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Communication

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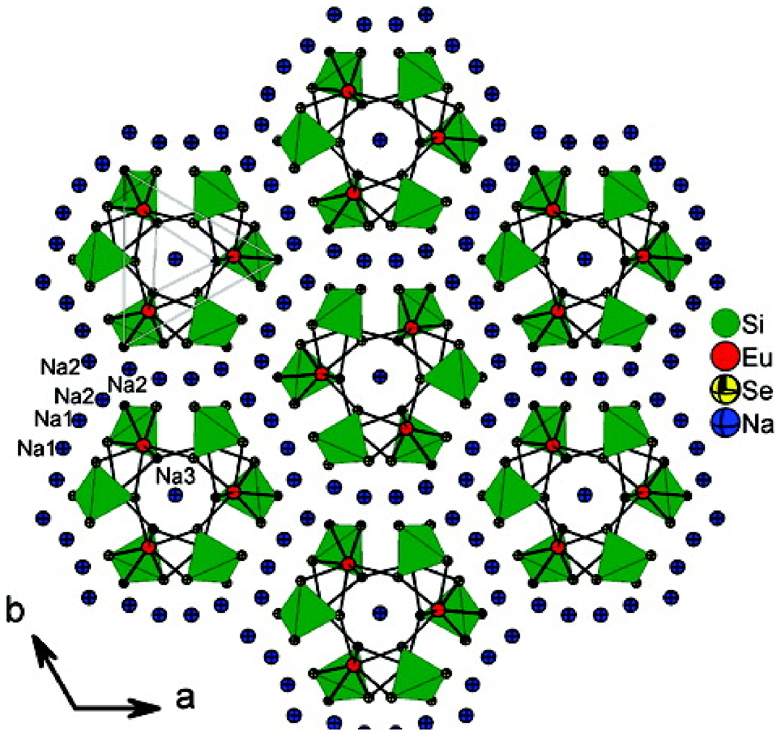

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An Ordered Assembly of Filled Nanoscale Tubules of Europium Seleno-silicate in the Crystal Structure of a Quaternary Compound

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Recently, there have been several reports of an attractive class of compounds containing nanoscale features in extended solids.[1] These nanoscale features include tubules and spheres in well-defined compounds, especially in oxides and chalcogenides. For example, nanotubules are observed in the structures of $Na_2V_3O_7$,[2] $(C_4H_{12}N)_{14}[(UO_2)_{10}(SeO_4)_{17}(H_2O)]$,[3] $K_5[(UO_2)_3(SeO_4)_5](NO_3)(H_2O)_{3.5}$[4] and $SbPS_4$[5] and nanospheres in some actinyl peroxides.[6] These compounds with nanotube features are different from those compounds having one-dimensional (1-D) channels or tunnels fused through covalent bonds to form three-dimensional (3-D) structures as in open framework compounds.[7] Moreover, they are also different from the so-called "inorganic nanotubes", which are formed by rolling up exfoliated single or multilayered sheets of a layered compound.[8] The nanotubes in well-defined compounds are often negatively charged and held together in the crystal through ionic or other weaker forces in the 3-D crystalline assembly. In this Communication, we report the first example of a rare-earth based chalcogenide material featuring a tubular structure.

The title compound $Na_2EuSiSe_4$ (**1**) was isolated during our exploratory synthesis of rare-earth containing quaternary chalcogenides using the polychalcogenide flux method.[9] The very air-sensitive pale orange needle-shaped crystals were suitable for single-crystal X-ray data collection, and the structure was solved by direct methods.[10] The structure of **1** consists of nanoscale tubules of $[EuSiSe_4]^{2-}$ oriented parallel to the *c*-axis, packed hexagonally, and held together by ionic interactions between the negatively charged tubules and intertubular Na^+ ions as shown in Figure 1. Na^+ ions also fill the inner channels of the tubules. We can envision that the tubules are formed by the folding of a single two-dimensional (2D) layer of $[Eu^{2+}SiSe_4]^{2-}{}_n$ creating a very narrow hexagonal channel. The inner and the outer diameter of the tubules are 4.05(2) and 12.14(1) Å, respectively. The inner and the outer diameters of the tubules were calculated from the circum-circle of isosceles triangles formed by three inner- and outermost Se atoms, respectively.

The asymmetric unit of **1** contains atoms in nine crystallographically distinct sites with four Se, one Si, one Eu, and one Na (Na1) occupying general positions with no disorder. The Na2 and Na3 sites are disordered with vacancies (85 and 45% occupancies, respectively), where Na3 sits on a special position related by a 3-fold rotation symmetry. The tetrahedral $SiSe_4$ forms with Si−Se distances between 2.246(2) and 2.288(2) Å ($d(\mathrm{Si{-}Se})_{av}$ = 2.269(2) Å). Eu1 is coordinated by seven Se atoms in a monocapped trigonal prismatic geometry with Eu1−Se distances ranging from 3.127(1) to 3.229(1) Å ($d(\mathrm{Eu{-}Se})_{av}$ = 3.181(3) Å). The sodium atom sites Na1, Na2, and Na3 are six-coordinate where the Na1−Se, Na2−Se, and Na3−Se distances range from 2.910(3) to 3.019(3), 2.935(5) to 3.452(5), and 2.978(9) to 3.046(9) Å, respectively. The octahedra $Na1Se_6$ and $Na3Se_6$ adopt nearly regular octahedral geometries while $Na2Se_6$ adopts a distorted octahedral geometry. Bond valence sum calculations[11] suggest that Eu1 [BVS = 1.72(2)] is in the +2 oxidation state, leading to a charge-balanced formula, $Na_2Eu^{2+}SiSe_4$.

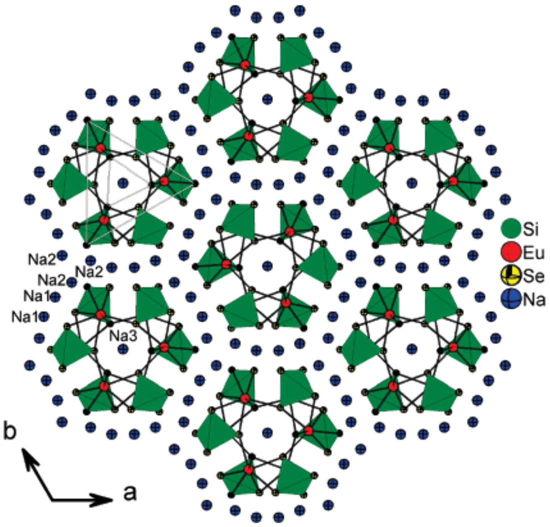

Figure 1. The structure of **1** projected along the *c*-axis. $SiSe_4$ tetrahedra are shown in green.

The tubule is constructed through the complex network of $EuSe_7$ monocapped trigonal prisms (mtps) and $SiSe_4$ tetrahedra. Close examination reveals that each Eu is connected to four Si and six Eu atoms through the Eu−Se−Si and Eu−Se−Eu linkages. Each $EuSe_7$ mtp shares edges with three $SiSe_4$ tetrahedra and two $EuSe_7$ mtps, while also sharing corners with one $SiSe_4$ tetrahedron and four $EuSe_7$ mtps. When two such corner-shared $EuSe_7$ polyhedra are projected out from the two corners of one single edge of the $EuSe_7$ mtp, they are within connecting distance through a Se-atom, thus the connection among the polyhedra may be made and a tubular structure is created. One possible way to envision the growth of a tubule in a chemical reaction may be considered as follows. The three $EuSe_7$ polyhedra share corners to form an isosceles triangle or a cyclic trimer, which may be stacked one over the other in a staggered way and fused through their edges to form a tubule. This may also be how tubular MoS_2 forms from solutions of $[Mo_3S_{13}]^{n-}$ clusters.[8b] The $SiSe_4$ tetrahedra cap the metal−chalcogen network. The Na^+ (Na3) ions located inside this tubule are octahedrally coordinated by the Se atoms of the tube walls; morever, these $Na3Se_6$ octahedra are trigonally distorted and face-shared along the *c*-axis forming a chain in which the Na^+ ion is slightly displaced along the shared face reminiscent of the anionic chains found in the polar hexagonal ternay chlorides of AMX_3 (A = alkali metal, M = transition metal, X = halogen) (Figure 2).[12] The trigonal distortion with three short bonds and three long bonds also explains the lack of center of inversion at Na3 site and as the chain of $Na3Se_6$ octahedra exactly traces the path of the innerspace of the tubule, the tubules are chiral. The intertubular space is filled by Na^+ (Na1

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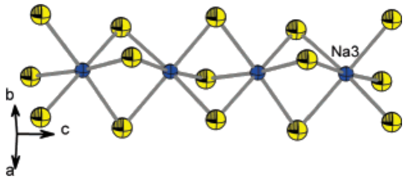

Figure 2. The face-shared chain of Na3Se$_6$ octahedra.

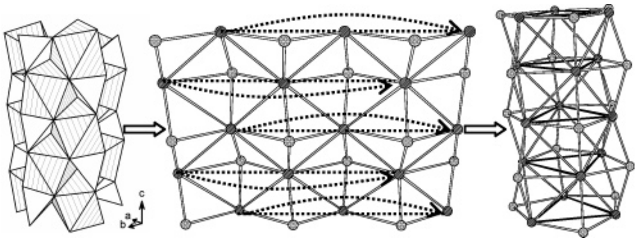

Figure 3. (a) Polyhedral representation of a tubule in **1**; where striped EuSe$_7$ mtps and solid white tetrahedra of SiSe$_4$ are shown; (b) the idealized nodal representation of an unfolded tubule; (c) the nodal representation of the tubule. The solid black lines indicate the isosceles triangles formed by connecting three Eu atoms. Eu are shown as striped spheres and Si are shown as dotted spheres.

and Na2) ions, which are responsible for the cohesion between the tubules via the participation of ionic interactions, thus forming an organized assembly of the tubules. Both Na1Se$_6$ and Na2Se$_6$ octahedra form 1-D chains along the *c*-axis through edge- and face-sharing, respectively.

It is worth investigating the nature of the layer that is derived when the tubule is hypothetically cut and unrolled. The analysis of such an unrolled layer and its comparison to any similar layer in the same family has its relevance in terms of finding a layered counterpart as in the case of “inorganic nanotubes”. The topology of the unrolled layer can be described in terms of a nodal representation, where EuSe$_7$ and SiSe$_4$ polyhedra are represented by two different symbols and are connected by a line if they share a common Se atom as shown in Figure 3. In the nodal representation, the dotted lines indicate the how three EuSe$_7$ mtps are connected to form a cyclic trimer of EuSe$_7$−mtps responsible for the formation of the tubule. Unrolling the tube, one ends up with the layered topology found in KEuGeS$_4$, where Eu is in the +3 oxidation state,[13] and belonging to a family of layered solids represented by the general formula ALnTtQ$_4$ (A = K, Rb, Cs; Ln = lanthanide elements; Tt = Si, Ge; Q = S, Se),[14] having a closely related corrugated layer topology. Another interesting feature of these layered structures is that they also crystallize in a noncentrosymmetric space group and may retain the chirality on rolling up into a tube. In the structures of ALnTtQ$_4$, rare-earth polyhedra are always trigonal prismatic with mono- or bicapping; however, the way they connect to the neighboring polyhedra, TtQ$_4$ or LnQ$_{7/8}$, differ in terms of corner- or edge-sharing, which are responsible for the formation of layers with different degrees of undulations, or tubules as with the current example. The nodal representation, however, does not distinguish these differences in topologies.

The formation of the nanoscale tubules in some well-defined compounds probably depends on the relative spatial disposition of the M−X−M (M = metal, X = ligand atom, e.g., O, S, Se) and M−X−T (T = any atom in tetrahedral center of TX$_4$ moiety) bonds of the layer. These tubules are filled with Na$^+$ ions, though different from the so-called inorganic nanotubes because they do not have any independent existence as a single free-standing tube,[15] and can be visualized as an ordered assembly of nanotubules forming a single crystal. Such self-assembly of nanotubes into a crystalline array leading to a nanotube single crystal has been reported by Remšker et al., for (MoS$_2$)-I$_x$.[16] These kinds of compounds may be exploited for use in ion-exchange and may also serve as structural models in the calculation of various properties of nanotube assemblies.

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Supporting Information Available: X-ray crystallographic data in CIF format for Na$_2$EuSiSe$_4$ (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Na$_2$Eu^{2+}SiSe$_4$, **1**, was synthesized by combining 60.8 mg of Eu (0.4 mmol), 28.1 mg of Si (1.0 mmol), 86.8 mg of Se (1.1 mmol), and 163.1 mg of Na$_2$Se$_2$ (0.8 mmol). Reactants were loaded into 10 mm diameter fused silica ampules inside a N$_2$-filled glovebox. The ampules were flame-sealed under vacuum and placed in a temperature-controlled furnace. The ampoule was 10 cm long after sealing. The furnace was ramped to 750 °C at a rate of 35 °C/h, and the temperature was held constant at 750 °C for 150 h. The furnace was then slowly cooled to ambient temperature at a rate of 5 °C/h. The ampule was opened in air, and the solid product contained pale orange colored needle shaped crystals. The solid product was soaked in DMF and sonicated for 30 sec to loosen the crystals and dissolve the excess alkali selenide flux. The crystals are stable in dry DMF in a stoppered vial; however, they decompose when the vial is kept open in air.
(10) X-ray diffraction data set on single crystal of Na$_2$Eu^{2+}SiSe$_4$ (pale orange needle) was collected on a Bruker Smart CCD diffractometer, and the structure was solved by direct methods and refined by using the SHELXTL program suite (Sheldrick, G. M. *SHELXTL 5.1*; Bruker AXS, Inc.: Madison, WI, 1997). Crystal data for **1**: Na$_2$EuSiSe$_4$, $M_r = 541.87$, trigonal, space group = $R3c$, $a = 24.398(2)$, $c = 7.147(4)$ Å, $V = 3684.2(6)$ Å^3, $T = 293(2)$ K, $Z = 18$, $\mu = 25.592$ mm^{-1}, $F(000) = 4230$, $\rho = 4.396$ Mg·m^{-3}, 11130 total data, 2018 unique data ($R_{int} = 0.0615$), wR_2 (all data, F^2) = 0.048, R_1 (1816 with $I > 2\sigma(I)$ = 0.029, $S = 1.006$.
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