This paper is published as part of a *Dalton Transactions* themed issue on:

# **Thermoelectric Materials**

Guest Editor Andrei Shevelkov Moscow State University, Russia

Published in issue 4, 2010 of Dalton Transactions



Image reproduced with permission of Ichiro Terasaki

Articles published in this issue include:

# **PERSPECTIVES:**

<u>Thermoelectric clathrates of type I</u> Mogens Christensen, Simon Johnsen and Bo Brummerstedt Iversen *Dalton Trans.*, 2010, DOI: 10.1039/b916400f

Wet chemical synthesis and thermoelectric properties of V-VI one- and two-dimensional nanostructures Gengiang Zhang, Qingxuan Yu and Xiaoguang Li

Dalton Trans., 2010, DOI: 10.1039/b913462j

# HOT ARTICLES:

<u>Novel thermoelectric properties of complex transition-metal oxides</u> Ichiro Terasaki, Manabu Iwakawa, Tomohito Nakano, Akira Tsukuda and Wataru Kobayashi, *Dalton Trans.,* 2010, DOI: 10.1039/b914661j

<u>Effect of Zn doping on improving crystal quality and thermoelectric properties of borosilicides</u> Takao Mori, David Berthebaud, Toshiyuki Nishimura, Akiko Nomura, Toetsu Shishido and Kazuo Nakajima, *Dalton Trans.*, 2010, DOI: 10.1039/b916028k

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research www.rsc.org/dalton

# Synthesis, crystallographic and theoretical studies of the new Zintl phases $Ba_2Cd_2Pn_3$ (Pn = As, Sb), and the solid solutions $(Ba_{1-x}Sr_x)_2Cd_2Sb_3$ and $Ba_2Cd_2(Sb_{1-x}As_x)_3$ <sup>†</sup>

Bayrammurad Saparov,<sup>a</sup> Hua He,<sup>a</sup> Xiaohang Zhang,<sup>b</sup> Richard Greene<sup>b</sup> and Svilen Bobev<sup>\*a</sup>

Received 20th July 2009, Accepted 4th November 2009 First published as an Advance Article on the web 1st December 2009 DOI: 10.1039/b914305j

Two new Zintl compounds  $Ba_2Cd_2As_3$  and  $Ba_2Cd_2Sb_3$  have been synthesized and structurally characterized. They crystallize in a novel monoclinic structure type with the space group C2/m (no. 12), featuring polyanionic layers made of  $CdPn_4$  tetrahedra (Pn = As, Sb) and homoatomic Pn-Pn bonds. The topological relationships between the structure of  $Ba_2Cd_2Sb_3$  and those of  $BaCd_2Sb_2$  ( $CaAl_2Si_2$ type) and  $Ba_3Cd_2Sb_4$  (own type) are discussed as well. Based on electronic structures calculations, carried out by the density-functional method, and resistivity measurements, pure  $Ba_2Cd_2As_3$  is shown to be a small-gap semiconductor and pure  $Ba_2Cd_2Sb_3$  to be a poor metal. The structures of the title compounds are amenable to doping on both cation and pnicogen sites, which could enable fine-tuning the transport properties, and make them promising materials for thermoelectric applications.

# Introduction

Zintl phases are intermetallic compounds, formed between metals and/or semi-metals with different electronegativities. They constitute a large class of inorganic materials with very diverse crystal structures.<sup>1</sup> The chemical bonding in Zintl phases can be understood by assuming a complete transfer of electrons from the more electropositive metal to the more electronegative element.<sup>1,2</sup> In this aspect, they are similar to the valence compounds, *i.e.*, the typical semiconductors.

Since the formulation of the phonon-glass electron-crystal (PGEC) concept by Slack,<sup>3</sup> Zintl phases have been identified as a promising class of materials for thermoelectric applications. According to this idea, the most efficient thermoelectric material would have the electrical conductivity ( $\sigma = 1/\rho$ ) of a small-gap semiconductor and the thermal conductivity ( $\kappa$ ) of a glass, thereby maximizing the thermoelectric figure of merit  $ZT = \sigma S^2 T/\kappa$ , where *T* is the absolute temperature and *S* is the thermopower.<sup>3,4</sup> Zintl phases fit ideally into this description because their complex crystal structures enable favorable thermal conductivity, while their electronic structures allow for the optimal charge-transport properties.<sup>4,5</sup> These desirable characteristics have long been recognized, and in recent years, advantageous thermoelectric figures of merit have been reported for many such compounds—

EuZn<sub>2</sub>Sb<sub>2</sub>,<sup>6</sup> CaZn<sub>2</sub>Sb<sub>2</sub>,<sup>7</sup> BaZn<sub>2</sub>Sb<sub>2</sub>,<sup>8</sup> and Yb<sub>14</sub>MnSb<sub>11</sub>,<sup>9</sup> to name just a few. Another important benefit of the Zintl phases is that their bonding characteristics typically favor isovalent substitutions (random or ordered), *i.e.*, the total valence electron count and the crystal structures are always preserved. This approach allows for rational fine-tuning of physical properties and has recently been demonstrated for Ca<sub>x</sub>Yb<sub>1-x</sub>Zn<sub>2</sub>Sb<sub>2</sub><sup>7</sup> and Yb<sub>14</sub>Mn<sub>1-x</sub>Zn<sub>x</sub>Sb<sub>11</sub>.<sup>10</sup> In rare cases, exemplified by Yb<sub>14</sub>Mn<sub>1-x</sub>Al<sub>x</sub>Sb<sub>11</sub>,<sup>11</sup> the structures can also tolerate small amounts of aliovalent replacements.

These findings prompted our interest in the search for new compounds formed between the alkali-, alkaline-earth or rareearth metals, group 12 metals, and the pnicogens (Pn). So far, our studies have yielded numerous new ternary and quaternary compounds, including the series  $A_9Cd_{4+x}Pn_9$  and  $A_9Zn_{4+x}Pn_{9}$ ,<sup>12</sup>  $A_{21}Cd_4Pn_{18}$ ,<sup>13</sup>  $KA_2Cd_2Sb_3$ ,<sup>14</sup>  $Eu_{10}Cd_6Bi_{12}$ ,<sup>15</sup>  $Ca_2CdSb_2$  and Yb2CdSb2,<sup>16</sup> Ba11Cd8Bi14,<sup>17</sup> Ba11Cd6Sb12,<sup>18</sup> Ba3Cd2Sb4,<sup>19</sup> where A denotes Ca, Sr, Ba, Eu, or Yb. With this paper, we report the syntheses, and the crystal and electronic structures of two new Zintl phases, Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>. They are isomorphous and crystallize in a new monoclinic structure type, which is closely related to that of the previously reported Ba<sub>3</sub>Cd<sub>2</sub>Sb<sub>4</sub>.<sup>19</sup> Based on crystallographic data for Ba<sub>2</sub>Cd<sub>2</sub>(Sb<sub>1-x</sub>As<sub>x</sub>)<sub>3</sub> with x = 0.163(3) and x = 0.907(3), we speculate that a wide range of solid solutions exists between the end members. In addition, the structure of the new compounds is shown to be prone to a partial substitution of Ba with other divalent cations, as inferred by the mixedcation phase  $(Ba_{1-x}Sr_x)_2Cd_2As_3$  (x = 0.265(5)). These traits are presented in the context of the crystallographic sites preferences, alongside a theoretical treatment of that problem. Discussed as well are the prospects for property-tuning using the cationic and/or anionic substitutions. A short analysis of the bonding and the structural trends, as well as the electrical resistivity and the thermopower, measured on a single-crystal of Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> are also provided.

<sup>&</sup>lt;sup>a</sup>Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware, 19716, USA. E-mail: bobev@udel.edu; Fax: 3028316335; Tel: 3028318720

<sup>&</sup>lt;sup>b</sup>Department of Physics, University of Maryland, College Park, Maryland, 20742, USA.

<sup>†</sup> Electronic supplementary information (ESI) available: Tables with distances and angles and with refined occupancies for the solid solutions; plot of the dependence on the unit cell volume for Ba<sub>2</sub>Cd<sub>2</sub>(Sb<sub>1-x</sub>As<sub>x</sub>)<sub>3</sub> as a function of "x"; plot of the thermopower of Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> as a function of temperature. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b914305j

Table 1	Selected crystal data for Ba <sub>2</sub> Cd <sub>2</sub> Pn	(Pn = As, St)	) and the substitution derivatives	Ba <sub>2</sub> Cd <sub>2</sub> (Sb	$(I_{1-x}As_x)_3$ and $(I_{1-x}As_x)_3$	$Ba_{1-x}Sr_x)_2Cd_2As_3$
---------	--	---------------	------------------------------------	-------------------------------------	---	---------------------------

Chemical formula	Ba <sub>2</sub> Cd <sub>2</sub> As <sub>3</sub>	Ba <sub>2</sub> Cd <sub>2</sub> Sb <sub>3</sub>	$Ba_{2}Cd_{2}Sb_{0.28(1)}As_{2.72}$	$Ba_{2}Cd_{2}Sb_{2.51(2)}As_{0.49}$	$Ba_{1.47(1)}Sr_{0.53}Cd_2As_3$
Formula weight/g mol <sup>-1</sup> Crystal system Space group Z T/K	724.24	864.73	737.59 Monoclinic <i>C2/m</i> (No. 12) 4 170(2)	841.67	698.09
a/Å	17.188(2)	18.072(4)	17.255(3)	17.897(5)	17.011(5)
b/Å	4.5472(4)	4.824(1)	4.5691(8)	4.768(1)	4.537(1)
c/Å $\beta/^{\circ}$ $V/Å^{3}$ $\rho_{c}/g \text{ cm}^{-3}$ $\mu(Mo-K\alpha)/mm^{-1}$ Crystal size/mm Reflections collected Independent reflections $R_{int}$	$12.725(1) 126.639(1) 798.0(1) 6.028 27.227 0.09 \times 0.05 \times 0.05546411060.0251$	$\begin{array}{c} 13.403(3) \\ 126.747(2) \\ 936.2(3) \\ 6.135 \\ 21.157 \\ 0.05 \times 0.05 \times 0.02 \\ 5324 \\ 1303 \\ 0.0318 \end{array}$	$\begin{array}{c} 12.785(2) \\ 126.567(2) \\ 809.6(2) \\ 6.052 \\ 26.614 \\ 0.05 \times 0.04 \times 0.02 \\ 4497 \\ 1120 \\ 0.0330 \end{array}$	$\begin{array}{c} 13.276(4) \\ 126.615(4) \\ 909.4(4) \\ 6.148 \\ 22.129 \\ 0.04 \times 0.02 \times 0.02 \\ 3147 \\ 1262 \\ 0.0455 \end{array}$	$12.651(4)  12.6788(3)  781.9(4)  5.930  28.741  0.05 \times 0.04 \times 0.03526910860.0343$
Goodness-of-fit $R_1 (I > 2\sigma_{(1)})^a$ $wR_2 (I > 2\sigma_{(1)})^a$ Largest peak and hole/e <sup>-</sup> Å <sup>-3</sup>	1.077 0.0158 0.0353 0.98/-0.76	1.101 0.0232 0.0517 1.19/-1.68	1.049 0.0226 0.0419 1.12/-1.30	1.020 0.0403 0.0722 2.27/-2.65	1.043 0.0217 0.0439 1.13/-1.50

 ${}^{a}R_{1} = \sum ||F_{o}|| - |F_{c}|| / \sum |F_{o}|; wR_{2} = [\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}]^{1/2}, where w = 1/[\sigma^{2}F_{o}^{2} + (AP)^{2} + BP], and P = (F_{o}^{2} + 2F_{c}^{2}) / 3 (A and B are weight coefficients).$ 

**Table 2** Crystallographic coordinates and equivalent isotropic displacement parameters  $(U_{eq})^a$  for Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>

Atom	Multiplicity Wyckoff site	X	у	z	$U_{ m eq}/{ m \AA}^2$
Ba1	4 <i>i</i>	0.26447(3)	0	0.66315(4)	0.0097(1)
Ba2	4i	0.39784(3)	0	0.05511(4)	0.0107(1)
Cd1	4i	0.04105(4)	0	0.31104(5)	0.0118(1)
Cd2	4i	0.40899(4)	0	0.34633(5)	0.0125(1)
Sb1	4i	0.08039(4)	0	0.12521(5)	0.0101(1)
Sb2	4i	0.15526(4)	0	0.80402(5)	0.0099(1)
Sb3	4i	0.38686(4)	0	0.54197(4)	0.0091(1)

#### **Results and discussions**

#### Crystal structures

A summary from the single-crystal X-ray diffraction studies of the title compounds is presented in Table 1. Because they are isotypic and isoelectronic, for the sake of simplicity, the focus of the structural discussions will be primarily on only one of them,  $Ba_2Cd_2Sb_3$ .

Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> crystallizes in the monoclinic space group C2/m (no. 12, Pearson's symbol mS28). The crystal structure is shown schematically in Fig. 1; it contains 7 symmetry independent atoms, all in special positions—two Ba, two Cd and three pnicogens (Table 2). According to the Pearson's Handbook<sup>20</sup> and the Inorganic Crystal Structure Database (ICSD),<sup>21</sup> there are no other reported compounds with the same atomic arrangement,‡ making this structure type unique.

The structure can be conveniently explained following the Zintl concept<sup>1,2</sup> as two-dimensional  $\frac{2}{\infty}$  [Cd<sub>2</sub>Sb<sub>3</sub>]<sup>4-</sup> layers, made up of



Fig. 1 A perspective view of the monoclinic crystal structure of  $Ba_2Cd_2Sb_3$ , projected down the *b* axis. Red spheres denote the Sb atoms, occupying corners of the Cd-centered tetrahedra. The latter are shown both in skeletal and polyhedral mode, where small green spheres represent Cd. Interlayer Ba1 atoms and intralayer Ba2 are shown as large yellow and purple spheres, respectively. Unit cell is outlined.

edge-shared [CdSb<sub>4</sub>]<sup>10-</sup> tetrahedra, and Ba<sup>2+</sup> cations, occupying positions in between and within the layers (Fig. 1). The layers can also be envisioned as being formed of tetrameric  ${}^1_{\infty}$  [Cd<sub>4</sub>Sb<sub>6</sub>]<sup>10-</sup> fragments of 4 fused 1 [CdSb<sub>3</sub>]<sup>7-</sup> chains, running parallel to the crystallographic b-axis. These "ribbons" are further interconnected along the c-axis via homoatomic Sb-Sb interactions to give  $\frac{2}{2}$  [Cd<sub>4</sub>Sb<sub>6</sub>]<sup>8-</sup>, *i.e.*,  $\frac{2}{2}$  [Cd<sub>2</sub>Sb<sub>3</sub>]<sup>4-</sup>. The Sb–Sb and Cd–Sb distances listed in Table 3 support the assigned formal chargescertainly, a Sb-Sb bond that measures 2.835(1) Å long, shorter than in elemental Sb (2.908 Å),<sup>20</sup> points towards a strong covalent character. Equally strong Sb<sub>2</sub>-dimers, as judged by the distances, are known from the structures of  $Ba_{11}Cd_6Sb_{12},^{18}\ Eu_{11}Zn_6Sb_{12},^{22}$ Ba21Cd4Sb18,13 and Ba3Cd2Sb4.19 Likewise, Cd-Sb contacts ranging from 2.8794(9) Å to 3.040(1) Å are on par with the sum of the covalent radii,23 and comparable to those observed for NaCdSb,24 Sr<sub>9</sub>Cd<sub>4.49(1)</sub>Sb<sub>9</sub>,<sup>12</sup> Ca<sub>2</sub>CdSb<sub>2</sub>,<sup>16</sup> and SrCd<sub>2</sub>Sb<sub>2</sub>.<sup>25</sup> In agreement with

<sup>‡</sup> Although there are number of compounds with the same Pearson's code and similar Wyckoff sequence, their atomic coordinates are very different, and therefore, their structure and bonding are different too.

Table 3Selected distances (Å) in Ba2Cd2Sb3

Pair		Distance	Pair		Distance
Cd1–	Sb1	2.9712(9)	Ba1–	$Sb1 \times 2$	3.4940(6)
	Sb2	2.901(1)		Sb2	3.4524(8)
	$Sb3 \times 2$	2.8853(6)		Sb3	3.4394(9)
Cd2-	$Sb2 \times 2$	2.9029(6)		$Sb3 \times 2$	3.4436(6)
	Sb3	2.8794(9)	Ba2–	$Sb1 \times 2$	3.5988(7)
	Sb3	3.040(1)		$Sb2 \times 2$	3.5313(7)
Sb1-	Sb1	2.835(1)		Sb2	3.5904(9)
	Cd1	2.9712(9)		$Sb1 \times 2$	3.7249(8)
Sb2-	Cd1	2.901(1)		$Cd1 \times 2$	3.6959(8)
	$Cd2 \times 2$	2.9029(6)			
Sb3-	$Cd1 \times 2$	2.8853(6)			
	Cd2	2.8794(9)			
	Cd2	3.040(1)			

earlier calculations on  $A_2B_2$ -type layers, the longest Cd–Sb bonds have the characteristics of the weaker "handle" bonds in the CaAl<sub>2</sub>Si<sub>2</sub> type (*vide infra*).<sup>26</sup>

Before turning our attention to the cation polyhedra, a short comparison between the bonding in the <sup>2</sup> [Cd<sub>2</sub>Sb<sub>3</sub>]<sup>4-</sup> and <sup>2</sup> [Cd<sub>2</sub>As<sub>3</sub>]<sup>4-</sup> layers is in order. Selected distances and angles in  $Ba_2Cd_2As_3$  and its substitution derivatives  $(Ba_{1-x}Sr_x)_2Cd_2As_3$  and  $Ba_2Cd_2(Sb_{1-x}As_x)_3$  are provided as ESI.<sup>†</sup> Two observations from the side-by-side comparison of their metrics must be explicitly pointed out: (i) all Cd-As distances (within the range 2.7151(6)-2.9093(7) Å) are systematically shorter than the Cd–Sb ones, but the differences do not scale with the covalent radii of Sb and As, 1.39 and 1.19 Å, respectively.<sup>23</sup> (ii) The CdAs<sub>4</sub> tetrahedra are slightly less distorted than CdSb<sub>4</sub> ones, as evidenced by the narrower angle ranges: 107.31(1)-113.09(2)° and 101.81(1)-114.11(1)° for As-Cd1-As and As-Cd2-As in the former, and 105.78(2)-113.43(2)° and 101.85(2)-114.61(2)° for Sb-Cd1-Sb and Sb-Cd2-Sb in the latter.<sup>†</sup> This suggests that in addition to the geometric factors (*i.e.*, crystal packing), electronic effects such as sp orbital mixing and/or polarization of bonds, due to the increased electronegativity of As,<sup>27</sup> also play an important role here.

Another base for comparison can be established between  $Ba_2Cd_2As_3$  and  $Ba_{1.47(1)}Sr_{0.53}Cd_2As_3$ . In this case, of particular interest are the following facts: (i) not all of the Cd–As in the Ba–Sr mixed phase are shorter than those in  $Ba_2Cd_2As_3$ , as could be expected from the contraction of the unit cell volume (Table 1); (ii) the As–As bonds are elongated by about 0.5% in the mixed phase compared to  $Ba_2Cd_2As_3$  ( $d_{As-As} = 2.512(2)$  Å

*vs*  $d_{As-As} = 2.498(1)$  Å, respectively). This is in accord with the trends reported for the pairs  $Sr_{11}Cd_6Sb_{12}/Ba_{11}Cd_6Sb_{12}$ ,<sup>18</sup> and  $Ba_3Cd_2Sb_4/Ba_{2.37(1)}Sr_{0.63}Cd_2Sb_4$ ,<sup>19</sup> where homoatomic Sb–Sb interactions are also slightly weakened. The likely reasons for that are changes in the orbital overlap caused by the size and electronegativity differences between Ba and the smaller and more electronegative Sr.

Last in this section, we discuss the cation coordination. As seen in Table 2, there are two Ba positions and they have very different polyhedra. Bal is dubbed the interlayer cation, and it centers an octahedron of Sb atoms from adjacent layers with an average distance  $d_{\text{Bal-Sb}} = 3.461(2)$  Å (Table 3). Ba2, in turn, is the intralayer cation, and it is surrounded by 5 closest Sb atoms in a severely distorted square-pyramidal fashion (Table 3). Here, four of the five Sb atoms around Ba2 belong to the same <sup>2</sup>  $[Cd_2Sb_3]^{4-}$  layer, which is the reason the two sites are given such descriptors. Ba2 is not at the center of the pyramid, but shifted towards its base. The average Ba2-Sb distance is appreciably longer, 3.570(1) Å. The polyhedron is augmented by two Sb atoms and two Cd atoms in capping positions, located at 3.7249(8) Å and 3.6959(8) Å away from Ba2, respectively. Virtually identical cation site coordinations were noted for Ba<sub>3</sub>Cd<sub>2</sub>Sb<sub>4</sub>,<sup>19</sup> a clear indication to a close relationship between the two structure types. Such considerations are elaborated in the following section.

#### **Related structures**

A topological relationship between  $Ba_2Cd_2Sb_3$ ,  $BaCd_2Sb_2^{28}$  with the ubiquitous  $CaAl_2Si_2$  type,<sup>20,26</sup> and the recently reported  $Ba_3Cd_2Sb_4^{19}$  structures is worth special attention. The idea is simple, and the schematic illustration in Fig. 2 makes it readily recognizable—an insertion of a BaSb segment into the  $BaCd_2Sb_2$  structure results in  $Ba_2Cd_2Sb_3$ . Since both  $Ba_2Cd_2Sb_3$ and  $BaCd_2Sb_2$  represent electron-balanced Zintl compounds,§ the inserted fragment BaSb is also electron-precise. The structure of this imaginary compound should consist of a Sb<sub>2</sub>-dimer and two  $Ba^{2+}$  cations. Although such a compound with the abovedescribed atomic arrangement does not exist, the isoelectronic  $Cs_4Sb_2$  can be used as a proof-of-principle analog.<sup>29</sup> Another close structure is that of  $K_5Sb_4$ ,<sup>30</sup> which contains a butadiene-like

 $BaCd_2Sb_2$  can be formulated as  $(Ba^{2+})(Cd^{2+})_2(Sb^{3-})_2$ , and  $Ba_2Cd_2Sb_3$  can be viewed as  $(Ba^{2+})_2(Cd^{2+})_2(Sb^{3-})_2(Sb^{2-})$ , respectively.



**Fig. 2** A schematic representation showing the relationship between the structures of  $BaCd_2Sb_2$ ,  $Ba_2Cd_2Sb_3$  and  $Ba_3Cd_2Sb_4$ . Emphasized is the successive addition of a BaSb slab into  $BaCd_2Sb_2$  to yield  $Ba_2Cd_2Sb_3$ , and then into  $Ba_2Cd_2Sb_3$  to form  $Ba_3Cd_2Sb_4$ . See text for further discussion.

tetramer of Sb atoms, *i.e.*, dimerized Sb<sub>2</sub> units with K<sup>+</sup> as counterions. Notwithstanding the lack of a "real" BaSb compound, the imaginary breaking of the  $\frac{2}{\infty}$  [Cd<sub>2</sub>Sb<sub>2</sub>]<sup>2-</sup> layers in BaCd<sub>2</sub>Sb<sub>2</sub>, as shown in Fig. 2, and the addition a BaSb slab leads to the "formation" of the Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> structure. In the next step, another equivalent of BaSb is added to Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> in order to obtain the Ba<sub>3</sub>Cd<sub>2</sub>Sb<sub>4</sub> structure.<sup>19</sup> As a consequence, the coordination of the interlayer and intralayer Ba atoms in both Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> and Ba<sub>3</sub>Cd<sub>2</sub>Sb<sub>4</sub> remain unchanged.

All of the above seems to suggest that BaCd<sub>2</sub>Sb<sub>2</sub>,<sup>28</sup> Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>, and Ba<sub>3</sub>Cd<sub>2</sub>Sb<sub>4</sub><sup>19</sup> are the simplest members of a homologous series. We attempted to synthesize other members, such as Ba<sub>3</sub>Cd<sub>4</sub>Sb<sub>5</sub> (2:1 intergrowth of BaCd<sub>2</sub>Sb<sub>2</sub> and BaSb) and Ba<sub>7</sub>Cd<sub>6</sub>Sb<sub>10</sub> (2:1 intergrowth of Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> and Ba<sub>3</sub>Cd<sub>2</sub>Sb<sub>4</sub>), and Ba<sub>4</sub>Cd<sub>2</sub>Sb<sub>5</sub> (1:3 intergrowth of BaCd<sub>2</sub>Sb<sub>2</sub> and BaSb), but all our attempts proved unsuccessful-BaCd<sub>2</sub>Sb<sub>2</sub>, Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>, Ba<sub>3</sub>Cd<sub>2</sub>Sb<sub>4</sub>, Ba<sub>11</sub>Cd<sub>6</sub>Sb<sub>12</sub> or combinations of these compounds were products of the reactions. This indicates that those, presumably metastable phases are difficult to crystallize and likely decompose to other, more stable compounds. However, since the structures in question are very sensitive to the sizes of the participating elements, one might be able to find mixtures of cations and anions that stabilize one structure over another. This point is exemplified by our recent success in synthesizing ordered quaternary phases  $KA_2Cd_2Sb_3$ Eu, Yb),<sup>31</sup> with novel structures.

#### **Electronic structure**

To better understand the nuances of the bonding in Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>, computations based on the density functional method were carried out for both structures. The calculated total and partial density of states (DOS) curves for Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> are plotted in Fig. 3a and 3b, respectively. As seen from the plots, the bonding is optimized in both compounds and the electron count obeys the Zintl rules, *i.e.*,  $(Ba^{2+})_2(Cd^{2+})_2(Sb^{2-})(Sb^{3-})_2$  (or alternatively,  $(Ba^{2+})_2[(4b-Cd^{2-})_2(3b-Sb^0)(2b-Sb^{1-})(4b-Sb^{1+})])$ . The DOS plots show that states just below the Fermi level, in the energy range from ca. -3.75 to 0 eV, originate predominantly from As and Sb p-orbitals, with noticeable contributions from Ba d-orbitals. This indicates appreciable cation-anion p-d orbital mixing-a subtle departure from the classic Zintl formalism, according to which the cations are just electron-donors and space-fillers within the polyanionic skeleton of the structure. Small contributions from Cd 5p orbitals in this energy range could be noticed too. The maximum below this region, falling in the energy range from ca.-5



Fig. 3 Density of states (DOS) for (a)  $Ba_2Cd_2As_3$  and (b)  $Ba_2Cd_2Sb_3$  including partial components with Ba contributions in grey, Cd contributions in black, and As and Sb contributions as dotted curves.

to -3.75 eV is composed of Cd s-orbitals, together with pnicogen p-orbitals. The fact that Cd s- and p-states are clearly separated in both figures implies that the classical sp<sup>3</sup> hybridization concept for Cd*Pn*<sub>4</sub> tetrahedra is inapplicable in Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>.

Since the pnicogen p-orbitals contributions are dominant in close proximity of the Fermi level, it is clear that these play the most important roles in determining the electrical transport properties of both compounds. A clear signature of a band gap is observable for Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub>, suggesting it to be a small band-gap semiconductor. In the case of Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>, the Fermi level falls into a pseudo-gap, and therefore,  $Ba_2Cd_2Sb_3$  is expected to be a poor metal. These predictions; however, should be put in perspective, since it is a well-known fact that TB-LMTO-ASA calculations underestimate, at times up to 50%, band gaps in semiconductors.<sup>32</sup> Despite this drawback of the method, the band structure is successful in explaining the subtle difference between Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba2Cd2Sb3-the compound with the more electronegative pnicogen, arsenic, as noted earlier, resembles more closely the characteristics of an ionic solid and therefore, has a wider band gap. Of course, the difference in size between As and Sb can be a contributing factor as well, although the electronic properties are expected to be dominated by the difference in electronegativity. This issue has recently been addressed by extensive theoretical calculations on various arsenides with the CaAl<sub>2</sub>Si<sub>2</sub> type and related structures.33

To further interrogate the nature of the interatomic interactions, the crystal orbital Hamiltonian populations (COHP) were calculated for selected atom pairs. Since the bonding picture is identical for both compounds, the COHP plots are very similar and only three integrated COHP curves for Ba2Cd2Sb3 are provided in Fig. 4. The average Cd-Sb interactions in the anionic layers are fully optimized, while the homoatomic Sb-Sb interactions have weakly antibonding character just below the Fermi level. On the contrary, the Ba-Sb interactions remain slightly bonding just above the Fermi level. This is not without a precedent as similar bonding characteristics have already been studied comprehensively and will not be discussed further.<sup>18,34,35</sup> From the COHP plots it can be inferred that had there been less electron(s) in the system, for example by virtue of K-doping on Ba sites, their net effect would be destabilization of Cd-Sb and Ba-Sb interactions and strengthening of the Sb-Sb bonds. Such alteration



Fig. 4 (a) COHP diagrams for Ba-Sb (solid line) and Cd–Sb interactions (dotted line) in  $Ba_2Cd_2Sb_3$ . (b) COHP diagram for Sb–Sb interactions in  $Ba_2Cd_2Sb_3$ .

 $\P$  In the COHP diagrams we plot the reverse COHP (–COHP) vs. E, so that the calculated peak values are negative for antibonding and positive for bonding interactions.

	Ba <sub>2</sub> Cd <sub>2</sub> As <sub>3</sub>	Ba <sub>2</sub> Cd <sub>2</sub> Sb <sub>3</sub>	
Pn1	4.457	4.499	
Pn2	4.785	4.796	
Pn3	4.961	4.941	

to the structure, clearly, will not be favored since there are eight Cd–Sb bonds and only one Sb–Sb bond per formula unit. The opposite effect, the addition of extra valence electron(s), would weaken the dominant Cd–Sb and Sb–Sb interactions, while Ba–Sb bonding would be strengthened.

Last, we turn our attention to the two types of solid solutions- $Ba_2Cd_2(Sb_{1-x}As_x)_3$  (0 < x < 1) and  $(Ba_{1-x}Sr_x)_2Cd_2As_3$  (x  $\approx 0.25$ ). They present a possibility for a "band-gap engineering" which may prove essential for property-tuning. Therefore, we decided to investigate which cationic and anionic positions are most susceptible to substitutions and how the structural variations impact the chemical bonding. Such studies in a given crystal structure are often referred to as "coloring problem", coined after a famous mathematical predicament.<sup>36,37</sup> Simple chemical reasoning could also be used to explain the site preference without an extensive amount of computational modeling-the argument here being that a more electronegative atom will prefer the site with the higher electron density. Although simplistic, this logic is widely used in predictions for simple molecules, based on their Lewis structures and the formal charges. As demonstrated by Burdett and Miller, the same ideas are applicable to solids, when the sums of atomic orbital populations (AOP), aka QVAL, are compared. The latter represents electron density on each atomic position, thereby, the sum of all QVAL in an asymmetric unit will give the total number of valence electrons per formula unit.<sup>38</sup>

The values of interest for the structures under consideration are provided in Table 4. According to the calculations, for both structures, the greatest electron density is at the *Pn3* positions. Therefore, based on this argument alone, in the solid solutions  $Ba_2Cd_2(Sb_{1-x}As_x)_3$  (0 < x < 1), the more electronegative As (Pauling electronegativity of 2.18)<sup>27</sup> will preferably occupy *Pn3* positions. Analogously, the *Pn1* sites, which have the lowest electron density will be preferred by Sb (Pauling electronegativity of 2.05).<sup>27</sup> The other major factor for site preferences, the sizes, also suggests the *Pn3* site, *i.e.*, the one with the closest neighbors to be preferred by arsenic, and *vice versa* for antimony. The experimental results corroborate with these predictions quite well.<sup>†</sup>

The analysis concerning the coloring of the cation sites is less straightforward. Here, cation–anion orbital mixing, as mentioned already, is important for the overall bonding, and the degree of covalency of the Ba–*Pn* and Sr–*Pn* must not be ignored when considering this conundrum. However, since the Sr-analogs of either Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> or Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> are still "missing", accurate calculations could not be done and Ba–Sb/Sr–Sb COHP could not be compared. Nevertheless, the structure refinements of Ba<sub>1.47(1)</sub>Sr<sub>0.53</sub>Cd<sub>2</sub>As<sub>3</sub> indicating that one of the cation sites is an equimolar mixture of Ba and Sr, while the second one is favored by Ba over Sr (*ca.* 10:1 ratio; Table S2 - ESI<sup>†</sup>), led us to conclude that an optimal balance between the electronic and geometric factors is achieved in Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>, but not in Sr<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> or Sr<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>. We can therefore hypothesize that if the covalency of the Sr–Sb interactions is not sufficient to compensate for the less efficient packing with the smaller in size  $Sr^{2+}$ , one might be able to find the "right" spatial/electronic characteristics in a more electronegative divalent metal. For example, Eu is such a metal—the radii of Eu<sup>2+</sup> (1.16 Å) and Sr<sup>2+</sup> (1.18 Å) are almost identical,<sup>39</sup> yet Eu is more electronegative than Sr. The above is suggestive of Eu<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Eu<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> being likely targets for future work, aimed at a better understanding of the cation sensitivity of this structure.

#### Physical properties

Resistivity was determined using the four-probe technique on a number of flux-grown single crystals of Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub>, and a representative plot of the measured electrical resistivity as a function of the temperature (100-300 K) is shown in Fig. 5. As seen from the graph, the resistivity increases with decreasing temperature, suggesting intrinsic semiconducting behaviour, as expected for a Zintl phase and in a good agreement with the electronic structure calculations discussed above. The inset in Fig. 5 shows the dependence of  $\ln \rho$  with the inverse temperature, which indicates that  $\rho(T)$  follows a thermally activated behaviour according to the Arrhenius-law.40 A linear fit of the data in the interval 200-300 K yields a band gap of ca. 0.1 eV, which is a quite reasonable estimate. Similar semiconducting properties and energy gaps have been reported for many related Zintl phases, such as Ca<sub>2</sub>CdSb<sub>2</sub> ( $E_g \approx 0.2 \text{ eV}$ ),<sup>16</sup> BaGa<sub>2</sub>Sb<sub>2</sub> ( $E_g \approx 0.3 \text{ eV}$ ),<sup>41</sup>  $BaIn_2Sb_4 (E_g \approx 0.1 \text{ eV}),^{42} Yb_{11}GaSb_9 (E_g \approx 0.05 \text{ eV}),^{43} although$ the resistance in our case is about three orders of magnitude higher—room temperature resistivity  $\rho_{300}$  is nearly 3  $\Omega$  cm. Since the presented values are reproducible for different batches, it is possible that oxidized insulating regions are formed on the surface or inside the crystal. To circumvent the problem, we attempted to clean the surface immediately before attaching the leads (by both mechanical and chemical means), but those efforts failed. Therefore, it is likely that a specialized set-up under an inert atmosphere will be required in order to accurately determine the resistivity of the pure material. Based on previous experience, we hypothesize that the sample would probably exhibit room temperature resistivity in the m $\Omega$  cm range. This assumption is corroborated by crude two-probe resistivity estimates of both Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>, done inside the glove-box.



**Fig. 5** Four-probe electrical resistivity ( $\rho$ ) of a single-crystal of Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> as a function of the temperature. Data is normalized to the value at 300 K. Inset shows  $\ln \rho vs 1/T$ .

If insulating oxide regions hinder the resistivity measurements, one should expect that the thermopower, measured on the same samples will also be affected. Indeed, the room temperature Seebeck coefficient was found to be  $S_{300}=170 \ \mu\text{V} \ \text{K}^{-1}$ . A comparison of the absolute thermopower values at 300 K, reported for some of the best known thermoelectric Zintl phases (122  $\mu\text{V} \ \text{K}^{-1}$  for EuZn<sub>2</sub>Sb<sub>2</sub>;<sup>6</sup> 120  $\mu\text{V} \ \text{K}^{-1}$  for CaZn<sub>2</sub>Sb<sub>2</sub>,<sup>7</sup> and 60  $\mu\text{V} \ \text{K}^{-1}$  for Yb<sub>14</sub>MnSb<sub>11</sub>;<sup>9</sup>) suggests that new measurements in a protective environment are needed to obtain better quantitative information. Nonetheless, the gathered *S*(*T*) data,<sup>†</sup> at least qualitatively, confirm the semiconducting properties, and the positive sign of the Seebeck coefficient indicates that the dominant charge carriers in the material are holes (p-type semiconductor).

Crystals of Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> could not be grown bigger than 1–2 mm, therefore attempts were made to record the transport properties on cold-pressed pellets. These were unsuccessful, presumably because of effects of grain boundaries and cracks, alongside the already mentioned problems with surface oxidation. However, based on the calculated electronic structures, we speculate, that Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> should be a better conductor than its As-analog. This could be advantageous for fine-tuning the electronic and thermal conductivity because of the possibility of forming homogeneous solid solutions between Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> in a very wide range. Similar characteristics are particularly desired in thermoelectrics and make these compounds good candidatematerials for such applications.

### Conclusions

Single crystals of two new ternary Zintl phases Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> were grown from high-temperature reactions in lead flux. The close relationship of their crystal structure (own monoclinic type) with the CaAl<sub>2</sub>Si<sub>2</sub> structure type, and Ba<sub>3</sub>Cd<sub>2</sub>Sb<sub>4</sub> structure type was discussed. These new compounds provide more examples of materials with a complicated structure, which can be effectively rationalized using classical approaches such as the Zintl concept. Our experimental and theoretical studies confirm that Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> are small band-gap semiconductors, in agreement with the Zintl reasoning. As such, Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and  $Ba_2Cd_2Sb_3$  and their  $Ba_2Cd_2(Sb_{1-x}As_x)_3$  (0 < x < 1) solid solutions, as well as the phases  $(Ba_{1-x}Sr_x)_2Cd_2As_3$  with mixed cations could be promising materials for thermoelectric conversion. Although their air-sensitivity might hinder widespread practical applications, the discovered structure-property relationships are certain to advance the research on thermoelectrics and Zintl phases in particular. Presently, efforts to synthesize magnetic members of this family (e.g.  $Eu_2Cd_2As_3$ ,  $Eu_2Cd_2Sb_3$ , or  $(Ba_{1-x}Eu_x)_2Cd_2As_3$ ) and test their thermoelectric performance are under way.

# Experimental

#### Materials and methods

All synthetic preparations were carried out in an argon-filled glove box or under vacuum. The elements—Ba (Aldrich, rod), Cd (Alfa, shot), Sb (Alfa, shot), As (Alfa, sponge), all with stated purity greater than 99.9%, were used as received. Two synthetic methods were employed—reactions in sealed tubes and flux reactions, using Pb as a flux. In both cases, metals in the desired stoichiometric amounts were loaded into niobium tubes, or alumina crucibles. The niobium tubes were subsequently sealed using an arc-welder. Prior to heating in high-temperature tube or muffle furnaces, equipped with programmable controllers, the reaction mixtures (either in a Nb tube or in an  $Al_2O_3$  container) were placed inside fused silica tubes and flame-sealed under vacuum (below discharge).

# Synthesis of Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>

 $Ba_2Cd_2Sb_3$  was first identified as a byproduct of a stoichiometric high temperature reaction in a welded niobium tube, aimed at producing  $Ba_3Cd_2Sb_4$ .<sup>19</sup> The reaction mixture was heated to 900 °C at a rate of 200 °C h<sup>-1</sup>, kept at 900 °C for 20 h, cooled to 500 °C at a rate of 5 °C h<sup>-1</sup>, and then annealed at 500 °C for 37 h. The outcome of this reaction consisted of small, needleshaped crystals of  $Ba_2Cd_2Sb_3$ , together with irregular crystals of  $Ba_{11}Cd_8Sb_{14}$  (isostructural with  $Ba_{11}Cd_8Bi_{14}$ )<sup>17</sup> and  $BaCd_2Sb_2$ .<sup>28</sup>

After the crystal structure of  $Ba_2Cd_2Sb_3$  was established by single-crystal X-ray diffraction, the stoichiometric reactions in niobium tubes were tried again with an elemental ratio of Ba:Cd:Sb = 2:2:3. Such reactions, even after optimizing the synthetic conditions failed to produce the desired compound in high yield. Instead, the products were mixtures of phases. Consequently, further actions were taken by using the flux method. After a number of tries at different temperatures, the best route for the synthesis of pure  $Ba_2Cd_2Sb_3$  was determined to be as follows: ratio Ba:Cd:Sb:Pb = 2:2:3:20 was heated to 760 °C at a rate of 150 °C h<sup>-1</sup>, homogenized at 760 °C for 40 h, cooled to 500 °C at a rate of 5 °C h<sup>-1</sup>, and kept at 500 °C for 40 h. After this step, the liquid Pb was removed (decanted) and the synthesized crystals were isolated.

# Synthesis of $Ba_2Cd_2As_3$ and $Ba_2Cd_2(Sb_{1-x}As_x)_3$

Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> can be synthesized in high yield by both methods, however, reactions in Pb flux produced long needle crystals, suitable for physical property measurements. They were done by loading the metals in a ratio of Ba : Cd : As : Pb = 2 : 2 : 3 : 20, but with a different heat treatment profile. Here, the reaction mixture was heated to 960 °C at a rate of 60 °C h<sup>-1</sup>, homogenized at 960 °C for 20 h, and cooled to 500 °C at a rate of 30 °C h<sup>-1</sup>. Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> crystals grew up to 5 mm long. BaCd<sub>2</sub>As<sub>2</sub><sup>44</sup> was a minor sideproduct, but these crystals had irregular morphology and were mechanically separated from the rest of the sample.

The synthesis of the solid solutions was carried out analogously. Reactions were set up with nominal composition BaSrCd<sub>2</sub>As<sub>3</sub>, Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>1.5</sub>As<sub>1.5</sub>, Ba<sub>2</sub>Cd<sub>2</sub>SbAs<sub>2</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>0.75</sub>As<sub>2.25</sub>, all with 20-fold excess of Pb and were subjected to the optimized heat treatment for Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub>, described above. The reaction of Cd and As with equimolar mixture of Ba and Sr produced a mixture of Ba<sub>1.47(1)</sub>Sr<sub>0.53</sub>Cd<sub>2</sub>As<sub>3</sub> and small amounts of BaCd<sub>2</sub>As<sub>2</sub> or rather Ba<sub>1-x</sub>Sr<sub>x</sub>Cd<sub>2</sub>Sb<sub>2.</sub> The other three reactions yielded Ba<sub>2</sub>Cd<sub>2</sub>(Sb<sub>1-x</sub>As<sub>x</sub>)<sub>3</sub> (0 < x < 1) with various degrees of Sb–As

<sup>||</sup> The unit cell parameters for this phase are a = 4.499(4) Å and c = 7.639(8) Å. In comparison, the unit cell dimensions of BaCd<sub>2</sub>As<sub>2</sub> and SrCd<sub>2</sub>As<sub>2</sub> are a = 4.513(3) Å and c = 7.674(7) Å, and a = 4.46(1) Å and c = 7.42(4) Å, respectively. This indicates that the product is indeed a solid solution Ba<sub>\*</sub>Sr<sub>1-x</sub>Cd<sub>2</sub>As<sub>2</sub>.

substitutions. Since studying the Sb–As solubility limits was not the focus of this work, based on the available experimental data, we can only speculate that continuous solid solutions exist throughout the whole range. A plot showing the dependence on the unit cell volume of the end-members  $Ba_2Cd_2As_3$  and  $Ba_2Cd_2Sb_3$  and the solid solutions  $Ba_2Cd_2(Sb_{1-x}As_x)_3$  (0 < x < 1) is provided as ESI.†

#### X-Ray powder diffraction

X-Ray powder diffraction patterns were taken on a Rigaku MiniFlex powder diffractometer using Cu-K $\alpha$  radiation. The diffractometer was operated at room temperature. Due to the limited instrument capabilities (450 W power) the collected powder diffraction patterns were not suitable for refinements, and were used only for phase identification. The data analysis was carried out using the JADE 6.5 package.

Since the instrument was enclosed inside a nitrogen-filled glove box, this allowed for testing the air-moisture-sensitivity of the samples. For this purpose, the powder diffraction patterns of a freshly synthesized (and prepared in the glove box) specimens were compared to those of samples left in the open air for a one week period. According to these, the polycrystalline Ba<sub>2</sub>Cd<sub>2</sub>*Pn*<sub>3</sub> (*Pn* = As, Sb) materials are stable and do not oxidize/hydrolyze. However, visual inspection of single-crystals of both compounds, also left in the open air for one week, shows that they becomes tarnished (more distinctive for the Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> crystals), suggesting that thin layers of oxides may form on their surfaces and protect the bulk of the sample from further degradation.

# X-Ray single-crystal diffraction

Crystals were selected inside the argon-filled glove box, cut in Paratone-N oil to suitable sizes (from ca. 0.02 to 0.09 mm), put on top of glass fibers and quickly transferred onto the goniometer of a Bruker SMART CCD-based diffractometer. A liquid nitrogen stream was used to cool (ca. 170(2) K) and protect crystals during data collections. A sealed-tube Mo-K $\alpha$  source ( $\lambda = 0.71073$  Å), operated at 2 kW was used. All data acquisitions were carried out by the same strategy-full sphere of diffraction data were acquired in four batch runs with a frame width of  $0.4^{\circ}$  in  $\omega$  and  $\theta$ angles and exposure times varying from 8-20 s/frame, depending on the individual characteristics of the crystal. The SMART software<sup>45</sup> controlled the process; the SAINTplus program<sup>46</sup> was used for integration and cell refinement. Semi-empirical absorption correction based on equivalent reflections was applied using SADABS.47 The structures were solved in C-centered monoclinic C2/m space group by direct methods, and refined by full matrix least-squares methods on  $F^2$  employing SHELXL.<sup>48</sup> Site occupation factors were checked by freeing the site occupancy factor of an individual site, while the remaining parameters were kept fixed. This resulted in no deviations greater than  $3\sigma$  for the sites in  $Ba_2Cd_2As_3$  and  $Ba_2Cd_2Sb_3$ . The same procedure for  $(Ba_{1-x}Sr_x)_2Cd_2As_3$  and  $Ba_2Cd_2(Sb_{1-x}As_x)_3$  indicated that Ba–Sr and Sb-As mixing, respectively. In the last refinement cycles, all sites were refined with anisotropic displacement parameters (ADP). The resultant ADPs were "well-behaved" and the final difference Fourier maps were featureless. Standardization of atomic positions was done using the software STRUCTURE TIDY.<sup>49</sup> Additional information on the crystal structure investigations can be obtained in the form of CIF files from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein–Leopoldshafer, Germany, (fax: +49 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers: CSD 420833 for Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub>, CSD 420834 for Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub>, CSD 420835 for Ba<sub>1.47(1)</sub>Sr<sub>0.53</sub>Cd<sub>2</sub>As<sub>3</sub>, CSD 420836 for Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>2.51(2)</sub>As<sub>0.49</sub> and CSD 420837 for Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>0.28(1)</sub>As<sub>2.72</sub>.

### **Electronic structure calculations**

Electronic structures of Ba<sub>2</sub>Cd<sub>2</sub>As<sub>3</sub> and Ba<sub>2</sub>Cd<sub>2</sub>Sb<sub>3</sub> were computed using the linear muffin-tin orbital (LMTO) method with the aid of the Stuttgart TB-LMTO 4.7 package.<sup>50</sup> This program uses the local density approximation (LDA)<sup>51</sup> to treat exchange and correlation. All relativistic effects except for spin-orbital coupling were taken into account by the scalar relativistic approximation.52 The TB-LMTO-ASA method the atomic sphere approximation (ASA) to fill the space with overlapping Wigner-Seitz (WS) spheres.<sup>53</sup> Interstitial empty spheres were used to achieve complete filling of the space. The basis set included 5d, 6s, and 6p orbitals for Ba, 4d, 5s, and 5p orbitals for Cd, and 5s, 5p, and 5d orbitals for Sb, and 4s, 4p, and 4d orbitals for As. The Ba 5p, Sb 5d and As 4d orbitals were treated by the Löwdin downfolding technique.<sup>54</sup> The Cd 4d orbitals were treated as core wave functions. The k-space integrations employing the tetrahedron method<sup>55</sup> were performed using 172 irreducible k-points ( $10 \times 10 \times 6$ ) in the Brillouin zone. The density of states (DOS) and crystal orbital Hamiltonian populations (COHP)56 were calculated and plotted. The Fermi level was set at 0 eV as a reference point.

#### Electrical resistivity and thermopower measurements

The temperature-dependent electrical resistivity measurements were carried out by the standard four-probe method on a commercial Quantum Design (QD-PPMS) system. To verify the obtained data, three other single crystals of  $Ba_2Cd_2As_3$  (from different batches) were independently measured with a Keithley 224 programmable current source and a Keithley 182 digital voltmeter.

The thermopower was measured by a custom-designed puck for the PPMS cryostat, interfacing with a Keithley 2182 nanovoltmeter. With two heaters attached to the ends of a single crystal, temperature gradients of +1 K and -1 K were established through the needle for each temperature point. Subsequently, the value of the thermopower was calculated from the corresponding voltage readings.

# Acknowledgements

The authors are indebted to the University of Delaware and the Petroleum Research Fund (ACS-PRF) for funding. Work at UMD was supported by an AFOSR MURI Award.

# Notes and references

- 1 E. Zintl, Angew. Chem., 1939, 52, 1; Chemistry, Structure, and Bonding of Zintl Phases and Ions, ed. S. M. Kauzlarich, VCH Publishers, New York, 1996.
- 2 R. Nesper, Prog. Solid State Chem., 1990, 20, 1.
- 3 G. A. Ślack, in *CRC Handbook of Thermoelectrics*, ed. M. Rowe, CRC Press, Boca Raton, 1995, ch. 34, pp. 407-440.
- 4 G. J. Snyder and E. S. Toberer, Nat. Mater., 2008, 7, 105.

- 5 S. M. Kauzlarich, S. R. Brown and G. J. Snyder, *Dalton Trans.*, 2007, 2099.
- 6 H. Zhang, J. T. Zhao, Yu. Grin, X. J. Wang, M. B. Tang, Z. Y. Man, H. H. Chen and X. X. Yang, *J. Chem. Phys.*, 2008, **129**, 164713.
- 7 F. Gascoin, S. Ottensmann, D. Stark, S. M. Haïle and G. J. Snyder, *Adv. Funct. Mater.*, 2005, **15**, 1860.
- 8 X. J. Wang, M. B. Tang, J. T. Zhao, H. H. Chen and X. X. Yang, *Appl. Phys. Lett.*, 2007, **90**, 232107.
- 9 S. R. Brown, S. M. Kauzlarich, F. Gascoin and G. J. Snyder, *Chem. Mater.*, 2006, 18, 1873.
- 10 S. R. Brown, E. S. Toberer, T. Ikeda, C. A. Cox, F. Gascoin, S. M. Kauzlarich and G. J. Snyder, *Chem. Mater.*, 2008, 20, 3412.
- 11 C. A. Cox, E. S. Toberer, A. A. Levchenko, S. R. Brown, G. J. Snyder, A. Navrotsky and S. M. Kauzlarich, *Chem. Mater.*, 2009, **21**, 1354; E. S. Toberer, C. A. Cox, S. R. Brown, T. Ikeda, A. F. May, S. M. Kauzlarich and G. J. Snyder, *Adv. Funct. Mater.*, 2008, **18**, 2795.
- 12 S. Q. Xia and S. Bobev, J. Am. Chem. Soc., 2007, 129, 10011.
- 13 S. Q. Xia and S. Bobev, Inorg. Chem., 2008, 47, 1919.
- 14 B. Saparov, M. Broda, K. V. Ramanujachary and S. Bobev, *Polyhedron*, 2009, DOI: 10.1016/j.poly.2009.06.031.
- 15 S. Q. Xia and S. Bobev, Chem.-Asian J., 2007, 2, 619.
- 16 S. Q. Xia and S. Bobev, J. Am. Chem. Soc., 2007, 129, 4049.
- 17 S. Q. Xia and S. Bobev, Inorg. Chem., 2006, 45, 7126.
- 18 S. Q. Xia and S. Bobev, J. Comput. Chem., 2008, 29, 2125.
- 19 B. Saparov, S. Q. Xia and S. Bobev, Inorg. Chem., 2008, 47, 11237.
- 20 Pearson's Handbook of Crystallographic Data for Intermetallic Phases, ed. P. Villars and L. D. Calvert, ASM International, Materials Park, OH, 2nd edn., 1991; P. Villars, Pearson's Handbook of Crystallographic Data for Intermetallic Phases, ASM International, Materials Park, OH, desktop edn., 1997.
- 21 ICSD Database, Fachinformationszentrum, Karlsruhe, Germany, 2008.
- 22 B. Saparov, S. Bobev, A. Ozbay and E. R. Nowak, J. Solid State Chem., 2008, 181, 2690.
- 23 B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans.*, 2008, 2832.
- 24 G. Savelsberg and H. Schäfer, Z. Naturforsch., B: Anorg. Chem. Org. Chem., 1978, 33, 370.
- 25 A. Mewis, Z. Naturforsch., B: Anorg. Chem. Org. Chem., 1978, 33, 382.
- 26 C. Zheng, R. Hoffmann, R. Nesper and H.-G. von Schnering, J. Am. Chem. Soc., 1986, 108, 1876; C. Zheng and R. Hoffmann, J. Solid State Chem., 1988, 72, 58.
- 27 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 3rd edn., 1960.
- 28 E. Brechtel, G. Cordier and H. Schäfer, Z. Naturforsch., B: Anorg. Chem. Org. Chem., 1979, 34, 921.

- 29 C. Hirschle and C. Rohr, Z. Anorg. Allg. Chem., 2000, 626, 1992.
- 30 F. Gascoin and S. C. Sevov, Inorg. Chem., 2001, 40, 5177.
- 31 B. Saparov, and S. Bobev, unpublished results.
- 32 R. Dronskowski, *Computational Chemistry of Solid State Materials*, Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim, 2005.
- 33 P. Alemany, M. Llunell and E. Canadell, J. Comput. Chem., 2008, 29, 2144.
- 34 P. Alemany, S. Alvarez and R. Hoffmann, *Inorg. Chem.*, 1990, 29, 3070.
- 35 J. X. Xu and H. Kleinke, J. Comput. Chem., 2008, 29, 2134.
- 36 J. K. Burdett, S. Lee and T. J. McLarnan, J. Am. Chem. Soc., 1985, 107, 3083; J. K. Burdett, E. Canadell and T. Hughbanks, J. Am. Chem. Soc., 1986, 108, 3971.
- 37 G. J. Miller, Eur. J. Inorg. Chem., 1998, 523.
- 38 S. Misra and G. J. Miller, J. Am. Chem. Soc., 2008, 130, 13900.
- 39 R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Cryst., 1976, 32, 751.
- 40 C. Kittel, Introduction to Solid-State Physics 7th edn., John Wiley & Sons, Inc., 1996.
- 41 S.-J. Kim and M. G. Kanatzidis, Inorg. Chem., 2001, 40, 3781.
- 42 S.-J. Kim, S. Hu, C. Uher and M. G. Kanatzidis, *Chem. Mater.*, 1999, 11, 3154.
- 43 S. Bobev, V. Fritsch, J. D. Thompson, J. L. Sarrao, B. Eck, R. Dronskowski and S. M. Kauzlarich, J. Solid State Chem., 2005, 178, 1071.
- 44 P. Klufers and A. Mewis, Z. Kristallogr., 1984, 169, 135.
- 45 SMART NT, version 5.63, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2003.
- 46 SAINT NT, version 6.45, Bruker Analytical X-ray Systems Inc., Madison, WI, USA, 2003.
- 47 G. M. Sheldrick, SADABS, University of Göttingen, Germany, 2003.
- 48 G. M. Sheldrick, *SHELXTL*, University of Göttingen, Germany, 2001.
- 49 L. M. Gelato and E. Parthe, J. Appl. Crystallogr., 1987, 20, 139.
- 50 O. Jepsen, O. K. Andersen, TB-LMTO-ASA Program, version 4.7, Max-Planck Institut f
  ür Festkörperforschung, Stuttgart, Germany, 1998.
- 51 U. von Barth and L. Hedin, J. Phys. C: Solid State Phys., 1972, 5, 1629.
- 52 D. D. Koelling and B. N. Harmon, J. Phys. C: Solid State Phys., 1977, 10, 3107.
- 53 O. Jepsen and O. K. Andersen, Z. Phys. B: Condens. Matter, 1995, 97, 35.
- 54 W. R. L. Lambrecht and O. K. Andersen, *Phys. Rev. B: Condens. Matter*, 1986, 34, 2439.
- 55 P. E. Blöchl, O. Jepsen and O. K. Andersen, *Phys. Rev. B: Condens. Matter*, 1994, **49**, 16223.
- 56 R. Dronskowski and P. E. Blöchl, J. Phys. Chem., 1993, 97, 8617.