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Redox-Induced "Zipper" Action in the Solid State. Unprecedented Single-Crystal to Single-Crystal to Single-Crystal Cascade Conversions in $Cs_3Bi_7Se_{12}$. Framework Evolution from 2D to 2D′ to 3D

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Topotactic *single-crystal to single-crystal* solid-state transformations are rare in the literature. Most of the documented cases involve reactions of organic[1] or organometallic[1] molecules enabled by heat, light, or loss of solvent from coordination complexes[2] or rigid framework structures.[3] The topotactic reduction of γ-MnO_2 to MnO(OH) with hydrazine and the reduction of $Mg_3(VO_4)_2$ to $Mg_3V_2O_6$ by hydrogen are some known examples.[4] Recently, we described a unique solid-state *redox* transformation in two-dimensional (2D) $A_2Bi_4Se_7$ (A = Rb, Cs) which involves the topotactic oxidative coupling of complete rows of Se^{2-} ions to rows of Se_2^{2-} groups in a cooperative way reminiscent of the closing action of a zipper.[5] This remarkable process involves the rapid expulsion of alkali ions from the crystals and produces the daughter compounds ABi_4Se_7 (A = Rb, Cs) in which the original layers connect to become a three-dimensional (3D) framework. Here we report a compound that exhibits an even more remarkable zipper closing reaction. Namely, $Cs_3Bi_7Se_{12}$[6] engages in *two successive single crystal to single-crystal oxidative transformations* which convert its original 2D framework to a novel 2D′ framework and finally to a full 3D framework. Well-defined solid-state processes of this type, besides being spectacular, are of fundamental importance in chemistry because they could provide basic systems for mechanistic studies, which are rare in solids due to lack of well-behaved systems.

$Cs_3Bi_7Se_{12}$ has a two-dimensional layered structure made of Bi_2Te_3-type blocks, see Figure 1A.[7] The $[Bi_7Se_{12}]^{3-}$ slabs consist of edge-sharing distorted $BiSe_6$ octahedra. An essential characteristic of the structure is that adjacent slabs come in close, nonbonding contact by rows of Se(4) atoms. The Se(4)−Se(4) contact is at 3.409(2) Å. Along the *b*-axis, the Se(4) atoms in each layer form parallel rows approaching one another side by side so that the Se atoms in one row are staggered with respect to those in the other row, see Figure 2. The Cs(1) site has a bicapped trigonal prismatic coordination with Cs−Se distances varying between 3.569(2) and 3.782(1) Å. Cs(2) has a trigonal prismatic coordination with Cs−Se distances varying between 3.559(2)−3.744(2) Å. The Cs(2) is only 50% occupied since it generates a symmetry equivalent atom 2.267(4) Å away from itself. This creates a situation in which the Cs(2) atoms reside in tunnels much larger than their size causing facile ion motion in them.

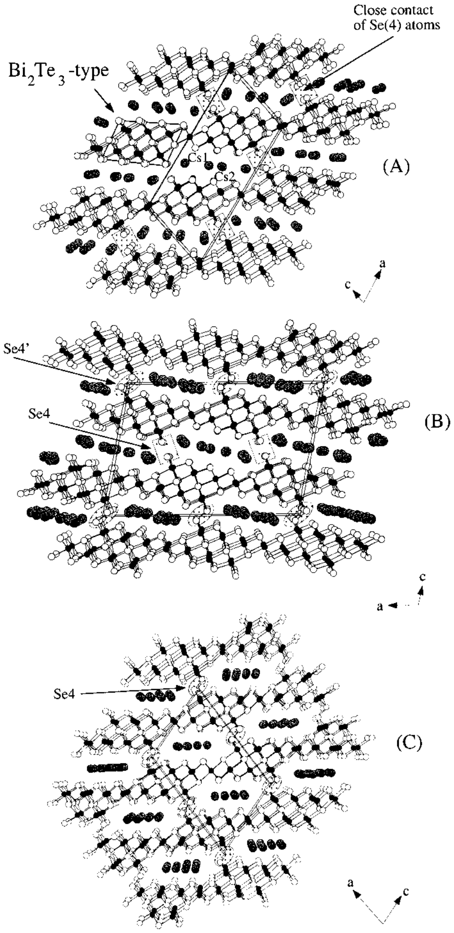

Figure 1. Projection down the *b*-axis of the structure of (A) $Cs_3Bi_7Se_{12}$, (B) $Cs_2Bi_7Se_{12}$, and (C) $CsBi_7Se_{12}$. The square-like shaded areas indicate the Se(4)−Se(4) contacts while the oval ones the Se(4)′−Se(4)′ bonds in $Cs_2Bi_7Se_{12}$ and the Se(4)−Se(4) bonds in $CsBi_7Se_{12}$.

When crystals of $Cs_3Bi_7Se_{12}$ are soaked in H_2O and air is bubbled through this suspension overnight, a clean conversion occurs to $Cs_2Bi_7Se_{12}$[8] as judged from the single-crystal diffraction

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[6] Synthesis of $Cs_3Bi_7Se_{12}$: A mixture of 0.100 g (0.290 mmol) of Cs_2Se and 0.354 g (0.541 mmol) of Bi_2Se_3 was transferred to a silica tube which was flame-sealed under vacuum. The tube was placed under the flame of a natural gas-oxygen torch until the sample melted and then the tube was removed from the flame and was let to solidify. The procedure was repeated two more times. The product consisted of a silver chunk with bladelike crystals growing across its surface. Semiquantitative energy dispersive analysis (EDS) using a scanning electron microscope (SEM) on several crystals gave an average composition of $Cs_{3.1}Bi_{6.7}Se_{12}$.

[7] A Bruker SMART Platform CCD diffractometer, using graphite monochromatized Mo Kα radiation, was used. The SMART software was used for data acquisition and SAINT for data extraction. The absorption correction was done with SADABS and the structure solution and refinement (full-matrix least squares on F^2) were done with the SHELXTL or/and SHELX97 package of crystallographic programs. (a) $Cs_3Bi_7Se_{12}$: monoclinic, space group $C2/m$,[7b,c] $a = 27.4432(1)$ Å, $b = 4.1815(1)$ Å, $c = 13.2100(1)$ Å, $\beta = 107.363(1)°$, $T = 173.1(1)$ K, $Z = 2$, $V = 1446.82(4)$ Å^3, final R indices $[I > 2\sigma(I)]$ $R1 = 3.54\%$, $wR2 = 8.25\%$, GOF on $F^2 = 1.005$. (b) $Cs_3Bi_7Se_{12}$ was reported[7c] earlier in space group *Cm*: (c) Cordier, G.; Schäfer, H.; Schwidetzky, C. *Rev. Chim. Miner.* **1985**, *22*, 676−683.

[8] Synthesis of $Cs_2Bi_7Se_{12}$: An 0.450 g sample of $Cs_3Bi_7Se_{12}$ was ground into powder and added into 250 mL of H_2O. This suspension was stirred and air was bubbled through it at very small flow. After 6 h, the transformation of $Cs_3Bi_7Se_{12}$ to $Cs_2Bi_7Se_{12}$ was complete as judged from X-ray powder diffraction. SEM/EDS on several crystals gave an average composition of $Cs_{1.8}Bi_{6.7}Se_{12}$.

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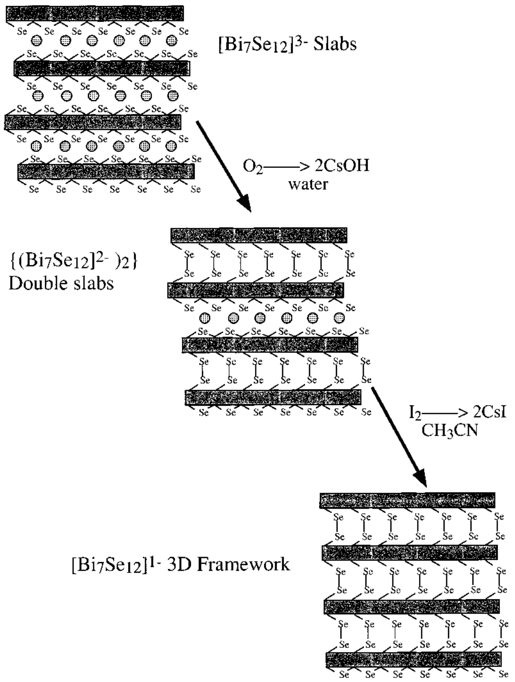

Figure 2. Schematic diagram showing the two different steps in the oxidative zipper-like action of two rows of Se atoms belonging to two adjacent $[Bi_7Se_{12}]^{3-}$ layers into a single row of diselenide groups. Single slabs join to double slabs, which finally couple to a full 3D-framework. The circles indicate the Cs atoms in the uncoupled layers.

patterns. The specimens now index to a new unit cell indicative of a new phase.

The structure of $Cs_2Bi_7Se_{12}$ was determined using the same specimen used above to determine the structure of $Cs_3Bi_7Se_{12}$. The two structures are very related[9] proving that their redox interconversion is fully topotactic. The structure of $Cs_2Bi_7Se_{12}$ contains the same framework found in $Cs_3Bi_7Se_{12}$ but now the layers are connected pairwise *through diselenide bonds* to form a two-dimensional structure, see Figure 1B. The newly formed Se(4)−Se(4′) bond is normal at 2.33(1) Å. This conversion can be imagined to occur over the entire length of the crystals via a concerted oxidative coupling of Se(4) atoms resembling the closing action of a zipper. In contrast to $A_2Bi_4Se_7$ (A = Rb, Cs), however, in the present case the zipper action occurs in a controlled way in selected places in the crystal so that only bilayers are formed.

Remarkably, when $Cs_2Bi_7Se_{12}$ is subjected to a concentrated solution of I_2 in wet CH_3CN a second oxidative step is enabled, which is complete overnight, to give $CsBi_7Se_{12}$,[10] see Figure 1C. Again, the structure of $CsBi_7Se_{12}$ was determined using the same specimen used above to determine the structure of $Cs_3Bi_7Se_{12}$. The structure features essentially the same $[Bi_7Se_{12}]^{3-}$ framework[11] only now the original layers are all linked with a new set of Se(4)−Se(4) bonds forming a truly 3D framework, see Figure 2. The Se_2^{2-} groups act as the pillars between the original layers. Again the new Se(4)−Se(4) bonds are normal at 2.39(3) Å. $CsBi_7Se_{12}$ contains only $^1/_3$ of the original Cs atoms present in $Cs_3Bi_7Se_{12}$ and because of all the void space now created they show a rather diffuse character (i.e. high-temperature factors).

The $Cs_3Bi_7Se_{12} \rightarrow Cs_2Bi_7Se_{12} \rightarrow CsBi_7Se_{12}$ shift can be promptly controlled with the proper oxidants such as I_2 in wet CH_3CN or O_2 and H_2O. The formation of Se−Se bonds in both samples was independently confirmed with Raman spectroscopy by observing the Se−Se stretch shift at 233 cm^{-1}.

To the best of our knowledge, this is a singular example of a *two-step* long-range topotactic solid state process involving the making of intracrystal bonds over the entire body of a single crystal. Because of steric reasons the Se(4) atoms, which become diselenide groups, are not actually chemically accessible by the iodine or oxygen molecules. These molecules cannot diffuse in the interior of these crystals due to the lack of micropores. The redox processes are thus electrochemical in nature where electrons are removed from the semiconductive $[Bi_7Se_{12}]^{3-}$ framework generating holes. The holes migrate to the electron-rich $Se(4)^{2-}$ atoms causing them to couple to Se−Se bonds stitching the layers. The $[Bi_7Se_{12}]^{3-}$ slab serves as an electron conduit between the $Se(4)^{2-}$ atoms (electron donors) and the electron acceptors (I_2 or O_2).[12]

In conclusion, we have identified the first example of a single-crystal to single-crystal to single-crystal cascade conversion, which involves two successive topotactic structural transformations accompanied by electron transfer, ion diffusion, and bond making in a process resembling the closing action of a zipper. The uniqueness of this process is emphasized by the fact that, unlike other solid-state transformations which do not involve movement of atoms in and out of the structure, large amount of cations are orderly and rapidly removed from the system without structural collapse. The ease of diffusion of the Cs atoms out of these lattices suggests that these compounds, particularly $CsBi_7Se_{12}$, may be excellent ion-conductors and good ion-exchange hosts.

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Supporting Information Available: X-ray crystallographic details with positional parameters, bond lengths, and angles for all compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[9] The crystal used for the determination of $Cs_2Bi_7Se_{12}$ was the actual crystal of $Cs_3Bi_7Se_{12}$ after it was let to stand in moist air. $Cs_2Bi_7Se_{12}$: monoclinic, space group *C*2/*m*, $a = 31.974(6)$ Å, $b = 4.1367(8)$ Å, $c = 22.045(4)$ Å, $\beta = 100.659(3)°$, $T = 173.1(1)$ K, $Z = 4$, $V = 2865.6(9)$ Å^3, final *R* indices [$I > 2\sigma(I)$] $R1 = 7.51\%$, $wR2 = 18.85\%$, GOF on $F^2 = 1.02$.

[10] Synthesis of $CsBi_7Se_{12}$: An 0.100 g (0.290 mmol) sample of $Cs_3Bi_7Se_{12}$ was ground into powder and added into 350 mL of a 2.25 mM I_2 in wet CH_3CN (H_2O-CH_3CN 1:7 v/v). The mixture was continuously stirred and kept under an N_2 atmosphere. The solution was left overnight and the next day the transformation of $Cs_3Bi_7Se_{12}$ to $CsBi_7Se_{12}$ was complete as judged from X-ray powder diffraction. SEM/EDS on several crystals gave an average composition of $Cs_{1.2}Bi_{6.5}Se_{12}$.

[11] The crystal used for the determination of $CsBi_7Se_{12}$ was a crystal of $Cs_3Bi_7Se_{12}$ dipped in an I_2 solution in wet CH_3CN. $CsBi_7Se_{12}$: monoclinic, space group *C*2/*m*, $a = 22.70(2)$ Å, $b = 4.179(3)$ Å, $c = 15.71(1)$ Å, $\beta = 108.97(1)°$, $T = 298(2)$ K, $Z = 2$, $V = 1409(2)$ Å^3, final *R* indices [$I > 2\sigma(I)$] $R1 = 11.79\%$, $wR2 = 31\%$, GOF on $F^2 = 1.09$. Data were collected in several crystals of $CsBi_7Se_{12}$. Unfortunately, due to the broad shape of the peaks, the integration and the subsequent absorption correction with SADABS were not optimal; consequently, there were residual peaks around the heavy atoms, relatively high *R* values, and large atomic displacement parameters, particularly for the Cs atoms. Nevertheless, the overall crystal structure, atom connectivity, and presence of Se−Se bonds were clearly determined.

[12] The room-temperature electrical conductivity of these systems (∼0.2−2 S/cm) is adequate to carry out this process.