

Ionic Liquid-Driven Formation of and Cation Exchange in Layered Sulfido Stannates – a CH₂ Group Makes the Difference

Bertram Peters, Martin Möbs, Nick Michel, Frank Tambornino, and Stefanie Dehnen^{*[a]}

Two types of layered sulfido stannates or a molecular cluster compound are obtained upon ionothermal treatment of the simple sulfido stannate salt $K_4[SnS_4] \cdot 4H_2O$ that is based on binary tetrahedral $[SnS_4]^{4-}$ anions. The formation of the respective products, novel compounds $(C_4C_1C_1Im)_2[Sn_3S_7]$ (**1a**), $(C_4C_1C_2Im)_2[Sn_3S_7]$ (**1b**), and $(C_4C_1C_2Im)_2[Sn_4S_9]$ (**2**) with layered anionic substructures, or the recently reported compound $(C_4C_1C_1Im)_{4+x}[Sn_{10}O_4S_{16}(SMe)_4][An]_x$ (**A**) comprising a molecular cluster anion, is controlled by both the choice of the ionic liquid

and the reaction temperature. We report the scale-up of the syntheses by a factor of 100 with regard to other reported ionothermal syntheses of related compounds, and a procedure of how to isolate them in phase-pure form – both being rare observations in chalcogenido stannate chemistry in ionic liquids. Moreover, the synthesis of compound **1a** can be achieved by rapid cation exchange starting out from **1b**, which has not been reported for organic cations in any chalcogenido stannate salt to date.

1. Introduction

The optoelectronic properties of chalcogenido (semi)metalate compounds can be fine-tuned by different approaches. One approach is the introduction of further elemental components – other types of (semi)metal or chalcogen atoms – in order to change the charger carrier concentration,^[1–6] such as done in compounds comprising the cluster ions $[M_xE_yCh_{18}]^{z-}$ ($M=Ga, In$; $E=Ge, Sn$; $x+y=10$, $Ch=S, Se$), $[M_{10}S_{18}]^{6-}$ ($M=Ga, In$), or $[Zn_{25}In_{31}S_{84}]^{25-, [7–9]}$ for instance. Another approach is the change of the chalcogenido metalate network structure (with or without alteration of the network composition), which has an impact on the electronic band structure, as well.^[10–18] An example for this is found in four related compounds that are based on anionic selenido stannate networks of different dimensionalities, 3D- $[Sn_2Se_3]$, 1D- $[Sn_6Se_{14}]$, 2D- $[Sn_{24}Se_{56}]$, and 3D- $[Sn_{18}Se_{40}]$.^[13]

To vary the network architecture, one may choose specific synthetic strategies, which mainly differ in the absence or presence of liquid reaction media, the variation of the latter in solution- or flux-based approaches, potentially used additives,

and in the temperature during the synthesis. Another means of affecting the chalcogenido metalate substructures is the application of post-synthetic treatments. For this, the application of ionic liquids has become very popular in recent times.^[19–22] Especially in the presence of amines as auxiliaries, one observes processes that involve partial or local dissolution and re-assembly of the metalate units, usually under slightly elevated temperatures – so-called ionothermal conditions.^[23]

Herein, we report a series of chalcogenido stannate compounds that were obtained by ionothermal treatment of $K_4[SnS_4] \cdot 4H_2O$ ^[24] in the presence of 2,6-dimethylmorpholine (DMMP). The reactions were carried out in different imidazolium-based ionic liquids of the type $(C_4C_1C_nIm)Br$ (with C_4 , C_1 , and C_n representing a butyl, a methyl and an alkyl chain with n carbon atoms as substituents of the cationic imidazolium ring Im). To scan the chosen reaction room, which address the heretofore relatively rarely explored sulfido stannates, we chose two different ionic liquids, $(C_4C_1C_1Im)Br$ and $(C_4C_1C_2Im)Br$, and two different reaction temperatures, 120 °C and 180 °C. Both parameters led to changes of the product spectrum, indicating the subtle influence of the counterions, which differ by one CH₂ group only.

We present the syntheses and single-crystal structures of the products, which were obtained with a remarkably high phase purity, and demonstrate the impact of the sulfido stannate architecture on the optical absorption properties and demonstrate the feasibility of a cation exchange of one ionic liquid cation for another. Band gap energies of the new compounds were determined to be 2.93 – 2.96 eV.

[a] B. Peters, M. Möbs, N. Michel, Dr. F. Tambornino, Prof. Dr. S. Dehnen
Fachbereich Chemie, Wissenschaftliches Zentrum für Materialwissenschaften (WZMW)
Philipps-Universität Marburg
Hans-Meerwein-Straße 4
35043 Marburg (Germany)
E-mail: dehnen@chemie.uni-marburg.de

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/open.202000287>

An invited contribution to a Special Issue dedicated to Material Synthesis in Ionic Liquids

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2. Results and Discussion

Syntheses and crystal structures. The ionothermal treatment of the starting compound $K_4[SnS_4] \cdot 4H_2O$ in the ionic liquids

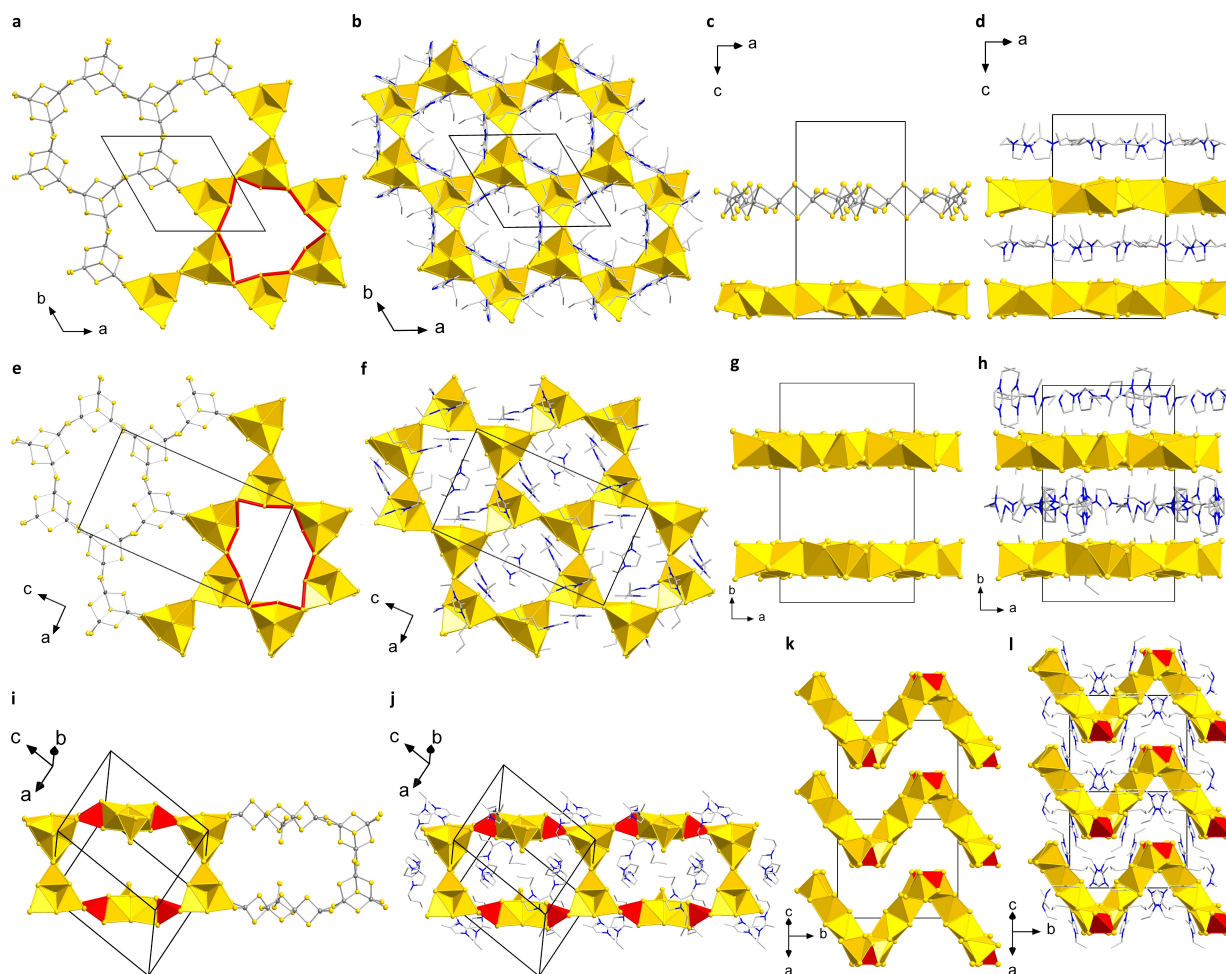


Figure 1. View of the crystal structure of **1 a** along the crystallographic *c* axis (a, b) and *b* axis (c, d) in different representations each. View of the crystal structure of **1 b** along the crystallographic *b* axis (e, f) and *c* axis (g, h) in different representations each. Unit cell of **2** in two perpendicular views and different representations (i–l). $[\text{SnS}_4]$ units are shown as yellow tetrahedra if they are part of defect-heterocubane-type units, or as red tetrahedra if they represent a separate building units. Organic cations are drawn as wires. Displacement ellipsoids are shown at a 50% probability level.

trivial. To achieve higher quantities, the mixture of the starting materials was prepared in a Schlenk tube and treated (under stirring) in an oil bath instead of being kept un-stirred in an oven. This methodology allowed to increase the amount of reacted material by a factor of 100. For obtaining pure products, we developed a washing process consisting of three steps: (1) Removal of the ionic liquid by treatment with acetonitrile that serves to dissolve the ionic liquid, yet not the sulfido stannate salt. (2) Removal of binary salts (KCl or KBr) by washing the raw-product with an aqueous ionic liquid solution, 10% (m/m) (**1 a** and **2**) or an ionic liquid solution in methanol, 25% (m/m) (**1 b**). (3) One more washing step with acetonitrile to eliminate ionic liquid residues that were imported by the previous step. The purity of the product was verified by powder X-ray diffraction (PXRD, see Figure 2) and elemental analysis (see Tables S1 and S2, and Figure S1).

Upon treatment of 25 mg isolated, pure single-crystals of **1 b** with 1.0 g of a $(\text{C}_4\text{C}_1\text{Im})\text{X}:\text{MeOH}$ mixture ($\text{X} = [\text{BF}_4], \text{Br}; 1:3, \text{m/m}$), a change of the structure is observed and confirmed by means of PXRD (Figure 3). The diffraction pattern recorded on

the product of this procedure does not correlate to the PXRD pattern of compound **1 b** anymore (blue line in Figure 3), but is in excellent agreement with the PXRD pattern of compound **1 a**, which clearly demonstrates the clean structure conversion of **1 b** to **1 a** (beside a certain degree of amorphization, as recognized by a larger background in the measured diffractogram). We take this observation as a strong indication for a cation exchange. The driving force behind this procedure is probably the recovery of the undistorted anionic substructure in **1 a**. There are several evidences for ion exchange properties of this compound class in the literature, yet notably not for the replacement and incorporation of ionic liquid counterions or other (organic) cations of a comparable size.^[10,16,33]

In order to estimate the band gap energy and the nature of the electronic transition to take place in these layered sulfido stannate salts, we performed UV-visible spectroscopy. The spectra were recorded in diffuse reflectance mode, and the data were transferred into a Tauc plot using the Kubelka-Munk function.^[34,35] $(F(R_\infty)h\nu)^{1/\gamma}$ was plotted as a function of the photon energy, while γ as the power coefficient corresponds to

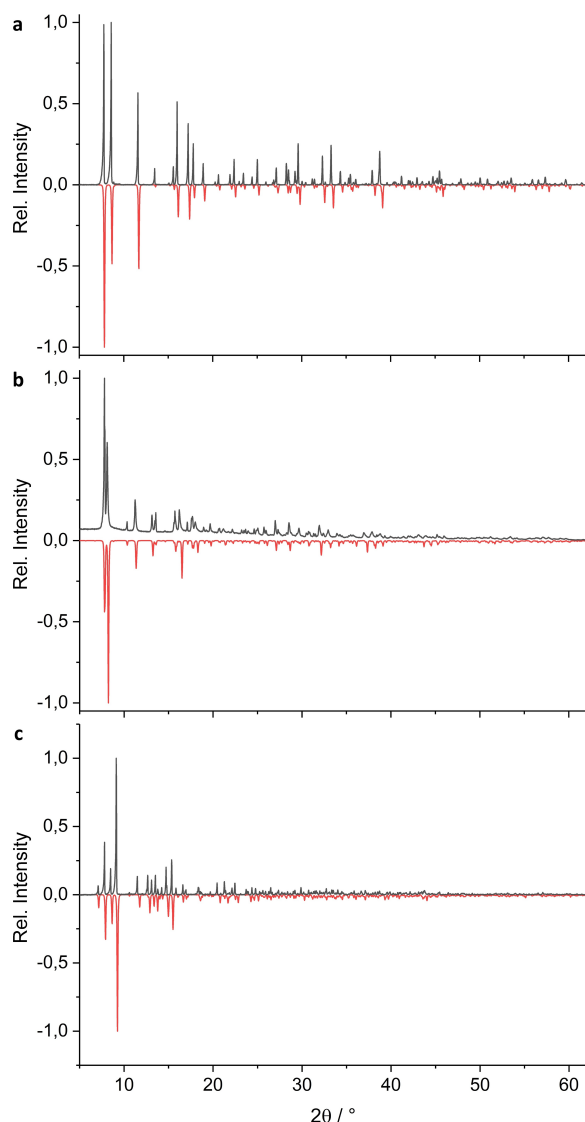


Figure 2. PXRD patterns of **1a** (a), **1b** (b), and **2** (c), shown as black lines, with the simulated PXRD patterns (using the corresponding SC-XRD data) shown as mirrored lines in red.

the nature of the transition ($\gamma=0.5$: direct allowed; $\gamma=2$: indirect allowed). Additionally, the spectra measured in diffuse reflectance mode were transformed into absorbance spectra.^[36] The absorbance data show a typical behavior and indicate band gaps close to 3.0 eV, with the “more open” structure of **2** causing a slightly larger band gap: 2.94 eV (**1a**), 2.93 eV (**1b**), 2.96 eV (**2**). The Tauc plots indicate that the transition is of indirect allowed nature. The results of the optical absorption measurements are illustrated in Figure 4.

3. Conclusion

We presented the synthesis, scale-up and purification of three new sulfido stannate salts with imidazolium-based organic counterions, $(C_4C_1C_1Im)_2[Sn_3S_7]$ (**1a**), $(C_4C_1C_2Im)_2[Sn_3S_7]$ (**1b**), and $(C_4C_1C_2Im)_2[Sn_4S_9]$ (**2**). The compounds were obtained upon

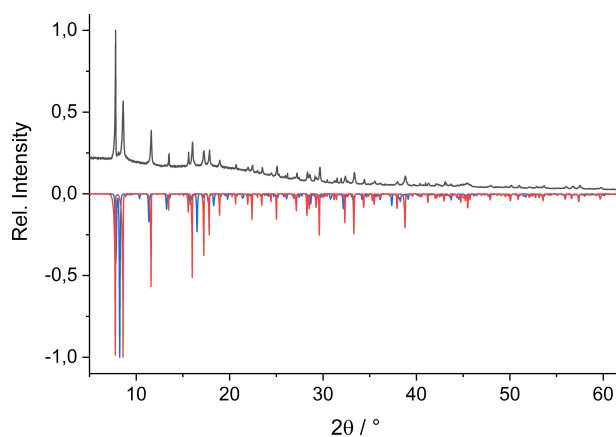


Figure 3. PXRD pattern recorded upon treatment of purified compound **1b** with a solution of $(C_4C_1C_1Im)[BF_4]$ in MeOH solution (1:3, m/m) (black), and PXRD patterns of **1a** (red; measured) and **1b** (blue; simulated from the single-crystal data) for comparison. A reflection of very low intensity observed at 8.1° (between the major reflections at 7.8° and 8.6°) is a minimal reminiscence of the diffraction pattern of **1b**, thus indicating its nearly complete absence in the product.

ionothermal treatment of $K_4[SnS_4] \cdot 4H_2O$ with ionic liquids that comprised the respective cations besides X^- (Cl^- or Br^-) anions, which serve to form KX in a salt metathesis process. The two types of ionic liquid cations and the application of two different reaction temperatures (120 or $180^\circ C$) control the product formation, with the fourth combination affording the known compound $(C_4C_1C_1Im)_{4+x}[Sn_{10}O_4S_{16}(SMe)_4][An]_x$ (**A**) as a fourth product. While the sulfido stannate substructure of **2** differs significantly from that observed in compounds **1a** and **1b**, the latter two also show differences in structural details that we put down on the subtle differences of sizes and shapes between $(C_4C_1C_1Im)^+$ and $(C_4C_1C_2Im)^+$ as templating counterions. Post-synthetic treatment of **1b** with a $(C_4C_1C_1Im)[BF_4]/MeOH$ mixture affords a product that produces the diffraction pattern of **1a** in high phase-purity. We attribute this observation to an exchange of the imidazolium cations, which has not been observed for chalcogenido stannate compounds comprising such organic cations. Measurement of the optical absorption behavior indicates band gap energies of 2.93–2.96 eV.

Experimental Section

General

All manipulations were performed under dry Ar atmosphere using standard Schlenk or glovebox techniques. Elements were used as received: K lumps (Acros Organics, 98%), Sn powder (Sigma-Aldrich, 99%), and S powder (Alpha Aesar, 99,999%). Ethane-1,2-diamine (en, 99%, Acros Organics) and 2,6-dimethylmorpholine (DMMP; 97%; Acros Organics) was distilled from CaH_2 and stored over molecular sieve (3 Å). 1-Butyl-2,3-methylimidazolium chloride/bromide, $(C_4C_1C_1Im)Cl/Br$, were treated under reduced pressure for several days. The literature-known synthesis of 1-butyl-2-methyl-3-ethylimidazolium bromide, $(C_4C_1C_2Im)Br$,^[25] was modified by several steps: 1) The reactions were not performed under inert conditions. NaH was not reacted in pure form, but as a suspension in white

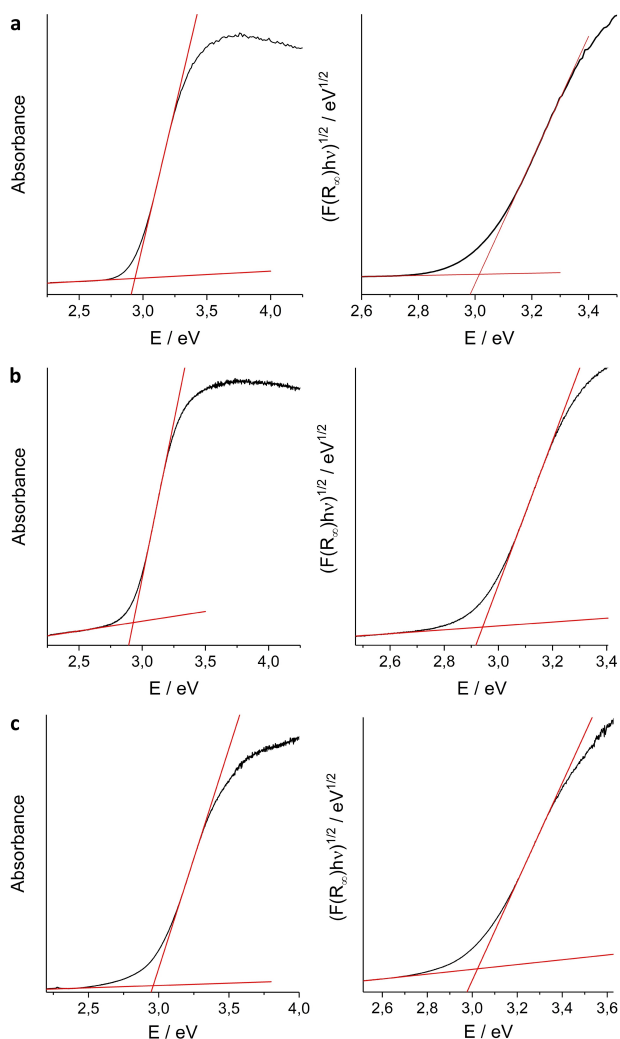


Figure 4. UV-visible absorbance spectra (left) and Tauc plots (right), generated by application of the Kubelka-Munk function $(F(R_{\infty})h\nu)^{1/2}$ with $\gamma = 0.5$ of **1a** (a), **1b** (b), and **2** (c). The measurement was performed under inert conditions employing a Praying Mantis device.^[34–36]

mineral oil. Therefore, the oil had to be separated from the product by extraction with pentane. 2) Monitoring the reaction by ^1H NMR spectroscopy indicated that longer reaction times of 1 week for the first reaction step and 1–2 weeks for the second step were necessary. 3) The reaction batch was scaled-up by a factor of 50. Single crystals of $(\text{C}_4\text{C}_1\text{C}_2\text{Im})\text{Br}$ (denoted here as **B**) were obtained that were of sufficiently high quality for an X-ray diffraction study (see Supporting Information). The inorganic starting material $\text{K}_4[\text{SnS}_4] \cdot 4\text{H}_2\text{O}$ was prepared by solid state reaction of K_2S , Sn and S according to the literature.^[24] The raw product was purified by extraction with degassed water. Note that the isolated products are stable under (humid) air and do not decompose over a period of several weeks according to powder X-ray diffraction analysis.

Synthesis of $(\text{C}_4\text{C}_1\text{C}_2\text{Im})_2[\text{Sn}_3\text{S}_7]$ (**1a**)

50 mg of $\text{K}_4[\text{SnS}_4] \cdot 4\text{H}_2\text{O}$ (0.11 mmol), 500 mg of $(\text{C}_4\text{C}_1\text{C}_2\text{Im})\text{Cl}$, and 100 μL of *en* or DMMP were placed in a Duran glass ampoule that was sealed thereafter, heated to 120°C and kept at this temperature for three days. The mixture was then allowed to cool down to room temperature. Colorless crystals of **1a** were obtained as

colorless hexagonal plates. The raw product was washed three times with acetonitrile, three times with a $(\text{C}_4\text{C}_1\text{C}_2\text{Im})\text{Cl}/\text{H}_2\text{O}$ (1:9) and three times with acetonitrile again. The purified product was obtained as colorless powder in approximately 65 % yield.

Synthesis of $(\text{C}_4\text{C}_1\text{C}_2\text{Im})_2[\text{Sn}_3\text{S}_7]$ (**1b**)

50 mg of $\text{K}_4[\text{SnS}_4] \cdot 4\text{H}_2\text{O}$ (0.11 mmol), 500 mg of $(\text{C}_4\text{C}_1\text{C}_2\text{Im})\text{Br}$, and 100 μL of DMMP were placed in a Duran glass ampoule that was sealed thereafter, heated to 120°C and kept at this temperature for three days. The mixture was then allowed to cool down to room temperature. Colorless crystals of **1b** were obtained as colorless rhombic plates. The raw product was washed three times with acetonitrile, three times with a $(\text{C}_4\text{C}_1\text{C}_2\text{Im})\text{Br}/\text{MeOH}$ (1:3) and three times with acetonitrile again. The purified product was obtained as colorless powder in approximately 50 % yield.

Synthesis of $(\text{C}_4\text{C}_1\text{C}_2\text{Im})_2[\text{Sn}_4\text{S}_9]$ (**2**)

80 mg of $\text{K}_4[\text{SnS}_4] \cdot 4\text{H}_2\text{O}$ (0.17 mmol), 500 mg of $(\text{C}_4\text{C}_1\text{C}_2\text{Im})\text{Br}$, and 160 μL of DMMP were placed in a Duran glass ampoule that was sealed thereafter, heated to 180°C and kept at this temperature for three days. The mixture was then allowed to cool down to room temperature. Colorless crystals of **2** were obtained as colorless plates. The raw product was washed three times with acetonitrile, three times with a $(\text{C}_4\text{C}_1\text{C}_2\text{Im})\text{Br}/\text{H}_2\text{O}$ (1:9) and three times with acetonitrile again. The purified product was obtained as colorless powder in approximately 60 % yield.

Single Crystal X-Ray Diffraction

X-ray data were collected on a Stoe StadiVari diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54186 \text{ \AA}$; $T = 100 \text{ K}$) equipped with an Oxford Cryosystems module. Structure solution by dual space methods and full-matrix least-squares refinement against F^2 were carried out using SHELXT15, SHELXL15, and OLEX2 software.^[37] The non-hydrogen atoms were anisotropically refined. <https://www.ccdc.cam.ac.uk/services/structures?id=doi:10.1002/open.202000287>, deposition numbers 2032832 (**1a**), 2032833 (for **1b**), 2032834 (**2**), 2032835 (**B**), contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service <https://www.ccdc.cam.ac.uk/structures>. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) +44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk].

Powder X-ray diffraction

PXRD data were obtained on a Stoe StadiMP $\text{Cu K}\alpha_1$ in transmission using a Mythen detector system. The data were examined by using WinXPOW.

UV-visible spectroscopy

Optical absorption spectra were recorded on a Varian Cary 5000 UV/VIS/NIR spectrometer between 200 and 800 nm in the diffuse reflectance mode employing a Praying Mantis™ accessory from Harrick. For ease of viewing, the raw data was transformed from % Reflectance (R) to Absorbance (A) according to the relation $A = \log(1/R)$.^[36] Additionally, the measured diffuse reflectance spectra were converted in Tauc plots by application of the Kubelka-Munk function (K-M) in order to estimate the respective band gap energies of allowed (in-)direct transitions.^[34,35]

$$F(R) = \frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty}$$

where k is the K-M absorption coefficient, R_∞ is the diffuse reflection, and s is the K-M scattering coefficient.^[38,39] Tauc plots were generated by plotting

$$(F(R) \cdot h\nu)^{1/\gamma}$$

as a function of the photon energy $h\nu$. The power coefficient can be $\gamma = 1/2, 2/3, 2$ or 3 , depending on the nature of the transition, which corresponds to direct allowed, direct forbidden, indirect allowed or indirect forbidden transitions, respectively. E_g is estimated from the intercept with the x axis of the linear fit from the corresponding region.^[40]

Acknowledgements

This work was supported by the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG), within the framework of the Priority Programme SPP1708 and the Graduate School GRK1782. Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: ionic liquids · ionothermal synthesis · optical absorption · scale-up · sulfido stannates salts · X-ray diffraction

- [1] P. Feng, X. Bu, N. Zheng, *Acc. Chem. Res.* **2005**, *38*, 293–303.
- [2] M. J. Manosa, M. G. Kanatzidis, *Chem. Sci.* **2016**, *7*, 4804–4824.
- [3] B. Peters, N. Lichtenberger, E. Dornsiepen, S. Dehnen, *Chem. Sci.* **2020**, *11*, 16–26.
- [4] B. Peters, C. Krampe, J. Klärner, S. Dehnen, *Chem. Eur. J.* **2020**, *26*, doi.org/10.1002/chem.202003887, in the print.
- [5] a) M. Langenmaier, S. Wissinger, C. Röhr, *Z. Anorg. Allg. Chem.* **2020**, *646*, 1–11; b) Michael Langenmaier, Julian Brantl, Caroline Röhr, *J. Solid State Chem.* **2020**, doi.org/10.1016/j.jssc.2020.121455.
- [6] J. F. Houry, J. He, J. E. Pfluger, I. Hadar, M. Balasubramanian, C. C. Stoumpos, R. Zu, V. Gopalan, C. Wolverton, M. G. Kanatzidis, *Chem. Sci.* **2020**, *11*, 870–878.
- [7] N. Zheng, X. Bu, B. Wang, P. Feng, *Science* **2002**, *298*, 2366–2369.
- [8] N. Zheng, X. Bu, P. Feng, *J. Am. Chem. Soc.* **2003**, *125*, 1138–1139.
- [9] X. Xu, W. Wang, D. Liu, D. Hu, T. Wu, X. Bu, P. Feng, *J. Am. Chem. Soc.* **2018**, *140*, 888–891.
- [10] Y.-J. Gao, H.-Y. Sun, J.-L. Li, X.-H. Qi, K.-Z. Du, Y.-Y. Liao, X.-Y. Huang, M.-L. Feng, M. G. Kanatzidis, *Chem. Mater.* **2020**, *32*, 1957–1963.
- [11] W. S. Sheldrick, *Z. Naturforsch.* **1988**, *43b*, 249–252.
- [12] J.-R. Li, Z.-L. Xie, X.-W. He, L.-H. Li, X.-Y. Huang, *Angew. Chem. Int. Ed.* **2011**, *50*, 11395–11399; *Angew. Chem.* **2011**, *123*, 11597–11601.
- [13] Y. Lin, D. Xie, W. Massa, L. Mayrhofer, S. Lippert, B. Ewers, A. Chernikov, M. Koch, S. Dehnen, *Chem. Eur. J.* **2013**, *19*, 8806–8813.
- [14] J.-R. Li, W.-W. Xiong, Z.-L. Xie, C.-F. Du, G.-D. Zou, X.-Y. Huang, *Chem. Commun.* **2013**, *49*, 181–183.
- [15] X.-H. Qi, K.-Z. Du, M.-L. Feng, J.-R. Li, C.-F. Du, B. Zhang, X.-Y. Huang, *J. Mater. Chem. A* **2015**, *3*, 5665–5673.
- [16] M.-L. Feng, D. Sarma, X.-H. Qi, K.-Z. Du, X.-Y. Huang, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2016**, *138*, 12578–12585.
- [17] C.-F. Du, N.-N. Shen, J.-R. Li, M.-T. Hao, Z. Wang, X.-Y. Huang, *Chem. Asian J.* **2016**, *11*, 1555–1564.
- [18] Y. Lin, W. Massa, S. Dehnen, *Chem. Eur. J.* **2012**, *18*, 13427–13434.
- [19] P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis*, Wiley, **2008**.
- [20] J. Richter, M. Ruck, *Molecules* **2020**, *25*, 78–108.
- [21] L. Schmolke, S. Lerch, M. Bülow, M. Siebels, A. Schmitz, J. Thomas, G. Dehm, C. Held, T. Strassner, C. Janiak, *Nanoscale* **2019**, *11*, 4073–4082.
- [22] R. E. Morris, *Chem. Commun.* **2009**, *21*, 2990–2998.
- [23] S. Santner, J. Heine, S. Dehnen, *Angew. Chem. Int. Ed.* **2016**, *55*, 876–893; *Angew. Chem.* **2016**, *128*, 886–904.
- [24] E. Ruzin, S. Jakobi, S. Dehnen, *Z. Anorg. Allg. Chem.* **2008**, *634*, 995–1001.
- [25] K. Boruah, R. Borah, *ChemistrySelect* **2019**, *4*, 3479–3485.
- [26] (C₄C₂Im)Br (**B**) crystallizes as colorless blocks in the monoclinic crystal system, space group type P2₁/c. The cell parameters are $a = 16.5236(12)$ Å, $b = 12.7360(8)$ Å, $c = 11.9433(9)$ Å, $\beta = 105.538(6)^\circ$, $V = 2421.5(3)$ Å³ with eight formula units in the unit cell. Further information is given in the supporting information.
- [27] B. Peters, S. Santner, C. Donsbach, P. Vöpel, B. Smarsly, S. Dehnen, *Chem. Sci.* **2019**, *10*, 5211–5217.
- [28] J. B. Parise, Y. Ko, J. Rijssenbeek, D. M. Nellis, K. Tana, S. Koch, J. Chem. Soc., *Chem. Commun.* **1994**, 527–527.
- [29] N. Pienack, D. Schinkel, A. Puls, M.-E. Ordoloff, H. Lühmann, C. Näther, W. Bensch, *Z. Naturforsch.* **2012**, *67b*, 1098–1106.
- [30] R. Walther, A. K. Winther, A. S. Fruergaard, W. van den Akker, L. Sørensen, S. M. Nielsen, M. T. Jarlstad Olesen, Y. Dai, H. S. Jeppesen, P. Lamagni, A. Savateev, S. L. Pedersen, C. K. Frich, C. Vigier-Carrière, N. Lock, M. Singh, V. Bansal, R. L. Meyer, A. N. Zelikin, *Angew. Chem. Int. Ed.* **2019**, *58*, 278–282.
- [31] a) Y. Lin, W. Massa, S. Dehnen, *Chem. Eur. J.* **2012**, *18*, 13427–13434; b) Y. Ko, K. Tan, D. M. Nellis, S. Koch, J. B. Parise, *J. Solid State Chem.* **1995**, *114*, 506–511.
- [32] C.-F. Du, N.-N. Shen, J.-R. Li, M.-T. Hao, Z. Wang, C.-C. Cheng, X.-Y. Huang, *Dalton Trans.* **2016**, *45*, 9523–9528.
- [33] X.-H. Qi, K.-Z. Du, M.-L. Feng, Y.-J. Gao, X.-Y. Huang, M. G. Kanatzidis, *J. Am. Chem. Soc.* **2017**, *139*, 4314–4317.
- [34] A. Escobedo-Morales, I. I. Ruiz-López, M. deL. Ruiz-Peralta, L. Tepech-Carrillo, M. Sánchez-Cantú, J. E. Moreno-Orea, *Heliyon* **2019**, *5*, e01505.
- [35] K. A. Michalow, D. Logvinovich, A. Weidenkaff, M. Amberg, G. Fortunato, A. Heel, T. Graule, M. Rekas, *Catal. Today* **2009**, *144*, 7–12.
- [36] S. I. Boldish, W. B. White, *Am. Mineral.* **1998**, *83*, 865–871.
- [37] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3–8; b) G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8; c) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [38] P. Kubelka, F. Z. Munk, *Tech. Phys.* **1931**, *12*, 593–601.
- [39] A. B. Murphy, *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1326–1337.
- [40] J. Tauc, R. Grigorovici, A. Vancu, *Phys. Status Solidi* **1966**, *15*, 627–637.

Manuscript received: September 23, 2020

Revised manuscript received: October 22, 2020

Correction added on 13.04.2022, after first online publication: Projekt DEAL funding statement has been added.