

Supporting Information

Low Temperature Synthesis and Structures of the Alkaline Earth Metal Chalcogenides $\text{Ba}_3\text{Cu}_4\text{SbS}_6\text{OH}$, BaCuSbS_3 and BaCu_2S_2

Zhimin Ma^a, Fan Weng^b, Qiuran Wang^b, Qun Tang^b, Ganghua Zhang^c, Chong Zheng^d,
Ray P.S. Han^a and Fuqiang Huang^{a,b,c,*}

^a*Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China. E-mail: huangfq@pku.edu.cn; Fax: +86-10-62767628; Tel: +86-10-62758225*

^b*State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*

^c*State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China*

^d*Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL 60115, USA*

Experimental Details

Materials and synthesis

All the reactants were used as purchased from commercialized company without further purification except for specifying otherwise.

Compound **1** and **2** were yielded from the following procedures: The mixture of Cu (2.5mmol), Sb (2.5mol), S (25mol) was ground uniformly in a agate mortar and added into a teflon liner (25ml) with 5mL deionized water in. Then, $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (12g) was gradually added and stirred by a glass bar. The Teflon liner sealed into a steel autoclave was put into the oven at 200°C for 48~82 hours. Crystals of compound **1** (most) and **2** (minority) remained in the product were washed with deionized water and ethanol for several times in the open air. Both compound **1** and **2** seem to be the stable phases under such reaction situation. Although we tried to modify the reagent ratio of Cu/Sb and use various temperature, they were failed to separate the compounds to obtain their pure samples. However, a relatively pure phase of **1** was obtained by the ratio of Cu/Sb mentioned above. 82 hours, a long time, was used for the growing of the suitable single crystals for X-ray diffraction. Actually, 48 hours, even shorter, was enough to get the mixture of compounds **1** and **2**. Compound **3** was obtained by the same procedure but without Sb.

Powder XRD

Powder X-ray diffraction analysis was performed on Bruker D8 FOCUS system using a Cu $K\alpha$ radiation source operating at 40kV/40mA and a scanning speed of 30° per minute in reflection mode.

SEM and EDS

The SEM images and semiquantitative energy dispersive X-ray analysis were obtained with a HITACHI-S4800 field emission scanning electron microscope equipped with a Bruker XFlash® 5010 detector. The SEM images were obtained with 10kV accelerating voltage. An acquisition time of 60s was used when collecting EDS spectra at an accelerating voltage of 10 kV.

UV-vis spectrum

The ultraviolet-visible (UV-Vis) absorption spectrum was recorded on the UV-4100 Shimadzu ultraviolet-visible-infrared spectrophotometer. The powder sample was pressed into the round groove of a Teflon stage. Then, the sample stage was covered with a quartz plate for test.

FT-IR spectrum

Fourier transform infrared (FTIR) spectrum was recorded from KBr pellet in a Nicolet Nexus 670 spectrophotometer.

Raman Spectroscopy

The Raman measurement was taken with Renishaw in Via-Reflex spectrometer system consisting of a deep depletion CCD and the spectroscopy was calibrated with a clean Si wafer. The excitation wavelength was 532nm from a solid state laser.

Single crystal X-ray Crystallography

Crystallographic data were collected on a Bruker Smart-1000 CCD diffractometer system using graphite-monochromatic Mo K α ($\lambda=0.71073\text{\AA}$) radiation with the ω -2 θ method at room temperature. Data absorption corrections were applied on the structures via SADABS program.¹ The structures were all solved by direct methods

and refined on F^2 by full-matrix least-squares methods with the help of SHELXS-97 and SHELXL-97 software suit respectively.² The final refinement involved anisotropic displacement parameters and a secondary extinction correction.

Computational Study

The density of states (DOS) and band structure were computed using the self-consistent linear muffin-tin orbital local density approximation method (LDA) as implemented in the Stuttgart-TB-LMTO-ASA program.³ 50 k-points were used during the self-consistent convergence part in the LDA calculations.

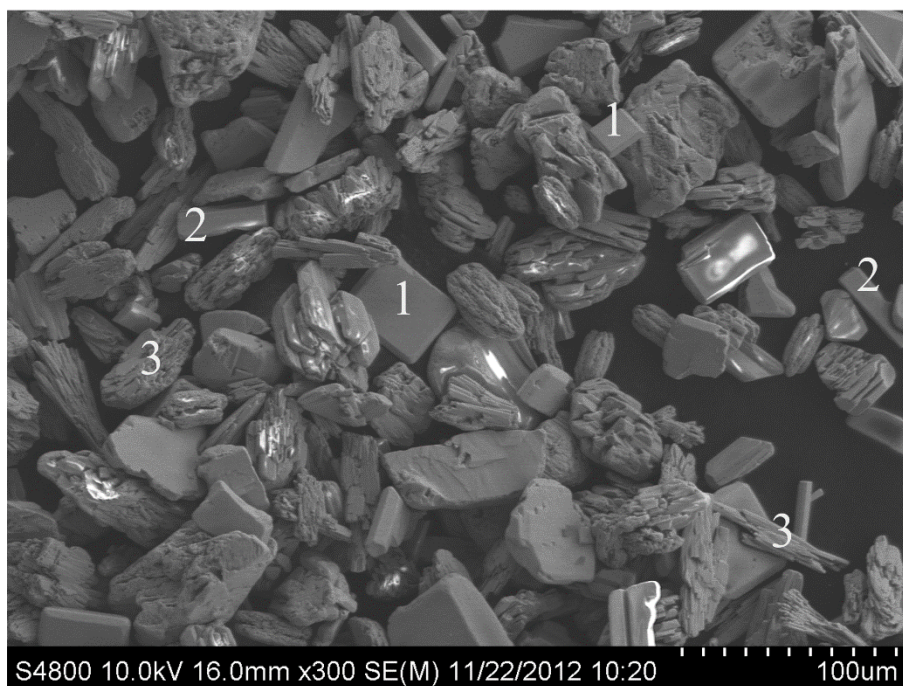


Figure S1. SEM image of the original sample presenting different morphologies. Slab-like, rod-like and bundle-like shape crystals were marked by 1, 2 and 3.

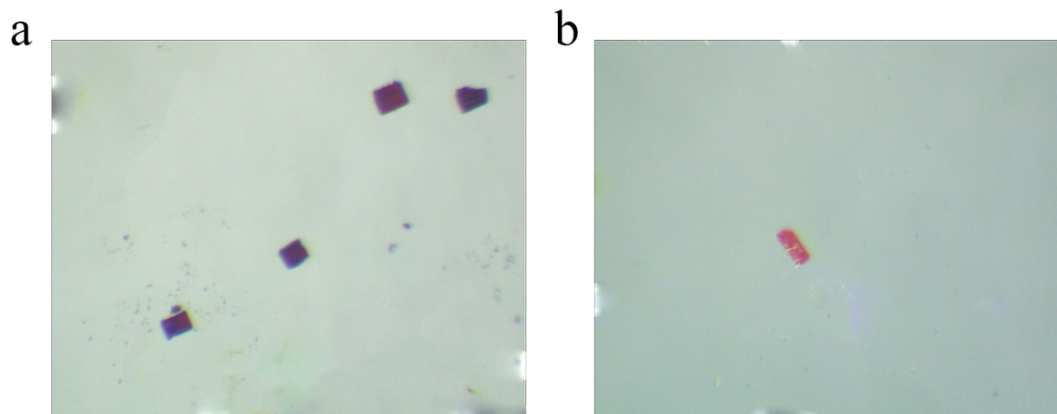


Figure S2. Optical microscope images of the slab-like(a) and rod-like(b) crystals.

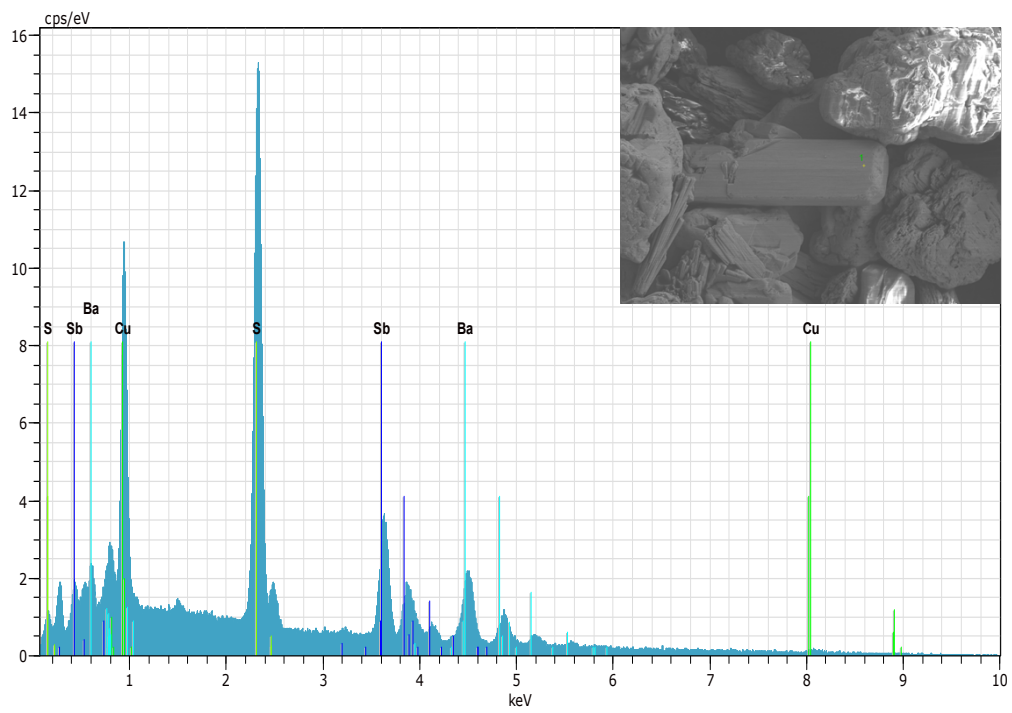
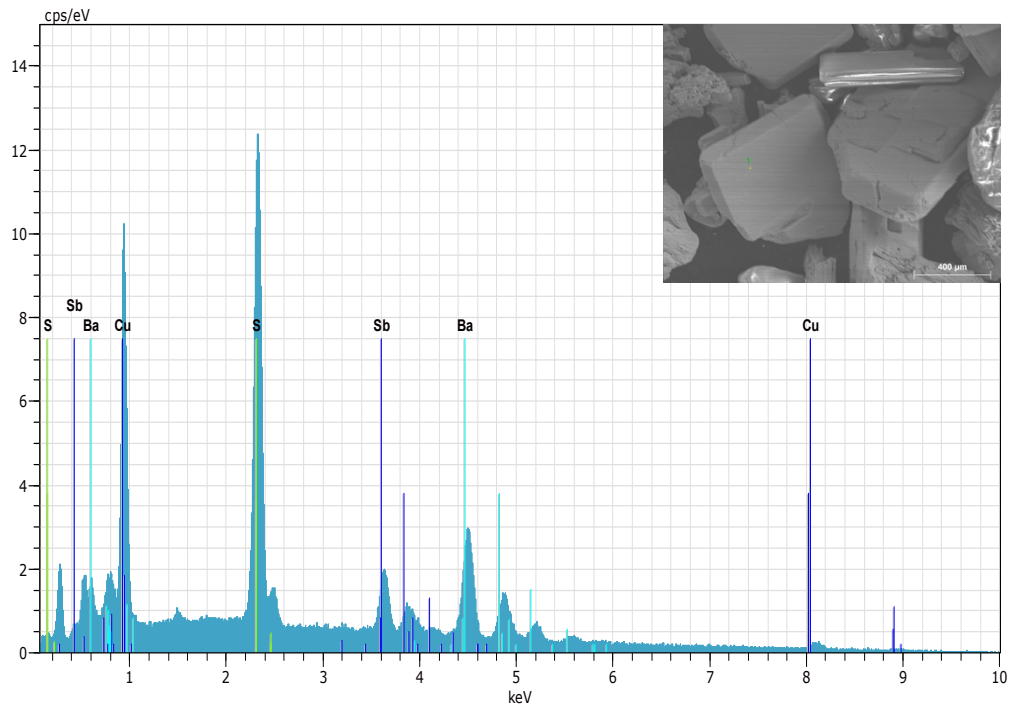


Figure S3. EDS analysis of slab-like(up) and rod-like crystals(bottom).

Table S1. The stoichiometric ratio statistics of Slab-like crystals (compound **1**) and Rod-like crystals (compound **2**) tested by Energy Dispersive Spectra.

	Slab-like crystals (at.%)				Rod-like crystals (at.%)			
	Ba	Cu	Sb	S	Ba	Cu	Sb	S
Test1	14.35	49.20	5.15	31.30	11.72	37.75	12.22	38.32
Test2	14.12	48.68	5.18	32.02	12.73	35.03	11.87	40.37
Test3	13.76	49.90	4.95	31.37	12.30	36.73	12.18	38.79
average	14.08	49.26	5.09	31.56	12.25	36.50	12.09	39.16

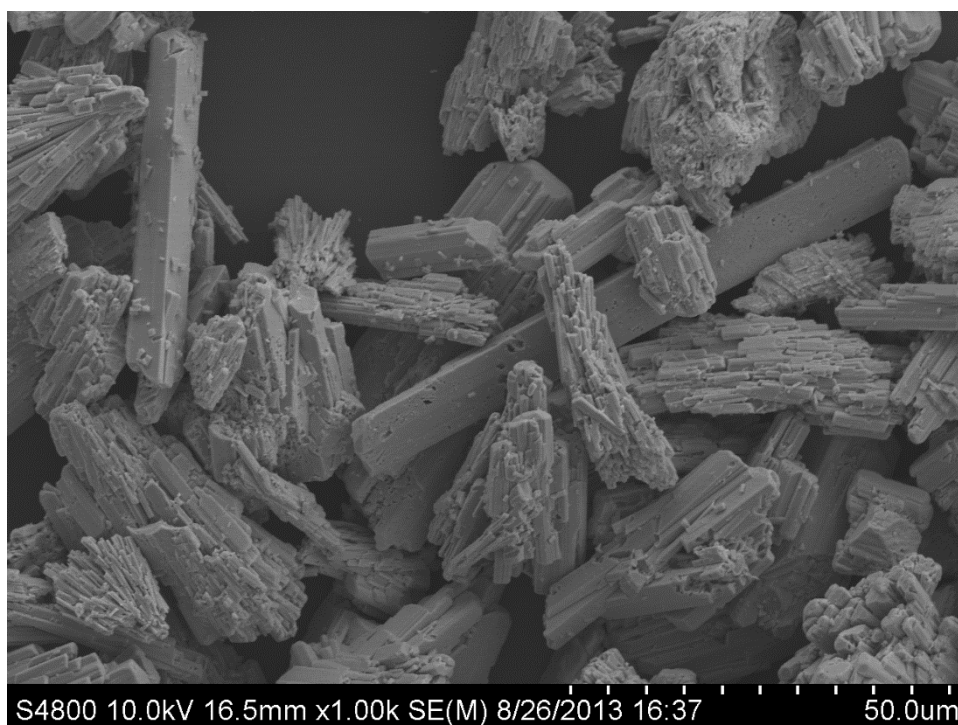


Figure S4. SEM image of compound **3**'s pure phase. Bundle-like shape crystals mainly distributed in the view. Rod-like single crystals were rare.

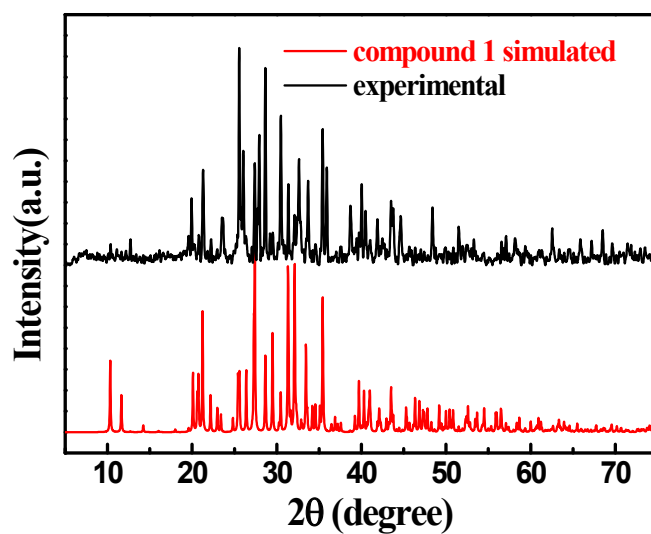


Figure S5. Powder XRD pattern of a relatively pure sample of compound **1**.

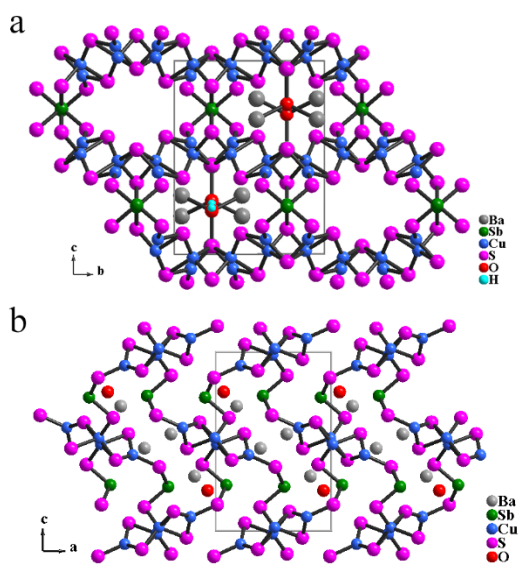


Figure S6. Images of (a) Star-like channels and (b) S shape channels in the structure of **1** viewed down the [100] and [010] directions, respectively.

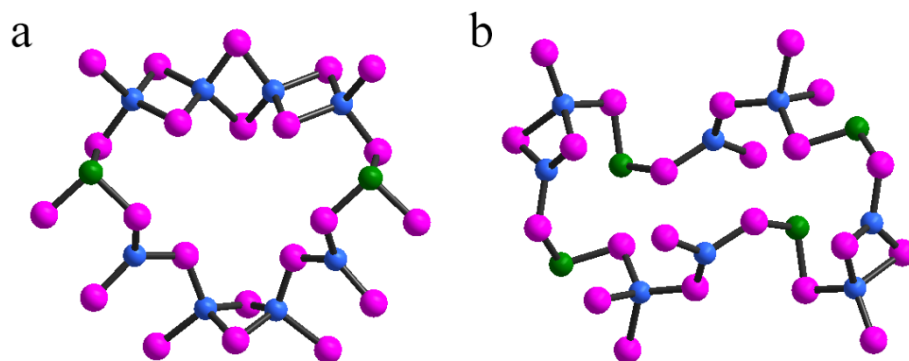


Figure S7. Images of (a) 20-membered rings and (b) 24-membered rings in the structure of **1**.

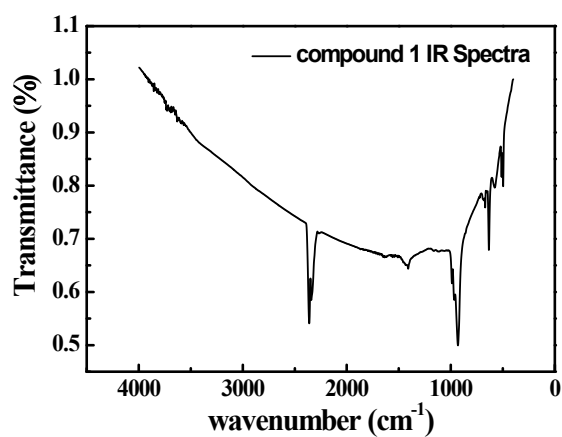


Fig. S8. FT-IR spectrum of compound **1**

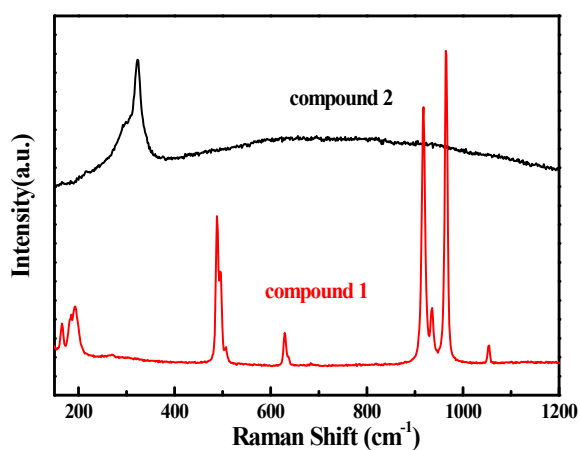


Figure S9. Raman spectra of **1** and **2**.

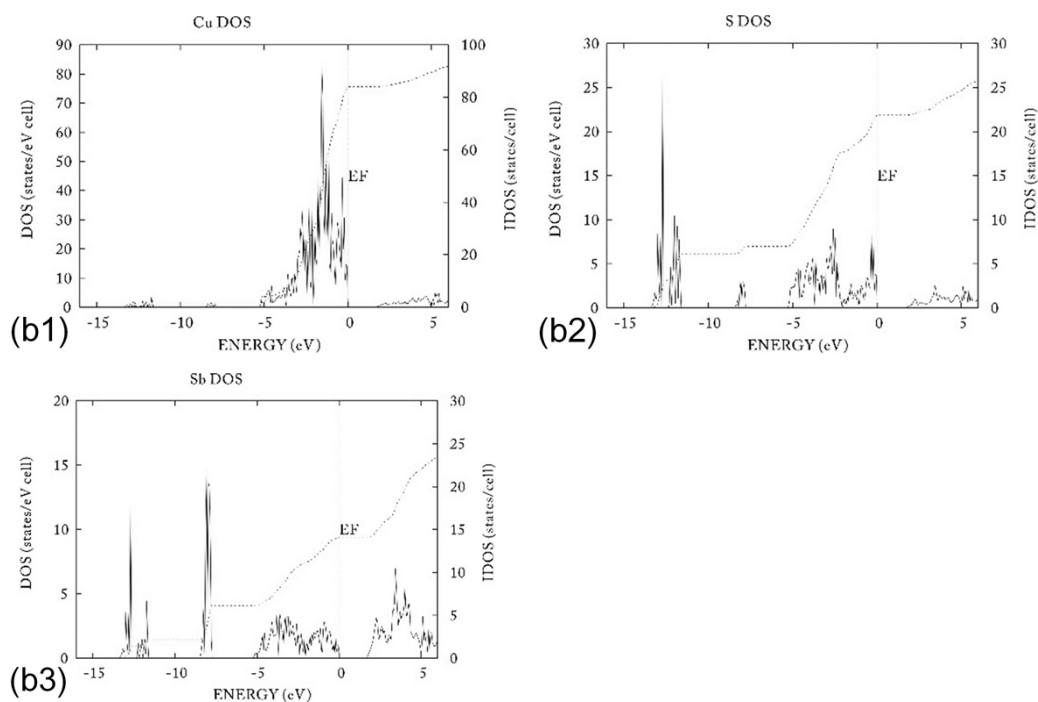


Figure S10. The density of states (*DOS*) and band structure calculation results of **2**.

Reference

1. G. Sheldrick, Bruker AXS Inc., Madison, Wisconsin, USA 2007.
2. (a) G. Sheldrick, University of Göttingen, Germany, 1997. (b) G. M. Sheldrick, University of Göttingen, Germany 1997.
3. Andersen, O.K.; Jepsen, O. *Phys. Rev. Lett.* **1984**, *53*, 2571.