Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Structural Dimension Modulation in the New Oxysulfide System of $Ae_2Sb_2O_2S_3$ (Ae = Ca, Ba)

Ruiqi Wang,[a] Yantao Zhao,[a] Xian Zhang,*[,b] and Fuqiang Huang,*[,a,c]

[a] *Beijing National Laboratory for Molecular Sciences and State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China*

[b] *Qian Xuesen Laboratory of Space Technology, China Academy of Space Technology, Beijing, 100094 P. R. China*

[c] *State Key Laboratory of High-Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China*

List of contents:

1. Supplementary figures.

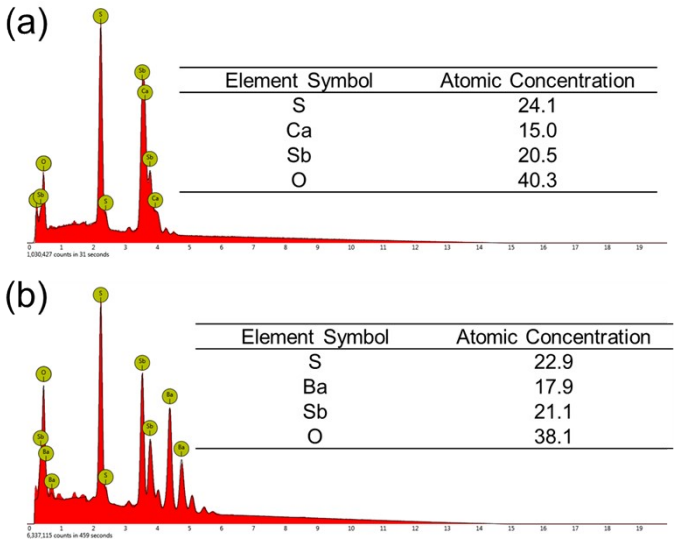

Figure S1 EDS spectrum and element contents of (a) $Ca_2Sb_2O_2S_3$ and (b) $Ba_2Sb_2O_2S_3$.

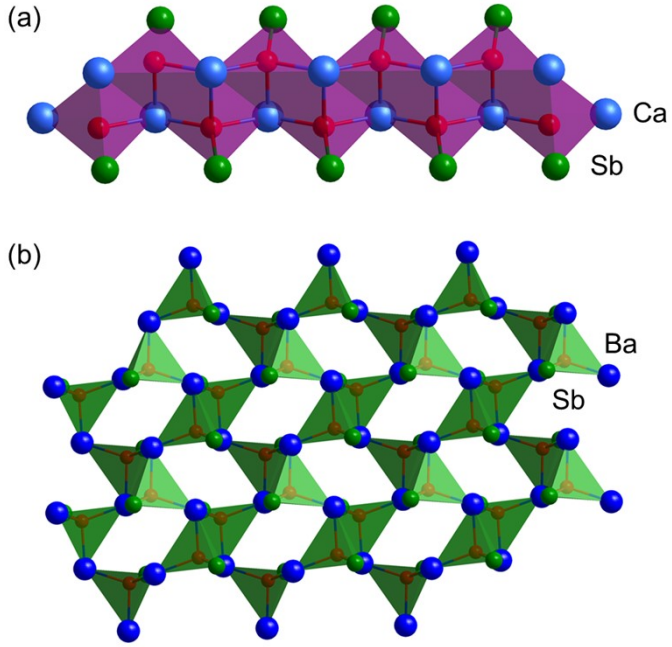

Figure S2. Oxygen coordination environments of (a) $Ca_2Sb_2O_2S_3$ and (b) $Ba_2Sb_2O_2S_3$.

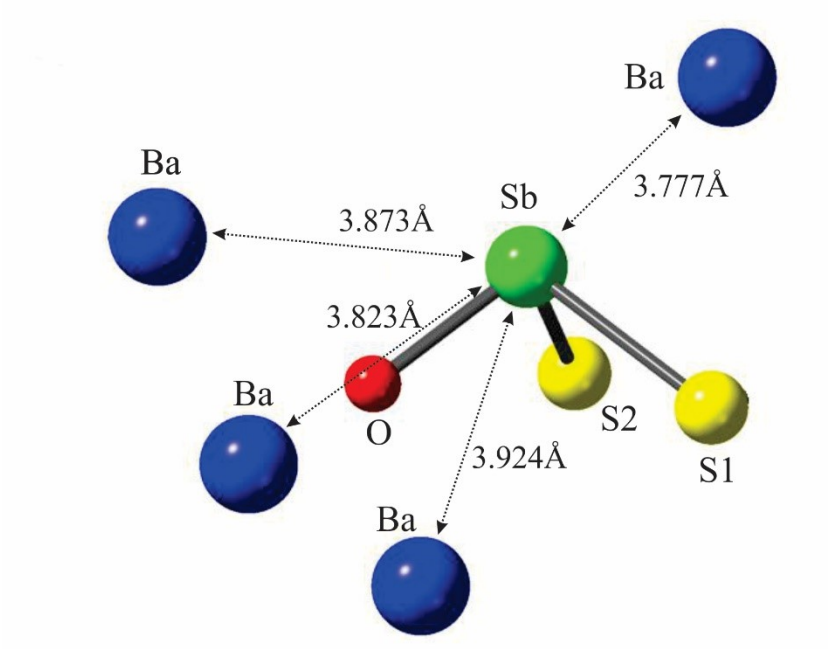

Figure S3. Coordination Sphere of Sb. All four Ba atoms are equivalent.

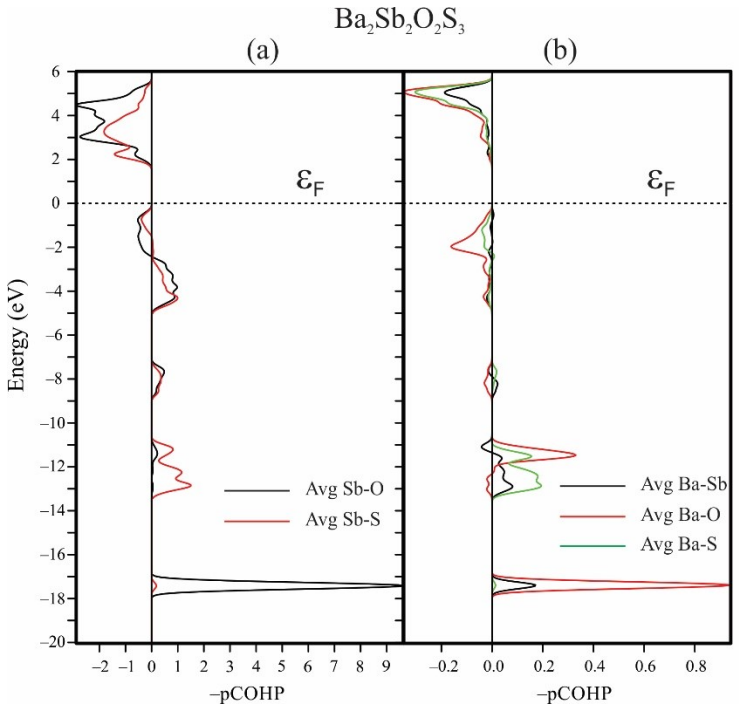

Figure S4. (a) The COHP curves of Sb–O, Sb–S, (b) Ba–Sb, Ba–O and Ba–S bond. The dotted horizontal line is the Fermi level.

2. Supplementary tables.

Table S1. Crystallographic data and details of the structure refinement of $Ae_2Sb_2O_2S_3$ (*Ae* = Ca, Ba)

Formula	$Ca_2Sb_2O_2S_3$	$Ba_2Sb_2O_2S_3$
Space group	*C*2/*c*	*C*2/*c*
F_w(g·mol^{-1})	451.84	646.36
a (Å)	14.8616(7)	16.0862(9)
b (Å)	4.0014(2)	7.8909(5)
c (Å)	12.7811(6)	7.1929(5)
β (°)	100.313(4)	113.867(5)
V(Å^3)	747.78(6)	834.95(9)
crystal color	yellow	pale yellow
ρ_c (g·cm^{-3})	4.013	5.142
μ (mm^{-1})	9.351	16.385
F(000)	824	1112
data/parameters	995/42	1052/42
R_{int}	0.0195	0.0182
$R1[I>2\sigma(I)]$	0.0111	0.0144
wR_2 (all data)	0.0259	0.0328
GOF	1.124	1.079

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \Sigma\{[w(|F_o|^2-|F_c|^2)^2]/\Sigma[w(|F_o|^4)]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2)+(0.0114P)^2+0.0699P]$ for A=Ca, and $w = 1/[\sigma^2(F_o^2)+(0.0135P)^2]$ for A = Ba, where $P = (F_o^2+2F_c^2)/3$

Table S2. Selected bond lengths and angles for $Ae_2Sb_2O_2S_3$ (*Ae* = Ca, Ba)

$Ca_2Sb_2O_2S_3$		$Ba_2Sb_2O_2S_3$	
bond type	distance (Å)	bond type	distance (Å)
Sb–S1	2.6076(4)	Sb–S1	2.6122(8)
Sb–S1	3.0566(5)	Sb–S2	2.4148(8)
Sb–S2	2.4785(4)	Sb–O1	1.932(2)
Sb–S2	3.0070(5)	Ba–S1	3.4379(6)
Sb–O1	1.966(2)	Ba–S1	3.4934(4)
Ca–S1	2.9678(4)	Ba–S2	3.3139(7)
Ca–S2	3.0596(5)	Ba–S2	3.4696(8)
Ca–S2	2.8620(5)	Ba–S2	3.2458(8)
Ca–O1	2.350(1)	Ba–S2	3.4617(8)
Ca–O1	2.322(1)		
Ca–O1	2.363(1)		

$Ca_2Sb_2O_2S_3$		$Ba_2Sb_2O_2S_3$	
angle type	angle (°)	angle type	angle (°)
O1–Sb–S1	87.05(3)	O1–Sb–S1	96.94(7)
O1–Sb–S2	89.85(3)	O1–Sb–S2	94.56(7)
O1–Sb–S1	78.83(3)	S1–Sb–S2	94.59(2)
O1–Sb–S2	81.17(4)		
S1–Sb–S2	97.22(3)		
S1–Sb–S1	89.528(4)		
S2–Sb–S2	93.18(2)		

Table S3. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of $Ca_2Sb_2O_2S_3$ at 180 K

Label	x	y	z	Occupancy	U_{eq}*
Sb	0.56554(2)	0.35092(3)	0.62702(2)	1	0.00626(5)
Ca	0.69871(2)	0.90271(8)	0.83792(2)	1	0.00616(7)
S	0.5	-0.06966(14)	0.75	1	0.00681(10)
S	0.65424(3)	-0.05856(10)	0.54120(3)	1	0.00824(8)
O	0.67046(7)	0.4068(3)	0.74341(9)	1	0.0062(2)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of $Ba_2Sb_2O_2S_3$ at 180 K

Label	x	y	z	Occupancy	U_{eq}*
Ba	0.17774(2)	0.34732(2)	0.21999(3)	1	0.00649(6)
Sb	0.06426(2)	0.79591(3)	0.07709(3)	1	0.00669(6)
S	0	0.57037(14)	0.25	1	0.0078(2)
S	0.35316(5)	0.45050(10)	0.11276(12)	1	0.00823(15)
O	0.16854(15)	0.6668(3)	0.0901(3)	1	0.0077(4)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S5. Anisotropic displacement parameters (Å^2) of $Ca_2Sb_2O_2S_3$ at 180 K

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb1	0.00540(7)	0.00704(7)	0.00583(7)	-0.00033(3)	-0.00033(4)	0.00060(3)
Ca1	0.00629(14)	0.00585(14)	0.00662(15)	0.00002(11)	0.00193(11)	0.00048(11)
S1	0.0059(2)	0.0063(2)	0.0086(2)	0	0.00242(18)	0
S2	0.01015(18)	0.00818(18)	0.00683(17)	-0.00059(13)	0.00270(13)	0.00070(15)
O1	0.0051(5)	0.0070(5)	0.0058(5)	0.0002(4)	-0.0006(4)	0.0003(4)

Table S6. Anisotropic displacement parameters (Å^2) of $Ba_2Sb_2O_2S_3$ at 180 K

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	0.00709(10)	0.00600(10)	0.00675(10)	0.00065(7)	0.00320(8)	0.00047(6)
Sb1	0.00570(10)	0.00710(12)	0.00692(11)	-0.00043(8)	0.00218(8)	0.00109(7)
S1	0.0091(5)	0.0065(5)	0.0096(5)	0	0.0056(4)	0
S2	0.0103(3)	0.0077(3)	0.0078(3)	0.0022(3)	0.0047(3)	0.0010(3)
O1	0.0071(10)	0.0066(11)	0.0095(11)	-0.0003(9)	0.0037(9)	0.0011(8)