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Polar Titanium Polychalcogenides: Syntheses and Characterization of $Cs_6Ti_6S_{27}$, $Cs_4BaTi_6Se_{27}$, $Rb_5AgTi_6Se_{27}$, and $Cs_5AgTi_6Se_{27}$

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The compounds $Cs_6Ti_6S_{27}$ and $Cs_4BaTi_6Se_{27}$ have been synthesized by means of the reactive flux method. $Cs_6Ti_6S_{27}$ and $Cs_4BaTi_6Se_{27}$ crystallize in a new structure type in the trigonal space group C_3^4-$R3$ with three formula units in cells with hexagonal axes at $T = 153(2)$ K of $a = 13.5203(8)$ Å, $c = 19.784(1)$ Å and $a = 13.804(2)$ Å, $c = 20.850(2)$ Å, respectively. The compounds $Rb_5AgTi_6Se_{27}$ and $Cs_5AgTi_6Se_{27}$ have also been synthesized by the reactive flux method. $Rb_5AgTi_6Se_{27}$ and $Cs_5AgTi_6Se_{27}$ crystallize in the trigonal space group C_{3v}^4-$P31c$ with two formula units in cells with hexagonal axes at $T = 153(2)$ K of $a = 13.266(1)$ Å, $c = 13.908(2)$ Å and $a = 13.5713(4)$ Å, $c = 13.9367(6)$ Å, respectively. The polar structures are closely related and consist of similar infinite one-dimensional $^{1}_{\infty}[Ti_2(Q_2)_4(Q)^{2-}]$ (Q = S, Se) chains that run along [001] and are separated by cations. If these chains are considered to be cylinders, then these structures adopt hexagonal closest-packing along [001], a general feature of the packing for known A/group IV/Q compounds (A = alkali metal). These chains are built from seven-coordinate TiQ_7 pentagonal bipyramids that are bonded together by edge- and face-sharing in turn. Four Q_2^{2-} groups are in the translational unit of the chain. An unusual feature of the Ag chalcogenides is octahedral coordination about Ag.

Introduction

A remarkable variety of low-dimensional metal polychalcogenides A/M/Q (A = Na, K, Rb, Cs; M = Ti, Zr, Hf, Nb, Ta; Q = S, Se, Te) have been synthesized with the aid of the reactive flux method,[1−10] following its discovery and application to the synthesis of $K_4Ti_3S_{14}$ from the reaction of K_2S with S and Ti at 648 K.[1,2] Many different structure types have been discovered; most consist of one-dimensional $^{1}_{\infty}[M/Q]$ chains separated by alkali-metal cations. In the A/group IV/Q system, a variety of compounds, for example, $K_4Ti_3S_{14}$ (648 K),[1,2] $Na_2Ti_2Se_8$ (618 K),[3] $Cs_3Ti_3Te_{11}$ (773 K),[6] $Cs_4Zr_3Te_{16}$ (1173 K),[5] $K_4M_3Te_{17}$ (M = Zr, Hf; 1173 K),[4] and $Cs_5Hf_5Te_{26}$ (1173 K),[6] with different compositions and different structures result from different coordination geometries about the M centers (coordination numbers from 6 to 8) and different connections between the polyhedra (face-sharing or edge-sharing). However, with the exception of $NaNbS_6$,[9] the M_2Q_{11} unit (M = Nb, Ta; Q = S, Se) is the building block of similar one-dimensional $^{1}_{\infty}[M/Q]$ chains in the A/group V/Q systems.[8,10,11] Here we report the syntheses and structures of the parent compound $Cs_6Ti_6S_{27}$ ($Cs_2Ti_2S_9$) and three related compounds, all of which consist of similar infinite one-dimensional $^{1}_{\infty}[Ti_2(Q_2)_4(Q)^{2-}]$ (Q = S, Se) chains.

Experimental Details

Synthesis. The following reagents were used as obtained: Cs (Aldrich, 99.5%), Rb (Aldrich, 98+%), Ti (Aldrich, 99.7%), Ag (Alfa, 99.99%), BaSe (Aldrich, 99%), S (Alfa, 99.5%), and Se (Aldrich, 99.5%). The reactive fluxes A_2Q_3 (A = Cs, Rb; Q = S, Se) were synthesized from reactions of stoichiometric amounts of elemental A and Q dissolved in liquid ammonia at 194 K under an N_2 atmosphere. The compound $Cs_6Ti_6S_{27}$ was prepared by the reaction of 0.50 mmol of Cs_2S_3, 0.50 mmol of Ti, and 2.50 mmol of S. The compound $Cs_4BaTi_6Se_{27}$ was prepared by the reaction of the mixture of 0.50 mmol of Cs_2Se_3, 0.125 mmol of BaSe, 0.50 mmol of Ti, and 2.50 mmol of Se. The compounds $Rb_5AgTi_6Se_{27}$ and $Cs_5AgTi_6Se_{27}$ were prepared by the reactions of 0.50 mmol of Ti, 0.125 mmol of Ag, 2.25 mmol of Se, and 0.50 mmol of either Rb_2Se_3 or Cs_2Se_3. The mixtures were loaded into fused-silica tubes under an argon atmosphere in a glovebox. The tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The samples were heated to 873 K at 1 K/min, kept at 873 K for 3 days, very slowly cooled at 0.05 K/min to 373 K, and then cooled to room temperature. The reaction mixtures were washed free of any remaining flux with dimethylformamide and then dried with acetone. Although final compositions were established from the X-ray structure determinations, energy dispersive X-ray (EDX) analyses with an EDX-equipped Hitachi S-4500 scanning electron microscope of crystals obtained in these various reactions were satisfactory: $Cs_6Ti_6S_{27}$, black needles, Cs/Ti/S = 1:1:4; $Cs_4BaTi_6Se_{27}$, black polyhedral blocks, Cs/Ba/Ti/Se = 2:0.5:3:12; $Rb_5AgTi_6Se_{27}$ and $Cs_5AgTi_6Se_{27}$, black needles, A/Ag/Ti/Se = 1:0.2:1:5. Yields were about 70−80% (based on Ti). These compounds are stable in air for several weeks.

Structure Determinations. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer.[12] The crystal-to-detector distance was 5.023 cm. Crystal

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Table 1. Crystal Data and Structure Refinements for $Cs_6Ti_6S_{27}$, $Cs_4BaTi_6Se_{27}$, $Rb_5AgTi_6Se_{27}$, and $Cs_5AgTi_6Se_{27}$

	$Cs_6Ti_6S_{27}$	$Cs_4BaTi_6Se_{27}$	$Rb_5AgTi_6Se_{27}$	$Cs_5AgTi_6Se_{27}$
fw	1950.48	3088.30	2954.54	3191.74
space group	C_3^4-$R3$	C_3^4-$R3$	C_{3v}^4-$P31c$	C_{3v}^4-$P31c$
a (Å)	13.5203(8)	13.804(2)	13.266(1)	13.5713(4)
c (Å)	19.784(1)	20.850(2)	13.908(2)	13.9367(6)
V (Å^3)	3132.0(3)	3440.7(7)	2119.6(5)	2223.0(1)
Z	3	3	2	2
temp (K)	153 (2)	153 (2)	153 (2)	153 (2)
λ (Mo Kα_1) (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g/cm^3)	3.102	4.471	4.629	4.768
linear abs coeff (cm^{-1})	76.06	263.93	304.20	276.02
$R(F)^a$ ($F_o^2 > 2\sigma(F_o^2)$)	0.0167	0.0372	0.0233	0.0199
R_w (F_o^2)^b (all data)	0.0452	0.0926	0.0514	0.0473

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $F_o^2 > 2\sigma(F_o^2)$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$, $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 > 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606 frames each at φ settings of 0°, 90°, 180°, and 270° for $Cs_6Ti_6S_{27}$ and $Cs_4BaTi_6Se_{27}$ and φ settings of 0°, 120°, and 240° for the two Ag compounds. The exposure time was 15 s/frame. The collection of the intensity data was carried out with the program SMART.[12] Cell refinement and data reduction were carried out with the use of the program SAINT,[12] and face-indexed absorption corrections were performed numerically with the use of XPREP.[13] Then the program SADABS[12] was employed to make incident beam and decay corrections.

Systematic absences and Laue symmetry led to the trigonal space group $R\bar{3}$ or $R3$ for $Cs_6Ti_6S_{27}$ and $Cs_4BaTi_6Se_{27}$ and to the trigonal space groups $P31c$ and $P\bar{3}1c$ for $Rb_5AgTi_6Se_{27}$ and $Cs_5AgTi_6Se_{27}$. No solutions for any of these structures were found in the centrosymmetric space groups. The structures were solved in the noncentrosymmetric space groups with the direct-methods program SHELXS of the SHELXTL-PC suite of programs and refined by full-matrix least-squares techniques.[13] The refinements for $Cs_6Ti_6S_{27}$, $Rb_5AgTi_6Se_{27}$, and $Cs_5AgTi_6Se_{27}$ were straightforward, but that for $Cs_4BaTi_6Se_{27}$ was not. Initial isotropic refinement of the $Cs_4BaTi_6Se_{27}$ solution led to a structure that was very similar to that of $Cs_6Ti_6S_{27}$ except that two of the four original Cs positions were about half-occupied. The mean distances from these two positions to the Se atoms were about 3.34 Å, closer to a Ba−Se distance (3.36 Å in $BaSe_3$)[14] than to a Cs−Se distance (3.545 Å in Cs_2Se_5).[15] In the final anisotropic refinement, Ba atoms were placed in these two positions and the sum of their occupancies was set to 1 to maintain charge balance. The resultant occupancies of atoms Ba1 and Ba2 are 0.553(3) and 0.447(3), respectively. In the refinements of $Cs_6Ti_6S_{27}$ and $Cs_4BaTi_6Se_{27}$ the Flack parameters were near 0.5 and 0.6, respectively, consistent either with a racemic twin or with $R\bar{3}$ being the correct space group. However, examination of the resultant atomic coordinates with the program MISSYM in the PLATON suite of programs did not suggest the presence of an inversion center.[16,17] In the refinements of $Rb_5AgTi_6Se_{27}$ and $Cs_5AgTi_6Se_{27}$ the Flack parameters were near 0. Note, however, that the structure of $Cs_5AgTi_6Se_{27}$ is inverted relative to that of $Rb_5AgTi_6Se_{27}$. This results from a simple change in the polar direction of the chosen crystal relative to the laboratory coordinate system. Additional experimental details are shown in Table 1. Tables 2 and 3 present selected bond distances for $Cs_6Ti_6S_{27}$ and $Cs_4BaTi_6Se_{27}$, and $Rb_5AgTi_6Se_{27}$ and $Cs_5AgTi_6Se_{27}$, respectively.

Table 2. Selected Bond Lengths (Å) for $Cs_6Ti_6S_{27}$ and $Cs_4BaTi_6Se_{27}$

$Cs_6Ti_6S_{27}$		$Cs_4BaTi_6Se_{27}$	
Cs1−S1	3.6058(9)	Cs1−Se1	3.632(1)
Cs1−S2	3.6940(9)	Cs1−Se1	4.168(1)
Cs1−S4	3.5743(8)	Cs1−Se2	3.708(1)
Cs1−S5	3.6045(8)	Cs1−Se3	4.157(1)
Cs1−S6	3.8845(8)	Cs1−Se4	3.636(1)
Cs1−S7	3.6289(8)	Cs1−Se5	3.717(1)
Cs1−S8	3.8515(9)	Cs1−Se6	4.040(1)
Cs1−S9	3.5070(9)	Cs1−Se7	3.733(1)
Cs1−S9	4.0236(9)	Cs1−Se8	3.921(1)
Cs2−S1 × 3	3.5770(8)	Cs1−Se9	3.606(1)
Cs2−S3 × 3	3.8739(8)	Cs1−Se9	4.160(2)
Cs2−S8 × 3	3.5081(8)	Cs2−Se1 × 3	3.654(1)
Cs3−S4 × 3	3.3133(8)	Cs2−Se3 × 3	3.985(1)
Cs3−S5 × 3	3.6468(8)	Cs2−Se8 × 3	3.626(1)
Cs3−S7 × 3	3.7215(8)	Ba1−Se4 × 3	3.349(1)
Cs3−S9 × 3	3.6144(8)	Ba1−Se5 × 3	3.838(2)
Cs4−S1 × 3	3.4922(8)	Ba1−Se9 × 3	3.666(2)
Cs4−S2 × 3	4.0491(8)	Ba2−Se1 × 3	3.494(2)
Cs4−S6 × 3	3.3155(8)	Ba2−Se6 × 3	3.352(2)
Ti1−S1	2.3656(9)	Ti1−Se1	2.503(2)
Ti1−S2	2.4218(9)	Ti1−Se2	2.578(2)
Ti1−S3	2.539(1)	Ti1−Se3	2.666(2)
Ti1−S5	2.4020(9)	Ti1−Se5	2.544(2)
Ti1−S6	2.6689(9)	Ti1−Se6	2.791(2)
Ti1−S7	2.3910(9)	Ti1−Se7	2.529(2)
Ti1−S9	2.383(1)	Ti1−Se9	2.513(2)
Ti2−S1	2.3809(9)	Ti2−Se1	2.514(2)
Ti2−S3	2.4595(9)	Ti2−Se3	2.622(2)
Ti2−S4	2.391(1)	Ti2−Se4	2.528(2)
Ti2−S5	2.5197(9)	Ti2−Se5	2.630(2)
Ti2−S6	2.3908(9)	Ti2−Se6	2.551(2)
Ti2−S7	2.6177(9)	Ti2−Se7	2.722(2)
Ti2−S8	2.427(1)	Ti2−Se8	2.572(2)
S2−S5	2.073(1)	Se2−Se5	2.352(1)
S3−S8	2.077(1)	Se3−Se8	2.357(1)
S4−S6	2.057(1)	Se4−Se6	2.338(2)
S7−S9	2.071(1)	Se7−Se9	2.362(2)

Electrical Conductivity. The electrical conductivities of single crystals of $Cs_5AgTi_6Se_{27}$ were measured with the use of a computer-controlled, four-probe technique.[18]

Results and Discussion

The compounds $Cs_6Ti_6S_{27}$ and $Cs_4BaTi_6Se_{27}$ belong to a new structure type. The structure of $Cs_6Ti_6S_{27}$ (Figure 1) contains ${}^1_\infty[Ti_2S_9{}^{2-}]$ chains running along the [001] direction with Cs atoms isolating these chains. Closely related are the structures of $Rb_5AgTi_6Se_{27}$ and $Cs_5AgTi_6Se_{27}$ (Figure 2). In the structure of $Cs_6Ti_6S_{27}$, there are four independent Cs atoms. Some of

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Table 3. Selected Bond Lengths (Å) for $A_5AgTi_6Se_{27}$ (A = Rb, Cs)

$Rb_5AgTi_6Se_{27}$		$Cs_5AgTi_6Se_{27}$	
Rb1−Se1	3.839(1)	Cs1−Se1	3.8231(7)
Rb1−Se2	3.628(1)	Cs1−Se2	3.5606(7)
Rb1−Se3	3.428(1)	Cs1−Se3	3.8095(7)
Rb1−Se4	3.341(1)	Cs1−Se4	3.4738(6)
Rb1−Se4	3.488(1)	Cs1−Se4	3.5863(6)
Rb1−Se6	3.291(1)	Cs1−Se5	4.0050(7)
Rb1−Se7	4.000(1)	Cs1−Se6	3.3887(6)
Rb1−Se8	4.119(1)	Cs1−Se8	4.0708(8)
Rb1−Se8	4.142(1)	Cs1−Se8	4.2007(8)
Rb1−Se9	3.509(1)	Cs1−Se9	3.6286(7)
Rb2−Se1 × 3	3.7990(8)	Cs2−Se1 × 3	4.2054(6)
Rb2−Se4 × 3	3.626(1)	Cs2−Se4 × 3	3.6269(7)
Rb2−Se5 × 3	3.8332(7)	Cs2−Se5 × 3	3.8777(6)
Rb2−Se8 × 3	3.861(1)	Cs2−Se9 × 3	3.5827(7)
Rb3−Se1 × 3	4.1110(8)	Cs3−Se1 × 3	3.8852(6)
Rb3−Se4 × 3	3.521(1)	Cs3−Se4 × 3	3.7812(7)
Rb3−Se7 × 3	3.7053(8)	Cs3−Se7 × 3	3.9718(5)
Rb3−Se9 × 3	3.488(1)	Cs3−Se8 × 3	3.9130(7)
Ag−Se2 × 3	2.8099(9)	Ag−Se2 × 3	2.8267(7)
Ag−Se3 × 3	2.8110(9)	Ag−Se3 × 3	2.8062(7)
Ti1−Se1	2.654(1)	Ti1−Se1	2.619(1)
Ti1−Se3	2.518(1)	Ti1−Se3	2.566(1)
Ti1−Se4	2.524(1)	Ti1−Se4	2.509(1)
Ti1−Se5	2.789(1)	Ti1−Se5	2.751(1)
Ti1−Se6	2.520(1)	Ti1−Se6	2.589(1)
Ti1−Se7	2.540(1)	Ti1−Se7	2.520(1)
Ti1−Se8	2.594(1)	Ti1−Se9	2.536(1)
Ti2−Se1	2.619(1)	Ti2−Se1	2.658(1)
Ti2−Se2	2.562(1)	Ti2−Se2	2.515(1)
Ti2−Se4	2.522(1)	Ti2−Se4	2.527(1)
Ti2−Se5	2.520(1)	Ti2−Se5	2.538(1)
Ti2−Se6	2.597(1)	Ti2−Se6	2.517(1)
Ti2−Se7	2.741(1)	Ti2−Se7	2.790(1)
Ti2−Se9	2.540(1)	Ti2−Se8	2.602(1)
Se1−Se9	2.3623(9)	Se1−Se9	2.3646(8)
Se2−Se5	2.3601(9)	Se2−Se5	2.3476(8)
Se3−Se7	2.3466(9)	Se3−Se7	2.3592(8)
Se6−Se8	2.3698(9)	Se6−Se8	2.3725(8)

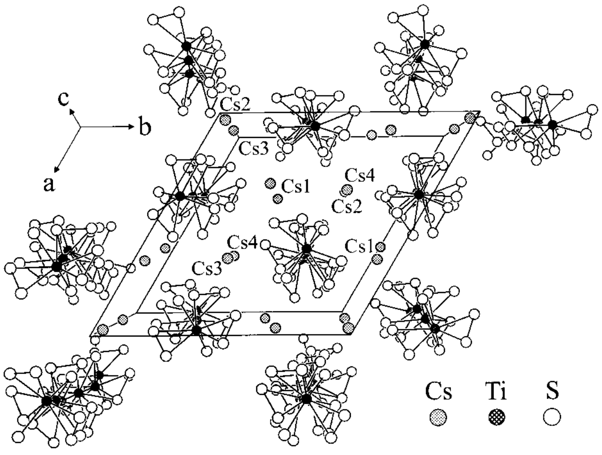

Figure 1. Unit cell of $Cs_6Ti_6S_{27}$ viewed along [001].

these may be substituted by Ba or Ag atoms. In $Cs_4BaTi_6Se_{27}$ two of the Cs atoms are replaced by Ba atoms, S atoms are replaced by Se atoms, and there is no change in structure. In $A_5AgTi_6Se_{27}$ (A = Rb, Cs) one of the Cs atoms is replaced by a Ag atom, the S atoms are replaced by Se atoms, and the structure and space group change.

In the structure of $Cs_6Ti_6S_{27}$, atom Cs1 is coordinated to an irregular polyhedron of nine S atoms whereas atoms Cs2, Cs3, and Cs4 are coordinated to 9, 12, and 9 S atoms, respectively, as shown in Figure 3a−c. The Cs−S distances range from 3.3133(8) to 4.0491(8) Å, which are comparable to those in Cs_2S_5 (3.435(3)−4.128(3) Å).[19] In $Cs_4BaTi_6Se_{27}$, atoms Ba1 and Ba2 replace atoms Cs3 and Cs4 in $Cs_6Ti_6Se_{27}$ with occupancies of 0.553(3) and 0.447(3), respectively. The coordination numbers of Cs1, Cs2, Ba1, and Ba2 of 11, 9, 9, and 6, respectively, differ from those of the corresponding Cs atoms in $Cs_6Ti_6S_{27}$. The environments of atoms Cs2, Ba1, and Ba2 are displayed in Figure 3d−f. The Cs−Se distances range from 3.606(1) to 4.168(1) Å and Ba−Se distances range from 3.349(1) to 3.838(2) Å, comparable to the corresponding distances in Cs_2Se_5 and $BaSe_3$.[14,15] The three independent A atoms (A1, A2, and A3) in $A_5AgTi_6Se_{27}$ are coordinated by 10, 12, and 12 Se atoms, respectively. The environments of atoms Rb2 and Rb3 are shown in Figure 3g,h. The Rb−Se distances range from 3.291(1) to 4.142(1) Å, and the Cs−Se distances range from 3.3887(6) to 4.2007(8) Å.

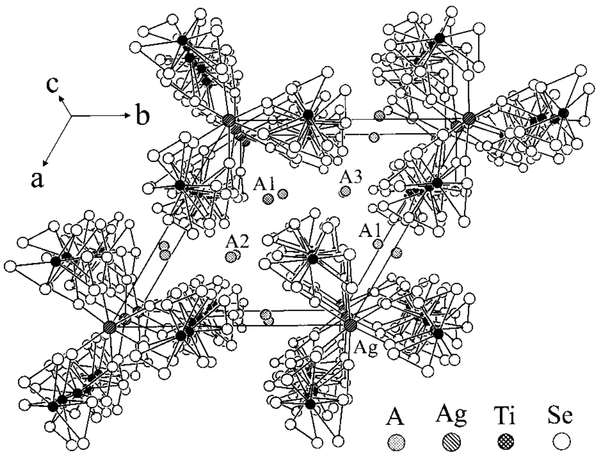

Figure 2. Unit cell of $A_5AgTi_6Se_{27}$ (A = Rb, Cs) viewed along [001].

Of particular interest in the structure of $A_5AgTi_6Se_{27}$ are the facts that the Ag atoms are coordinated to a distorted octahedron of six Se atoms (three Se2 and three Se3) (Figure 3i) and that Ag−Se distances range from 2.8062(7) to 2.8267(7) Å. Ag−Se distances in the $AgSe_4$ tetrahedron of $BaYAgSe_3$ range from 2.600(1) to 2.624(1) Å.[20] Octahedrally coordinated Ag is a rarity in chalcogenides. One of the few examples is $AgTe_3$.[21]

As shown in Figure 4, the ${}^{1}_{\infty}[Ti_2Q_9{}^{2-}]$ chains in these four structures, including the parent structure, consist of two independent Ti atoms (Ti1 and Ti2), each in the center of a pentagonal bipyramid of seven Q atoms, with each Ti atom sharing two Q atoms with one Ti neighbor and three Q atoms with the other to form the chain. The S−S bonded distances range from 2.057(1) to 2.077(1) Å, and the Se−Se bonded distances range from 2.338(2) to 2.3725(8) Å, typical values for single bonds. Consequently the chains in all four of these compounds may be written as ${}^{1}_{\infty}[Ti_2(Q_2)_4(Q)^{2-}]$ (Q = S, Se).

Ti−S distances in $Cs_6Ti_6S_{27}$ vary from 2.3656(9) to 2.6689(9) Å, in good agreement with Ti−S distances (2.283(2)−2.652(2) Å) in $K_4Ti_3S_{14}$.[1] The Ti−Se distances in $Cs_4BaTi_6Se_{27}$, $Rb_5AgTi_6Se_{27}$, and $Cs_5AgTi_6Se_{27}$ range from 2.503(2) to 2.791(2) Å, consistent with the distances of 2.383(4)−2.822(4) Å in $Na_2Ti_2Se_8$.[3]

Not only MQ_7 units but also MQ_8 units are the most common building blocks for the A/M/Q compounds. $Na_2Ti_2Se_8$[3] consists of ${}^{1}_{\infty}[Ti_2Se_8{}^{2-}]$ chains built by face-sharing $TiSe_7$ units. The ${}^{1}_{\infty}[Ti_3S_{14}{}^{4-}]$ chain in $K_4Ti_3S_{14}$[1] is constructed from both TiS_7

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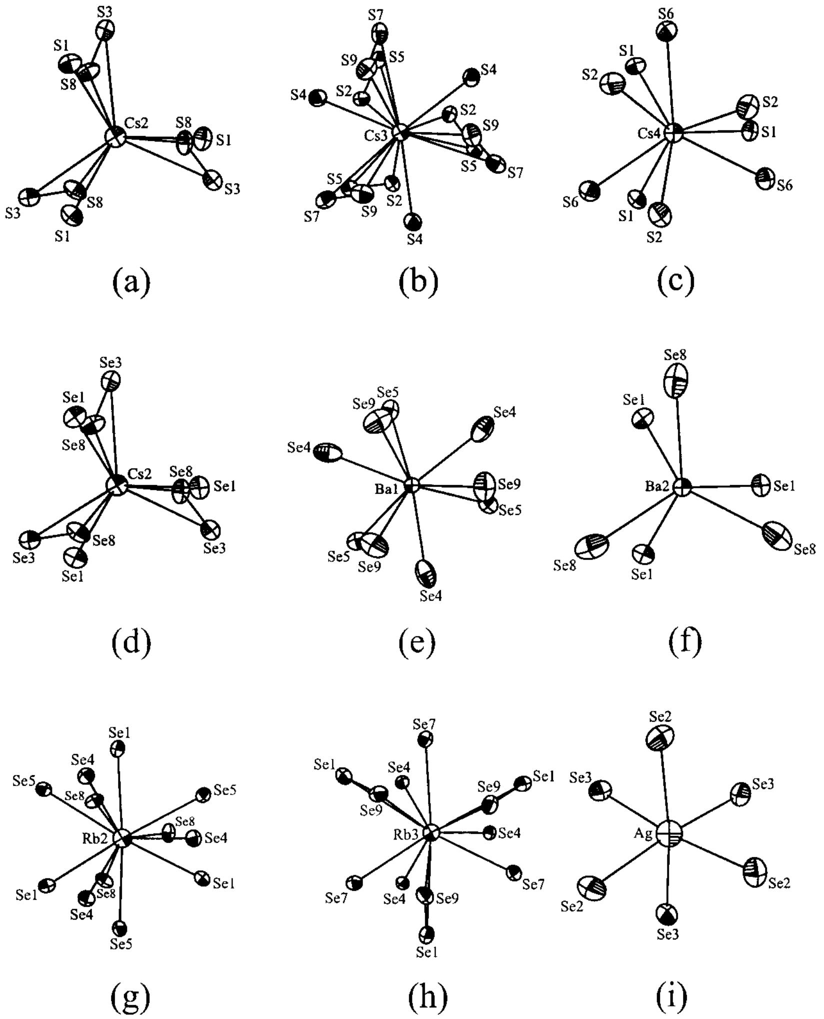

Figure 3. Coordination environments of (a) Cs2, (b) Cs3, and (c) Cs4 in $Cs_6Ti_6S_{27}$; (d) Cs2, (e) Ba1, and (f) Ba2 in $Cs_4BaTi_6Se_{27}$; (g) Rb2, (h) Rb3, and (i) Ag in $Rb_5AgTi_6Se_{27}$. All polyhedra have crystallographic symmetry 3. Here and in Figure 4 the 90% probability displacement ellipsoids are shown.

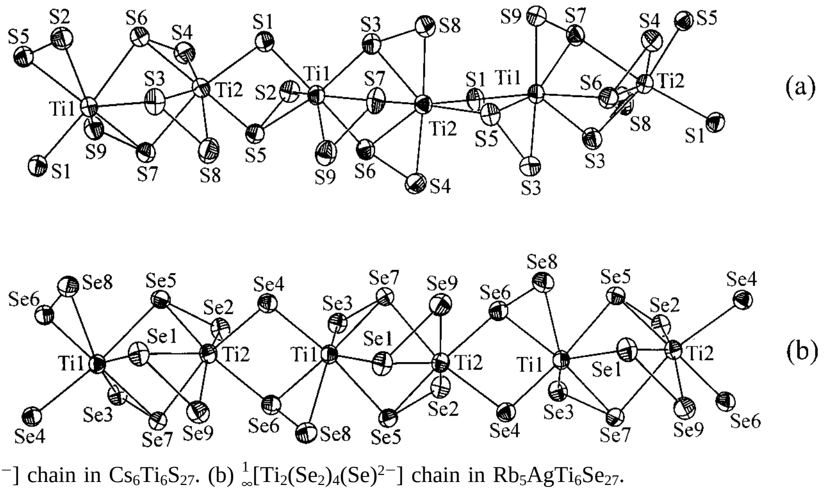

Figure 4. (a) $^{1}_{\infty}[Ti_2(S_2)_4(S)^{2-}]$ chain in $Cs_6Ti_6S_{27}$. (b) $^{1}_{\infty}[Ti_2(Se_2)_4(Se)^{2-}]$ chain in $Rb_5AgTi_6Se_{27}$.

and TiS_8 units. Most metal polytellurides, such as $Cs_4Zr_3Te_{16}$,[5] $K_4M_3Te_{17}$ (M = Zr, Hf),[4] and $Cs_5Hf_5Te_{26}$,[6] contain MTe_8 units in their $^{1}_{\infty}[M/Te]$ chains.

It is interesting that if the $^{1}_{\infty}[Ti_2Q_9{}^{2-}]$ chains in the present structures are considered to be cylinders, then each cylinder is surrounded by six nearest-neighboring cylinders and cations are located in the gaps of three neighboring cylinders. This is an hexagonal closest-packing arrangement. It turns out that all other A/group IV/Q compounds of this type contain similar one-dimensional chains and adopt hexagonal closest packing. One-dimensional columns and hexagonal packing can be found in elemental chalcogens. Conceptually, these ternary compounds can be considered to result from the breaking of some Q−Q bonds with insertion of M and A atoms inside the columns and between the columns, as shown in Figure 1.

$K_4Ti_3S_{14}$ and $Cs_4Zr_3Te_{16}$ are semiconducting.[2,5] $Cs_5AgTi_6Se_{27}$ is highly insulating with a conductivity at room temperature of about 4.0×10^{-6} S/cm.

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Supporting Information Available: Crystallographic files in CIF format for $Cs_6Ti_6S_{27}$, $Cs_4BaTi_6Se_{27}$, $Rb_5AgTi_6Se_{27}$, and $Cs_5AgTi_6Se_{27}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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