Electronic Supplementary Information for Dalton Transactions

Synthesis, crystal and electronic structures of the new quaternary phases $A_5Cd_2Sb_5F$ (A=Sr, Ba, Eu), and the solid solutions $Ba_5Cd_2Sb_5O_x$ ($0.5<x<0.7$)

Bayrammurad Saparov and Svilen Bobev*

Department of Chemistry, University of Delaware, Newark, Delaware 19716

SUPPORTING INFORMATION

Contents

Synthesis

Many reactions with varied compositions and temperature ranges have been tried. From these, several important observations have been made: 1) Lower temperature reactions at 860°C for 10 h with cooling to 500°C at a rate of 20°C/h, followed by annealing at that temperature for 5 days failed to produce target compounds. Products of such reactions included binary, ternary and quaternary phases such as BaF_2, $Ba_3Cd_2Sb_4$, $Ba_{11}Cd_6Sb_{12}$ and BaCdSbF in the reactions aimed at producing $Ba_5Cd_2Sb_5F$, and $Sr_9Cd_{4.5}Sb_9$, SrF_2 and $Sr_{16}Sb_{11}$ in the reactions directed at synthesizing $Sr_5Cd_2Sb_5F$. The quaternary phase BaCdSbF is a new compound with ZrCuSiAs type (*aka* filled PbFCl or $ZrCuSi_2$ type) structure (Figure S1). 2) Removing the annealing step at 500°C (heating to 900°C for 10 h and subsequent cooling to 300°C at a rate of 30°C/h) does yield $Ba_5Cd_2Sb_5F$, however, $Ba_{11}Cd_6Sb_{12}$ is also present as a major product. 3) At lower temperatures (860°C – 900°C), BaF_2 is a minor impurity, but as the reaction temperatures are increased, the BaF_2 content also increases, and conversely, the $Ba_{11}Cd_6Sb_{12}$ content decreases. Thus, the reactions carried out at 1200°C for 2 h, then cooling to 1000°C for 20 h, and keeping at that temperature 5 h, followed by cooling to 700°C at a rate of 10°C/h have a minor amount of $Ba_{11}Cd_6Sb_{12}$ as impurity, while BaF_2 is present as a major product. Similar product distribution is obtained from the reaction conditions described in experimental section of the manuscript as well. These facts suggest that at higher temperatures (close or above the melting point of CdF_2 = 1110°C), the metathesis reaction between barium and cadmium fluoride becomes more pronounced. 4) Because of the loss of Ba to BaF_2, the loading composition, unsurprisingly, has a crucial influence to product composition as well. Thus, increasing the amount of barium to compensate for the loss in BaF_2 does increase the BaF_2 in the reaction products as well. Increasing the fluorine amount has similar implications as well, whereas the stoichiometric reactions have higher amounts of ternary side products, most notably $Ba_{11}Cd_6Sb_{12}$.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters (U_{eq}) for $Sr_5Cd_2Sb_5F$.

Atom	Wyckoff Site	*x*	*y*	*z*	U_{eq} /Å^2
Sr1	8*f*	0	0.27137(2)	0.61987(3)	0.00895(11)
Sr2	4*c*	0	0.10062(3)	1/4	0.01104(15)
Sr3	4*c*	0	0.90247(3)	1/4	0.00924(14)
Sr4	4*a*	0	0	0	0.00922(14)
Cd	8*f*	0	0.36792(2)	0.08579(2)	0.01001(9)
Sb1	8*f*	0	0.14936(2)	0.01877(2)	0.00847(9)
Sb2	8*f*	0	0.494566(14)	0.15472(2)	0.00940(9)
Sb3	4*c*	0	0.29342(2)	1/4	0.00824(11)
F	4*c*	0	0.6555(2)	1/4	0.0127(9)

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (U_{eq}) for $Eu_5Cd_2Sb_5F$.

Atom	Wyckoff Site	*x*	*y*	*z*	U_{eq} /Å^2
Eu1	8*f*	0	0.27066(2)	0.61946(3)	0.00831(10)
Eu2	4*c*	0	0.10030(3)	1/4	0.01008(13)
Eu3	4*c*	0	0.90284(2)	1/4	0.00865(12)
Eu4	4*a*	0	0	0	0.00849(12)
Cd	8*f*	0	0.36823(3)	0.08516(4)	0.00956(13)
Sb1	8*f*	0	0.14957(2)	0.02057(3)	0.00803(12)
Sb2	8*f*	0	0.49537(2)	0.15371(3)	0.00850(11)
Sb3	4*c*	0	0.29303(3)	1/4	0.00779(15)
F	4*c*	0	0.6543(3)	1/4	0.0118(13)

Table S3. Selected bond distances (Å) in $Sr_5Cd_2Sb_5F$ and $Eu_5Cd_2Sb_5F$.

Atom pair (*A*=Sr or Eu)		$Sr_5Cd_2Sb_5F$	$Eu_5Cd_2Sb_5F$
*A*1–	F	2.509(3)	2.519(4)
	Sb1×2	3.3103(9)	3.2696(9)
	Sb1	3.3867(11)	3.3517(11)
	Sb3×2	3.3751(9)	3.3369(9)
*A*2–	F×2	2.672(2)	2.635(3)
	Sb1×2	3.5724(14)	3.5232(14)
	Sb2×4	3.6255(10)	3.5799(10)
*A*3–	Sb2×4	3.4334(10)	3.4115(9)
	Sb3×2	3.3899(11)	3.3671(11)
	Cd×4	3.4776(10)	3.4533(10)
*A*4–	Sb1×2	3.3191(14)	3.2923(14)
	Sb2×4	3.2964(10)	3.2561(10)
Cd–	Sb1×2	2.8596(9)	2.8434(9)
	Sb2	2.9826(12)	2.9614(13)
	Sb3	2.9275(10)	2.9192(11)
Sb2–	Sb2	2.806(1)	2.815(2)
F–	Ba1×2	2.509(3)	2.519(4)
	Ba2×2	2.672(2)	2.635(3)

Table S4. Calculated bond valence sums and Madelung potentials of crystallographic positions in $Ba_5Cd_2Sb_5F$, $Ba_5Cd_2Sb_5O$ and $Ba_5Cd_2Sb_5$.

Atom	Input charge	Bond valence sum	Madelung potential/ V
$Ba_5Cd_2Sb_5F$			
Ba1	+2	2.63	–14.95
Ba2	+2	1.74	–15.62
Ba3	+2	2.71	–12.16
Ba4	+2	3.17	–14.64
Cd	+2	1.92	–15.73
Sb1	–3	3.32	22.03
Sb2	–2	3.81	13.12
Sb3	–3	3.52	22.81
F	–1	0.98	10.61
$Ba_5Cd_2Sb_5O$ (using the parameters and coordinates of $Ba_5Cd_2Sb_5O_{0.59(3)}$)			
Ba1	+2	2.60	–14.70
Ba2	+2	1.66	–15.42
Ba3	+2	2.63	–12.24
Ba4	+2	3.06	–14.75
Cd	+2	1.89	–15.74
Sb1	–3	3.16	21.97
Sb2	–2	3.70	12.96
Sb3	–3	3.42	22.80
O	–1	1.24	10.67
$Ba_5Cd_2Sb_5$ (using the parameters and coordinates of $Ba_5Cd_2Sb_5O_{0.59(3)}$) **not electro-neutral*			
Ba1	+2	2.23	–13.76
Ba2	+2	1.17	–13.26
Ba3	+2	2.63	–14.12
Ba4	+2	3.06	–16.34
Cd	+2	1.89	–17.24
Sb1	–3	3.16	21.24
Sb2	–2	3.70	11.66
Sb3	–3	3.42	22.32

The charge balance for $Ba_5Cd_2Sb_5F$ can be written as $(Ba^{2+})_5(Cd^{2+})_2(Sb^{3-})_3(Sb^{2-})_2(F^-)$. If purely ionic interactions are assumed to exist in these compounds, one can calculate the bond valence sums and Madelung site potentials using the program EUTAX. The

program replaces atom positions with point charges equivalent to the entered charge for a given site. Although the program has been successfully used for more covalent chalcogenides and pnictides, the method works best for highly ionic oxides and halides. Three different cases—$Ba_5Cd_2Sb_5O$ and $Ba_5Cd_2Sb_5$ using the cell dimensions and atomic coordinates of $Ba_5Cd_2Sb_5O_{0.59(3)}$, and $Ba_5Cd_2Sb_5F$ were chosen for calculations. Partial occupancy of 50% in oxygen position for $Ba_5Cd_2Sb_5O$ is given by –1 charge on that position. The results of the calculations are provided in Table S4. In an ionic compound, the bond valence sums for elements are expected to be identical to their valences, while Madelung site potentials are around 10 times the formal charge of the ion. It is clear that both F and O positions in $Ba_5Cd_2Sb_5O_{0.59(3)}$ and $Ba_5Cd_2Sb_5F$ do carry –1 charge, on the other hand a compound with a vacant tetrahedral cavity and $Ba_5Cd_2Sb_5$ formula is calculated to be an unbalanced, i.e. ionic species, supporting the simple electron count mentioned above. The input charges of –2 on Sb2 sites in all three cases is due to the fact that Sb2 atoms are bonded to each other and are expected to carry a –2 charge to complete its octet, while all other Sb atoms need 3 electrons to achieve closed-shell configuration. Elements other than O and F display some noticeable deviations from the expected bond valence sums and Madelung site potentials due to the fact that these compounds are not purely ionic and the constituent elements are not fully oxidized except for the most electronegative elements such as oxygen and fluorine. A more detailed discussion of the bonding in these compounds is given in electronic structure calculations section.

Figure S1. Perspective view of the tetragonal structure of BaCdSbF viewed down approximately *a*-axis. The Ba, Cd, Sb and F atoms are shown as large maroon, pink, green and blue spheres, respectively.

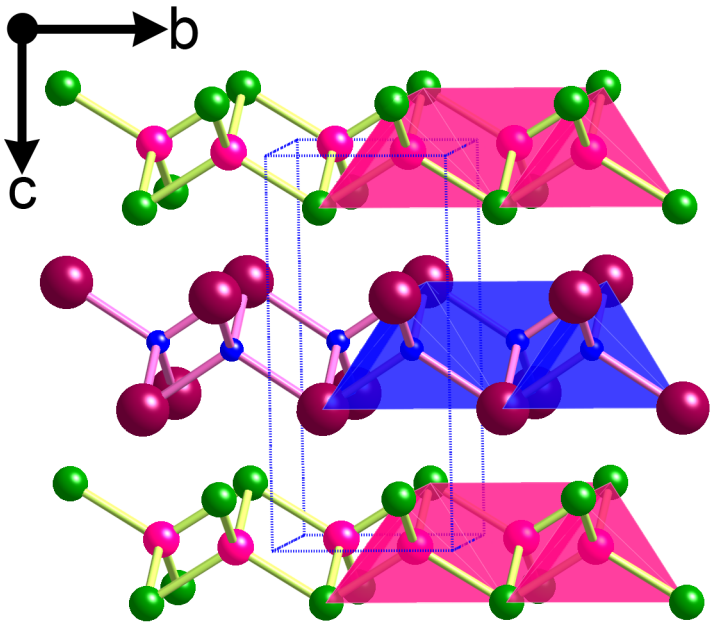

Table S5. Selected single-crystal data collection and refinement parameters for BaCdSbF.

Formula	BaCdSbF
Formula weight /g mol^{-1}	390.49
Radiation, wavelength /Å	Mo Kα, 0.71073
Crystal system	Tetragonal
Space group	*P*4/*nmm* (No. 129)
Z	2
Temperature/ °C	–73(2)
Unit cell parameters /Å	a = 4.5792(9) c = 9.740(4)
Volume /Å^3	204.24(9)
Density (ρ_{calc}) /g cm^{-3}	6.350
θ range / °	2.09 – 28.26
Absorption coefficient (μ) /cm^{-1}	210.55
Transmission factors min/max	0.4577/0.5614
Crystal dimensions /mm^3	0.04×0.03×0.03
Total reflections collected	2625
Independent reflections	185
Final R_1 ($I > 2\sigma_{(I)}$)[a]	0.0194
Final wR_2 ($I > 2\sigma_{(I)}$)[a]	0.0386
Largest peak and deepest hole /e$^-$ Å^{-3}	1.87/–1.41

[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 $w = 1/[\sigma^2F_o^2+(0.0168\cdot P)^2 + 0.338\cdot P]$, and $P = (F_o^2+2F_c^2)/3$.

Table S6. Atomic coordinates and equivalent isotropic displacement parameters (U_{eq}) for BaCdSbF/

Atom	Wyckoff Site	*x*	*y*	*z*	U_{eq} /Å^2
Ba	8*f*	0	1/2	0.35865(8)	0.0118(2)
Cd	4*c*	0	0	0	0.0137(2)
Sb	4*c*	0	1/2	0.81486(9)	0.0115(2)
F	4*c*	0	0	1/2	0.0132(16)

Table S7. Selected bond distances (Å) in $Ba_5Cd_2Sb_5F$ and BaCdSbF at 200K.

Atom pair		$Ba_5Cd_2Sb_5F$	BaCdSbF
Ba–	F	2.667(4) – 2.776(3)	2.6717(6)
Ba–	Sb	3.4516(13) – 3.9000(13)	3.6525(8)
Cd–	Sb	2.9166(9) – 3.0553(12)	2.9145(8)
Sb2–	Sb2	2.8191(14)	-

Figure S2. The DOS and COHP plots for BaCdSbF.