Synthesis and Crystal Structure of New Ternary Chalcogenides of Group IV Metals: K₂ZrS₄, Rb₂ZrS₄, and Rb₂HfS₄

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The new ternary one-dimensional chain compounds K_2ZrS_4 , Rb_2ZrS_4 and Rb_2HfS_4 were prepared at 350 °C by reacting A_2S_3 and S with elemental M (A = K, Rb; M = Zr, Hf). They are isostructural, crystallizing in the orthorhombic space group Pbca with Z = 8. The M atoms are in a distorted octahedral environment of four S^{2–} anions and one S₂^{2–} unit. The structure consists of infinite anionic chains comprised of edge-sharing MS₆ octahedra running parallel to the [001] direction separated by the alkali metal cations. The composition of the chain may be formulated as $\frac{1}{2}[MS_{4/2}(S_2)^{2^-}]$. The two crystallographically independent alkali cations are in eight- and ninefold coordination of S atoms.

Introduction

Ternary group 4 transition metal alkali chalcogenides have received much attention with respect to their low dimensional crystal structures. The metal atoms show a high flexibility of the coordination environment in the $M^{IV}Q_x$ polyhedra with x ranging from 4 to 8. These polyhedra are interconnected in different ways. Examples containing 1D anionic chains are Tl₂TiS₄ [1], Rb₄Zr₃Te₁₆ [2], and $K_4Ti_3S_{14}$ [3]. In Tl_2TiS_4 distorted TiS_6 octahedra are connected via common edges to form zig-zag chains (angle Ti-Ti-Ti 132.5°). In Rb₄Zr₃Te₁₆ each Zr atom is surrounded by eight Te atoms forming distorted bicapped trigonal prisms. The polyhedra share opposite triangular faces. Finally, in K₄Ti₃S₁₄ TiS₇ and TiS₈ polyhedra are connected by sharing common edges or trigonal faces to build linear chains.

Experimental

 A_2MS_4 was prepared by reacting A_2S_3 (A = K, Rb) with elemental M (M = Zr, Hf) and S in a 3:2:6 molar ratio. A_2S_3 was made from the stoichiometric reaction of elemental A with S in liquid ammonia. The starting materials were thoroughly mixed in a dry-box and loaded into a glass tube which was evacuated to 10^{-5} mbar and sealed.

Table 1. Atomic coordinates $(\cdot 10^4)$ and equivalent displacement parameters U_{eq} $(\mathring{A}^2 \cdot 10^3).$

	x	у	z	U_{eq}
K_2ZrS_4 :				
Zr	3294(1)	5531(1)	6316(1)	5(1)
S(1)	1652(1)	3666(1)	5660(1)	9(1)
S(2)	2707(1)	2883(1)	7055(1)	9(1)
S(3)	5922(1)	5705(1)	6610(1)	12(1)
S(4)	5515(1)	3860(1)	5884(1)	12(1)
K(1)	692(1)	625(1)	8022(1)	16(1)
K(2)	1430(1)	7014(1)	4683(1)	16(1)
Rb_2ZrS_4 .	:			
Zr	3271(1)	5377(1)	6311(1)	8(1)
S(1)	1694(1)	3504(1)	5676(1)	11(1)
S(2)	2670(1)	2762(1)	7028(1)	12(1)
S(3)	5840(1)	5517(1)	6590(1)	14(1)
S(4)	5417(1)	3729(1)	5881(1)	15(1)
Rb (1)	688(1)	465(1)	8012(1)	16(1)
Rb(2)	1431(1)	6910(1)	4656(1)	18(1)
Rb_2HfS_4	:			
Hf	3265(1)	5334(1)	6312(1)	7(1)
S(1)	1685(1)	3476(2)	5683(1)	9(1)
S(2)	2724(1)	2669(2)	7022(1)	10(1)
S(3)	5818(1)	5499(2)	6592(1)	12(1)
S(4)	5404(1)	3718(2)	5874(1)	13(1)
Rb (1)	720(1)	433(1)	8015(1)	14(1)
Rb(2)	1433(1)	6897(1)	4656(1)	16(1)

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	K_2ZrS_4	Rb_2ZrS_4	Rb_2HfS_4
a [Å]	9.4541(6)	9.7488(4)	9.7430(6)
<i>b</i> [Å]	6.7021(4)	6.7234(3)	6.6754(3)
c [Å]	22.966(2)	23.675(2)	23.602(2)
$V [Å^3]$	1455.2(2)	1551.8(2)	1535.1(3)
Calc. density [g/cm ³]	2.717	3.342	4.134
T [K]	180	180	180
$\mu [\mathrm{mm}^{-1}]$	3.68	14.85	27.17
F(000)	1136.0	1424.0	1680.0
Index range	$-13 \le h \le 13, 8 \le k \le 8,$	$-13 \le h \le 13, 8 \le k \le 8,$	$-13 \le h \le 13, 9 \le k \le 9,$
	$-32 \le l \le 32$	$-33 \le l \le 33$	$-33 \le l \le 33$
Reflections collected	14494	16247	18124
Independent refl.	2062	2121	2280
Refl. with $F \ge 4 \sigma(F)$	1949	1978	2139
$R_{\rm int}$ [%]	4.80	4.05	4.80
Min./max. transm.	0.4612/0.6774	0.1357 / 0.1906	0.0471/0.0914
Number of parameters	65	65	65
x ^[a]	0.0020(5)	0.0021(4)	0.0009(2)
$y, z^{[b]}$	0.0320, 0.35	0.0349, 0.74	0.0351, 6.16
<i>R</i> 1 for all $F_o \ge 4 \sigma(F_o)$ [%]	1.96	2.12	2.53
wR2 for all reflections [%]	5.11	5.28	6.68
GOOF	1.114	1.071	1.205
$\delta F [e \check{A}^{-3}]$	0.57 / -1.06	0.69 / -1.24	5.57 / -2.00

Table 2. Technical details of data acquisition and some refinement results for A2MS4.

^[a] $F^* = F_c (k[1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^3 / \sin(2\theta)]^{-0.25}); {}^{[b]} w = 1/[\sigma^2(F_o^2) + (y \cdot P)^2 + z \cdot P]; P = (Max (F_o^2, 0) + 2 \cdot F_c^2)/3.$

Table 3. Selected bond distances [Å] and angles [°] for the compounds A_2MS_4 .

	K_2ZrS_4	Rb_2ZrS_4	Rb_2HfS_4
Bond distances [Å]:			
M-S(1) M-S(2) M-S(2) M-S(4) M-S(1) M-S(3) S(3)-S(4) Shortest interchain	2.4993(4) 2.5013(4) 2.5163(4) 2.5782(4) 2.5775(4) 2.1105(5) 3.635	2.4930(6) 2.5092(6) 2.5132(6) 2.5766(6) 2.5859(6) 2.5918(6) 2.1061(8) 3.884	2.472(1) 2.484(1) 2.500(1) 2.564(1) 2.570(1) 2.576(1) 2.110(2) 3.850
S-S distance Angles [°]:			
S(3)-M-S(4) M-M-M	48.33(2) 131.75	48.09(2) 131.8	48.48(4) 131.85

The ampoules were placed in a computer controlled furnace and heated from r.t. to 350 °C within 5 h. They were held at this temperature for 6 d and then slowly cooled down to r.t. with a cooling rate of 3 °C/h. To remove unreacted alkali metal polychalcogenides the resultant melt was washed with DMF and ether.

The compounds consist of yellow coloured crystals (yield: $\sim 20\%$ based on M) which are highly unstable in humid air.



Fig. 1. The coordination of the M atom in A_2MS_4 together with the numbering scheme.

All single crystal X-ray investigations were performed on a STOE imaging plate diffraction system (IPDS) with an area detector, monochromated Mo-K_{α} radiation (λ = 0.71073 Å), and a low temperature device from Oxford Cryosystems. Technical details of the data acquisition as well as some refinement results are summarized in Table 2. Atomic coordinates are listed in Table 1 and selected interatomic separations are given in Table 3.

Structure solution was performed using SHELXS-97. Refinement was done against F² using SHELXL-97. A



Fig. 2. Crystal structure of A₂MS₄ viewed along [010].

face indexed absorption correction was applied. All atoms were refined using anisotropic displacement parameters. All compounds are isostructural and were refined in the orthorhombic space group Pbca.

Further details on the structure determination can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Fax: +49 (0)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) under No. CSD-411329 (K_2ZrS_4), CSD-411330 (Rb_2HfS_4), and CSD-411331 (Rb_2ZrS_4).

Results and Discussion

The ternary compounds crystallize in the orthorhombic space group Pbca with Z = 8. The transition metal ions in A₂MS₄ are in an octahedral environment of four μ -S²⁻ anions and one η^2 -S₂²⁻ unit. The average M-S distances range from 2.54 Å (Zr-S) to 2.53 Å (Hf-S) and correspond well with the sum of the ionic radii of Zr^{IV}, Hf^{IV} and S²⁻. They are comparable to those in other Zr and Hf sulfides like Na₂ZrS₃ [4], Ba₃Zr₂S₇ [5] and Cu₂HfS₃ [6]. The S-S bond length in the S_2 unit (S3 - S4) is about 2.11 Å which is typical for single bonds (see Table 3).

Because the S_2^{2-} unit is bound to M^{IV} in an η^2 mode the resulting angle S3-M-S4 is fixed and it ranges from $48.09(2)^\circ$ to $48.48(4)^\circ$. As a consequence the other angles in the octahedra deviate from the ideal geometry giving rise to a strong distortion (see Fig. 1).

The octahedra are connected by two μ -S atoms leading to the formation of one-dimensional infinite ${}_{\infty}^{1}[MS_{4/2}(S_2)^{2-}]$ anionic chains running parallel to the [010] direction.

A view of the unit cell of A_2MS_4 (A = K and Rb, M = Zr and Hf) is shown in Figure 2. The zigzag chains (M-M-M = 131.8°) are separated by two crystallographically unique alkali metal cations: A1 is coordinated by nine, A2 by seven S atoms (cutoff A-S = 3.9 Å) within irregular polyhedra. The A-S distances correspond to the sum of their ionic



Fig. 3. Comparison of the $\frac{1}{\infty}[MS_{4/2}(S_2)^{2-}]$ chain in A_2MS_4 (a) with the $\frac{1}{\infty}[TiS_{4/2}(S)^{2-}]$ chain in Cs_2TiS_3 (b).

radii and agree with those found in K_2TiS_3 [7] or Rb_2S_2 [8]. The shortest S-S distance between the chains is about 3.64 Å for the potassium compound and is larger as expected for Rb_2ZrS_4 (3.88 Å) and Rb_2HfS_4 (3.85 Å) indicating no S-S interaction. Therefore, the formal oxidating states may be assigned as A^I , M^{IV} , S^{2-} and S_2^{2-} .

Obviously the increase of the **b** axis with increasing size of the alkali cation $(Rb^+ > K^+)$ is very small due to the rigidity of the metal centered octahedra. However, the **a** as well as the **c** axis are strongly influenced by the alkali cation size. The lattice parameters of Rb_2ZrS_4 are very similar to those of Rb_2HfS_4 due to the very similar radii of Zr^{IV} (0.72 Å) and Hf^{IV} (0.71 Å) [9].

The structures of the title compounds are isostructural to Tl_2TiS_4 [1] and can be derived from Cs_2TiS_3 [10] in a simple way. In Cs_2TiS_3 the Ti atom is coordinated by five S atoms within a square pyramid. The TiS_5 units are connected by common edges to form $\frac{1}{\infty}[TiS_{4/2}(S)^{2-}]$ chains. The chains of Cs_2TiS_3 and A_2MS_4 are compared in Fig. 3, where the structural differences are obvious.

The structures of the title compounds result when a single S²⁻ anion in A₂MS₃ is replaced by the η^2 -S₂²⁻-unit to give A₂MS₄. Further substitution of chalcogen atoms (Q²⁻) by Q₂²⁻-units leads to higher coordinated M atoms as in Cs₄Zr₃Te₁₆ [11], Cs₃Ti₃Te₁₁, Cs₅Hf₅Te₂₆ [12] and A₄M₃Q₁₄ (A = K, Rb, Cs; M = Ti, Zr, Hf; Q = S, Se) [13].

Our attemps to prepare the Cs compound Cs_2ZrS_4 led to the formation of $Cs_4Zr_3S_{14}$ [13] which is isostructural with $K_4Ti_3S_{14}$. In this compound the Ti atoms are seven- and eightfold coordinated. Obviously, the coordination number of M depends on the charge/radii ratio and the stoichiometry of the compound.

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