Supporting Information

A Facile Approach to Hexanary Chalcogenoborate Featuring 3-D Chiral Honeycomb-Like Open-Framework Constructed From Rare-Earth Consolidating Thiogallate-*Closo*-Dodecaborate

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Reagents and Syntheses

All chemicals of analytical grade were purchased and used without further purification. A 500 mg mixture of Sm_2O_3 (194 mg, 99.9%), Ga_2O_3 (104 mg, 99.9%), S (142 mg, 99.999%) and B (60 mg, 99.9%) in the molar ratio of Sm : Ga : S : B = 1 : 1 : 8 : 10, and 400 mg KI (99%) as flux. The starting materials was ground into fine powders in an agate mortar and pressed into one pellet, followed by being loaded into one quartz tube. The tube was evacuated to 1×10^{-4} torr and flame-sealed. The sample was placed into a muffle furnace, heated from the room temperature to 300 °C in 5 h, kept at 300 °C for 10 h, then heated to 650 °C in 5 h, kept at 650 °C for 10 h, then heated to 950 °C in 5 h, kept at 950 °C for 10 days, then cooled down to 300 °C in 5 days, and powered off, some small yellow block crystals of **1** were obtained. Later, we repeated this experiment for many times, and yellow crystals with the same cell parameters with **1** can be obtained every time.

EDS Analyses

Semiquantitative microscopic element analyses on single crystals were performed on a field-emission scanning electron microscope (JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA). It confirmed the presence of Sm, K, I, B, S, Ga,

and no other elements were detected. The exact composition was established from the X-ray structure determination.

Structure Determination

Single crystal of **1** was mounted on a glass fiber for the X-ray diffraction analyses. The data set was collected on a Rigaku Scxmini CCD diffractometer equipped with a graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71073 Å) at 293 K. Intensities were corrected for *Lp* factors, and for empirical absorption using ω scan technique. The structure was solved by direct methods and refined on F^2 with full-matrix least-squares techniques using the SHELXTL^{TM} version 5 package of crystallographic software.[1] The final refinement included anisotropic displacement parameters for all atoms and a secondary extinction correction.

Second Harmonic Generation Measurement

Powder SHG measurement on hand-selected unsieved crystalline sample of **1** was performed on a modified Kurtz-NLO system using 1.06 and 1.94 um laser radiation, respectively. The SHG signal was collected in a reflection geometry from the excitation surface and focused into a fiber optic bundle. The output of the fiber optic bundle was coupled to the entrance slit of a spectrometer and detected using a CCD detector. KDP powder was used as a reference to assume the second-order NLO effect. No obvious SHG signals were detected when irradiated by 1.06 um laser due to their absorption in the visible-light region. A SHG efficiency of about 0.3 times that of KDP (KH_2PO_4) was detected when irradiated by 1.94 um laser.

Infrared and UV–Vis–NIR Diffuse Reflectance Spectroscopies

The IR spectrum was recorded by using a Nicolet Magana 750 FT-IR spectrophotometer in the range of 4000–400 cm^{-1}. Powdery sample was pressed into one pellet with KBr. Diffuse reflectance measurement was taken at the room temperature on a computer-controlled Lambda 900 UV-Vis-NIR spectrometer equipped with an integrating sphere in the wavelength range 300–1700 nm. A $BaSO_4$ plate was used as a reference. The spectrum was calculated

from reflection spectrum by the Kubelka-Munk function.[2]

Table S1. Selected bond distances (Å) for **1**.

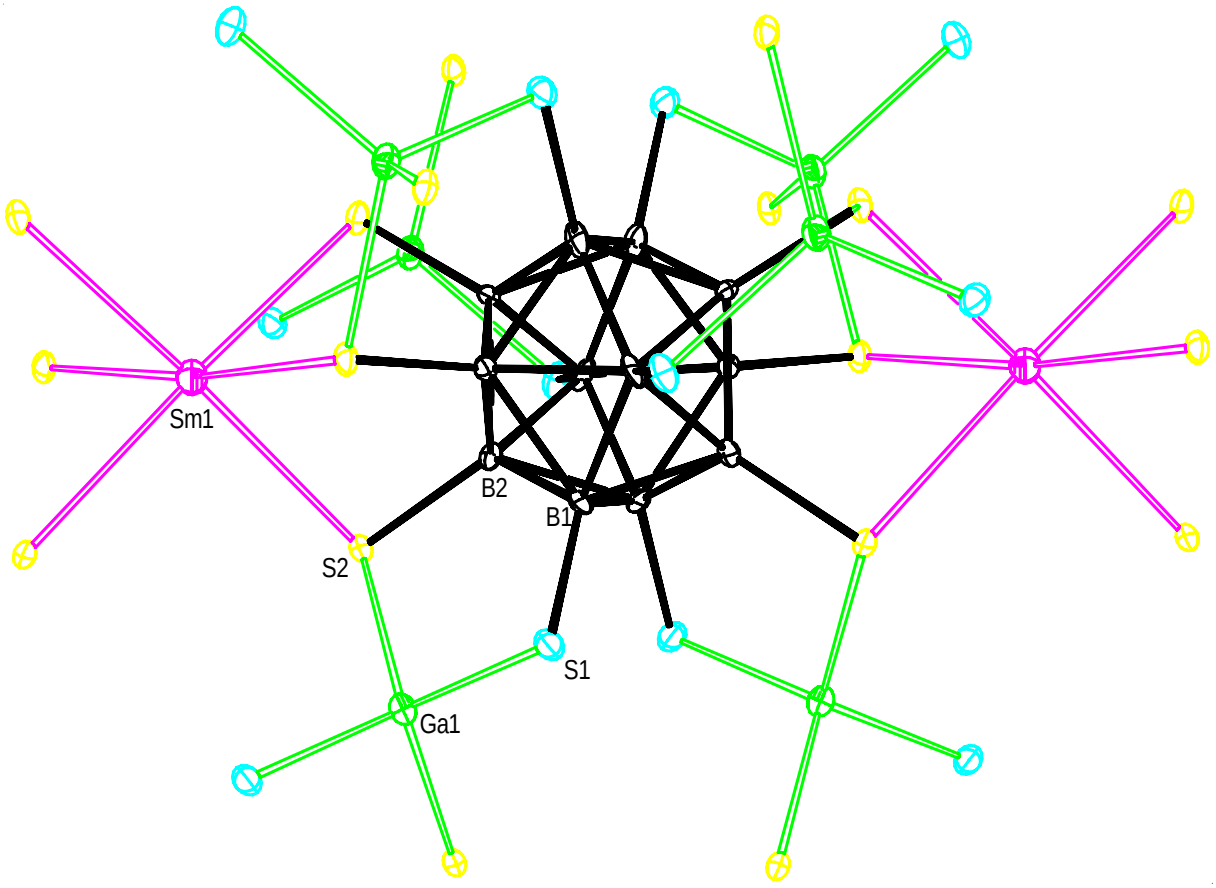
Bond	Dist.	Bond	Dist.	Bond	Dist.
Sm(1)-S(2)#1	2.832(1)	Ga(1)-S(2)	2.342(1)	B(1)-B(1)#16	1.777(5)
Sm(1)-S(2)#2	2.832(1)	K(1)-S(2)	3.308(2)	B(1)-B(1)#12	1.813(8)
Sm(1)-S(2)	2.832(1)	K(1)-S(2)#11	3.308(2)	B(1)-B(2)#2	1.830(5)
Sm(1)-S(2)#3	2.832(1)	K(1)-S(1)#12	3.604(1)	B(2)-B(1)#12	1.770(4)
Sm(1)-S(2)#4	2.832(1)	K(1)-S(1)#13	3.604(1)	B(2)-B(2)#2	1.811(4)
Sm(1)-S(2)#5	2.832(1)	K(1)-I(1)#14	3.625(1)	B(2)-B(2)#4	1.811(4)
Ga(1)-S(1)	2.242(1)	K(1)-I(1)	3.625(1)	B(2)-B(1)#4	1.830(5)
Ga(1)-S(1)#11	2.242(1)	B(1)-B(2)	1.765(6)	S(2)-B(2)	1.867(3)
Ga(1)-S(2)#11	2.342(1)	B(1)-B(2)#12	1.770(4)	S(1)-B(1)	1.853(4)

Symmetry codes: #1 *x*, *x*-*y*+1, -*z*+1/2; #2 -*x*+*y*, -*x*+1, *z*; #3 -*y*+1, -*x*+1, -*z*+1/2; #4 -*y*+1, *x*-*y*+1, *z*; #5 -*x*+*y*, *y*, -*z*+1/2; #6 -*y*, *x*-*y*, *z*; #7 *y*, -*x*+*y*, *z*+1/2; #8 *x*-*y*, *x*, *z*+1/2; #9 -*x*, -*y*, *z*+1/2; #10 -*x*+*y*, -*x*, *z*; #11 -*x*, -*x*+*y*, -*z*+1; #12 *x*, *x*-*y*+1, -*z*+3/2; #13 -*x*, -*y*+1, *z*-1/2; #14 -*x*, -*y*, *z*-1/2; #15 -*x*, -*y*+1, *z*+1/2; #16 -*y*+1, -*x*+1, -*z*+3/2.

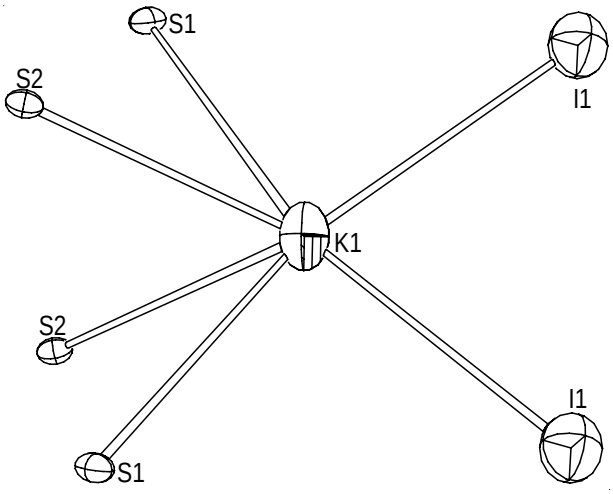
Table S2. List of known chalcogenoborato- *closo*-dodecaborates.[3]

Compounds	Structure [a]	Space Group	*d*(B–S/Se) / Å	*d*(B–B) / Å
$Cs_8[B_{12}(BSe_3)_6]$	0-D	*P*-1	1.981(8) – 2.011 (8)	1.753 (12) – 1.803 (12)
$Rb_8[B_{12}(BSe_3)_6]$	0-D	*P*-1	1.977 (14) – 2.027 (15)	1.696 (19) – 1.817 (16)
$Na_8[B_{12}(BSe_3)_6]$	0-D	$P2_1/c$	1.967 (4) – 2.021 (4)	1.764 (5) – 1.805 (5)
$K_8[B_{12}(BSe_3)_6]$	0-D	*C*m	1.963 (15) – 2.042 (19)	1.720 (18) – 1.830 (20)
$Rb_4Hg_2[B_{12}(BSe_3)_6]$	0-D	*P*-1	1.975 (16) – 1.999 (13)	1.770 (20) – 1.810 (20)
$Cs_4Hg_2[B_{12}(BSe_3)_6]$	0-D	*P*-1	1.989 (8) – 2.003 (9)	1.758 (13) – 1.803 (12)
$Rb_8[B_{12}(BS_3)_6]$	0-D	*P*-1	1.842(5) – 1.862 (5)	1.752 (6) – 1.809 (6)
$Cs_8[B_{12}(BS_3)_6]$	0-D	*P*-1	1.851 (6) – 1.866 (6)	1.767 (8) – 1.811 (8)
$Na_2[B_{18}Se_{16}]$	3-D	*P*-3	1.991 (7) – 1.997 (5)	1.752 (9) – 1.811(8)
$Na_6[B_{18}Se_{17}]$	1-D	*C*2/c	1.985 (7) – 2.005 (8)	1.742 (11) – 1.794 (11)

[a] 0-D, 1-D and 3-D represent discrete, chain and three dimensional structures, respectively.



(a)



(b)

Figure S1. Coordination geometries of B, Sm, Ga and K in **1** with 30% thermal ellipsoids.

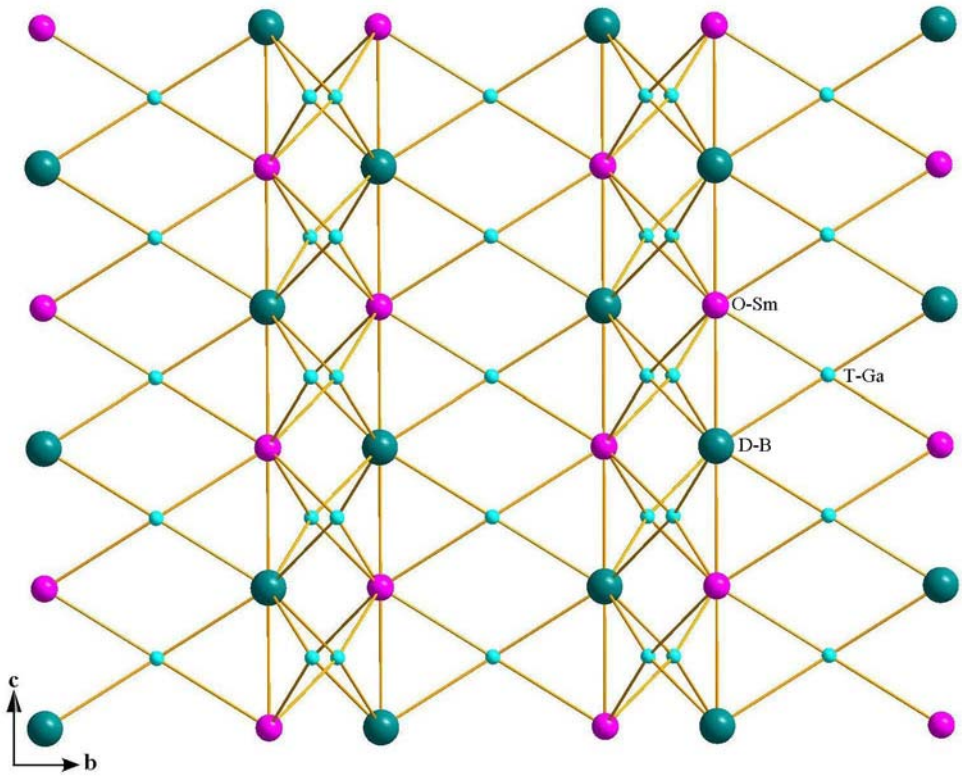


Figure S2. Simplified honeycomb-like open-framework of **1** along the *a* direction, where the dark yellow, turquoise and pink balls represent B_{12} dodecaborate (D-B), GaS_4 tetrahedra (T-Ga) and SmS_6 octahedra (O-Sm), respectively.

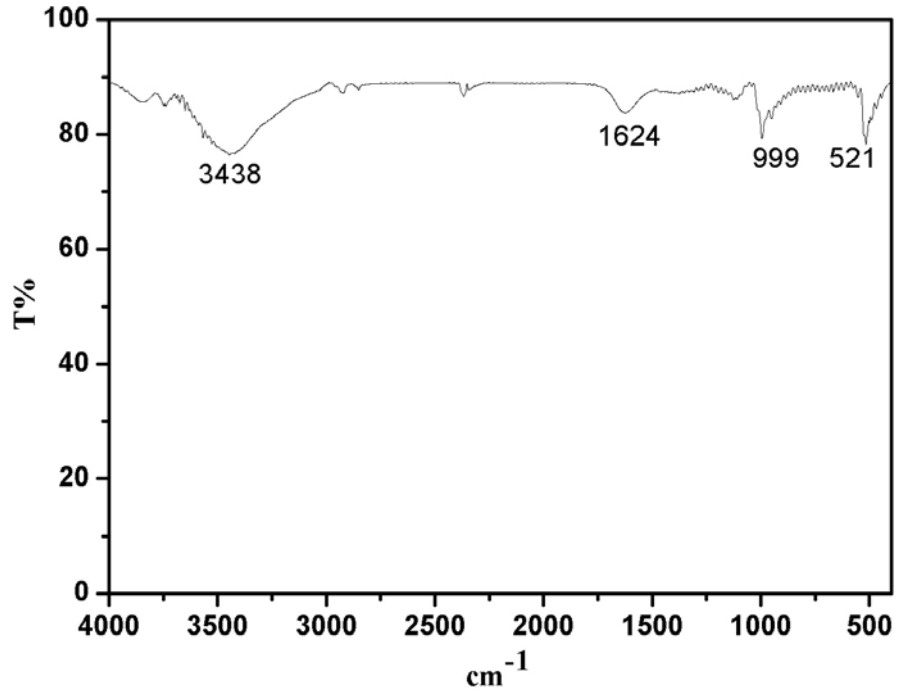


Figure S3. FT-IR spectrum of **1**.

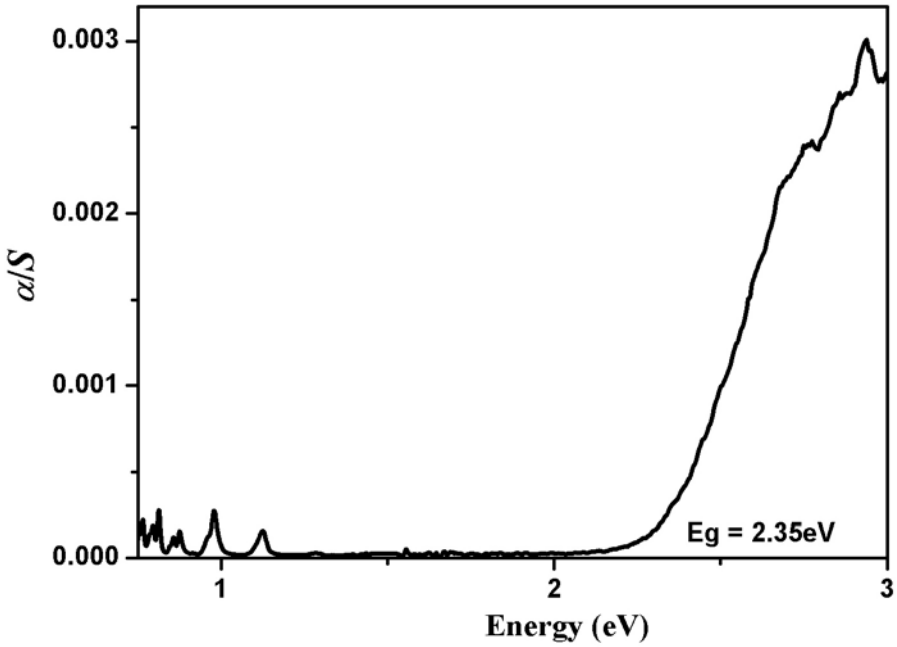


Figure S4. Diffuse reflectance spectrum of **1**.

References**:**

1 Siemens, *SHELXTL*^{TM} *Version 5 Reference Manual*, Siemens Energy & Automation Inc., Madison, Wisconsin, USA, **1994**.

2 (a) W. W. Wendlandt, H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, **1966**; (b) G. Kortüm, *Reflectance Spectroscopy*, Springer, **1969**.

3 See the reference 5 in the manuscript.