

[BMIm]₄[Sn₉Se₂₀]: Ionothermal Synthesis of a Selenidostannate with a 3D Open-Framework Structure

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Supporting Information

ABSTRACT: The reaction of [K₄(H₂O)₄][SnSe₄] with [BMIm][BF₄] at 130–180 °C afforded [BMIm]₄[Sn₉Se₂₀] (**1**). The anion of the title compound represents a unique three-dimensional (3D) open framework, based on a variety of interconnectivity modes of Sn/Se units that lead to a system of six intersecting channels. **1** comprises the first example of a binary 3D open-framework selenidostannate anion and the first 3D open-framework chalcogenido metalate to be conveniently obtained by ionothermal synthesis.

Since the first open-framework chalcogenide was synthesized in 1989,¹ research on crystalline porous chalcogenide frameworks has received increasing attention.^{2–6} Because of the intrinsic combination of porosity with further properties like the semiconductivity or polarity of the chalcogenides, such materials are promising for applications in optoelectronic devices,^{3b,d} photocatalysis,^{3f} fast ionic conductivity,^{3c,6e} and ion exchange.^{2f–h}

Open-framework materials are typically synthesized using hydro/solvothermal methods. In 2004, Morris and co-workers first reported a new method for the synthesis of open-framework aluminum phosphates known as ionothermal synthesis.⁷ In the meantime, more and more activity is noticeable for the ionothermal method because of the excellent solvating properties of ionic liquids (ILs), such as negligible vapor pressure, high thermal stability, wide liquidus range, and the ability to dissolve a variety of materials.⁸ Hence, ionothermal methods have been employed in the synthesis of zeolites,⁹ metal–organic frameworks,¹⁰ and nanomaterials.¹¹ Nevertheless, the application of this technique for the preparation of chalcogenides is less explored. Most of the chalcogenides that have been prepared in ILs are binary metal–chalcogenide nanoparticles and nanorods.¹² Research on the preparation of highly crystalline chalcogenides by ionothermal syntheses is still scarce.¹³ The only examples are the cluster compound [Sb₇S₈Br₂][AlCl₄]₃^{13a} and the 2D structure [Bi₂Te₂Br][AlCl₄]₃^{13b} reported recently by Kanatzidis and co-workers.

Here, we describe the synthesis of [BMIm]₄[Sn₉Se₂₀] (**1**, BMIm = 1-butyl-3-methyl-imidazolium) with a new three-dimensional (3D) open-framework selenidostannate. **1** was prepared in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF₄]). It is worth noting that, even though significant progress has been made in sulfides, very few 3D open-framework selenides have been reported to date.¹⁴ To the best of our knowledge, no binary 3D open-framework selenidostannate anion, hence based on Sn/Se as linkers, has been known prior to this work, although examples of structures that are based on ternary or quaternary phases using metal or organic linkers have been reported.^{14,15}

Compound **1** was synthesized by reacting [K₄(H₂O)₄][SnSe₄]¹⁶ (136 mg, 0.020 mmol) with 0.7 mL of [BMIm][BF₄] in a Teflon-lined steel autoclave at 130 °C for 7 days. Upon cooling to room temperature, red platelike crystals were obtained by filtration, washed several times with deionized water and ethanol, and dried under air. The title compound can be obtained in a wide temperature range (from 130 to 180 °C), however, resulting in different yields. Furthermore, it can also be prepared directly from the starting materials of [K₄(H₂O)₄][SnSe₄], i.e., K₂Se and Sn, heated in [BMIm][BF₄] in the presence of MnCl₂·4H₂O at 160 °C for 6 days. The powder X-ray diffraction (XRD) pattern of the resulting product accords very well with the one simulated on the basis of the single-crystal structure, indicating phase purity (Figure S5). The role of the manganese salt is not clear yet; it is assumed that the Lewis acidic Mn²⁺ ion subtly affects the basicity of the reaction mixture by withdrawing selenide anions under the formation of MnSe.

The structure of compound **1** (monoclinic space group *Cc*) was determined by single-crystal XRD. It consists of a macroanionic [Sn₉Se₂₀]^{4–} framework, and the charge neutrality is balanced by four [BMIm]⁺ cations. As shown in Figure 1, the Se^{2–} ligand adopts two different coordination modes in the asymmetric [Sn₉Se₂₀]^{4–} unit of compound **1**; besides 18 bicoordinated μ -Se sites, there are two μ_3 -Se atoms (Se9 and Se19), each of which link three Sn atoms. For the Sn atoms, in turn, one also observes two different coordination environments; six Sn sites, which occupy the corners of two [Sn₃Se₄] semicubes in the asymmetric unit, form [SnSe₅] trigonal bipyramids, while the other three Sn atoms (Sn1, Sn5, and Sn6) possess a tetrahedral coordination environment.

The [Sn₃Se₄] semicubes act as the basic building unit in the 3D structure; they are interconnected by three different kinds of Sn/Se linkers. As shown in Figure 2, two [Sn₃Se₄] semicubes are linked by two μ -Se bridges to form a Sn₂Se₂ ring; the whole unit is further connected via edge-bridging [SnSe₄] tetrahedra along the [102] direction to form an infinite zigzag [Sn₇Se₁₄] chain. Four adjacent chains of this type are interconnected via corner-sharing, ditetrahedral, [Sn₂Se₆] spacers into the unique 3D framework (Figure 3). Although tetrahedral monomeric [SnSe₄] and its dimeric species [Sn₂Se₆] are well-known building blocks in selenidostannates, the few examples of structures that contain both types of units comprise either isolated anions, K₄[Sn₃Se₈], or layered selenidostannate structures, A₆[Sn₄Se₁₁]·xH₂O (A = K, Rb).¹⁷ Thus, the formation of a 3D structure based on both types of linkers for the [Sn₃Se₄] semicubes is unique.

The complicated connectivity patterns in **1** result in the formation of a channel system, formed by intertwining helical

Received: April 5, 2011

Published: August 02, 2011

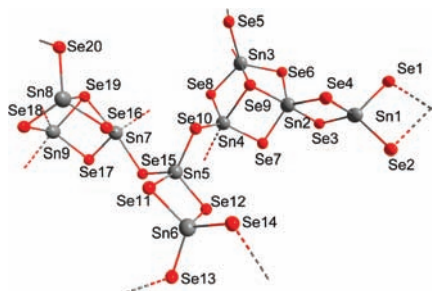


Figure 1. Asymmetric unit in the crystal structure of compound **1**. Dashed lines indicate the continuation of the 3D infinite structure. The $[\text{BMIm}]^+$ cations are omitted for clarity.

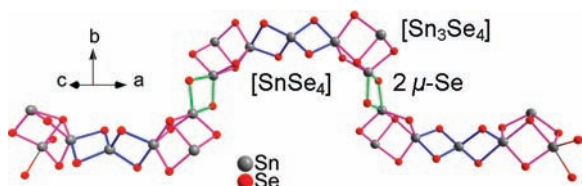


Figure 2. Infinite zigzag $[\text{Sn}_7\text{Se}_{14}]$ chain in the anionic structure of **1**, formed by two μ -Se-bridged $[\text{Sn}_3\text{Se}_4]$ semicubes that are further linked via edge-bridged $[\text{SnSe}_4]$ tetrahedra.

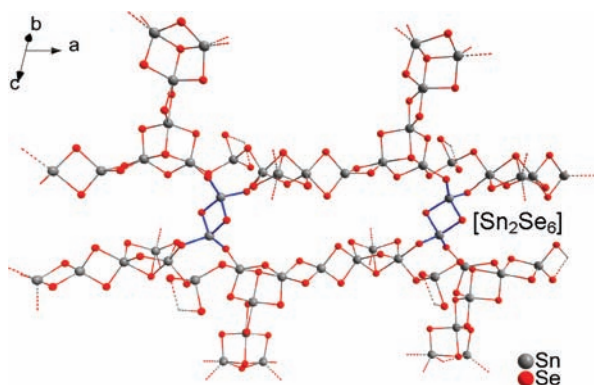


Figure 3. Linkage of four adjacent $[\text{Sn}_7\text{Se}_{14}]$ chains by $[\text{Sn}_2\text{Se}_6]$ units along the $[011]$ direction to form the 3D framework. Dashed lines indicate the continuation of the structure.

chains of the linked Sn/Se moieties as channel walls. The aperture cross sections of the six channels (Figure S4), running along the $[11\bar{2}]$, $[001]$, $[110]$, $[101]$, $[112]$, or $[100]$ direction, are approximately 13.1×4.5 , 12.4×9.2 , 11.9×6.8 , 11.5×8.7 , 10.9×7.4 , and $10.3 \times 10.0 \text{ \AA}^2$, respectively (Figures 4 and S4), indicating the extra-large microporosity of **1**. A PLATON analysis¹⁸ performed on the anionic $[\text{Sn}_9\text{Se}_{20}]^{4-}$ framework suggests a solvent- or counterion-accessible volume of approximately 4184.3 \AA^3 per unit cell (7361.0 \AA^3), amounting to 56.8% of the crystal lattice.

It was confirmed previously that the role of ILs in ionothermal syntheses can be templating, cotemplating, and no templating.⁸ At the synthesis of **1**, the IL $[\text{BMIm}][\text{BF}_4]$ seems to act as both a template and a solvent: the use of another related IL, $[\text{EMIm}]\text{Br}$, leads to production of the layered compound $[\text{EMIm}]_2[\text{Sn}_3\text{Se}_7]$ with a known 2D Sn/Se framework.¹⁹ The charge-compensation and space-filling effects appear to occur in a self-assembly mechanism. The dual role of the IL in this system serves to inhibit any competition between a template framework and a solvent

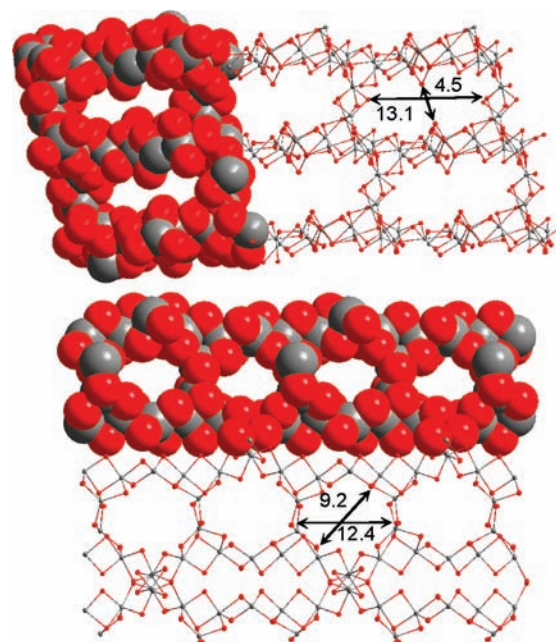


Figure 4. Illustrations of two of the channels in the framework of compound **1**: along $[11\bar{2}]$ (top) and $[001]$ (bottom). Measures are given in angstroms. The $[\text{BMIm}]^+$ cations that are located in the channels are omitted for clarity. Color code: grey, Sn; red, Se.

framework, such as the generation of the quoted 2D framework (as $[\text{BMIm}]_2[\text{Sn}_3\text{Se}_7]$, see the Supporting Information) upon the addition of the amine $\text{H}_2\text{NC}_8\text{H}_{16}\text{NH}_2$. Indeed, the chalcogenidostannates that were synthesized so far by molten flux or hydro/solvothermal techniques mostly turned out to be low-dimensional structures.^{17,20} Thus, the unique structural features observed for the title compound **1** shed light on the high synthetic potential of the ionothermal technique in this field.

A Raman spectrum of **1** was recorded at room temperature on a single crystal with a 633 nm red laser. As shown in Figure 5, at least seven vibrational modes were observed in the region of $50\text{--}350 \text{ cm}^{-1}$, which accords with the presence of several different types of Sn/Se patterns in **1**.

The sharp, intense peak centered at 199 cm^{-1} can be assigned to the symmetric Sn–Se stretching mode in the $[\text{SnSe}_4]$ and $[\text{Sn}_2\text{Se}_6]$ units, corresponding to those of reported values 199 cm^{-1} in $\text{Na}_4\text{SnSe}_4 \cdot 2\text{en}$ ^{21a} and 202 cm^{-1} in $\text{K}[\text{N}(\text{CH}_3)_3]\text{-Sn}_2\text{Se}_6$.^{21b} The asymmetric Sn–Se stretching mode is observed at 253 and 184 cm^{-1} .^{21a,c} The low-frequency vibrations at 102 and 80 cm^{-1} can be assigned to the partially overlapping antisymmetric Se–Sn–Se bends.^{21a,c} The cage mode of the semicube $[\text{Sn}_3\text{Se}_4]$ is expected to be similar to those of the cage modes observed for $(\text{CH}_3)_4\text{Sn}_4\text{Se}_6$ (252 , 248 , 210 , 208.5 , 191 , and 80 cm^{-1}); thus, they should accord with the signals at 253 , 248 , 208 , 199 , 190 , and 80 cm^{-1} .^{21b}

According to thermogravimetric analyses (TGA; Figures S8 and S9) under an argon atmosphere in the temperature ranges $25\text{--}800$ and $25\text{--}500 \text{ }^\circ\text{C}$, compound **1** is stable up to $257 \text{ }^\circ\text{C}$. A steep and significant weight loss is observed between 257 and $296 \text{ }^\circ\text{C}$. A second weight loss occurs at $596 \text{ }^\circ\text{C}$. The steps are attributed to the release of $[\text{BMIm}]^+$ cations and H_2Se molecules, giving rise to the formation of SnSe_2 after heating the sample at $500 \text{ }^\circ\text{C}$, and SnSe as a final decomposition product. This was confirmed by powder XRD (Figures S6 and S7).

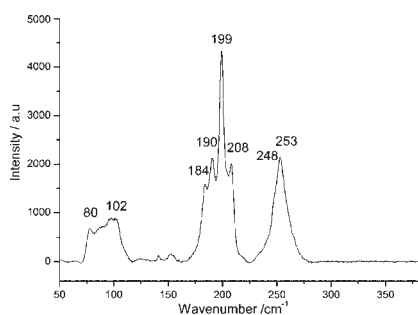


Figure 5. Single-crystal Raman spectrum of compound 1.

The optical absorption behavior of compound **1** was investigated by means of UV–vis spectroscopy, recorded on suspensions of single crystals in Nujol oil (Figure S10). An onset of absorption at 2.2 eV is followed by a maximum of around 2.3 eV, in good agreement with the red color of the compound. The absorption can be assigned to $p(\text{Se}) \rightarrow p(\text{Sn})$ charge-transfer processes, according to similar values that were previously reported for further Sn/Se complexes.²² It also shows a second onset of absorption at around 4.30 eV, assignable to charge transfer involving the organic cation to Sn.²³

■ ASSOCIATED CONTENT

S Supporting Information. SEM image, details on EDX, powder XRD, single-crystal X-ray diffraction, TGA, UV/vis and Raman spectroscopy, and CIF for compound **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

This work was supported by the Alexander von Humboldt Foundation and the DFG. We thank R. Riedel, Dr. M. Hołyńska (X-ray data collection and disorder modeling), M. Hellwig (EDX), J. Heine (discussion), and Dr. I. Kuzu (Raman spectrum) for their help.

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