Supplementary Information

Structure and opto-thermo electronic property of a newly $(Bi(Bi_2S_3)_9I_3)_{2/3}$ hexagonal nano-/micro- rod

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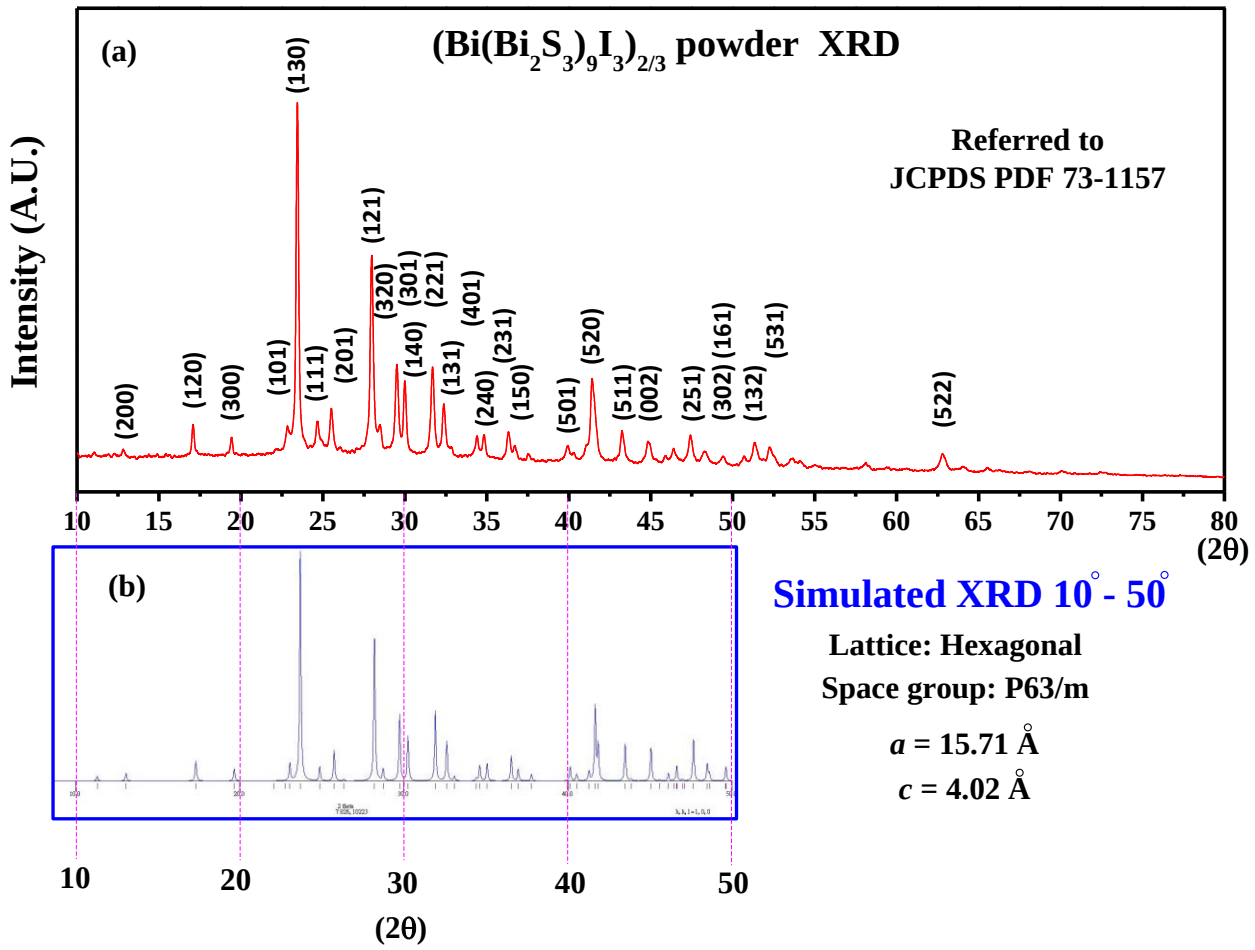
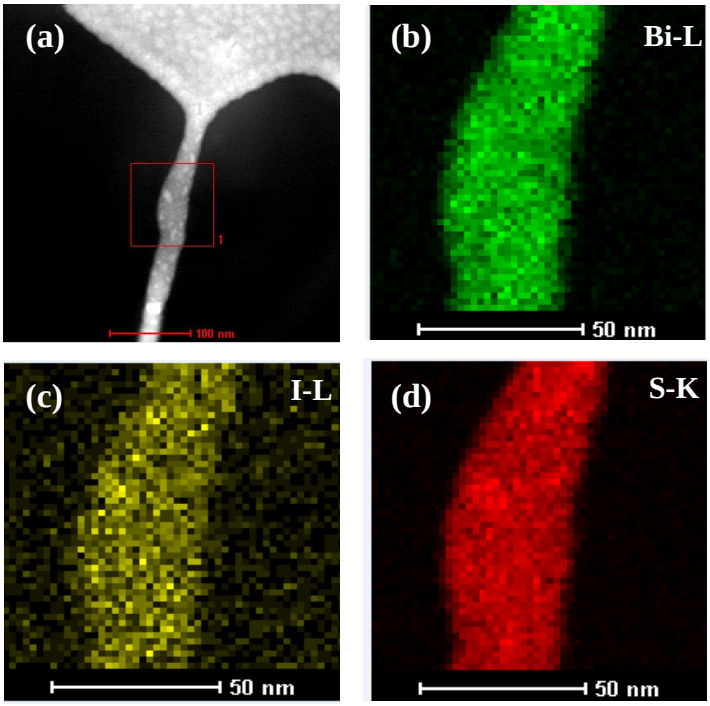


Fig. S1. (a) Experimental X-ray diffraction (XRD) pattern of the $(Bi(Bi_2S_3)_9I_3)_{0.667}$ grown by CVT. The sample preparation is accomplished by finely ground some small crystals of $(Bi(Bi_2S_3)_9I_3)_{0.667}$ into powder, and the powder XRD pattern is taken and recorded by means of a Cu K_α radiation in the 2θ range of 10° - 80°. The peak angle (2θ) and plane index for each of the diffraction peaks are compared and referred to previous JCPDS card No. 73-1157 [18]. The lattice constants determined from the experimental XRD results in (a) are *a*=15.71 Å and *c*=4.02 Å, respectively. The structure of crystal lattice is hexagonal. (b) Simulated XRD curve of $(Bi(Bi_2S_3)_9I_3)_{0.667}$ using the obtained lattice constants and crystal structure from 10° - 50°. The relative intensities and peak positions of the simulated XRD pattern approximately agree well with the experimental data of the same 2θ range in (a).

$(Bi(Bi_2S_3)_9I_3)_{2/3}$ EDX mapping



Element	Weight %	Atomic %
S(K)	17.509	54±3
I(K)	9.499	6±2
Bi(L)	78.991	40 ±2

$(Bi(Bi_2S_3)_9I_3)_{2/3} \sim Bi_{12.667}S_{18}I_2$

Expected: S ~ 55.1%
I ~ 6.1%
Bi ~ 38.8%

Fig. S2. The energy dispersive X-ray (EDX) mapping of $(Bi(Bi_2S_3)_9I_3)_{0.667}$ from HRTEM analysis. (a) The HRTEM picture of $(Bi(Bi_2S_3)_9I_3)_{0.667}$ after a focused-ion-beam cutting. The area for mapping the element content is displayed by a red square. (b) Green color mapping of Bi L line from the square in (a). (c) The composition of iodine is shown by yellow-color mapping with the I L line. (d) Red color mapping of S K line. The EDX analysis of atomic percentage of the as-grown crystal is 54±3 % for sulfur, 6±2 % for iodine, and 40±2 % for bismuth, respectively. The values are in good agreements with those of $(Bi(Bi_2S_3)_9I_3)_{0.667}$ corresponding to a $Bi_{12.667}S_{18}I_2$ stoichiometric content (i.e. S ~ 55.1 %, I ~ 6.1 %, and Bi ~ 38.8 %).

Figure S1(a) displays the experimental powder XRD pattern of the as-grown $(Bi(Bi_2S_3)_9I_3)_{0.667}$ by CVT. The powdered sample was obtained by finely ground the small bulk crystals of $(Bi(Bi_2S_3)_9I_3)_{0.667}$ into powder. The XRD pattern is similar to that of previous JCPDS card No. 73-1157 [18] and that of the needle-like crystals grown by polyol method.[17] The analysis of

XRD result in Fig. S1(a) reveals the lattice constants of $(Bi(Bi_2S_3)_9I_3)_{0.667}$ are a=15.71 Å and c=4.02 Å and crystal structure is hexagonal with a symmetry of space group P63/m. Detailed analysis of the structure, atomic coordination and stoichiometry using XRD are also included in APPENDIX 1. Figure S1(b) shows the simulation curve of XRD from 2θ=10° to 50° using the obtained structure and lattice parameters in Fig. S1(a). The relative intensity and peak pattern of the simulation curve show good agreement with the experimental data in Fig. S1(a). It verifies hexagonal structure of the $(Bi(Bi_2S_3)_9I_3)_{0.667}$ nano-/micro- rods grown by CVT.

To verify the stoichiometry of the as-grown $(Bi(Bi_2S_3)_9I_3)_{0.667}$ single crystals, the EDX experiment was also implemented. Fig. S2 shows the EDX analysis of the as-grown $(Bi(Bi_2S_3)_9I_3)_{0.667}$ nano rod from the HRTEM experiment. Fig. S2(a) shows the area of EDX analysis, Fig. S2(b) shows the Bi L-line mapping, Fig. S2(c) shows the I L-line mapping and Fig. S2(d) shows the S K-line mapping, respectively. The values of stoichiometric content of the nano rod are calculated to be 54±3 % for sulfur, 6±2 % for iodine, and 40±2 % for bismuth, respectively. The obtained stoichiometric compositions are corresponding to $Bi_{12.667}S_{18}I_2$, and which matches well with $(Bi(Bi_2S_3)_9I_3)_{2/3}$. The result also matches well with the XRD analysis in APPENDIX 1.

Optical characterization

Thermoreflectance (TR) experiments of the m-plane $(Bi(Bi_2S_3)_9I_3)_{0.667}$ were implemented using indirect heating manner with a gold-evaporated quartz plate as the heating element.[25,26] Prior

to the TR experiment, the sheet-type sample of the rod was polished from a thick rod into a thin sample. The thin m-plane sample was closely attached on the heating element by silicone grease. The on-off heating disturbance uniformly modulates the thin m-plane $(Bi(Bi_2S_3)_9I_3)_{0.667}$ periodically. An 150 W tungsten halogen lamp (or an 150 W xenon-arc lamp) filtered by a PTI 0.2-m monochromator provided the monochromatic light. The incident light is focused onto the sample with a spot size less than hundred μm^2. An InGaAs photodetector acted as the detection unit and the TR signal was measured and recorded via an EG&G model 7265 lock-in amplifier. For transmittance measurement, the same monochromatic system and light source as those of TR were used. The thickness of the m-plane $(Bi(Bi_2S_3)_9I_3)_{0.667}$ sample is about 50 μm. The incident monochromatic light was chopped (200 Hz), and the transmission signal was measured and recorded via an EG&G model 7265 lock-in amplifier that combined with the InGaAs photodetector. A closed-cycle cryogenic refrigerator with a thermometer controller facilitates the low-temperature measurements for transmittance and TR measurements.

The μRaman measurement of the m-plane $(Bi(Bi_2S_3)_9I_3)_{0.667}$ hexagonal micro rod was carried out by using a RAMaker integrated micro-Raman-PL identified system equipped with one 532-nm solid-state diode pumped laser as the excitation sources. A light-guiding microscope (LGM) equipped with one Olympus objective lens (50x, working distance ~8 mm) acts as the inter-connection coupled medium between the nano rod sample, incident and reflected lights, and charge-coupled-device (CCD) spectrometer. A pair of dichroic sheet polarizers (in visible to infrared range) was utilized for polarization-dependent measurements. The measurement

configuration of polarized μRaman is setting as $Z(XX)\bar{Z}$ and $Z(XY)\bar{Z}$ on the m-plane $(Bi(Bi_2S_3)_9I_3)_{0.667}$, where X is along the *c* axis of the hexagonal rod.

Supplementary Information Reference:

25 C. H. Ho, H. W. Lee, and Z. H. Cheng, *Rev. Sci. Instrum.* 2004, **75**, 1098-1102.

26 C. H. Ho and H. H. Chen, *Sci Rep.* 2014, **4**, 6143.

APPENDIX 1

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Table 1. Crystal data and structure refinement for 1.

Identification code	1
Empirical formula	Bi12.667 I2 S18
Formula weight	3547.62
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Hexagonal, P6(3)/m
Unit cell dimensions	a = 15.6203(6) A alpha = 90 deg. b = 15.6203(6) A beta = 90 deg. c = 4.0211(2) A gamma = 120 deg.
Volume	849.68(8) A^3
Z, Calculated density	1, 6.933 Mg/m^3
Absorption coefficient	69.960 mm^-1
F(000)	1473
Crystal size	0.400 x 0.060 x 0.040 mm
Theta range for data collection	1.505 to 28.271 deg.
Limiting indices	-20<=h<=20, -19<=k<=20, -5<=l<=5
Reflections collected / unique	6454 / 807 [R(int) = 0.0386]
Completeness to theta = 25.242	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	807 / 0 / 37
Goodness-of-fit on F^2	1.138
Final R indices [I>2 sigma(I)]	R1 = 0.0205, wR2 = 0.0453
R indices (all data)	R1 = 0.0208, wR2 = 0.0455
Extinction coefficient	0.00113(8)
Largest diff. peak and hole	3.719 and -2.379 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Bi(1)	8785(1)	4891(1)	7500	15(1)
Bi(2)	10556(1)	7591(1)	2500	20(1)
Bi(3)	10000	10000	-3944(5)	33(1)
I(1)	6667	3333	2500	16(1)
S(1)	9828(2)	8148(2)	-2500	13(1)
S(2)	8682(1)	6052(1)	2500	12(1)
S(3)	10669(1)	6128(1)	7500	12(1)

Table 3. Anisotropic displacement parameters (A^2 x 10^3) for 1.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Bi(1)	12(1)	14(1)	18(1)	0	0	6(1)
Bi(2)	21(1)	29(1)	17(1)	0	0	18(1)
Bi(3)	27(1)	27(1)	45(1)	0	0	14(1)
I(1)	15(1)	15(1)	17(1)	0	0	7(1)
S(1)	13(1)	15(1)	13(1)	0	0	8(1)
S(2)	12(1)	12(1)	12(1)	0	0	6(1)
S(3)	11(1)	11(1)	12(1)	0	0	6(1)