Supporting Information

$KEu_2In_3B_{12}S_{13}$: A Novel Type of Thioborate Featuring $B_{12}S_{12}$ Cluster and Unique In_6S_6 12-membered Ring

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Experimental Section

Synthesis. High-temperature solid-state method was taken to synthesize the crystals of $KEu_2In_3B_{12}S_{13}$ (**1**). All starting materials were used as received without further purification. Considerable efforts have been devoted to systhesize **1**, and eventually an optimized routine with a high yield was found. For which, a 500 mg mixture of Eu_2O_3 (99.9 %), In_2O_3 (99.9 %), S (99.95 %) and B (99 %) with the molar ratios of Eu : 3In : 32B : 17S, and additional 400 mg KI (99 %) as reactive flux, were used as the starting materials; which were hand-ground in an agate mortar for 30 minutes. The obtained mixture was pressed into a pellet and then loaded into an evacuated quartz ampoule with a vacuum degree of 1×10^{-4} Torr. The quartz tube was put in a muffle furnace and heated to 950 °C in 25 h and kept for 7 days, and then cooled down to 300 °C in 5 days, and powered off.

Structure Determination. Single crystal X-ray diffraction experiment was performed on a Bruker D8 QUEST X-ray diffractometer equipped with a graphite-monochromated Mo-Kα (λ

= 0.71073 Å) radiation at 296 K. Within Olex2, the structure was solved by Direct Methods with ShelXT (Sheldrick, 2015) and refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters for all atoms.[1] The final refinement included anisotropic displacement parameters for all atoms and a secondary extinction correction. The crystallographic data of **1** are listed in Table S1, and the atom positions and anisotropic displacement parameters (ADP), and bond distances are listed in Table S2 and Table S3, respectively. The cif document of **1** is also deposited with the CCDC number of 2143270.

Semiquantitative microscopic element analysis on single crystals of **1** was performed on a field-emission scanning electron microscope (JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDS, Oxford INCA). The EDS analysis reveals approximate K/Eu/In/S ratios of 1 : 1.82 : 2.74 : 10.25 (B could not be detected since it is too light), and no other elements were detected (Fig. S1 and Table S4). The exact compositions were established from the X-ray structure determination.

Considering the structure of **1** is heavily disordered, involving cooccupation and spilt sites, it is necessary to make a detailed description about the structure solution process, which can be described below. (1) The following EDS analysis results on several single crystals of **1** indicate that K, Eu, In and S exist in the crystals of **1**, and their molar ratios are close to the chemical formula determined from structure solution. (2) All the B and In sites are fully occupied with reasonable anisotropic displacement parameters (ADPs). (3) There are three independent S atoms in the structure, and two of them are fully occupied without disorder, while the third one having no bonding with B and In atoms splits into two neighboring sites with a total occupancy of 0.5. (4) Firstly, when one Eu, one In, two B, and three S atoms were assigned, there was a large residual peak with the electron density of 6.7 near the Eu site; so, it must consider splitting it into two neighboring sites as suggested. On the other hand, as evidenced by the EDS result, K element exists in the structure. When considering the reasonable chemical bond distances, K could only occupy the Eu site. Therefore, K and Eu were assigned to co-occupy the same sites. When freely refining the two Eu/K sites, the chemical formula $KEu_2In_3B_{12}S_{13}$ could be obtained. It must be mentioned that the R1 and wR2 values were 0.0665 and 0.2064, respectively, if no split considered. When split was considered, the R1 and wR2 values were decreased to 0.0354 and 0.0776, respectively.

Power X-Ray Diffraction Characterization. Powder X-ray diffraction (PXRD) measurement of **1** was carried out with a Bruker D8 Advance diffractometer at 40 kV and 100 mA for Cu-Kα radiation (λ = 1.5406 Å) at room temperature. The 2θ range was 10–60° with a scan step width of 1°. The calculated pattern was generated using the Mercury program with its single-crystal structure data.

X-Ray Photoelectron Spectroscopy Analysis. X-ray photoelectron spectroscopy (XPS) (Thermofisher Scientific, ESCALAB250Xi) measurement was carried out to determine the oxidation states of Eu atoms in **1**. It was carried out with a commercially-available X-ray generator, equipped with an Al/Mg dual anode. The operating conditions were 15 kV and 20 mA. Ejected photoelectrons were analyzed in energy with a double-pass cylindrical mirror analyzer (CMA) (Perkin-Elmer Instrument, model 15-255G).

UV–vis–NIR Diffuse Reflectance Spectroscopy. The UV-vis-NIR diffuse reflectance spectrum was recorded at room temperature using a powder $BaSO_4$ sample as a standard on a computer-controlled Cary 5000 UV–vis–NIR spectrometer equipped with a diffuse reflectance accessory in 200−2500 nm. The spectrum was calculated from the reflection spectrum by the Kubelka-Munk function:[2]

$$F(R) = (1-R)^2/(2R) = K/S$$

where R is the reflectance, K is the absorption, and S is the scattering. In the (K/S) versus E plot, extrapolating the linear portion of the rising curve to zero gives rise to the onset of absorption.

Magnetic Susceptibility Measurement. Field-cooled (FC) direct-current (*dc*) variable temperature magnetic susceptibility was measured by Quantum Design PPMS from 2 to 300 K in an applied magnetic field of 1000 Oe. Freshly prepared polycrystalline powdery sample of **1** was secured in a gel capsule. The polycrystalline powdery sample of **1** was secured in a gel capsule. The diamagnetic correction was made using Pascal's constants

Calculation Details. The electronic structure calculation including band structure and density of states (DOS) were performed using the CASTEP module in Material Studio[3]. Generalized gradient approximation (GGA) by PBE was adopted to describe the exchange-correlation energy. The electronic configurations for In, B, S, K, and Eu were 5s and 5p, 2s and 2p, 3s and 3p, 4s , 5s/6s and 4f, respectively, and the cutoff energy 700 eV was set. The numerical integration of the Brillouin zone was implemented by employing 2 × 2 × 4 Monkhorst-Pack *k*-point sampling. The Fermi level at 0 eV was chosen as the reference.

Table S1. Crystal data and structure refinement parameters for **1**.

Chemical formula	**$KEu_2In_3B_{12}S_{13}$**
Fw	1234
T (K)	296
Crystal system	trigonal
Space group	$R\bar{3}m$
Z	3
a (Å)	9.8053(3)
c (Å)	20.7184(11)
V (Å^3)	1725.08(14)
D_{calcd} (g cm^{-3})	3.571
μ (mm^{-1})	9.737
F(000)	1683.0
2θ range (°)	5.9 to 49.968
Indep. Reflns./R_{int}	403/0.0220
Data/restraints/parameters	403/8/49
GOF on F^2	1.081
$R1^a$ ($I > 2\sigma(I)$)	0.0354
$wR2^b$ (all data)	0.0786

$^aR1 = ||F_o| - |F_c||/|F_o|$. $^bwR2 = [w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($U_{eq}{}^a$, Å^2 × 10^3) for **1**.

Atom	***x***	***y***	***z***	**U_{eq}/Å^2**
Eu(1A)	2754(2)	1377.1(11)	6089.6(9)	32.6(7)
K(1A)	2754(2)	1377.1(11)	6089.6(9)	32.6(7)
Eu(1B)	2850(20)	1425(11)	6377(9)	32.6(7)
K(1B)	2850(20)	1425(11)	6377(9)	32.6(7)
In(1)	5000	5000	5000	24.4 (4)
B(1)	4328(6)	5672(6)	6506(4)	13.9(18)
B(2)	4559(10)	7280(5)	6031(4)	11.9(18)
S(1)	5886(3)	7942.8(13)	5320.6(9)	16.9(5)
S(2)	5365.8(13)	4634.2(13)	6241.2(10)	19.2(5)
S(3A)	0	0	5478(15)	59(6)
S(3B)	0	0	5478(15)	59(6)

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

Table S3. Selected bond distances (Å) for **1**.

Bond	**Dist.**	**Bond**	**Dist.**
K/Eu(1A)–S(1) × 2	3.470(2)	In(1)–S(2) × 2	2.646(2)
K/Eu(1A)–S(1)	3.142(3)	B(1)–B(1) × 2	1.816(10)
K/Eu(1A)–S(2) × 2	3.082(2)	B(1)–B(2) × 3	1.774(9)
K/Eu(1A)–S(2)	2.946(2)	B(2)–B(2) × 2	1.803(15)
K/Eu(1A)–S(2)	2.946(2)	B(1)–S(2)	1.846(9)
K/Eu(1A)–S(3A)	2.660(15)	B(2)–S(1)	1.853(9)
In(1)–S(1) × 4	2.649(1)	S(3A)–S(3A)#13	1.98(6)

Table S4. EDS analysis result for **1**.

Single crystal	**#1**	**#2**	**#3**
Eu	12.1%	11.27%	11.18%
In	18.1%	17.23%	16.57%
K	6.1%	6.21%	6.68%
S	63.6%	65.30%	65.58%

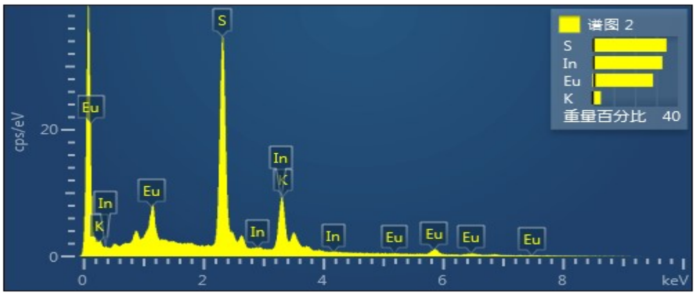

Fig. S1 EDS analysis for **1**.

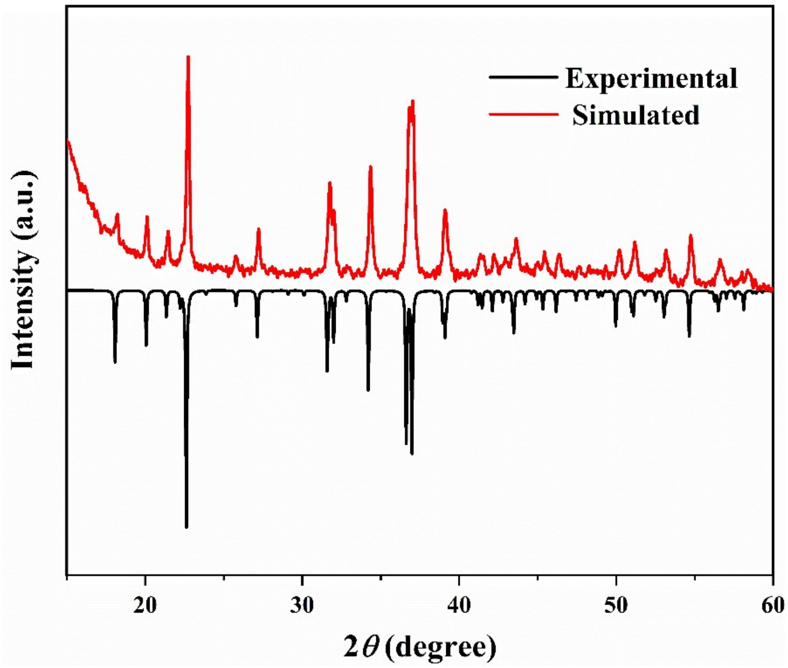

Fig. S2 Powder X-ray diffraction pattern for **1**.

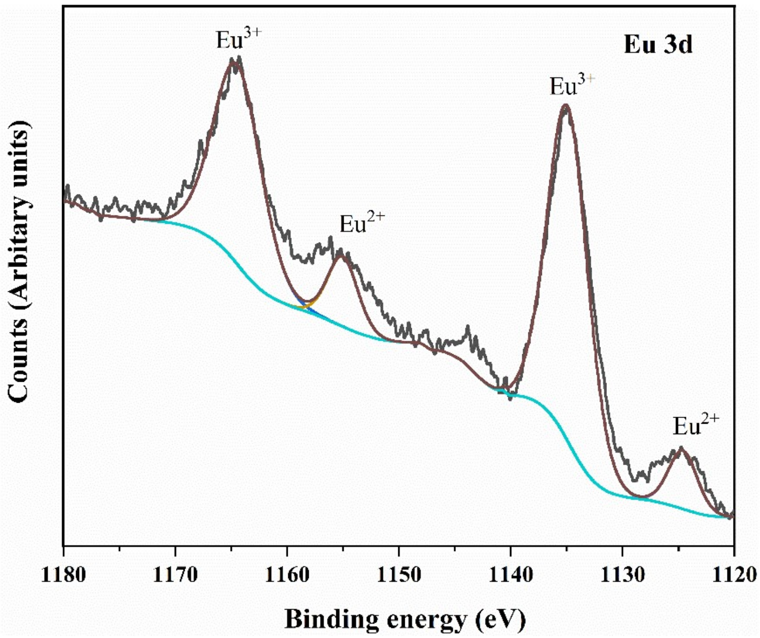

Fig. S3 XPS Eu-3d spectrum of **1**.

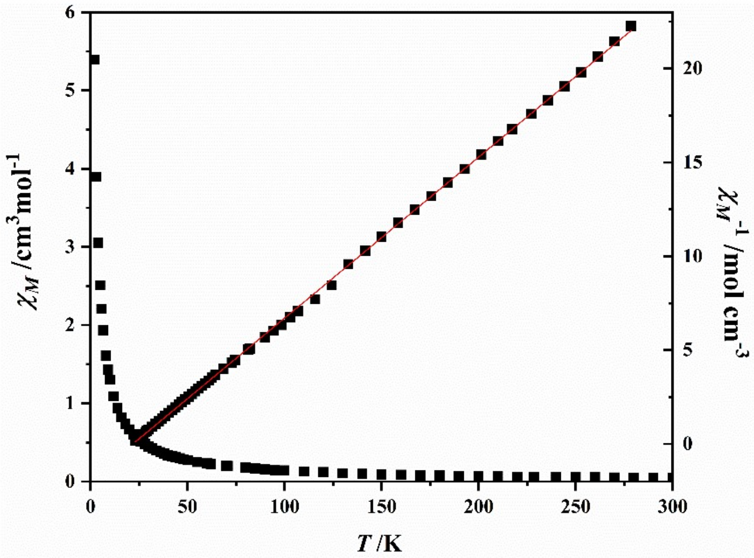

Fig. S4 Temperature-dependent magnetic susceptibilities of **1**.

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2. (a) W. W. Wendlandt and H. G. Hecht, *Reflectance Spectroscopy*, Interscience Publishers, New York, **1966**; (b) G. Kortüm, *Reflectance Spectroscopy*, Springer, **1969**.
3. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. Probert, K. Refson and M. C. Payne, *Z. Kristallogr. - Cryst. Mater*., 2005, **220**, 567−570.