Abstract: Multinary chalcogenido (semi)metalate salts exhibit finely tunable optical properties based on the combination of metal and chalcogenide ions in their polyanionic substructure. Here, we present the structural expansion of chalcogenido germanate(IV) or stannate(IV) architectures with $\text{Sb}^3+$, which clearly affects the vibrational and optical absorption properties of the solid compounds. For the synthesis of the title compounds, $[\text{K}[(\text{H}_2\text{O})_n][\text{Ge}_2\text{S}_7\text{O}]_3]$ or $[\text{K}[(\text{H}_2\text{O})_n][\text{Sn}_2\text{S}_7\text{O}]_3]$ were reacted with $\text{SbCl}_3$ under ionothermal conditions in imidazolium-based ionic liquids. Salt metathesis at relatively low temperatures (120 °C or 150 °C) enabled the incorporation of (formally) $\text{Sb}^3+$ ions into the anionic substructure of the precursors, and their modification to form $(\text{Cat})_4[\text{Ge}_2\text{S}_7\text{S}_3]_2[\text{GeS}_4]$ (1) and $(\text{Cat})_4[\text{Sn}_2\text{O}_4\text{S}_2][\text{Sb}_2\text{S}_5]^2_2$ (2a and 2b), wherein Cat = $(\text{C}_m\text{C}_n\text{C}_l\text{Im})^+$ (1 and 2a) or $(\text{C}_m\text{C}_n\text{C}_l\text{Im})^+$ (2b). In 1, germanium and antimony atoms are combined to form a rare noradamanthane-type ternary molecular anion, six of which surround an [Ge$S_3$] un unit in a highly symmetric secondary structure, and finally crystallize in a diamond-like superstructure. In 2, supertetrahedral oxsulfido stannate clusters are generated, as known from the ionothermal treatment of the stannate precursor alone, yet, linked here into unprecedented one-dimensional strands with [Sb$_2$S$_5$] units as linkers. We discuss the single-crystal structures of these uncommon salts of ternary and quaternary chalcogenido (semi)metalate anions, as well as their electronic properties.

Introduction

Metal chalcogenide compounds possess a variety of desirable properties, mostly based on their intrinsic semiconducting, photo-conducting or ion conducting properties.\textsuperscript{[11–9]} However, beside the native features of corresponding binary M,E compounds (M = d-block or p-block (semi)metal, E = O, S, Se, or Te), the combination of different M or different E atoms, and the formation of chalcogenido (semi)metalates by (formal) incorporation of Cat,E (Cat = alkali metal or non-metal cation) can be used to additionally tune the corresponding structural and electronic properties.\textsuperscript{[10–15]}

In order to achieve a targeted synthesis of such compounds, various synthetic methods have been applied.\textsuperscript{[16–21]} Approaches at moderate temperatures were particularly successful in the construction of a large diversity of architectures that would not be accessible with traditional solid state methods at high temperatures. Besides comparably established syntheses under solvothermal reaction conditions\textsuperscript{[16–20]} or in alkali metal polychalcogenide flux\textsuperscript{[21]} reactions in ionic liquids have become a very popular method in more recent times for the transformation of chalcogenido (semi)metalates. The products are usually obtained as single-crystalline material, which allows the subsequent investigation of their structural as well as comonstant physical properties.\textsuperscript{[20,22–29]}

In our work, we have been particularly interested in the formation and transformation of chalcogenido tetrelate anions \{Tt$_x$E$_y$$^+$ (Tt = Ge, Sn), thereby addressing changes of structures and physical properties in a threefold manner, by a) dimensional changes within binary networks,\textsuperscript{[23,30–34]} b) combination of two types of tetrel atoms,\textsuperscript{[20,22] 35} and c) admixture of transition metal atoms.\textsuperscript{[34,35]} In all three cases, the whole reaction space—including the nature of the ionic liquid, the used precursors, potential auxiliary compounds, reaction temperature and time—needs to be scanned to get a sufficiently deep insight into the corresponding reaction system. As a side effect, we could recently show that alkylimidazolium-based ionic liquids (C$_m$C$_n$C$_l$Im)[An] (C$_m$C$_n$C$_l$ = alkyl groups with l, m, or n C atoms in 1, 2, or 3 position of the imidazolium (Im) ring; [An] = Cl, Br, $\text{BF}_4$) can serve as mild and relatively benign alkylolation reagents for these weakly nucleophilic chalcogenido (semi)metalate compounds, which has also been the only way of achieving their post-synthetic alklylation to date.\textsuperscript{[37]}

As a new means of tuning the chalcogenido (semi)metalates’ structural and electronic properties, we intended to mix two main group (semi)metal atoms of different main groups in cor-
responding networks. This was achieved by reacting salts of tetrahedral sulfido germanate or stannate anions, such as $[\text{K(H}_2\text{O)}_3]_2\text{Ge}_2\text{S}_4\text{O}_4$ or $[\text{K(H}_2\text{O)}_3]_4\text{SnS}_4\text{O}_4$, with $\text{SbCl}_3$ in imidazolium-based ionic liquids ($\text{C}_6\text{C}_1\text{mx}$)[$\text{Im}$]. Instead of a mere cation exchange, potentially along with a reorganization of the anionic substructure (as observed at the formation of $1\text{D}-(\text{C}_6\text{C}_1\text{Im})_2[\text{Ge}_2\text{Se}_4]$), or $[\text{Cat}]_2\text{Sn}_2\text{O}_2\text{S}_2\text{Br}_2\text{Me}_4$ with $\text{Cat}=\text{C}_6\text{C}_1\text{Im}$, for instance, which form in the absence of other metal compounds), the pnictogen atoms were incorporated in the structures under ionothermal conditions. This way of combining tin sulfide and antimony sulfide subunits has been unprecedented. It should be noted that another compound with antimony sulfide subunits that was prepared in ionic liquids, $[\text{Sb}_2\text{S}_3\text{Br}_3]_2[\text{AlCl}_4]_2$, was synthesized from the elements in an acidic ionic liquid mixture. As a result, the clusters in this very interesting compound bearing non-linear optical properties are cationic, and thus differ significantly from the compounds presented in this work.

Here, we report about the synthesis, structures, and optical absorption properties of the products of the mentioned reactions, (Cat)$_2$[Ge$_2$Sn$_3$S$_4$] or [Ge$_2$Sn$_4$O$_4$S$_4$][SnS$_4$] (2a and 2b), wherein Cat = $\text{C}_6\text{C}_1\text{Im}^+$ (1 and 2a) or ($\text{C}_6\text{C}_1\text{Im}$)$^-$ (2b).

### Results and Discussion

The synthesis of 1 and 2 proceeded according to Scheme 1, by ionothermal treatment of $[\text{K(H}_2\text{O)}_3]_2\text{Ge}_2\text{S}_4\text{O}_4$ or $[\text{K(H}_2\text{O)}_3]_4\text{SnS}_4\text{O}_4$ with $\text{SbCl}_3$ in the ionic liquid ($\text{C}_6\text{C}_1\text{Im}$)[BF$_4$], in the ionic liquid mixture ($\text{C}_6\text{C}_1\text{Im}$)[BF$_4$]/($\text{C}_6\text{C}_1\text{Im}$)[Cl] (1:1), or in ($\text{C}_6\text{C}_1\text{Im}$)Br, respectively. The structural data in detail. The two subunits within the anionic substructure of compound 1, a) Tetrahedral anion $[\text{Ge}_2\text{S}_4\text{O}_4]^-$; b) Noradamanantane-type anion $[\text{Ge}_2\text{S}_4\text{O}_4]^-$; c) Relative orientation of the two types of anions in crystal structure of 1; d) Structure of the resulting supramolecular subunit $\text{[(}[\text{Ge}_2\text{Sn}_3\text{S}_4]_2[\text{Ge}_2\text{S}_4\text{S}_4])^{16-}$, consisting of seven chalcogenido (sem)metalate anions in sum (Figure 1).

![Figure 1](image_url)
then packed in a diamond-like superstructure in the crystal. Figure 2 illustrates the arrangement of the anions in the crystal structure of 1.

The $\left\langle \left\langle \left\langle \text{GeSbS}_3\right\rangle \text{GeS}_6\right\rangle\right\rangle^{16-}$ assemblies are separated from each other by the counterions. Although not crystallographically detectable owing to heavy disorder (which is rather common in salts obtained from ionothermal syntheses), we assume that the counterions be $(\text{C}_3\text{C}_6\text{C}_1\text{Im})^{+}$, based on the volume of the voids between the anionic assemblies (30530.3 Å³ according to accessible void calculations done with PLATON). We note that we cannot exclude a fraction of 2–3 counterions to be $\text{K}^+$, based on a small $\text{K}$ abundance ($\approx 4$ at%) in the $\mu$-XRF spectrum (Figure S2, Table S1).

The ‘accessible’ void matches relatively well the volume of 16 $(\text{C}_3\text{C}_6\text{C}_1\text{Im})^{+}$ cations per formula unit, hence 128 cations within the unit cell ($\approx 28160$ Å³ for an estimated 20 Å³ per C or N atom), given that there are additional voids between the cation molecules. Although we cannot exclude with certainty the presence of $\text{K}^+$ cations as counterions between the anionic assemblies, we can exclude the presence of any cations between the $\left\langle \left\langle \text{GeSbS}_3\right\rangle \text{GeS}_6\right\rangle^{16-}$ and $\left\langle \text{GeS}_6\right\rangle^{16-}$ units of one such assembly, given the small interatomic distances between them (see above).

Compound 2 was obtained in two different versions, one crystallizing from $(\text{C}_3\text{C}_6\text{C}_1\text{Im})\text{[BF}_4]\text{Cl}$ (1:1) as yellow blocks in the tetragonal crystal system, space group $P4_1/mbc$, with four formula units per unit cell (2a), and one crystallizing from $(\text{C}_3\text{C}_6\text{C}_1\text{Im})\text{B}$ as yellow blocks (see Figure S1) in the triclinic crystal system, space group $P1$, with two formula units per unit cell (2b). While the two compounds differ in their counterions (see below), they comprise the same anionic substructure. The lower crystallographically observed for compound 2b results from the fact that the symmetry-reducing counterions are localizable; hence the high symmetry of 2a is likely a pseudo-symmetry, as the heavily disordered cations form an isotropic ‘solid solution’.

As in 1, the anion in 2 is based on two structural motifs: a supertetrahedral $\left\langle [\text{Sn}_{10}\text{O}_{20}]^{10-}\right\rangle$ cluster (with the O atoms stemming from water residues in the ionic liquids) and a distorted defect-heterocubane unit with two terminal sulfide ligands, $\left\langle [\text{SbS}_3]\right\rangle^{3-}$. However, in contrast to 1, the two building units are covalently linked in compound 2 to form quaternary one-dimensional strands of the formula $\left\langle [\left\langle [\text{Sn}_{10}\text{O}_{20}]^{10-}\right\rangle [\text{SnS}_3]\right\rangle^{6-}$ (Figure 3).

The strands are formed by sharing all terminal sulfide (S1) atoms of both structural motifs. Thus, two atoms each on opposite edges of the supertetrahedral moiety serve as $\mu$-S bridges to two $\left\langle [\text{SbS}_3]\right\rangle^{3-}$ subunits on each side. The $\left\langle [\text{SbS}_3]\right\rangle^{3-}$ moiety has been reported as a building unit in the sulfido antimonate salt $(\text{C}_3\text{H}_7\text{N})\text{[SnS}_3\text{]}$ (see Figure 4b). In 2, it is based on a central $(\text{Sb}_2(\mu$-$\text{S})_4)$ ring $(\text{Sb}_2\text{--}\text{Sb}_2 2.445(3)–2.451(4) Å)$, which is capped in an unsymmetric $\mu$-type manner by $\text{Sb}_2$ $(\text{Sb}_2\text{--}\text{Sb}_2 2.357(5) Å);\text{Sb}_1$ $–\text{Sb}_1 3.092(3)$ Å). The length of the Sb1–S1 bond, which serves as a bridge to the supertetrahedral oxo-sulfido stannate units, amounts to...
2.446(3) Å. A comparison of the structural parameters of the anionic substructure of 2 with those reported for \((\text{C}_3\text{H}_5\text{N})_2[\text{Sb}_3\text{S}_3]\) (Sb–(μ-S) 2.468(2)–2.491(3) Å; Sb–(μ-S) 2.406(3) Å; Sb–(μ-S) 3.113(2), 3.137(2) Å; Sb–Sn, Sn–Sn 2.489(2)–2.496(2) Å)\(^{(46)}\) indicates slight deviations of up to ≈5 pm, with slight elongation of the Sb–(μ-S) bonds in 2 on the one hand, and a slight shortening of the Sb–(μ-S) and Sb–Sn bonds in 2 on the other hand. Very obviously, this is a consequence of the different types of network structures and counterions: while ethane-1,2-ammonium dications connect through close H-bonds with the anion in \((\text{C}_3\text{H}_5\text{N})_2[\text{Sb}_3\text{S}_3]\), the imidazolium cations in 2b are found to stay farther apart. The disorder of the cations in 2a is another hint towards only weak interactions with the anionic network, which we take as an indirect proof for our assumption.

The \([\text{Sn}_{10}\text{O}_{13}\text{S}_{20}]^{8-}\) cluster anion has been known as part of a three-dimensional network (see Figure 4c)\(^{(46)}\) or as discrete anion, either with\(^{(37)}\) or without\(^{(46,47)}\) methyl groups at the terminal S atoms. In 2a, the cluster possesses crystallographic \(S_4\) symmetry—with only slight deviation from \(T_d\)—owing to the formation of the infinite strands. One observes the following interatomic distances: Sn1–S1 2.409(3) Å, Sn1,2,3–S2,3,4 2.383(3)–2.472(3) Å, Sn–S5 2.604(3)–2.625(3) Å, Sn–O 2.074(6), Sn–O 2.504(6) Å. The reported clusters with terminal SMe groups showed very similar structural parameters (Sn–S(Me) 2.407(9) Å, Sn–(μ-S) 2.395(10)–2.473(9) Å, Sn–(μ-S) 2.607(8)–2.650(8) Å, Sn–O and Sn–O 2.073(19)–2.552(20) Å)\(^{(37)}\) as the ‘terminal’ S atoms are actually μ-bridging in both cases. The purely inorganic versions of the isolated supertetrahedral architectures naturally show significantly shorter Sn–Sn bonds (2.355–2.374 Å)\(^{(46,47)}\) for these S atoms indeed terminate the anion’s molecular structure.

The structural motifs of the related compounds that were quoted above for comparison with the substructures of compounds 1, 2a, and 2b are illustrated in Figure 4.

As the linkage of the two building units in the anionic substructure of 2 occurs via trans-edges of the supertetrahedra, the entire strand possesses idealized \(D_2h\) symmetry (\(S_4\) in the crystal, see above), and thus, the position of the two \([\text{Sb}_3\text{S}_3]\) units alternates with respect to the twofold axis (Figure 5a). All strands run through the crystal in parallel fashion, in the direction of the crystallographic c axis. Neighboring strands along \(<0,0,1>\) and \(<1/3,1/3,1>\) are oriented perpendicularly to each other, which allows to optimize the positions of the \([\text{Sb}_3\text{S}_3]\) groups (Figure 5).

As proven by the crystal structure of 2b, the cations are located between the strands, thereby forming ‘belts’ around the two alternating subunits (see Figure 3c). In order to get an experimental hint for the actual presence of imidazolium counterions in 2a, we recorded Raman spectra of single-crystals of 2a, and of the pure ionic liquid that was used for the reaction (Figure 6).

Comparison of the two Raman spectra indicate clearly the presence of the IL cation in compound 2a, as visible from the characteristic signals observed between 700 and 1600 cm\(^{-1}\). Another signal group which stems from C–H valence vibrations can be found between 2700 and 3200 cm\(^{-1}\) (inset in Figure 6). The signals observed at lower wavenumbers (up to 400 cm\(^{-1}\)) are assigned to vibrations of the anionic substructures. These regions of the spectra of all three compounds reported herein, 1, 2a, and 2b, and the Raman spectrum obtained from the related compound (Cat)\(_4[\text{Sn}_{10}\text{O}_{13}\text{S}_{20}(\text{SMe})_4]\)\(^{(37)}\) are presented together in Figure 7.

The spectra of 1, 2a and 2b exhibit a broad signal consisting of two bands centered around 275 cm\(^{-1}\). As this signal is missing in the Raman spectrum of (Cat)\(_4[\text{Sn}_{10}\text{O}_{13}\text{S}_{20}(\text{SMe})_4]\),\(^{(37)}\) we attribute it to Sb–S vibrations in 1, 2a, and 2b.

All four spectra exhibit a predominant signal at around 350 cm\(^{-1}\), which occurs as a single band in 1 and (Cat)\(_4[\text{Sn}_{10}\text{O}_{13}\text{S}_{20}(\text{SMe})_4]\) or a double band in 2a (shoulder) and 2b. As there is no structural feature that all four compounds have in common, we ascribe this signal, and another one at
around 150 cm\(^{-1}\) in all spectra, to combined vibrations of the sulfido (semi)metalate substructures that are averaged around similar vibrational modes.

Some signals are only observed in the spectra of 2a, 2b, and the reference compound: a Raman signal of medium strength at ca. 125 cm\(^{-1}\), a strong band at 174–180 cm\(^{-1}\), and a signal at ca. 320 cm\(^{-1}\) in the spectrum of (Cat)\(_4[Sn_2O_5S_4(SMe)\_4]\), which in the case of 2a and 2b appears slightly blue shifted (ca. 325 cm\(^{-1}\)) as a shoulder in the slightly red-shifted, strongest signal centered around 345 cm\(^{-1}\) as said signals are missing in the spectrum of 1, they likely stem from Sn–S and Sn–O vibrations within the supertetrahedral o xo-sulfido stannate substructure.

A strong signal that is found exclusively in the Raman spectrum of compound 1 (ca. 140 cm\(^{-1}\)), in turn, can be unambiguously assigned to Ge–S or Sb–Sb vibrations of the [Ge\(_2\)Sb\(_2\)]\(^{2-}\) and [GeS\(_4\)]\(^{2-}\) anions that occur exclusively in this compound.

As outlined in the introduction, we aimed at affecting not only the development of structural motifs, but also the electronic structures by introducing Sb\(^{+3}\) into group 14 chalcogeno (semi-)metalate substructures. To probe the impact on the electronic properties, optical absorption spectra were recorded, which served to illustrate the presence of building units with different elemental compositions, [Ge\(_2\)Sb\(_2\)]\(^{2-}\) and [GeS\(_4\)]\(^{2-}\) in 1, or [Sn\(_2\)O\(_5\)S\(_4\)]\(^{6-}\) and [Sb\(_2\)S\(_4\)]\(^{2+}\) which are linked by \(\mu\)-S-sharing in 2a and 2b. Figure 8 summarizes the UV-visible spectra that were obtained from single crystalline material. The diffuse reflectance spectra (left hand side of Figure 8) were converted to Tauc plots (right hand side of Figure 8) by using the Kubelka-Munk function, for estimating the nature of the electronic transition. The indicated band gaps (2.62 eV in 1, 2.44 eV in 2a, and 2.58 eV in 2b) agree well with an allowed indirect transition in the three compounds according to the corresponding Tauc plots (2.61 eV in 1, 2.45 eV in 2a, and 2.62 eV in 2b). The allowed direct transitions derived from the Tauc plot (see Figure S5) possess larger energies: 2.78 eV (1), 2.74 eV (2a), and 2.80 eV (2b).

We cannot explain the difference of the band gap energies of 2a and 2b with certainty, but we assume that the highly disordered cations in 2a allow for a denser packing of the anions. This is in agreement with a slightly smaller unit cell volume observed for 2a (11 098 4(17) \(\text{Å}^3\)) as compared to the unit cell in 2b (11 431.8(12) \(\text{Å}^3\)), see Table S4.

A comparison with the band gaps of the formally underlying binary compounds, Ge\(_2\)S\(_4\) (3.43 eV, direct allowed transition),\(^{[48]}\) Sn\(_2\)S\(_4\) (2.38 eV, direct allowed transition),\(^{[49]}\) and Sb\(_2\)S\(_4\) (1.78 eV, direct allowed transition),\(^{[49]}\) clearly reflect the multinary elemental composition of the anionic substructures: in 1, the relatively large amount of Sb\(^{+5}\) leads to a significant narrowing of the band gap, which is distinctly smaller than that of bulk Ge\(_2\)S\(_4\). The comparably small degree of Sb\(^{+5}\) incorporation into compound 2, in contrast, is reflected by a band gap that is relatively close to (a bit larger than) that of Sn\(_2\)S\(_4\), yet one needs to keep in mind that (a) this is a cluster substructure, not bulk Sn\(_2\)S\(_4\), and (b) the cluster composition is furthermore optically ‘diluted’ by Sn–O units. Beyond this background, a band gap that is similar to the one in Sn\(_2\)S\(_4\) also indicates a notable effect of Sb\(^{+5}\) incorporation. This is additionally supported by the fact that similarly-sized crystals of (Cat)\(_4[Sn_2O_5S_4(SMe)\_4]\) possess a lighter yellow color.

**Conclusions**

We report about the successful incorporation of (formally) Sb\(^{+3}\) ions in anionic substructures of sulfido germanates and sulfido stannates \([K(H_2O)\_4][GeS_4]\_4 or [K(H_2O)\_4][SnS_4]\_4\) by treatment of these salts with SbCl\(_3\) in the ionic liquid (C\(_5\)C\(_3\)Im)\_4[BF\(_4\)]\(_4\). In the ionic liquid mixture (C\(_5\)C\(_3\)Im)\_4[BF\(_4\)]\(_4\)/(C\(_5\)C\(_3\)Im)Cl (1:1), or in (C\(_5\)C\(_3\)Im)Br under ionothermal conditions at 120 °C. The structures of the products, (Cat)\(_4[Ge\_2Sb\_2S\_4][GeS\_4]\_4\) (1) and (Cat)\(_4[Sn\_2O\_5S\_4][Sb\_2S\_4]\_4\) (2), reveal a re-organization of the original sulfide tetrelate anions. Notably, the [GeS\(_4\)]\(^{2-}\) anion is degraded to form [Ge\(_3\)]\(^{2-}\) anions in the substructure of 1, while the [Sn\(_2\)]\(^{2+}\) anions are linked to form supertetrahedral Sn/O/S clusters in the substructure of 2. Both compounds comprise further anionic subunits involving Sb\(^{+5}\), with a noradamantane-type ternary anion in 1 and a cyclic moiety in 2. The sulfido (semi)metalate units form complex (non-bonded) assemblies of a total of seven ternary Ge/Sb/S and binary Ge/S anions in 1 and polymeric 1D-stands of alternating Sn/O/S and Sb/S units in 2. Owing to a high tendency for disorder of the (C\(_5\)C\(_3\)Im)\(^{+}\) molecules, the counterions could only be located in the crystal structure of 2b, comprising (C\(_5\)C\(_3\)Im)\(^{+}\). However, Raman spectra served to corroborate the presence of ionic liquid cations in the other salt. Raman spectra of all three compounds in comparison with that of recently reported...
Single crystal X-ray diffraction: X-ray data was collected on a Stoe StadiVario diffractometer using Cu Kα radiation (λ = 1.54186 Å; T = 100 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 SHELXTL, SHELXL15, and OLEX2 software. The non-hydrogen atoms were refined using anisotropic displacement parameters. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

Deposition Numbers 2024786 (1), 2024787 (2a), and 2024788 (2b) 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 www.ccdc.cam.ac.uk/structures.

UV-visible spectroscopy: Optical absorption spectra were recorded on a Varian Cary 5000/UV/Vis/NIR spectrometer in the range of 200–800 nm in diffuse reflectance mode employing a Praying Manth fiber accessory (Harrick). For ease of viewing, raw data was transformed from %Reflectance R to Absorbance A according to A = log (1/R) [50]. The recorded diffuse reflectance spectra were converted in Tauc plots by using the Kubelka-Munk function (K-M) to estimate the indicated band gap energies of allowed (in)direct transitions [51, 52] (Eq. (1)):

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

where k is the K-M absorption coefficient, R_\infty is the diffuse reflection, and s is the K-M scattering coefficient. Tauc plots were generated by plotting (F(R) × hν) ^ 1/2 as a function of the photon energy hν. The power coefficient might be y = 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 [53].

Raman spectroscopy: Raman data was collected on an Sdb MonoVista CRS+ device. The measurements were performed with a laser wavelength of 633 nm and a grating of 300 and 1200 grooves/mm. Each measurement had a duration of 5 s with 10 coadditions and 10 s with 25 coadditions.

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Conflict of interest

The authors declare no conflict of interest.

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[1] D. Hu, Y. Zhang, J. Lin, Y. Hou, D. Lib, T. Wu, Dalton Trans. 2017, 46, 3929–3933.
[2] B. Zhang, M.-L. Feng, J. Li, Q.-Q. Xu, H.-X. Qi, X.-Y. Huang, Cryst. Growth Des. 2017, 17, 1235–1244.
[3] H. Yang, L. Wang, D. Han, J. Lin, L. Luo, H. Wang, T. Wu, Chem. Commun. 2016, 52, 4140–4143.
[4] H. Yang, M. Luo, L. Luo, H. Wang, D. Han, J. Lin, X. Wang, Y. Wang, S. Wang, X. Bu, P. Feng, T. Wu, Chem. Mater. 2016, 28, 8774–8780.
[5] 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.
[6] L. A. Burton, T. J. Whitles, D. Hesp, W. M. Linnart, J. M. Skelton, B. Hou, R. F. Webster, G. O'Dowd, C. Reece, D. Cherns, D. J. Fermin, T. D. Veal, V. R. Dhanak, A. Walsh, J. Mater. Chem. A 2016, 4, 1312–1318.
[7] L. Nie, G. Liu, J. Xie, T. Lim, G. S. Armatas, R. Xu, Q. Zhang, Inorg. Chem. Front. 2017, 4, 954–959.
[8] N. Zheng, X. Bu, P. Feng, Nature 2003, 426, 428–432.
[9] N. Zheng, X. Bu, H. Yu, P. Feng, Angew. Chem. Int. Ed. 2005, 44, 5299–5303; Angew. Chem. 2005, 117, 5433–5437.
[10] P. Feng, X. Bu, N. Zheng, Acc. Chem. Res. 2005, 38, 293–303.
[11] T. Wu, X. Bu, P. Liao, L. Wang, S.-T. Zheng, R. Ma, P. Feng, J. Am. Chem. Soc. 2012, 134, 3619–3622.
