$K_{1.10}Zr_2Se_6$, $Rb_{0.86}Zr_2Se_6$ and $Cs_{0.80}Zr_2Se_6$. The First Intercalation Compounds of Zirconium Triselenide

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Single crystals of $K_{1.10}Zr_2Se_6$, $Rb_{0.86}Zr_2Se_6$ and $Cs_{0.80}Zr_2Se_6$ were obtained by reacting powdered mixtures of A_2Se (A = K, Rb, Cs), Zr and Se at 850 °C. $K_{1.10}Zr_2Se_6$ and $Rb_{0.86}Zr_2Se_6$ crystallize in space group *Immm* ($Z = 2$), with $a = 3.746(3)$, $b = 5.354(8)$, $c = 21.929(3)$ Å and $a = 3.756(1)$, $b = 5.354(8)$, $c = 22.81(1)$ Å, respectively. $Cs_{0.80}Zr_2Se_6$ crystallizes in space group $Cmc2_1$ ($Z = 2$), with $a = 3.747(1)$, $b = 24.102(5)$, $c = 5.332(2)$ Å. The compounds are characterized by complex anionic layers $^{2}_{\infty}[Zr_2Se_6]^{x-}$ with intercalated alkali cations. As in $ZrSe_3$, the layers are built from columns of trigonal prisms $^{1}_{\infty}[ZrSe_3]$, connected by additional waist contacts, yielding an eightfold coordination for the Zr atoms. The mean Zr-Se bond lengths correspond to those found in the binary compound. The Se-Se bond lengths are significantly altered, however, indicating a reduction of the Se-Se bond order due to the electron transfer from the alkali metal.

Introduction

Recent investigations in the chalcogen rich sections of the ternary systems $A/T^{IV}/Q$ (A = alkali metal, T = Ti, Zr, Hf, Q = Se, Te) have revealed numerous new ternary polychalcogenides [1 - 5]. As a common structural feature they are built from infinite polyanionic chains, $^{1}_{\infty}[T_mQ_n]^{p-}$, with different chalcogen contents. Typically these compounds are located at cation rich compositions beyond the equiatomic A:T ratio or along the equiatomic A:T line.

Diminishing the relative content of the alkali metal should favour the formation of polyanions of higher dimensionality towards layered or framework partial structures. The search for new layered compounds was the stimulus for our present investigation in the transition metal rich section of the ternary $A/T^{IV}/Q$ systems. As a first result the new ternary compounds $A_xZr_2Se_6$ of the heavier alkali metals are presented below.

Experimental Section

The starting materials A_2Se (A = K, Rb, Cs) were synthesized at –40 °C by reacting alkali metals (99.9%, Alfa Ventron, 5% excess) with Se powder (99.999%, Asarco) in liquid ammonia. The reaction products were dried and finally heated in a vacuum to 200 °C in order to remove the excess of the alkali metals.

In an argon glove box the A_2Se educts were intimately mixed with Zr powder (300 mesh, Alfa Ventron) and grey Se powder in the molar ratio 1:4:11 (75.5 mg K_2Se, 176.1 mg Zr, 425.9 mg Se; 252.9 mg Rb_2Se, 369.3 mg Zr, 880.6 mg Se and 284.7 mg Cs_2Se, 306.5 mg Zr, 717.7 mg Se, resp.), transferred to silica ampoules which were sealed in a vacuum of 10^{-2} Pa.

The samples were gradually heated to 850 °C, held at this temperature for 3d and finally allowed to attain ambient temperature at a constant cooling rate of 2 °C/h.

The reaction products consisted of needle shaped crystals which showed metallic luster and were extremely delicate to handle because of their fragility. They had to be handled under inert conditions. Attempts to synthesize homologous selenohafnates by this high temperature method were unsuccessful.

Preliminary X-ray investigations by Weissenberg methods revealed an orthorhombic body-centered unit-cell for the potassium- and the rubidium phase and an orthorhombic C-centered unit-cell for the cesium phase. For the determination of the crystal structures, fragments with the approximate dimensions $0.175 \times 0.025 \times 0.007$ mm^3 for the potassium phase, $0.125 \times 0.025 \times 0.025$ mm^3 for the rubidium phase and $0.175 \times 0.175 \times 0.025$ for the cesium phase were selected, embedded in a thin walled glass capillary and transferred to a Kappa diffractometer (Enraf Nonius Turbo CAD 4) operated with graphite

Table 1. Crystallographic data of $K_{1.10}Zr_2Se_6$, $Rb_{0.86}Zr_2Se_6$ and $Cs_{0.80}Zr_2Se_6$

	$K_{1.10}Zr_2Se_6$	$Rb_{0.86}Zr_2Se_6$	$Cs_{0.80}Zr_2Se_6$
Pearson symbol	*oI18*	*oI18*	*oC18*
a [Å]	3.746(3)	3.756(1)	3.747(1)
b [Å]	5.354(8)	5.359(4)	24.102(5)
c [Å]	21.929(3)	22.81(1)	5.332(2)
Space group	*Immm* (No.71)	*Immm* (No.71)	$Cmc2_1$ (No. 36)
Z	2	2	2
V [Å^3]	439.8	459.1	481.5
d_x [g cm^{-3}]	5.28	5.26	5.26
M_r	699.21	729.70	762.53
μ (Mo-K$_\alpha$) [cm^{-1}]	276.33	303.52	277.48
Structure refinement:			
Unique reflections	414	356	438
Observed reflections	268	292	336
Cutoff	3.00 $\sigma[F_o]^2$	3.00 $\sigma[F_o]^2$	3.00 $\sigma[F_o]^2$
Variables	22	22	32
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert \,/\, \Sigma \lvert F_o\rvert$	0.052	0.035	0.045
$R_w = [\Sigma\, w\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert^2 \,/\, \Sigma\, w\lvert F_o\rvert^2]^{1/2}$	0.047	0.034	0.051
Residual electron density [eÅ^{-3}]	2.96	1.72	2.95

$w = [\sigma[F_o{}^2]]^2 + [0.005\, F_o{}^2]^2]^{1/2}$.

Table 2. Positional parameters and temperature factors of $K_{1.10}Zr_2Se_6$, $Rb_{0.86}Zr_2Se_6$ and $Cs_{0.80}Zr_2Se_6$ (WP = Wyckoff position; PP = Population parameter; $B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_i U_{ij} a_i{}^* a_j{}^* a_i a_j$, where $U_{12} = U_{13} = 0$ by site and space group symmetry).

Atom	WP	x	y	z	PP	U_{11}	U_{22}	U_{33}	U_{23}	B_{eq}
$K_{1.10}Zr_2Se_6$:										
K(1)	2a	0	0	0	0.64	0.04(1)	0.13(2)	0.010(8)	0	4.6(6)
K(2)	2b	0	1/2	0	0.46	0.03(1)	0.12(3)	0.06(2)	0	5.(1)
Zr(1)	4j	1/2	0	0.3186(1)	1	0.006(1)	0.005(1)	0.008(1)	0	0.50(5)
Se(1)	4i	0	0	0.2287(1)	1	0.008(1)	0.003(1)	0.008(1)	0	0.50(5)
Se(2)	8l	0	–0.2431(5)	0.38953(9)	1	0.0117(7)	0.0153(9)	0.0110(7)	0.002(1)	1.00(3)
$Rb_{0.86}Zr_2Se_6$:										
Rb(1)	2a	0	0	0	0.5	0.042(4)	0.048(4)	0.016(3)	0	2.7(1)
Rb(2)	2b	0	1/2	0	0.36	0.034(5)	0.041(5)	0.007(4)	0	2.9(2)
Zr(1)	4j	1/2	0	0.31616(8)	1	0.0050(7)	0.0042(6)	0.0063(8)	0	0.42(3)
Se(1)	4i	0	0	0.22963(8)	1	0.0052(7)	0.0028(6)	0.0051(8)	0	0.37(3)
Se(2)	8l	0	–0.2429(3)	0.38414(6)	1	0.0093(5)	0.0105(5)	0.0107(6)	0.0011(5)	0.81(2)
$Cs_{0.80}Zr_2Se_6$:										
Cs(1)	4a	1/2	0.5017(3)	0.228(2)	0.40	0.040(2)	0.028(2)	0.040(3)	0	2.8(1)
Zr(1)	4a	1/2	0.31249(9)	0.208(2)	1	0.0034(7)	0.0162(9)	0.0047(7)	0	0.64(3)
Se(1)	4a	1/2	0.23045(9)	0.199	1	0.0041(7)	0.0142(9)	0.0043(7)	0	0.59(3)
Se(2)	4a	1/2	0.1225(2)	0.4592(6)	1	0.0009(9)	0.034(1)	0.011(1)	0	1.22(5)
Se(3)	4a	0	0.3775(1)	0.441(6)	1	0.010(1)	0.0075(9)	0.015(1)	0.0011(5)	0.86(4)

monochromated MoK$_\alpha$-radiation. Intensity data collections were performed at ambient temperatures over an octant of the reflection sphere. Crystal and orientation stability were monitored using three periodically determined control reflections. Finally precise lattice constants were obtained by least squares' refinements of the angular positions of 25 high angle reflections. Their values and other crystallographic data are summarized in Table 1.

The crystal structures were solved by direct methods (Multan 82) [6] in the centrosymmetric space groups *Immm* for the potassium- and the rubidium phase and in $Cmc2_1$ for the cesium phase which yielded the anionic

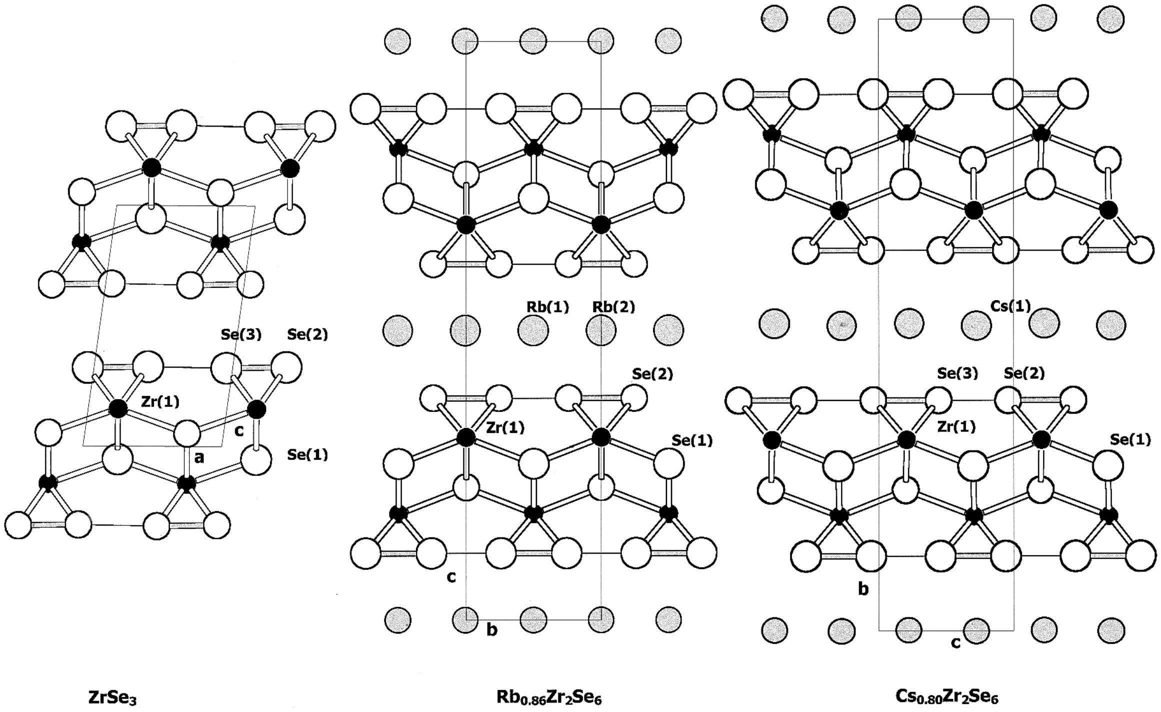

Fig. 1. Projection of the crystal structures of $ZrSe_3$, $Rb_{0.86}Zr_2Se_6$ and $Cs_{0.80}Zr_2Se_6$ along the shortest crystallographic axis. Zr-Se bonds are indicated by open, Se-Se bonds by hatched rods, resp.

network. The positions of the alkali metal atoms were obtained from difference Fourier syntheses. Full matrix least squares' refinements rapidly converged to R values of 0.052, R_w = 0.047 (K compound), R = 0.035, R_w = 0.034 (Rb compound), R = 0.045 and R_w = 0.051 (Cs compound). Subsequent difference Fourier maps were featureless. A refinement of the Flack parameter confirmed the enantiomorph chosen for $Cs_{0.80}Zr_2Se_6$.

All calculations were performed with programs of the MolEN [7] crystallographic software package using conventional scattering factors for neutral atoms. The data were corrected for absorption using an empirical method [8]. The final positions and anisotropic temperature factors are given in Table 2.

Further details on the structure refinements have been deposited with the Fachinformationszentrum Karlsruhe under CSD. Nos. 412723 ($K_{1.10}Zr_2Se_6$) 412724 ($Rb_{0.86}Zr_2Se_6$) 412732 ($Cs_{0.80}Zr_2Se_6$), respectively

Results and Discussion

The new ternary chalcogenides $K_{1.10}Zr_2Se_6$, $Rb_{0.86}Zr_2Se_6$ and $Cs_{0.80}Zr_2Se_6$ crystallize with novel structure types which are characterized by infinite complex anionic double layers, $^{2}_{\infty}[Zr_2Se_6]^{x-}$, running parallel to (001) (K and Rb compound) and (010) (Cs compound), respectively. These layers are separated from each other by planar sheets of alkali cations. While the K- and Rb- compounds are isotypic (space group *Immm* with Z = 2), the cesium compound adopts a different structure type (space group $Cmc2_1$ with Z = 2). Nevertheless the complex anions in both structure types are closely related with each other. They are built up by trigonal $ZrSe_6$-prisms sharing their basal faces to form columns which in turn are connected through additional Zr-Se waist contacts yielding double layers. The atomic arrangement within the layered anions are intimately related to that of the binary compound $ZrSe_3$ [9] (= $ZrSe(Se)_2$) which adopts the TiS_3 [10] structure type, $P2_1/n$ with a = 5.410 Å, b = 3.770 Å, c = 9.450 Å, β = 97.5°, Z = 2. A synoptic view of the three structure types is given in Fig. 1 in projection along the prism axes. In contrast to $ZrSe_3$, neighbouring layers in the ternary chalcogenides are alternatingly shifted by half the prism height which leads to a doubling of the stacking sequence and allows the formation of interstices of appropriate size hosting the alkali cations.

Table 3. Synoptic table of selected interatomic distances [Å] of $ZrSe_3$, $K_{1.10}Zr_2Se_6$, $Rb_{0.86}Zr_2Se_6$ and $Cs_{0.80}Zr_2Se_6$.

$ZrSe_3$ [9]			$K_{1.10}Zr_2Se_6$			$Rb_{0.86}Zr_2Se_6$			$Cs_{0.80}Zr_2Se_6$		
Coordination of the alkali cations											
			K(2)-Se(2)	3.327(1)	8×	Rb(2)-Se(2)	3.493(1)	8×	Cs(1)-Se(2)	3.68(1)	2×
									Cs(1)-Se(3)	3.71(1)	2×
			K(1)-Se(2)	3.357(1)	8×	Rb(1)-Se(2)	3.523(1)	8×	Cs(1)-Se(3)	3.78(1)	2×
									Cs(1)-Se(2)	3.81(1)	2×
Zr-Se Bond distances*											
Zr(1)-Se(1)	2.72	2x	Zr(1)-Se(1)	2.719(2)	4x	Zr(1)-Se(1)	2.725(2)	4x	Zr(1)-Se(1)	2.724(2)	2x
Zr(1)-Se(2)	2.74	2x	Zr(1)-Se(2)	2.761(1)	2x	Zr(1)-Se(2)	2.761(1)	2x	Zr(1)-Se(3)	2.743(6)	2x
Zr(1)-Se(3)	2.75	2x	Zr(1)-Se(3)	2.871(1)	2x	Zr(1)-Se(3)	2.876(1)	2x	Zr(1)-Se(2)	2.779(8)	2x
Zr(1)-Se(1)	2.87								Zr(1)-Se(1)	2.81(1)	
Zr(1)-Se(1)	2.87								Zr(1)-Se(1)	2.90(1)	
Mean value:	2.771			2.763			2.771			2.776	
Shortest Se-Se distances*											
Se(2)-Se(3)	2.34		Se(2)-Se(2)	2.603(2)		Se(2)-Se(2)	2.602(3)		Se(2)-Se(3)	2.572(4)	
Se(2)-Se(3)	3.06		Se(2)-Se(2)	2.751(2)		Se(2)-Se(2)	2.757(3)		Se(2)-Se(3)	2.760(4)	

* No estimated standard deviations are given in Ref. [9].

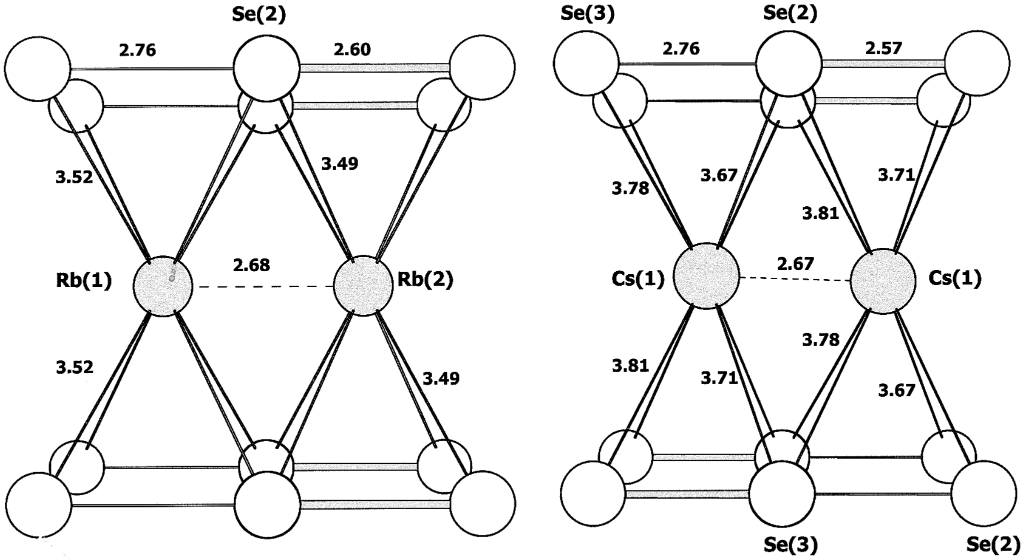

Fig. 2. The different coordination of the alkali cations in the crystal structures of $Rb_{0.86}Zr_2Se_6$ and $Cs_{0.80}Zr_2Se_6$. The alkali positions are only partially occupied, the occupation of the smaller Rb(2) site is significantly lower than that of the Rb(1) site.

The alkali cations adopt eightfold chalcogen coordinations in prismatic or almost prismatic configurations, shown in greater detail in Fig. 2. In $K_{1.10}Zr_2Se_6$ and $Rb_{0.86}Zr_2Se_6$ the cations occupy two crystallographically different split positions *2a* *A*(1) and *2b* *A*(2), respectively. The coordination prism around *2b* has shorter edges along [010] (four diselenide groups with a bond length of 2.60 Å). This is reflected by a significantly lower occupancy of this position. This site is apparently too small for the Cs^+ ions, which may be the main reason for the formation of a different structure in $Cs_{0.80}Zr_2Se_6$ where the Cs atoms occupy only one crystallographic site (*4a*).

Individual bond lengths within the anionic layers are summarized in Table 3 and compared to those of $ZrSe_3$. The zirconium atoms are in bicapped trigonal prismatic chalcogen coordinations. Zr-Se bonds within the trigonal prisms are in the range of 2.719(2) to 2.779(8) Å, while the two Zr-Se bonds provided by the waist contacts are only about 0.1 Å longer. The average Zr-Se bond lengths range from 2.763 to 2.776 Å, in excellent agreement with those found in $ZrSe_3$.

Since the insertion of the alkali metal apparently does not influence the Zr-Se bond lengths, it can be concluded that the oxidation state of the transition metal atom remains unchanged. This is corroborated by an inspection of the Se-Se distances. In the binary compound a discrete diselenide group with a homonuclear bond of 2.34 Å is found. The shortest distance between the diselenide groups is 3.06(7) Å, which indicates only weak Se-Se-interactions.

In the title compounds, however, the bond distances within the diselenide groups are widened significantly to 2.572(4) Å ($Cs_{0.80}Zr_2Se_6$) and 2.603 Å ($K_{1.10}Zr_2Se_6$ and $Rb_{0.86}Zr_2Se_6$), respectively.

This might be taken as an indication that an electron transfer has occurred from the alkali metal to the diselenide group causing a decrease of the Se-Se bond order. Application of Pauling's bond order / bond length relationship [11]

$$d = d_0 - 0.71 \log n$$

with d_0 = 2.34 Å yields bond orders of n = 0.47 ($Cs_{0.80}Zr_2Se_6$) and n = 0.43 ($Rb_{0.86}Zr_2Se_6$ and $K_{1.10}Zr_2Se_6$), respectively which is far lower than the expected value (0.75 for stoichiometric AZr_2Se_6). An inspection of the Se-Se intergroup distances of only ~2.75 Å shows that bonding Se-Se-interactions should no longer be neglected, since they correspond to bond orders of about 0.26. This yields "overall" bond orders of 0.73 (Cs compound) and 0.69 (Rb and K compound). Though these values are still too low for the substoichiometric Cs and Rb compounds, they reflect the trend correctly, *i. e.* the higher bond order is associated with the lower alkali metal content.

From the bonding considerations above and the close structural relationships it becomes evident, that the title compounds should be seen as intercalation compounds of $ZrSe_3$. It should therefore be interesting to study the reversibility of the intercalation process by electrochemical methods. The elevated displacement parameters U_{22} of the K cations in $K_{1.10}Zr_2Se_6$ in particular may indicate enhanced ionic mobility, making this compound a promising candidate for corresponding electrochemical experiments. Investigations in this field are currently in preparation.

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