Commensurate Columnar Composite Compounds: Synthesis and Structure of $Ba_{15}Zr_{14}Se_{42}$ and $Sr_{21}Ti_{19}Se_{57}$

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Among the ternary sulfide and selenide AMQ_3 compounds (A = alkaline earth ion, rare earth ion, M = early transition metal, Q = S, Se), the hexagonal $BaNiO_3$-type[2−5] and the $LaCrS_3$-type "misfit layer" structures[6−8] are most common.[9] Compounds reported to have the pseudo-one-dimensional $BaNiO_3$-type structure include $ATiS_3$ (A = Ba, Sr), $BaZrSe_3$, and $BaVQ_3$ (Q = S, Se).[2−4] The structures are characterized by $^{1}_{\infty}[MQ_{6/2}]$ chains of face-sharing octahedra (see **1**) extending along the *c*-axis of the hexagonal cell (prototypical crystal symmetry $P6_3/mmc$). The A-site ions are 12-coordinate (see **2**) and fill the interchain channels as shown by the projection down the *c*-axis given in **3**. In this structure type, the number of A and M atoms are equivalent and, therefore, the periodicities of the $^{1}_{\infty}[A]^{2+}$ and $^{1}_{\infty}[MQ_{6/2}]^{2-}$ chains are matched. An interesting new distorted version of this structure was recently found in the $CsTaQ_3$ phases (Q = S, Se, Te) in which the Ta^{5+} ions are displaced from the centers of the Q_6 octahedra.[10]

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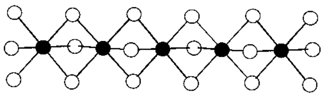

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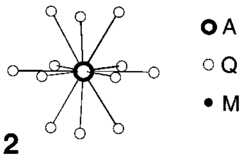

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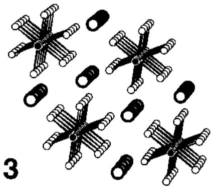

The elegant studies of Saeki, Onoda, and co-workers previously showed that some of these $BaNiO_3$-type compounds are slightly nonstoichiometric with actual compositions of $A_{1+x}TiS_3$ (where A = Ba, Sr; $x < 0.19$).[11−13] The compounds were shown to be highly adaptive with an infinite number of phases within given ranges of *x*.[11,12] The only structural data for these compounds, Rietveld analyses of powder X-ray data for $Sr_{1.145}TiS_3$ and $Sr_{1.19}TiS_3$, revealed a new type of columnar composite structure in which the $^{1}_{\infty}[TiS_{6/2}]^{2.29-}$ and $^{1}_{\infty}[Sr]^{2+}$ chains are mutually incommensurate along the *c*-axis of a $BaNiO_3$-related cell.[13,14] The incommensurate nature of the structure causes significant variations from the ideal $BaNiO_3$-type hcp lattice. We recently isolated single crystals of two members in this class of compounds; namely, "$BaZrSe_3$" and "$SrTiSe_3$". Herein we report the synthesis, structures, and preliminary characterization of these unusual chain compounds that contain commensurate rhombohedral crystal structures with large *c*-axes of 91.5 and 117.9 Å, respectively. The phases have actual compositions of $Ba_{15}Zr_{14}Se_{42}$ (or $Ba_{1.07}ZrSe_3$) and $Sr_{21}Ti_{19}Se_{57}$ (or $Sr_{1.11}TiSe_3$) with mixtures of $MSe_{6/2}$ octahedra (O) and distorted trigonal prisms (TP) in $BaNiO_3$-related structures.

Single phase $Ba_{15}Zr_{14}Se_{42}$ was prepared from BaSe, Zr, and Se in a 1:1:2 molar ratio at 1050 °C (80 h) with 40 wt % $BaCl_2$ flux. After the reaction, the flux was dissolved in water leaving thick black crystalline needles and a black powder in ~1:1 mass ratio. $Sr_{21}Ti_{19}Se_{57}$ was prepared in a similar manner from SrSe, Ti, and Se in a 1:1:2 molar ratio at 1050 °C (80 h) with 10 wt % $SrCl_2$ flux. Removal of the flux with water left small black needles (~30% of sample) of $Sr_{21}Ti_{19}Se_{57}$ along with a black powder containing unidentified impurities. The single crystals of both compounds have been characterized by EDX and single-crystal X-ray diffraction (conventional 4-circle and CCD diffractometers) and preliminary EPR spectroscopic studies, magnetic susceptibility, and 4-probe resistivity measurements have been made on $Ba_{15}Zr_{14}Se_{42}$. Wavelength dispersive X-ray analysis (WDS) on several crystals of $Ba_{15}Zr_{14}Se_{42}$ (or $Ba_{1.07}ZrSe_3$) gave a consistent composition $Ba_{1.12\pm0.02}Zr_{1.00\pm0.03}Se_{3.01\pm0.03}$ which is in excellent agreement with the refined X-ray compositions (see below). Attempts to prepare "stoichiometric" $BaZrSe_3$ or $SrTiSe_3$ were unsuccessful with or without added flux.

The structure of $Ba_{15}Zr_{14}Se_{42}$ comprises chains of $^{1}_{\infty}[ZrSe_{6/2}]^{2.14-}$ and $^{1}_{\infty}[Ba]^{2+}$ in a $BaNiO_3$-related cell. Unlike the parent $BaNiO_3$ structure, the repeat units for the chains are mismatched at 45.75 and 30.5 Å, respectively. In contrast to the $A_{1+x}TiS_3$ incommensurate columnar composite compounds,[11−13] the chains in $Ba_{15}Zr_{14}Se_{42}$ share a common repeat unit of 91.51 Å giving rise to a commensurate rhombohedral crystal structure, space group $R\bar{3}c$, with $a = 12.4366(1)$ Å and $c = 91.5069(2)$ Å.[15] The high residuals presumably reflect the abnormally long *c*-axis, the weakness of the diffraction data and the fact that the structure may be on the verge of becoming incommensurate. Several frame photographs collected with a CCD detector confirmed the space group choice and did not reveal any spurious satellite reflections that would indicate an incommensurate lattice. Despite the high residuals, the structure is well behaved and the final metric parameters are quite reasonable.

The most interesting feature is the $^{1}_{\infty}[ZrSe_{6/2}]^{2.14-}$ chains with eight crystallographically distinct Zr atoms. The 45.75 Å $[Zr_{14}Se_{42}]^{30-}$ repeat unit of the chain contains 12 $ZrSe_{6/2}$ octahedra (O) and two distorted trigonal prisms (TP) that order according to the following sequence: -O_{11}-TP-O-TP-O_{11}-TP-O-TP-O_{11}- (see Figure 1a). The Zr−Se contacts in both the O and TP polyhedra range from 2.612(4) to 2.769(4) Å with no statistical differences between the two types of polyhedra. The intrachain Zr−Zr separations range from 3.050(5) Å to 3.328(6) Å between adjacent octahedra whereas the O−TP separations are somewhat longer

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(15) *Crystal Data*. For $Ba_{15}Zr_{14}Se_{42}$: rhombohedral, $R\bar{3}c$; $a = 12.4366(1)$ and $c = 91.5069(6)$ Å; $V = 12257.1(2)$ Å^3, $Z = 6$, $\rho_{calcd} = 5.408$ g/cm^3; $\mu_{\mathrm{Mo\ K\alpha}} = 27.51$ mm^{-1}; $T = 298$ K; $R_1(F) = 9.89$ for those 1564 reflections with $F_o > 4\sigma F_o$, $R_1(F) = 11.58$ for all data and $wR(F^2) = 28.25$. For $Sr_{21}Ti_{19}Se_{57}$: rhombohedral, $R\bar{3}$ $a = 11.9517(5)$ and $c = 117.90$ (4) Å; $V = 14584$ (5) Å^3, $Z = 6$, $\rho_{calcd} = 4.953$ g/cm^3; $\mu_{\mathrm{Mo\ K\alpha}} = 34.22$ mm^{-1}. $R_1(F) = 8.34$ for those 1856 reflections with $F_o > 4\sigma F_o$, $R_1(F) = 19.59$ for all data, and $wR(F^2) = 29.10$. See the Supporting Information for full crystallographic details.

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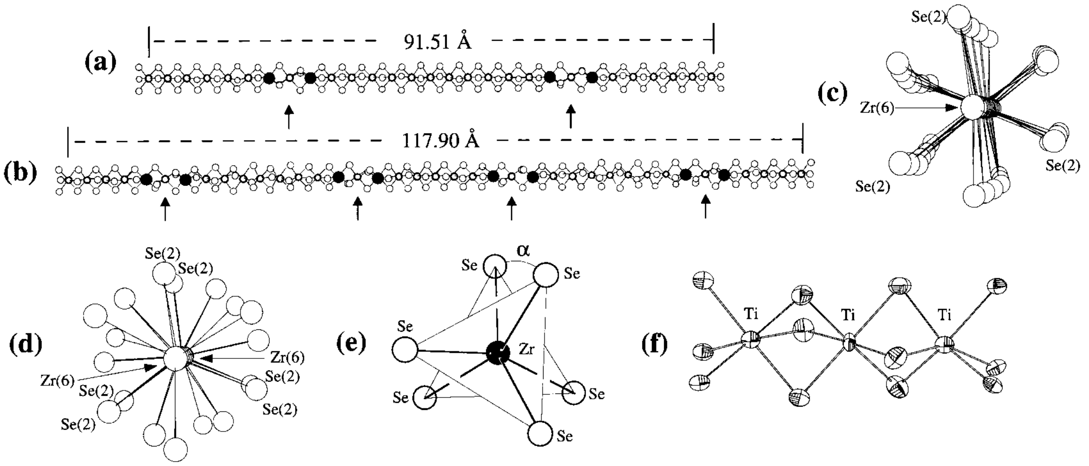

Figure 1. Graphical representations of the (**a**) -O_{11}-TP-O-TP-O_{11}-TP-O-TP- chains in $Ba_{15}Zr_{14}Se_{42}$ and (**b**) (-O_7-TP-O-TP)$_3$-O_5-TP-O-TP-(-O_7-TP-O-TP)$_3$-O_5-TP-O-TP- chains in $Sr_{21}Ti_{19}Se_{57}$. The large filled circles represent the "TP" in the -TP-O-TP- units. (**c**) An approximate (001) view down the "O_{11}" portion of the chain defined by Zr(6)-Zr(3)-...-Zr(3)-Zr(6). (**d**) An approximate (001) view down the "O-TP-O-TP-O" portion of the chain defined by Zr(6)-Zr(4)-Zr(2)-Zr(4)-Zr(6). (**e**) A view down the C_3-axis of a $TiSe_6$ distorted trigonal prism showing the nonideal dihedral angle (α). (**f**) An ORTEP drawing of an TP-O-TP $(Ti_3Se_{12})^{12-}$ unit in $Sr_{21}Ti_{19}Se_{57}$ with only the Ti atoms labeled.

at 3.386(6) Å and 3.413(5) Å. The 11 consecutive face-sharing $ZrSe_{6/2}$ octahedra (the O_{11} segments) are highly regular as evidenced by the view down the chain axis in Figure 1c. The eclipsed Se atoms show a periodic modulation in the O_{11} region which is similar to that observed in $Sr_{1.145}TiS_3$.[13,14] A similar view down the O-TP-O-TP-O segment (Figure 1d) shows the highly irregular arrangement of $ZrSe_{6/2}$ polyhedra in this region. The TP geometry is in fact intermediate between an octahedron and a trigonal prism as evidenced by the 36.02° (av) Zr(4)−Se(3)−Se(2)−Zr(4) dihedral angle (α in Figure 1e). This value is intermediate to those of an ideal octahedron (60°) and a trigonal prism (0°).

The average Zr oxidation state in the $[Zr_{14}Se_{42}]^{30-}$ segment is +3.86; however, if the Zr ions are partitioned into integral valencies, one finds 12 Zr^{IV} and 2 Zr^{III} ions per segment. One interpretation is that the two trigonal prismatic $ZrSe_{6/2}$ units in each segment contain the valence localized Zr^{III} ions. This proposal is supported by EPR and resistivity measurements (see below) but is not obvious from the Zr−Se distances.

$Sr_{21}Ti_{19}Se_{57}$ also possesses a commensurate rhombohedral structure, space group $R\bar{3}$, with $a = 11.9517(5)$ Å and $c = 117.90(4)$ Å.[15] The compound contains a 117.9 Å $[Ti_{38}Se_{114}]^{84-}$ repeat unit in the $^{1}_{\infty}[TiSe_{6/2}]^{2.21-}$ chains (Figure 1b) with TP−O−TP units (Figure 1f) virtually identical to those in $Ba_{15}Zr_{14}Se_{42}$. However, the number of octahedra separating the TP−O−TP units varies from five to seven according to the following sequence: (-O_7-TP-O-TP)$_3$-O_5-TP-O-TP-(-O_7-TP-O-TP)$_3$-O_5-TP-O-TP-

The average Ti oxidation state in the $[Ti_{38}Se_{114}]^{84-}$ repeat unit is +3.79 which gives 8 Ti^{III} and 30 Ti^{IV} when partitioned into integral valencies. Once again, the number of distorted trigonal prismatic and octahedral sites in the chain (8 TP, 30 O) mirrors the number of M^{III} and M^{IV} centers, respectively, suggesting that the d^1 Ti^{3+} ions are localized at the TP sites. As with the $Ba_{15}Zr_{14}Se_{42}$ phase, this proposal is not obvious from the structural parameters. The Ti−Se distances in the TP units range from 2.536 to 2.642 Å (2.583 Å, av) whereas the Ti−Se distances in the octahedra range from 2.496 to 2.652 Å (2.567 Å, av). The Ti−Ti separations between octahedra range from 2.935 to 3.064 Å with longer separations between O−TP units (3.1110−3.295 Å). The dihedral angles, α, for the trigonal prisms span 19.2 to 30.37°.

$Ba_{15}Zr_{14}Se_{42}$ is EPR active showing a broad signal at −170 °C with $g_{\parallel} = 2.056$ and $g_{\perp} = 1.998$. Magnetic susceptibility experiments show Curie−Weiss behavior above 150 K with $\mu_{\mathrm{eff}} = 1.63\ \mu_B$ per TP unit assuming all other ions are diamagnetic. Four-probe resistivity measurements (single crystal) between −180 and 25 °C show intrinsic semiconducting behavior with $E_g = 0.22$ eV. This measured gap is in good agreement with that reported for "$BaZrSe_3$" by Aslonov[3] suggesting that the compounds are the same. These data are consistent with the interpretation suggested by the stoichiometry and structure; namely, that the Zr^{III} centers are localized on the distorted trigonal prismatic sites of the $[Zr_{14}Se_{42}]^{30-}$ segments. We have been unable to prepare single-phase $Sr_{21}Ti_{19}Se_{57}$ and have therefore not investigated its properties. It is interesting to note that titanium oxide perovskites of similar stoichiometry and oxidation state are known to be metallic (i.e., metallic $Nd_{0.20}Ba_{0.80}TiO_3$, av Ti oxidation state +3.8)[16,17] as are the one-dimensional $BaNiO_3$-type sulfides $BaNbS_3$ (>620 K)[5] and $BaVS_3$.[18]

The origin of the alkaline earth "excess" in the $A_{1+x}MSe_3$ phases and the distortions in the $^{1}_{\infty}[MSe_{6/2}]^{(2+n)-}$ chains appear to stem from the reluctance of the A^{2+} ions (A = Ba, Sr) to reside in the 12-coordinate hcp lattice site required by an undistorted $BaNiO_3$ structure type. As with the $BaNiO_3$ structure type, there are three $^{1}_{\infty}[MSe_{6/2}]^{(2+n)-}$ chains defining the channels in each structure that host the A^{2+} ions (see **3**). The TP−O−TP "kinks" in the respective $^{1}_{\infty}[MSe_{6/2}]^{(2+n)-}$ chains effectively lower the A^{2+} coordination number at that point in the channel. By offsetting the chains relative to each other along the A^{2+} channels, all of the A^{2+} ions achieve lower coordination numbers but are in high concentration relative to the parent $BaNiO_3$ type. In $Ba_{15}Zr_{14}Se_{42}$, there are three crystallographically distinct pseudo-10-coordinate Ba^{2+} ions with Ba−Se contacts ranging from 3.201(6) to 4.138(3) Å. In $Sr_{21}Ti_{19}Se_{57}$, there is one 8-coordinate and six 9-coordinate Sr^{2+} ions with Sr−Se contacts ranging from 2.71(1) to 3.70(1) Å. Further studies are in progress.

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Supporting Information Available: X-ray crystallographic tables and details (115 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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