CuVS_4 and to the selenides K_2CuMSe_4 (M = Nb, Ta). In Table 4 selected geometrical parameters of the title compounds as well as of the isostructural compounds are summarized for comparison.

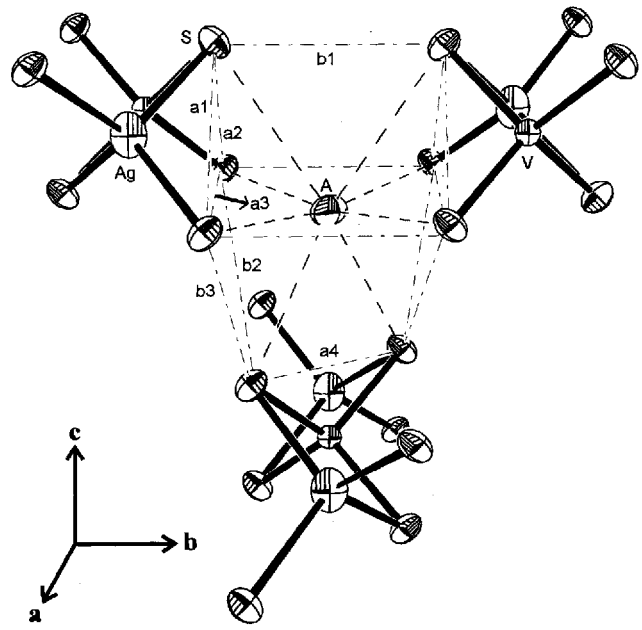
The larger ionic radius of Rb^+ (1.61 Å) compared to that of K^+ (1.51 Å)[12] only slightly affects the length of the *a* axis, but a pronounced enlargement of the *b* as well as the *c* axis is observed.

The alkali ions are in an eightfold coordination with K–S and Rb–S distances ranging from 3.267 to 3.723 Å for the K compound and from 3.352 to 3.793 Å for the Rb compound. The average ⟨K–S⟩ distance amounts to 3.422 Å. For ⟨Rb–S⟩ a value of 3.522 Å was calculated, an increase of 0.1 Å which is just the difference of the ionic radii of K^+ and Rb^+. In K_2S_3 and Rb_2S_3 the two crystallographically independent alkali ions are in a sevenfold coordination with average ⟨K–S⟩ distances of 3.237 and 3.312 Å and average ⟨Rb–S⟩ distances of 3.365 and 3.450 Å[14,15].

Each AS_8 polyhedron is connected to three different tetrahedra chains. The polyhedron shares trigonal faces with two of these chains and another edge with the third chain. This connection scheme is depicted in Figure 2. The lengths of these edges (denoted as a1 to a4 in Figure 2) of the AS_8 polyhedra are determined by the geometry of the tetrahedra chains. The tetrahedra are rigid and therefore these distances are only variable within a limited range. This rigidness is reflected by the nearly unchanged angles S–Ag–S and S–V–S. Consequently, the lengths of these edges in the K and Rb compound exhibit only very small variations [a1 = 4.296(1), a2 = 3.482(1), a3 = 5.807, and a4 = 3.523(1) Å in the K compound and a1 = 4.298(1), a2 = 3.489(1), a3 = 5.820, and a4 = 3.520(1) Å in the Rb compound]. The rigidness of the V^{5+}- and Ag^+-centered tetrahedra also explains why the *a* axis remains nearly unaffected when the smaller K^+ ion is replaced by the larger Rb^+ ion.

As a further consequence of the low flexibility of the tetrahedra the individual A–S distances cannot expand in the same manner. The larger Rb^+ ion causes an expansion of the unconstrained edges (denoted as b1 to b3 in Figure 2). These edges enlarge from b1 = 3.891(1), b2 = 4.897(1), and b3 = 3.666(1) Å to b1 = 4.111(1), b2 = 5.062(1), and b3 = 3.872(1) Å when K^+ is replaced by Rb^+. Therefore, the RbS_8 polyhedron shows a slightly different distortion compared to that around K^+ as evidenced by the distortion parameters for the S–A–S angles (see Table 3).

Figure 2. Coordination environment of the alkali ions in A_2AgVS_4 (A = K, Rb). Note: the labeling of the different edges is explained in the text



The uneven expansion of the *b* and *c* axis when going from the K to the Rb compound (Δb = 3.25%; Δc = 3.98%) can also be explained on the basis of the analysis given above. The expansion of the structure in the *b* direction is limited due to the rigid edge a4 of the tetrahedra (Figure 2). An elargement of the *b* axis comparable to the value obtained for the *c* axis would result in a strong distrotion of the RbS_8 polyhedron. In contrast, the expansion of the *c* axis is easily realized because the edges b2 and b3

(Figure 2) are not edges of the tetrahedra, and the Rb^+ can easily move out of the fourfold planar S^{2-} environment within the ab plane. This flexibility is reflected by the different displacements of K^+ (0.261 Å below the plane) and Rb^+ (0.344 Å).

Every AS_8 polyhedron is connected to 12 neighbors by 4 common corners, 6 common edges, and 2 common faces leading to a three-dimensional network in which the Ag−V−Ag chains are embedded.

Financial support by the *Deutsche Forschungsgemeinschaft* (DFG) as well as by the *Fonds der Chemischen Industrie* (FCI) is gratefully acknowledged.

Experimental

Preparations: The samples were prepared by reaction of A_2S_3 (A = K, Rb) with V and Ag metal with additional sulfur in the ratio 4:1:1:8. In a drybox the starting materials were thoroughly mixed and then placed into pyrex glass ampoules which were subsequently evacuated ($4 \cdot 10^{-5}$ mbar) and sealed. The ampoules were heated to 350 °C, held at this temp. for 6 d and afterwards cooled to room temp. at a rate of 2 K/h. The product was washed with DMF and diethyl ether. Deep violet needle-like crystals with a metallic lustre were isolated. The samples are slightly air-sensitive and must be handled under dry conditions. All reflections of the X-ray powder pattern of the products could be indexed on the basis of A_2AgVS_4. Homogeneity of the products was further confirmed by TXRF (Total Reflection X-ray Fluorescence Analysis) on an Atomica EXTRA II A spectrometer by using tungsten Bremsstrahlung and Mn as an internal standard. The resulting compositions are $K_{2.11}Ag_{1.1}V_{1.09}S_4$ and $Rb_{2.05}Ag_{1.08}V_{1.09}S_4$, respectively.

X-ray Crystallographic Study[16]: Single-crystal X-ray work was performed on a STOE AED II diffractometer by using monochromated Mo-K_α radiation (λ = 0.7107 Å), Ω-2Θ scan mode. Technical details of the data acquisition as well as some refinement results are summarized in Table 1. The observed intensities were reduced to F_o. Lorentz, polarization, and a numerical absorption correction were applied. A full-matrix least-squares refinement with anisotropic displacement parameters for all atoms was used. The final weighting scheme was varied until no significant dependence on F/F_{max} or $\sin\Theta/\lambda$ was observed. All calculations were performed with the software package SHELX TL plus. Atomic coordinates are listed in Table 2 and selected interatomic distances in Table 3.

Table 1. Technical details of data acquisition and some refinement results for K_2AgVS_4 and Rb_2AgVS_4

	K_2AgVS_4	Rb_2AgVS_4
a [Å]	5.807(1)	5.820(1)
b [Å]	12.939(3)	13.359(3)
c [Å]	22.296(4)	23.184(5)
V [Å^3]	1675.3(8)	1802.6(9)
Crystal system	orthorhombic	orthorhombic
Space group	*F*ddd	*F*ddd
Z	8	8
Mol. mass	365.3	458.0
ρ [Mg/m^3]	2.896	3.375
2 Θ [°]	3-60	3-60
Index Ranges	$-8 < h < 8$	$-2 < h < 8$
	$0 < k < 18$	$0 < k < 18$
	$-31 < l < 2$	$0 < l < 33$
Reflections collected	1419	1013
Independent refl.	613	667
R_{int} [%]	4.01	2.82
Observed reflections [$F > 4.0\sigma(F)$]	535	496
Min./Max. transm.	0.349/0.907	0.129/0.416
x[a]	0.00031(2)	0.00003(1)
y[b]	0.0001	0.0003
N_P	22	22
R [%]	2.54	2.83
wR [%]	2.86	3.60
GOOF	1.57	1.29
Difference [eÅ^{-3}]	1.09/-0.64	1.05/-0.65

[a] Extinction correction: $F^* = F[1 + 0.002 \times F^2/\sin 2\Theta]^{-1/4}$. – [b] Weighting scheme: $w^{-1} = \sigma^2(F) + yF^2$.

Table 2. Atomic coordinates (10^4) and equivalent isotropic displacement coefficients ($Å^2 \cdot 10^3$) for K_2AgVS_4 and Rb_2AgVS_4

K_2AgVS_4				
	x	*y*	*z*	U(eq)[a]
Ag	1250	1250	1250	36(1)
V	6250	1250	1250	16(1)
S	4219(1)	2261(1)	676(1)	27(1)
K	3750	3750	1942(1)	41(1)
Rb_2AgVS_4				
	x	*y*	*z*	U(eq)[a]
Ag	1250	1250	1250	35(1)
V	6250	1250	1250	17(1)
S	4215(2)	2225(1)	698(1)	27(1)
Rb	3750	3750	1951(1)	38(1)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

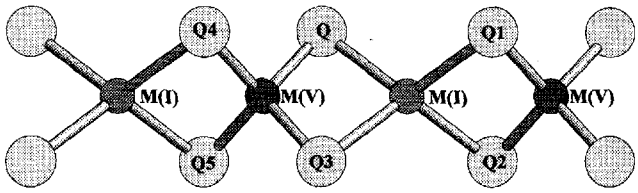
Table 3. Interatomic bond lengths [Å] and selected angles [°] in K_2AgVS_4 and Rb_2AgVS_4

K_2AgVS_4				**Rb_2AgVS_4**			
Ag–V	2.904(1)	S–K–S	69.1(1)	Ag–V	2.810(1)	S–Rb–S 2x	65.0(1)
Ag–S 4x	2.515(1)	S–K–S 2x	73.7(1)	Ag–S 4x	2.513(1)	S–Rb–S 2x	97.4(1)
V–S 4x	2.178(1)	S–K–S 2x	99.5(1)	V–S 4x	2.177(1)	S–Rb–S 2x	108.9(1)
		S–K–S 2x	62.6(1)			S–Rb–S	62.7(1)
K–S 2x	3.271(1)	S–K–S 2x	109.2(1)	Rb–S 2x	3.384(1)	S–Rb–S 2x	125.3(1)
K–S 2x	3.267(1)	S–K–S 2x	112.1(1)	Rb–S 2x	3.352(1)	S–Rb–S 2x	92.6(1)
K–S 2x	3.428(1)	S–K–S 2x	119.8(1)	Rb–S 2x	3.559(1)	S–Rb–S 2x	69.9(1)
K–S 2x	3.723(1)	S–K–S 2x	152.8(1)	Rb–S 2x	3.793(1)	S–Rb–S	168.2(1)
<K–S>	3.422	S–K–S 2x	62.9(1)	<Rb–S>	3.522	S–Rb–S	169.6(1)
DP_d[a]	0.0448	S–K–S 2x	97.0(1)	DP_d[a]	0.0437	S–Rb–S 2x	120.2(1)
		S–K–S 2x	67.2(1)			S–Rb–S 2x	71.5(1)
S–V–S 2x	108.0(1)	S–K–S	170.9(1)	S–V–S 2x	107.9(1)	S–Rb–S 2x	60.5(1)
S–V–S 2x	106.2(1)	S–K–S 2x	90.7(1)	S–V–S 2x	106.5(1)	S–Rb–S 2x	153.0(1)
S–V–S 2x	114.4(1)	S–K–S	172.0(1)	S–V–S 2x	114.1(1)	S–Rb–S 2x	108.9(1)
<S–V–S>	109.53	S–K–S 2x	125.0(1)	<S–V–S>	109.5	S–Rb–S 2x	99.8(1)
DP_a[b]	0.0296	S–K–S	65.3(1)	DP_a[b]	0.028	S–Rb–S	70.6(1)
		<S–K–S>	100.79			<S–Rb–S>	100.62
S–Ag–S 2x	118.8(1)	DP_a[c]	0.2630	S–Ag–S 2x	118.7(1)	DP_a[c]	0.2579
S–Ag–S 2x	117.3(1)			S–Ag–S 2x	117.6(1)		
S–Ag–S 2x	93.5(1)			S–Ag–S 2x	93.2(1)		
<S–Ag–S>	109.87			<S–Ag–S>	109.83		
DP_a[b]	0.0993			DP_a[b]	0.101		

[a] Distortion parameter DP_d for the AS_8 polyhedra: d_i = 8 A−S [Å]; $d_m = \langle A-S \rangle$ [Å]; $DP_d = (\Sigma_{i=1,8} |d_i - d_m|)/8\, d_m$. – [b] Distortion parameter DP_a for the MS_4 tetrahedra: a_i = 6 S−M−S [°]; $a_m = \langle S-M-S \rangle$ [°], $DP_a = (\Sigma_{i=1,6} |a_i - a_m|)/6a_m$. – [c] Distortion parameter DP_a for the AS_8 polyhedra: a_i = 28 S−A−S [°]; $a_m = \langle S-A-S \rangle$ [°]; $DP_a = (\Sigma_{i=1,28} |a_i - a_m|)/28\, a_m$.

To account for a possible partial cation disorder different refinements with isotropic (U_{iso}) and anisotropic displacement parameters (ADP) were performed. Firstly, it was assumed that a small amount of V is on the Ag site, and vice versa. The site occupation factors (*sof*) were refined with a tied common variable so that the sums of the obtained occupancies are equal to the possible values on the two different positions. In addition, the U_{iso} of V and Ag on the two sites were also refined with a tied common variable. This procedure yielded a *sof* for V on the Ag site of 0.015(8) [*sof*(Ag): 0.235(8); U_{iso} = 0.035(1)]. The *sof* for V is less than 3σ of the estimated standard deviation (*esd*). For Ag on the V site a

Table 4. Selected parameters compairing structural differences in the compounds $A_2M(I)M(V)Q_4$



Compound	K_2AgVS_4	Rb_2AgVS_4	K_2CuVS_4	$K_2CuNbSe_4$	$K_2CuTaSe_4$
Distance [Å]					
M(V)–M(I)	2.904	2.910	2.719	2.872	2.868
M(V)–Q	2.178	2.177	2.177	2.413	2.393
M(I)–Q	2.515	2.513	2.313	2.457	2.455
Q–Q3	3.662	3.658	3.568	3.932	3.908
Q–Q4	3.483	3.489	3.535	3.928	3.893
Q–Q1	4.295	4.298	3.865	4.038	4.046
Angle [°]					
Q–M(V)–Q4	108.0	107.9	108.6	109.0	108.9
Q–M(V)–Q5	106.2	106.5	109.7	110.3	110.0
Q–M(V)–Q3	114.4	114.1	110.1	109.2	109.5
Q2–M(I)–Q3	118.8	118.7	113.4	110.5	111.0
Q1–M(I)–Q3	117.3	117.6	114.4	111.7	112.1
Q–M(I)–Q3	93.5	93.2	100.9	106.3	105.5
r [M(I)]	1.00	1.00	0.60	0.60	0.60
r [M(V)]	0.355	0.355	0.355	0.48	0.64[a]

[a] Radius for coordination number 6.

negative *sof* was obtained [U_{iso} = 0.018(2)]. If the U_{iso} of all four atoms was tied with a common variable, the result did not change significantly. The *sof* for the V on the Ag site is still less than 3σ of the *esd* [U_{iso} for all atoms: 0.032(1)]. As expected the refinement with anisotropic displacement parameters (tied with common variables) did not lead to significantly different results. Hence we exclude the possiblity of *significant* cation disorder.

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[16] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-404770 (K_2AgVS_4) and CSD-404771 (Rb_2AgVS_4).

[96031]