# Crystal structure characterization and electronic structure of a rare-earth containing Zintl Phase in the Yb-Al-Sb family: Yb$_3$AlSb$_3$

**Rongqing Shang, $^a$ An T. Nguyen, $^a$ Allan He$^a$ and Susan M. Kauzlarich$^{a*}$**

$^a$Department of Chemistry, University of California, Davis, 1 Shields Ave, Davis, CA 95616, USA

*Correspondence email: smkauzlarich@ucdavis.edu

**Abstract**  A rare-earth containing compound, Yb$_3$AlSb$_3$ (Ca$_3$AlAs$_3$-type structure), has been successfully synthesized within the Yb-Al-Sb system through flux methods. According to the Zintl formalism, this structure is nominally made up of [Yb$^{2+}$]$_3$ [Al$^{1-}$] [$1b$ - Sb$^{2-}$]$_2$ [$2b$ - Sb$^{1-}$] where $1b$ and $2b$ indicate 1 bonded and 2 bonded, respectively, and Al is treated as part of the covalent anionic network. The crystal structure features infinite, corner-sharing AlSb$_4$ tetrahedra, $^1_\infty$[AlSb$_2$Sb$_{2/2}$]$^{6-}$, with Yb$^{2+}$ cations residing between the tetrahedra to provide charge balance. Herein, the synthetic conditions, the crystal structure determined from single-crystal X-ray diffraction data, and electronic structure calculations are reported.

**Keywords:  Zintl phase, electronic structure, semiconductor, crystal structure, ytterbium, aluminum, antimony, thermoelectric**

## 1. Introduction

A large variety of Zintl phase ternary compounds with the formula A$_3$MPn$_3$ (referred to as 3-1-3) where A = rare earth or alkaline earth metal; M = transition metal, alkaline earth, or triel (group 13 element); Pn = pnictogen (group 15 element) have been discovered.  To date there are five types of structures with the 3-1-3 composition and the different structure types are attributed to the size differences of each atomic species (Cordier *et al.*, 1987). Sr$_3$GaSb$_3$ (space group $P2_1/n$) (Cordier *et al.*, 1987) and Eu$_3$AlAs$_3$ (space group $P2_1/c$) (Radzieowski *et al.*, 2020) are the two structure types that crystallize in the monoclinic crystal system.  The other three, Ba$_3$GaSb$_3$ (space group $Pnma$) (Cordier *et al.*, 1985), Ca$_3$AlAs$_3$ (space group $Pnma$) (Cordier *et al.*, 1982) and Ba$_3$AlSb$_3$ (space group $Cmce$) (Cordier *et al.*, 1982) are all in the orthorhombic crystal system. The structure type of each

ternary compound depends on how the tetrahedra are connected in most cases (Kauzlarich

$et$ $al.$, 2016). For $Sr_3GaSb_3$ (Cordier $et$ $al.$, 1987), the tetrahedra are connected by shared Sb

corners and form an infinite distorted chain with four tetrahedra as the repeating unit. In

the $Ca_3AlAs_3$ structure type (Cordier $et$ $al.$, 1982), the infinite chain structure is similar to the

$Sr_3GaSb_3$ type (Cordier $et$ $al.$, 1987), but the tetrahedra form a straight line with one

tetrahedron as the repeating unit. In $Ba_3GaSb_3$ (Cordier $et$ $al.$, 1985), $Ba_3AlSb_3$ (Cordier $et$ $al.$,

1982) and $Eu_3AlAs_3$ types (Radzieowski $et$ $al.$, 2020), each two tetrahedra share a Pn-

containing edge (Pn = Ba, As) to form isolated dimeric anion pairs $(Al_2Pn_6)^{12-}$.

Early literature has shown various combinations of A = Ca, Sr, Ba, Eu; M = Al, Ga, In; Pn = P,

As, Sb exist with the 3:1:3 composition. The thermoelectric properties of some of the

$A_3MPn_3$ compounds have been reported, featuring an inherently low lattice thermal

conductivity and electron–crystal, phonon–glass properties (Zevalkink $et$ $al.$, 2011; Zevalkink

$et$ $al.$, 2012; Zevalkink $et$ $al.$, 2013). To date, all of the reported compositions, except the

rare earth phase, $Eu_3InAs_3$ (Rajput $et$ $al.$, 2020), are p-type semiconductors. $Yb_3AlSb_3$

appears as a new rare earth containing 3-1-3 phase and the only Yb containing phase to

date, after the reported Eu phases of $Eu_3AlAs_3$, $Eu_3GaAs_3$, (Radzieowski $et$ $al.$, 2020) $Eu_3InP_3$

(Jiang $et$ $al.$, 2005) and $Eu_3InAs_3$ (Rajput $et$ $al.$, 2020). It is isostructural with $Ca_3AlAs_3$ (Cordier

$et$ $al.$, 1982), $Ca_3AlSb_3$ (Cordier $et$ $al.$, 1984), $Ca_3InP_3$ (Cordier $et$ $al.$, 1985), $Ca_3GaAs_3$ (Cordier

$et$ $al.$, 1985), $Sr_3InP_3$ (Cordier $et$ $al.$, 1987), $Eu_3InP_3$ (Jiang $et$ $al.$, 2005), and $Ba_3InAs_3$ (Somer $et$

$al.$, 1996). The crystal structure of $Yb_3AlSb_3$ has been reported in the dissertation of Wu

(Wu, 2006), prepared from an Aluminum flux.

Four different phases have been reported to date containing the elements Yb-Al-Sb:

$Yb_5Al_2Sb_6$, $Yb_3AlSb_3$, $Yb_{11}AlSb_9$, and $Yb_{14}AlSb_{11}$. All of the structures feature $AlSb_4$ tetrahedra.

Unlike the single straight chain structure in $Yb_3AlSb_3$ reported herein, formed by anionic

species $[AlSb_3]^{6-}$, $Yb_5Al_2Sb_6$ contains straight chains formed by $[Al_2Sb_6]^{10-}$. These $_\infty^1[Al_2Sb_6]^{10-}$

chains can be described as a double chain ladder-type structure, where the tetrahedra in

two different chains are interconnected by a Sb-Sb bond (Todorov et al., 2009). When the

stoichiometry is more Al deficient, the tetrahedra become disconnected. Both $Yb_{11}AlSb_9$ and

$Yb_{14}AlSb_{11}$ contain isolated $[AlSb_4]^{9-}$ tetrahedra and $Sb^{3-}$ anions. $Yb_{11}AlSb_9$ contains

additional $[Sb_2]^{4-}$ dimers while the $Yb_{14}AlSb_{11}$ structure contains $[Sb_3]^{7-}$ linear units

(Kastbjerg et al., 2012; Toberer et al., 2008).

Herein, the crystal structure determined from single crystal X-ray diffraction and electronic

structure calculations using density functional theory are presented.

## 2. Experimental

### 2.1. Synthesis and crystallization

$Yb_3AlSb_3$ crystals were synthesized using flux methods.  All materials were handled in an

argon-filled dry box with <1 ppm $H_2O$.  The crystals were small, black and reflective and

were discovered serendipitously from attempts at growing an Al analog of $Yb_{21}Mn_4Sb_{18}$ (He

et al., 2019).  Stoichiometric amounts of Yb pieces (Metall Rare Earth Limited, 99.99 %), Al

shots (Alfa Aesar, 99.999 %), Sb shots (Alfa Aesar, 99.999 %), and Pb shots (Alfa Aesar, 99.99

%) were loaded with the ratio, $Yb_{21}Al_4Sb_{18}Pb_{172}$, for a total of 5 g into an alumina crucible set

(5 $cm^3$) (Canfield et al., 2016).  The crucible set was sealed in an evacuated fused silica tube

and placed in a programmable furnace.  The reaction vessel was heated to 500 °C at 120

°C/h (2 h dwell), brought to 950 °C at 120 °C/h (12 h dwell), and slowly cooled to 650 °C (2

°C/h). The reaction vessel was removed from the furnace at 650 °C and the molten flux was

removed through centrifugation and the crystals are air stable.  The reaction produced

multiple side phases.


**Table 1**   Crystal data and structure refinement for $Yb_3AlSb_3$.

| | |
|---|---|
| Empirical formula | $Yb_3AlSb_3$ |
| Formula weight | 911.35 |
| Temperature (K) | 100(2) |
| Radiation type | Mo $K\alpha$, 0.71073 Å |
| Crystal system, space group | Orthorhombic, *Pnma* |
| *a, b, c* (Å) | 12.803(3), 4.4751(9), 14.148(3) |
| *α, β, γ* (°) | 90, 90, 90 |
| V (Å$^3$) | 810.6(3) |
| Z | 4 |
| Crystal size (mm) | 0.027 x 0.049 x 0.063 |
| Θ-range for data collection (°) | 2.880 – 30.583 |
| Index ranges | −18 <= h <= 18, -6 <= k <= 6, -20 <= l <= 20 |
| Reflections collected | 16634 |
| Independent reflections | 1395 [$R_{int}$ = 0.0376] |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1395 / 0 / 44 |
| Goodness-of-fit on $F^2$ | 1.162 |
| Final R indices [I > 2σ(I)] | $R_1$ = 0.0158, $wR_2$ = 0.0335 |
| R indices (all data) | $R_1$ = 0.0185, $wR_2$ = 0.0340 |
| Extinction coefficient | 0.00046(3) |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e$^-$ Å$^{-3}$) | 1.389, -1.382 |


**2.2. Refinement**

Single crystal X-ray diffraction data were collected from a Bruker X-ray diffractometer with

Mo radiation and processed by APEX 3 and SADABS (see **Table 1**) (Bruker, 2016). The black

needle crystals were selected and cut to appropriate dimensions in Paratone-N oil. The

space group *Pnma* was determined by XPREP automatically (Sheldrick, 2008). The structure

was solved by direct methods in the SHELXTL suite of programs (Sheldrick, 2008). During the

refinement cycles, unphysical atomic positions based on van der Waals radius were ignored

manually, with the final refinement cycles obtained a highest residue peak 2.725 $e^-/Å^3$ and a deepest hole of -1.784 $e^-/Å^3$. The absorption correction was further employed in the refinement using SADABS (Bruker, 2016) resulting in a drop in the $R_1$ factor to 1.58 % with highest residue peak 1.389 $e^-/Å^3$ and the deepest hole -1.378 $e^-/Å^3$. Atomic coordinates were standardized using the STRUCTURE TIDY program (Gelato & Parthé, 1987).

### 2.3. Density Functional Theory (DFT) and Crystal Orbital Overlap Population (COOP)

Electronic structure calculations were done with DFT using the generalized gradient approximation (GGA) (Perdew *et al.*, 1996) for the semilocal exchange-correlation potential. The Kohn-Sham orbitals for the valence electrons were expanded on a plane wave basis set with a cutoff energy of 50 Ry for the wavefunctions. Chemical bonding analysis was performed by COOP calculations using the LOBSTER program (Maintz *et al.,* 2016). After calculation of the overlaps, the absolute total spilling was 2.33% and the absolute charge spilling was 1.64%. The first Brillouin zone of the unit cell was integrated over a uniform 3 x 9 x 3 k-point mesh (Monkhorst *et al.*, 1976) for self-consistent electronic structure calculations and geometry optimization. All the calculations were done using the Quantum ESPRESSO package v6.2. (Giannozzi *et al.*, 2009).

### 3. Results and discussion

### 3.1. Structural Description and Comparison

The crystal structure of $Yb_3AlSb_3$, viewed down the *b*-axis is shown in **Figure 1a** with the unit cell indicated in the bottom left corner. All atoms reside on the Wyckoff position 4*c* with *m* symmetry. According to the Zintl formalism (Kauzlarich, 1996), $Yb_3AlSb_3$ is nominally made up of 3 $Yb^{2+}$, 1 $Al^{1-}$, 2 $Sb^{2-}$, 1 $Sb^{1-}$. Since the electrons provided by the cations are not enough to satisfy octet for the anions, a covalent bonding framework is formed between anions.

5

(Kauzlarich *et al.*, 2007, Kauzlarich, 1996).  The aluminum atoms are bonded to four

antimony atoms (three unique positions) resulting in a formal charge of -1 for the aluminum

atom.  In the $AlSb_4$ tetrahedral chain, the antimony atoms that are shared between adjacent

tetrahedra have two bonds(*2b*) and can therefore be considered to be formally $Sb^{1-}$. The

remaining antimony only has one bond (*1b*), resulting in $Sb^{2-}$.  The remaining ytterbium

atoms are considered to be $Yb^{2+}$ cations, making the overall structure charge balanced.  In

sum, $Yb_3AlSb_3$ can be expressed as $(Yb^{2+})_3[(Al^{1-})(1b - Sb^{2-})_2(2b - Sb^{1-})]$.  For $Yb_3AlSb_3$, the

bonding between Yb atoms and $[AlSb_3]^{6-}$ anionic species is considered to be ionic. However,

because the difference between the electronegativity of Al and Sb, 1.61 and 2.05 in Pauling

scale, respectively, is not large enough to consider the bonding as ionic, the bonding

between them should be mostly covalent character, making the classification of this

compound as a polar intermetallic rather than a Zintl phase. However, for structural

considerations, the Zintl concept provides a consistent framework.  The structure contains

infinite chains of corner-shared $AlSb_4$ tetrahedra that make up the covalent anionic

substructure (**Figure 1b)**. The shortest Yb-Yb distance is 3.6097(6) Å, between Yb(1) and

Yb(2), bridged by three Sb(1) atoms. This distance is similar with that observed for the Ca

analog, $Ca_3AlSb_3$ (Cordier *et al.*, 1984) that has a distance of 3.642 (4) Å, and therefore is not

considered a covalent bond. All of the three Yb sites are in distorted octahedral

coordination as shown in **Figure 1c**. The Yb-Sb distance of the six Sb atoms surrounding the

Yb atoms are in the range of 3.1034(5) Å - 3.3906(8) Å. In each corner-shared $AlSb_4$

tetrahedra, one $Al^{1-}$ atom bonds to two *1b* Sb1 and *1b* Sb2, and two *2b* Sb atoms (Sb3),

formally considered $Sb^{2-}$ and $Sb^{1-}$, respectively (**Figure 1b)**. The Al-Sb distances, ranging from

2.7053(17) Å - 2.7302(10) Å, roughly matches the summed single-bonded covalent radii of Al

(1.214 Å) and Sb (1.395 Å) (Cordero *et al.*, 2008), which is 2.609 Å, in line with the Zintl

formalism. Two of the bond lengths for Al-Sb are the same (Al-Sb3, 2.7302(10) Å) while the

remaining two are different (Al-Sb1, 2.7053(17) Å, and Al-Sb2, 2.7245(18) Å).  The

tetrahedra are distorted with Sb-Al-Sb bond angles of 103.30(5)°, 109.09(4)°, 110.08(6)°,

112.50(4)°. The Sb(3)-Al-Sb(3)  angle of 110.08(6)° is the angle associated with the corner

sharing of the tetrahedra in the chain.

**Figure 1**     (a) The crystal structure of $Yb_3AlSb_3$, viewed down the *b*-axis. (b) The infinite chains of corner sharing $AlSb_4$ tetrahedral structures, viewed along the *b*-axis. Sb atoms are navy, Yb are gray, and Al are light blue. (c) The coordination picture of Yb.

Comparing $Yb_3AlSb_3$ to $Ca_3AlSb_3$, the only Al-Sb containing structural analog, the shortest Al-

Sb bond distance is slightly smaller for $Yb_3AlSb_3$ (2.7053(17) Å ) vs 2.709 Å in $Ca_3AlSb_3$

(Cordier *et al.*, 1984) and the tetrahedral bond angles are about the same; $Ca_3AlSb_3$ --

103.2°, 108.7°, 110.5°, 112.7° (Cordier *et al.*, 1984).  The obtained lattice parameters for

$Yb_3AlSb_3$, *a* = 12.803(3) Å, *b* = 4.4751(9) Å, *c* = 14.148(3) Å, are slightly smaller than those for

$Ca_3AlSb_3$, with *a* = 12.835(5) Å, *b* = 4.489(2) Å, *c* = 14.282(5) Å (Cordier *et al.*, 1984). The cell

volume of $Yb_3AlSb_3$ is 810.6(3) $Å^3$ which is also slightly smaller than the Ca analog (822.88

$Å^3$).

### 3.2. Electronic structure calculations

Electronic structure calculations were completed on $Yb_3AlSb_3$ to gain some understanding of

the chemical bonding in this new compound.  The calculated partial density of states (DOS)

and the band diagram are plotted in **Figure 2**.  These calculations show that $Yb_3AlSb_3$ is a

small band-gap (~0.1 eV) semiconductor. The experimental band-gap is expected to be

larger than the calculated result since DFT underestimates the band-gap value in general.

Compared with the Ca analog ($Ca_3AlSb_3$, calculated band gap ~ 0.25eV) (Zevalkink *et al.*,

2011), Yb is expected to be more metallic in character (Ca being a more ionic cation) and provide a smaller band gap because of the larger and more diffuse orbitals of Yb. In the valence band, the Al atoms show clear separation of the *s* and *p* orbitals with the *s* orbital contributions located within the region of -4.4 eV to -5.7 eV while the *p* orbital contributions are localized mainly from -1 to -4 eV.  For Sb, the *p* orbitals contribute the majority of states in the low lying region of -4.4 to -5.7 eV and close to the Fermi level between -1 to -4 eV. The lower lying states in the region between -4.4 to -5.7 eV is evidence of bonding interactions between the M and Pn atoms which is confirmed in the COOP calculations (**Figure 3**). The higher energy *p* states of Sb have a contribution from non-bonding lone pairs that is seen in electron density mapping for $Ca_3AlSb_3$ (Zevalkink *et al.*, 2011) where most of the charge is centered around the Sb atoms at -0.1 eV from the valence band edge.  The similarity in density of states between the Yb and Ca analog suggest that the same behavior is happening in $Yb_3AlSb_3$. The localization of charge on these Sb atoms suggest that the tetrahedral Sb atoms are responsible for hole transport/mobility as has been previously observed elsewhere (Sánchez-Portal *et al.*, 2002). The large majority of states in the valence band are contributed by the Sb *p* states while the majority of states in the conduction band is dominated by Yb *5d* states. The DOS curves for related phases $Ca_3AlSb_3$ and $Yb_5Al_2Sb_6$  are very similar due to the nature of the anionic moieties (M-Pn tetrahedra) (Zevalkink *et al.*, 2011, Todorov et al., 2009). In all of the compounds, the states deep in the valence band are dominated by Al and Sb states while those just below the Fermi level are dominated by Sb *p* states and the rare-earth or alkaline earth *d* states. The conduction band contains mainly higher energy cation electronic states of the rare-earth or alkaline earth atoms.

Similar to the Ca analog (Zevalkink *et al.*, 2011), $Yb_3AlSb_3$ is a direct band gap material with the valence band maximum and conduction band minimum both located at the Γ point.  The parabolic nature of the bands near the Fermi level suggest that this material can be modeled well with a single parabolic band (SPB) model.  This makes $Yb_3AlSb_3$ well positioned to be a good starting point for thermoelectric material optimization as the Ca analog was intrinsically shown to be too insulating and required hole doping for optimization.  From Wu's dissertation, the Seebeck values for $Yb_3AlSb_3$ is reported to be about 10 µV/K at the room temperature (300 K) and increased to around 21 µV/K at 700 K. The electrical conductivity was reported to be 435 µΩ cm (Wu, 2006). In comparison, the Seebeck value for $Ca_3AlSb_3$ is about 220 µV/K at the room temperature, and peaks at 650 K, with the value about 400 µV/K. The electrical conductivity is around 1100 µΩ cm (Zevalkink *et al.*, 2011), which is higher than the Yb analog, as expected. The SPB model is a common and powerful tool for characterizing thermoelectric transport that can provide insight on optimization pathways for this material.  Doping of this material to larger carrier concentrations will probe deeper into the valence band and will induce non-SPB behavior or through elevated temperatures.

**Figure 2**     The electronic density of states (DOS) for $Yb_3AlSb_3$ on the left shows the detailed DOS for each orbitals of the atoms. The inset highlights the DOS close to the Fermi energy. The band diagram of $Yb_3AlSb_3$ on the right reveals a direct band gap of ~ 0.1 eV. Fermi level is located at $E = 0$.

**Figure 3**     The crystal orbital overlap population for $Yb_3AlSb_3$ showing the average Yb-Sb (black) and Al-Sb (red) interactions.

## References

Bruker (2016). *APEX3*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Canfield, P. C., Kong, T., Kaluarachchi, U. S. & Jo, N. H. (2016). *Philos. Mag.* **96**, 84–92.

Cordero, B., Gómez, V., Platero-Prats, A. E., Revés, M., Echeverría, J., Cremades, E., Barragán, F. & Alvarez, S. (2008). *Dalton Trans.* **21**, 2832.

Cordier, G., Savelsberg, G. & Schäfer, H. (1982). *Z. Naturforsch. B*, **37**, 975–980.

Cordier, G., Schäfer, H. & Steher, M. (1985). *Z. Naturforsch. B*, **40**, 1100–1104.

Cordier, G., Schäfer, H. & Stelter, M. (1984). *Z. Naturforsch. B*, **39**, 727–732.

Cordier, G., Schäfer, H. & Stelter, M. (1987). *Z. Naturforsch. B*, **42**, 1268–1272.

Gelato, L. M. & Parthé, E. (1987). *J. Appl. Cryst.* **20**, 139–143.

Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G. L., Cococcioni, M., Dabo, I., Dal Corso, A., de Gironcoli, S., Fabris, S., Fratesi, G., Gebauer, R., Gerstmann, U., Gougoussis, C., Kokalj, A., Lazzeri, M. & Wentzcovitch, R. M. (2009). *J. Phys.: Condens. Matter*, **21**, 395502.

He, A., Bux, S. K., Hu, Y., Uhl, D., Li, L., Donadio, D. & Kauzlarich, S. M. (2019). *Chem. Mater.* **31**, 8076–8086.

Jiang, J., Payne, A. C., Olmstead, M. M., Lee, H., -o., Klavins, P., Fisk, Z., Kauzlarich, S. M., Hermann, R. P., Grandjean, F. & Long, G. J. (2005). *Inorg. Chem.* **44**, 2189–2197.

Kastbjerg, S., Uvarov, C. A., Kauzlarich, S. M., Chen, Y. S., Nishibori, E., Spackman, M. A., & Iversen, B. B. (2012). *Dalton Trans.* **41**, 10347-10353.

Kauzlarich, S. M. (1996). *Chemistry of Metal Clusters, 1st* ed. Wiley-VCH.

Kauzlarich, S. M., Brown, S. R. & Jeffrey Snyder, G. (2007). *Dalton Trans.* **21**, 2099-2107.

Kauzlarich, S. M., Zevalkink, A., Toberer, E. & Snyder, G. J. (2016). *Thermoelectric Mater. Devices.* 1–26.

Maintz, S., Deringer, V. L., Tchougréeff, A. L., Dronskowski, R. (2016). *J. Comput. Chem.* **37**, 1030-1035.

Monkhorst, H. J. & Pack, J. D. (1976). *Phys. Rev. B*, **13**, 5188–5192.

Perdew, J. P., Burke, K. & Ernzerhof, M. (1996). *Phys. Rev. Lett.* **77**, 3865–3868.

Radzieowski, M., Stegemann, F., Klenner, S., Zhang, Y., Fokwa, B. P. T. & Janka, O. (2020). *Mater. Chem. Front.* **4**, 1231–1248.

Rajput, K., Baranets, S. & Bobev, S. (2020). *Chem. Mater.* **32**, 9616–9626.

Sánchez-Portal, D., Martin, R. M., Kauzlarich, S. M. & Pickett, W. E. (2002). *Phys. Rev. B*, **65**, 144414.

Sheldrick, G. M. (2008). *Acta Crystallogr.* A**64**, 112–122.

Somer, M., Carrillo-Cabrera, W., Peters, K., von Schnering, H. G., & Cordier, G. (1996). *Z. Kristallogr. N. Cryst. Struct.* **211**, 632.

Toberer, E. S., Cox, C. A., Brown, S. R., Ikeda, T., May, A. F., Kauzlarich, S. M., & Snyder, G. J. (2008). *Adv. Funct. Mater.* **18**, 2795-2800.

Todorov, I., Chung, D. Y., Ye, L., Freeman, A. J., & Kanatzidis, M. G. (2009). *Inorg. Chem.* **48**, 4768-4776.

Wu, X., (2006). PhD thesis, Michigan State University, USA.

Zevalkink, A., Pomrehn, G., Takagiwa, Y., Swallow, J. & Snyder, G. J. (2013). *ChemSusChem*, **6**, 2316–2321.

Zevalkink, A., Toberer, E. S., Zeier, W. G., Flage-Larsen, E. & Snyder, G. J. (2011). *Energy Environ. Sci.* **4**, 510–518.

Zevalkink, A., Zeier, W. G., Pomrehn, G., Schechtel, E., Tremel, W. & Snyder, G. J. (2012). *Energy Environ. Sci.* **5**, 9121-9128.

**Table 2**

Fractional atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2$x $10^3$). U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

|     | x | y | z | U(eq) |
| --- | --- | --- | --- | --- |
| Yb1 | 5594(1) | 2500 | 6118(1) | 6(1) |
| Yb2 | 2726(1) | 2500 | 7213(1) | 6(1) |
| Yb3 | 3500(1) | 2500 | 59(1) | 6(1) |
| Sb1 | 2564(1) | 2500 | 3812(1) | 5(1) |
| Sb2 | 1139(1) | 2500 | 1092(1) | 5(1) |
| Sb3 | 401(1) | 2500 | 6492(1) | 5(1) |
| Al1 | 667(1) | 2500 | 2970(1) | 6(1) |

**Table 3**

Selected geometric parameters (Å, º)

| | | | |
|---|---|---|---|
| Yb1—Sb2$^{i}$ | 3.1509 (5) | Yb2—Al1$^{ii}$ | 3.2230 (12) |
| Yb1—Sb2$^{ii}$ | 3.1509 (5) | Yb2—Al1$^{i}$ | 3.2230 (12) |
| Yb1—Sb2$^{iii}$ | 3.2039 (7) | Yb2—Yb3$^{i}$ | 4.0939 (6) |
| Yb1—Sb1$^{iv}$ | 3.2520 (5) | Yb2—Yb3$^{ii}$ | 4.0939 (6) |
| Yb1—Sb1$^{v}$ | 3.2520 (5) | Yb2—Yb3$^{vii}$ | 4.1466 (8) |
| Yb1—Sb3$^{vi}$ | 3.3906 (8) | Yb3—Sb1$^{viii}$ | 3.1589 (5) |
| Yb1—Yb2$^{vi}$ | 3.6097 (6) | Yb3—Sb1$^{ix}$ | 3.1589 (5) |
| Yb1—Yb2 | 3.9849 (8) | Yb3—Sb3$^{iii}$ | 3.2760 (6) |
| Yb1—Yb3$^{iii}$ | 4.0764 (8) | Yb3—Sb3$^{ix}$ | 3.3313 (5) |
| Yb1—Yb1$^{v}$ | 4.1623 (7) | Yb3—Sb3$^{viii}$ | 3.3313 (5) |
| Yb1—Yb1$^{iv}$ | 4.1623 (7) | Yb3—Sb2 | 3.3590 (7) |
| Yb2—Sb2$^{i}$ | 3.1034 (5) | Sb1—Al1 | 2.7053 (17) |
| Yb2—Sb2$^{ii}$ | 3.1034 (5) | Sb2—Al1 | 2.7245 (18) |
| Yb2—Sb3 | 3.1470 (7) | Sb3—Al1$^{x}$ | 2.7302 (10) |
| Yb2—Sb1$^{ii}$ | 3.2034 (5) | Sb3—Al1$^{xi}$ | 2.7302 (10) |
| Yb2—Sb1$^{i}$ | 3.2034 (5) | | |
| Al1$^{x}$—Sb3—Al1$^{xi}$ | 110.08 (6) | Sb1—Al1—Sb3$^{xi}$ | 109.09 (4) |
| Sb1—Al1—Sb2 | 103.30 (5) | Sb2—Al1—Sb3$^{xi}$ | 112.50 (4) |
| Sb1—Al1—Sb3$^{x}$ | 109.09 (4) | Sb3$^{x}$—Al1—Sb3$^{xi}$ | 110.08 (6) |
| Sb2—Al1—Sb3$^{x}$ | 112.50 (4) | | |

Symmetry code(s): (i) −$x$+1/2, −$y$, $z$+1/2; (ii) −$x$+1/2, −$y$+1, $z$+1/2; (iii) $x$+1/2, $y$, −$z$+1/2; (iv) −$x$+1, −$y$+1, −$z$+1; (v) −$x$+1, −$y$, −$z$+1; (vi) $x$+1/2, $y$, −$z$+3/2; (vii) $x$, $y$, $z$+1; (viii) −$x$+1/2, −$y$, $z$−1/2; (ix) −$x$+1/2, −$y$+1, $z$−1/2; (x) −$x$, −$y$, −$z$+1; (xi) −$x$, −$y$+1, −$z$+1.

**Table 4**

Anisotropic displacement parameters (Å$^2$ x 10$^3$).

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Yb1 | 6(1) | 6(1) | 5(1) | 0 | 0(1) | 0 |
| Yb2 | 6(1) | 6(1) | 5(1) | 0 | 0(1) | 0 |
| Yb3 | 7(1) | 6(1) | 5(1) | 0 | 0(1) | 0 |
| Sb1 | 6(1) | 5(1) | 5(1) | 0 | 0(1) | 0 |
| Sb2 | 6(1) | 5(1) | 4(1) | 0 | 0(1) | 0 |
| Sb3 | 6(1) | 5(1) | 5(1) | 0 | 0(1) | 0 |
| Al1 | 7(1) | 5(1) | 6(1) | 0 | 1(1) | 0 |