

Destruction of Noncentrosymmetry through Chalcogenide Salt Inclusion

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A salt-inclusion samarium selenogermanate compound, $\text{NaSmGeSe}_4 \cdot 0.25\text{Na}_2\text{Se}$ was isolated from a reaction of Na_2Se , Sm, GeSe_2 , and Se. The new structure consists of isolated GeSe_4 units and bicapped trigonal-prismatic SmSe_8 , which are linked together to form corrugated anionic layers. The topology of the layer is similar to the well-known layered compounds ALnQE_4 ($A = \text{K, Rb, Cs}$; $\text{Ln} = \text{lanthanide ions}$; $\text{Q} = \text{Si, Ge}$; $\text{E} = \text{S, Se}$) with some subtle differences. A selenide anion and Na cations in the interlayer space form interesting structures where Se-centered trigonal-prismatic polyhedra of SeNa_6 are edge-shared and pass through a twofold rotation axis. Hence, this compound crystallizes in a centrosymmetric space group in contrast to the noncentrosymmetric structures adopted by the ALnQE_4 series of compounds. Raman and diffuse-reflectance spectra were also analyzed for the title compound.

Alkali halide salts reside in many oxide-based host frameworks such as phosphates, arsenates, silicates, and oxalates to form a large number of unique salt-inclusion phases with highly diverse structural chemistry.^{1–7} The roles of alkali halide salts in these structures are manifold; for example, the salt acts as a template to direct the formation of open-framework structures,¹ while the formation of noncentrosymmetric materials has been rationalized by the incorporation of salt lattices made of Cl-centered acentric secondary building units.⁵ Besides the structure-directing ability, the alkali halide salt sublattices themselves form fascinating structures as seen in $\text{Cr}_3\text{Si}_2\text{O}_7 \cdot 0.25\text{NaCl}^4$ and $[\text{Cd}(\text{C}_2\text{O}_4)_6] \cdot \text{KCl} \cdot 2\text{H}_2\text{O}$,⁷ where the NaCl and KCl lattices are expanded in three dimensions. Molten alkali halides are

excellent media for crystal growth, and their inclusion in the structures is sometimes “inevitable”.¹

Chalcogenide materials are quite often successfully synthesized by employing a low-melting alkali-metal polychalcogenide flux.⁸ The flux, composed of alkali metals and S, Se, or Te, often gets incorporated in the final structure, where S, Se, or Te becomes part of the negatively charged covalent framework and alkali-metal ions remain as framework charge-balancing cations, hence the term “reactive flux”. However, so far there has been no report of an alkali chalcogenide salt inclusion in any of the ternary or quaternary chalcogenide compounds. While attempting to make a single-phase sample of $\text{NaSm}_3\text{GeSe}_7$ for spectroscopic studies, we isolated a new compound $\text{NaSmGeSe}_4 \cdot 0.25\text{Na}_2\text{Se}$, where the selenide anion (Se^{2-}) is an extraframework species along with the Na cations, thus forming a salt-inclusion samarium selenogermanate. $\text{NaSmGeSe}_4 \cdot 0.25\text{Na}_2\text{Se}$ expands the ALnQE_4 family as well as being the first well-characterized Na analogue in the series.^{9–17} In this Communication, we will discuss the structure of the first alkali selenide salt inclusion in rare-earth chalcogenides that crystallizes in a centrosymmetric space group.

The red platelike crystals of $\text{NaSmGeSe}_4 \cdot 0.25\text{Na}_2\text{Se}$, **I**, were isolated from a typical high-temperature flux synthesis employing Na_2Se in combination with GeSe_2 , Sm, and Se.¹⁸ The single-crystal structure was determined by X-ray diffraction methods,¹⁹ and the crystallographic data are listed in Table 1. The asymmetric unit of **I** contains nine atoms, of which five (4Se, 1Ge, and 1Sm) belong to the covalently connected framework while one Se (Se5) and two Na atoms are extraframework species (Figure S1, Supporting Information). The site occupancies for Se5 and Na2 were first freely refined and then fixed to a value of 0.25 and 0.5, respectively, with a slight approximation (see the Supporting Information).

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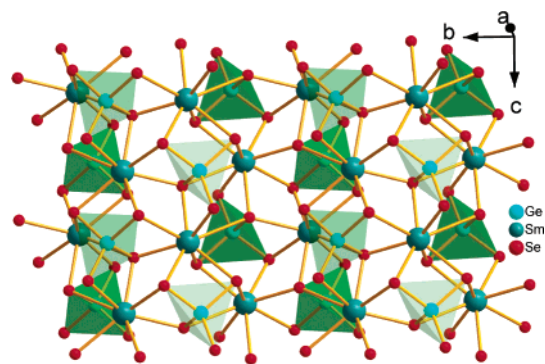
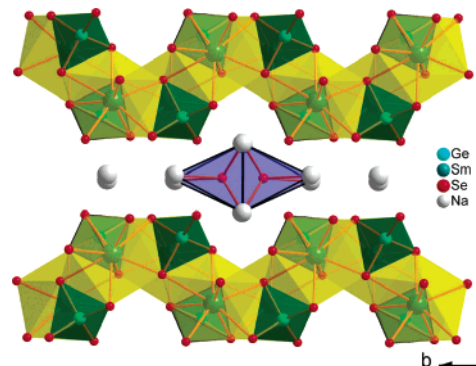
Table 1. Crystal Data and Structural Refinement for **I**

chemical formula	GeNa _{1.5} Se _{4.25} Sm
fw	593.01
space group	C2/c (No. 15)
<i>T</i> (K)	100(2)
wavelength (nm)	0.710 73
<i>a</i> (Å)	22.508(3)
<i>b</i> (Å)	11.0307(6)
<i>c</i> (Å)	6.8261(1)
α (deg)	90.0
β (deg)	103.038 (2)
γ (deg)	90.0
<i>V</i> (Å ³)	1651.1(4)
<i>Z</i>	8
ρ_{calc} (Mg m ⁻³)	4.771
μ (mm ⁻¹)	29.397
R [<i>F</i> ² > 2 σ (<i>F</i> ²)] ^a	0.0358
wR (<i>F</i> ²) (all data) ^b	0.0899

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$, $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [F_o^2 + 2F_c^2] / 3$; $a = 0.0384$ and $b = 28.1645$ for **I**.

The position of Se5 has also been fixed from thermal parameter and bond valence sum calculation [Se5 = 1.936(2)]. Bond valence sum calculations [Sm1 = 2.781(3); Ge1 = 4.050(2)] also establish the oxidation states of Sm and Ge to be +3 and +4, respectively.²⁰ Thus, the framework may be modeled as [SmGeSe₄]⁻ with a charge balanced by the fully occupied Na1 cation, while the two other extraframework species, Na2 and Se5, with occupancies of 0.5 and 0.25, balance the charge of each other and may be written as NaSmGeSe₄·0.25Na₂Se.

The crystallographically unique Sm atom is coordinated to eight Se atoms at the corners of a bicapped trigonal prism (btp), and the Ge atom is coordinated to four Se atoms at the corners of a tetrahedron. The structure of **I** is constructed from the extensive network of GeSe₄ tetrahedra and SmSe₈ btps, which form a corrugated anionic layer parallel to the *bc* plane (Figure 1). These layers are stacked one over the other along the *a* axis in an ABAB fashion. The interlayer space is occupied by the Na cations and Se²⁻ anions, where the coordination of Na⁺ ions is octahedral, while the Se²⁻ anion adopts a trigonal-prismatic geometry surrounded by

**Figure 1.** Perspective view of the covalently bonded layer viewed along the *a* axis.**Figure 2.** Polyhedral view of the covalently bonded layers in **I** along the *c* axis, showing the corrugated nature.

six Na cations. The Na–Se bond lengths are in the expected range 2.751(5)–3.152(4) and 2.954(9)–3.523(9) Å for Na1 and Na2, respectively. The six Sm–Se bond lengths in the trigonal-prismatic coordination are in the range 2.963(1)–3.0388(3) Å, while two capping Sm–Se bond lengths are slightly longer at 3.1453(2) and 3.3894(2) Å, respectively. The Ge–Se bond lengths are in the range 2.3341(4)–2.36269(5) Å and the Se–Ge–Se bond angles are in the range 102.73(5)–116.42(6)°, indicating a slightly distorted tetrahedron. Close examination reveals that each Sm is connected to four Ge and six Sm through Sm–Se–Ge and Sm–Se–Sm linkages, respectively. On the other hand, the SmSe₈ btp is edge-shared with four GeSe₄ tetrahedra and four SmSe₈ btps, while sharing corners with two SmSe₈ btps. The corner sharing between the SmSe₈ btps takes place through one of the capping Se atoms and another through the corner of the trigonal prism, which causes pronounced bending in the layer, giving it a corrugated shape (Figure 2). KCeSiS₄ is the only other layer that is centrosymmetric, and Ce has tricapped trigonal-prismatic coordination and an environment similar to that of SmSe₈ with six adjacent CeS₉ polyhedra, of which four are edge-shared and two are corner-shared through the capping S.¹³ This type of connectivity results in less curvature in the layer.

The ABAB stacking of the corrugated layer in **I** creates elliptical channels wherein the Se²⁻ anions and Na cations are packed. Though Na2 and Se5, which constitute Na₂Se in the formula, do not form any particular sublattice, both Na cations and Se5 anions form an interesting one-dimensional structure. Two face-shared chains of Na1Se₆

(18) NaSmGeSe₄·0.25Na₂Se was synthesized by combining 45.2 mg of Sm (0.3 mmol), 23 mg of GeSe₂ (0.1 mmol), 39.5 mg of Se (0.5 mmol), and 12.49 mg of Na₂Se (0.1 mmol). Reactants were loaded into fused-silica ampules inside an N₂-filled glovebox. The ampules were flame-sealed under vacuum and placed in a temperature-controlled furnace. The furnace was ramped to 825 °C at a rate of 20 °C h⁻¹, and the temperature was held constant at 825 °C for 72 h. The furnace was then slowly cooled (2 °C h⁻¹) to 550 °C and then to ambient temperature at a rate of 4 °C h⁻¹. The ampule was opened in air, and the solid product contained red platelike crystals and the little dark-colored product identified as SmSe_{1.9} (Dashjav et al. *Z. Kristallogr. New Cryst. Struct.* **2000**, *215*, 337). Although the title compound is stable in air and dry dimethylformamide for a period of days, it decomposes immediately in the presence of a trace amount of water.

(19) The intensity data set for the title compound was collected on a Bruker Smart CCD diffractometer. These data were integrated with *SAINT* (Data processing software for the SMART system; Bruker Analytical X-ray Instruments, Inc.: Madison, WI, 2000); the program *SADABS* (Sheldrick, G. M., University of Gottingen, Gottingen, Germany, 1997) was used for absorption correction. The structure was solved by direct methods using *SHELXS-97* (Sheldrick, G. M., 1997) and difference Fourier syntheses. Full-matrix least-squares refinement against [*F*²] was carried out using the *SHELXTL-PLUS* suit of programs (Bruker Analytical X-ray Instruments Inc., Madison, WI, 2000).

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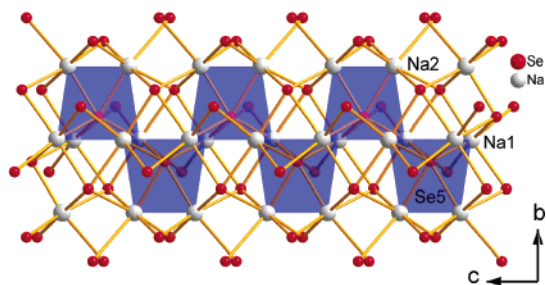


Figure 3. One-dimensional Na–Se network showing the chain of SeNa₆ trigonal prisms in the center.

along the *c* axis are fused through the edges formed by Se5–Se5 (Figure 3). Onto both sides of this chain are grafted a chain of alternate edge and face-shared Na₂Se₆. Such connectivity also leads to an edge-shared chain of trigonal-prismatic Se₅Na₆ down the *c* axis, which to our knowledge has not been observed previously. The presence of a twofold rotation axis through the Se5 anion also explains the destruction of noncentrosymmetry in the structure.

As mentioned earlier, the layered compounds ALnQE₄^{9–17} crystallize in the noncentrosymmetric space group of either *P*2₁ or *P*2₁2₁2₁ based on the types of alkali cations. Generally, K⁺ ions in the interlayer space favor the *P*2₁ space group, while bigger alkali cations (Rb and Cs) tend to force the space group to *P*2₁2₁2₁. The coordination environment of the lanthanide ion in these structures is a monocapped trigonal prism (mtp), and the corrugation of the layer, which is lesser in extent than **I**, is induced by the edge and corner sharing between the LnE₇ mtps. The layers are stacked in either ABAB or AAAA fashion along the *c* axis, and the chain of AE_{*x*} (*x* = 8–11; A = K, Rb, Cs; E = S, Se) polyhedra in the interlayer space traces a helical orientation in the case of *P*2₁2₁2₁, while in *P*2₁ examples, there often exists a center of symmetry between the edge-shared polyhedra as a result of the racemic twinning. Surprisingly, there is no report (crystallographically well-characterized) of similar layer topologies stabilized by Na cations. A probable reason could be the small size of the Na cation, which is not sufficient to interact with reasonable bonding to the framework chalcogen atoms due to longer Na–Se interactions, even when the corrugated layers are stacked in an AAAA fashion. In such a situation, the Na cation is left to “rattle” between more than one position to achieve a reasonable interaction with the framework, leading to a Na cation disorder in the interlayer space. A partially resolved structure of NaSmGeSe₄, different from the present one, may be an example of that above.¹⁵ Compound **I**, on the other hand, suggests that this problem may be resolved in a totally different way. If Na cation rattling is not sufficient for reasonable interactions, the introduction of more chemical species to fill the vacant space seems inevitable. Because

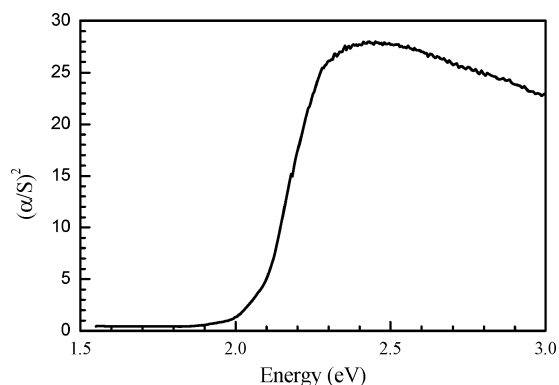


Figure 4. UV–vis diffuse-reflectance spectrum of **I**.

one Na cation is enough to balance the charge of the [SmGeSe₄][−] slab, any extra species must be accompanied by a charge-balancing counterion, hence the inclusion of a salt. This finding makes important insights into the situation where a salt can be incorporated in a structure, while the effect of simple substitution of alkali cations are being studied.

Raman analysis (Figure S2, Supporting Information) of **I** revealed only one strong peak at 214 cm^{−1} due to the primary symmetric stretch of GeSe₄ tetrahedra, while a weak broad peak at 150 cm^{−1} could be due to the bending vibration of GeSe₄ tetrahedra. The nature of the Raman spectrum is similar to the analogous ASmGeSe₄ (A = K, Rb, Cs) compounds, where a strong peak at 219 cm^{−1} was assigned to the symmetric stretch of GeSe₄ tetrahedra.¹⁵ Analysis of the diffuse-reflectance UV–vis spectrum of **I**, applying the Kubelka–Munk function, revealed the optical band gap of the compound to be 2.06 eV, consistent with the observed red color of the crystal. This value is slightly lower than the analogous ASmGeSe₄ (A = K, Rb, Cs) compounds, maybe because of the greater coordination number of Sm in **I** compared to ASmGeSe₄.¹⁵ We reported the first chalcogenide-based salt-inclusion rare-earth chalcogenide and discussed how the acentricity of the structure may be altered via salt inclusion. The current discovery also indicates that salt inclusion may be a possible route to the synthesis of unknown members in a family of compounds known with larger alkali cations.

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Supporting Information Available: X-ray crystallographic data in CIF format, details of the structural refinement, asymmetric unit, and Raman spectrum of NaSmGeSe₄·0.25Na₂Se. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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