

Supporting Information for

Cationic Quaternary Chalcogenide Nanobelts: $\text{Hg}_4\text{In}_2\text{Q}_3\text{Cl}_8$ (Q = S, Se, Te)

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1. Materials and methods

All the chemicals used for synthesis are of analytical grade and directly used without further purification. The optical diffuse reflectance spectra were measured at room temperature on a Perkin-Elmer Lambda 900 UV–vis-NIR spectro-meter equipped with an integrating sphere. BaSO_4 was used as the reference material, and the polycrystalline samples were ground well before the measurement. The absorption (α/S) data were calculated from the reflectance using the Kubelka–Munk function: $\alpha/S = (1-R)^2/2R$, in which R is the reflectance at a given wavelength, α is the absorption coefficient, and S is the scattering coefficient.¹ Thermal stability studies were carried out on a TGA Q500 instrument under N_2 at a heating rate of 10 °C. The elemental analyses of Hg, In, S, Se, Te and Cl have been examined with the aid of an EDX-equipped JEOL/JSM-6360A SEM. Powder X-ray diffraction data were recorded on a Bruker D8 Advance diffractometer with a graphite-monochromatized $\text{Cu } K\alpha$ radiation. The operating 2θ angle ranges from 10° to 70°. Simulation of the XRD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program version 1.4.2 available free of charge via the Internet at <http://www.iucr.org>.

2. Synthesis of $\text{Hg}_4\text{In}_2\text{Q}_3\text{Cl}_8$ (Q = S, Se, Te).

Hg_2Cl_2 (1.15 mmol), In_2Q_3 (0.30 mmol) and Q (1.15 mmol) were loaded and sealed in an evacuated fused silica tube (12 mm i.d.) under high vacuum ($\sim 10^{-3}$ Pa). Then it was placed into a box furnace and heated to 200 °C within 5 h, and kept at this temperature for 50 h, subsequently increased to 450 °C within 10 h, and kept at 450 °C for 100 h, followed by cooling to 50 °C at a rate of 5°C/h, finally the furnace was turned off. The presence of each element in the crystals was confirmed by the EDS analysis.

3. Single crystal X-ray data collections and structure determinations.

One crystal of $\text{Hg}_4\text{In}_2\text{Q}_3\text{Cl}_8$ (Q = S, Se, Te) with suitable dimensions was mounted on the glass fibers. Diffraction data were collected on a Bruker APEX II CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71073$ Å) at room temperature. The data sets were corrected by empirical absorption correction. The structures were solved by the direct methods and refined by the full-matrix least-squares fitting on F^2 in the orthorhombic Pnma (No. 62) space group with the aid of the SHELX-97 software package.² All of the atoms were refined with the anisotropic displacement parameters. The structure was verified using the ADDSYM algorithm from the program PLATON.³

4. Computational Methods.

The bands structures of the crystals were studied by Density Functional Theory (DFT) based quantum chemical calculations using Cambridge Series Total Energy Package (CASTEP) program, implemented in the Materials Studio 5.0. Single-crystal structural data determined by single-crystal X-ray diffraction analysis was used to generate the starting geometries of S, Se and Te based crystals. A complete geometry optimization of each lattice was performed till the forces on each atom were less than 0.05 Å/eV and the total stress on the cell was less than 0.05 GPa. All the calculations were done using GGA-PBE functional and ultrasoft pseudo-potentials with a kinetic energy cut off of 450 eV. For the geometry optimization of S, Se, and Te crystals a monkhorsth *k*-point grid of $3\times 2\times 2$ were employed

for the geometry optimization, respectively. The valence atomic configurations were $5d^{10}6s^2$ for Hg, $4d^{10}5s^25p^1$ for In, $3s^23p^5$ for Cl, $3s^23p^4$ for S, $4s^24p^4$ for Se and $5s^25p^4$ for Te. The other parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code.

Table S1. Crystal Data and Structure Refinements for $\text{Hg}_4\text{In}_2\text{Q}_3\text{Cl}_8$ (Q = S, Se, Te).^a

Empirical formula	$\text{Hg}_4\text{In}_2\text{S}_3\text{Cl}_8$	$\text{Hg}_4\text{In}_2\text{Se}_3\text{Cl}_8$	$\text{Hg}_4\text{In}_2\text{Te}_3\text{Cl}_8$
Formula weight	1411.78	1552.48	1698.40
<i>a</i> (Å)	13.510(3)	13.7113(11)	15.057(3)
<i>b</i> (Å)	7.3400(15)	7.4616(6)	7.6745(15)
<i>c</i> (Å)	18.190(4)	18.4305(15)	18.879(4)
<i>V</i> (Å ³)	1803.8(6)	1885.6(3)	2181.6(8)
<i>F</i> (000)	2408	2624	2839
<i>D</i> _{cal} (g/cm ³)	5.199	5.469	5.171
<i>RI</i> , <i>wR2</i> (<i>I</i> > 2σ(<i>I</i>)) ^b	0.0496, 0.1361	0.0356, 0.0776	0.0354, 0.0750
<i>RI</i> , <i>wR2</i> (all data)	0.0601, 0.1450	0.0415, 0.0805	0.0426, 0.0776
GOOF on <i>F</i> ²	1.079	1.059	1.074

^a For all structures, *Z* = 4, space group = *Pnma*, *T* = 293(2) K, and λ = 0.71073 Å.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

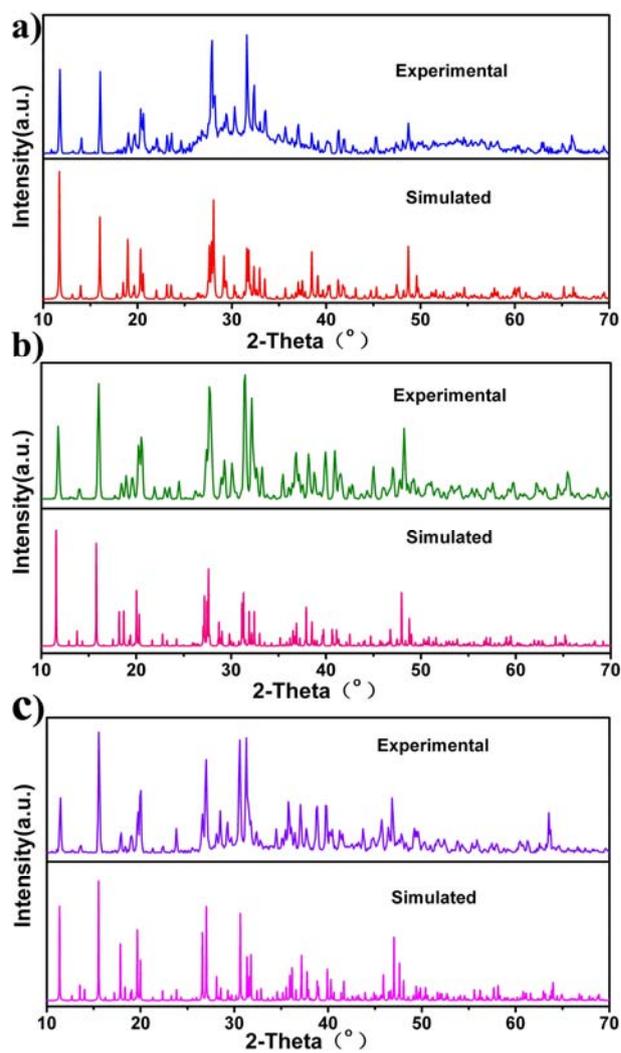


Fig. S1 Experimental and simulated XRD patterns of (a) $\text{Hg}_4\text{In}_2\text{S}_3\text{Cl}_8$
(b) $\text{Hg}_4\text{In}_2\text{Se}_3\text{Cl}_8$ (c) $\text{Hg}_4\text{In}_2\text{Te}_3\text{Cl}_8$

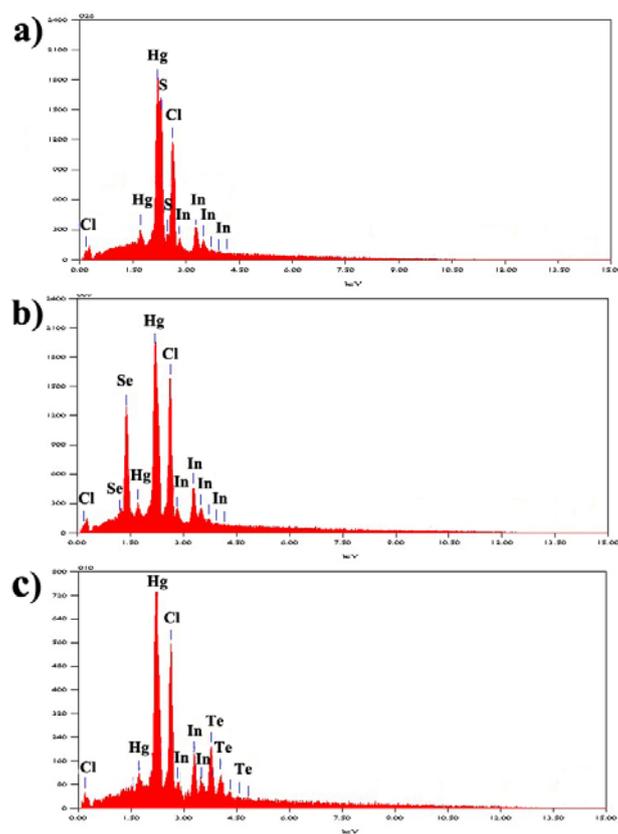


Fig. S2 Energy-dispersive X-ray spectroscopy analysis of (a) $\text{Hg}_4\text{In}_2\text{S}_3\text{Cl}_8$
(b) $\text{Hg}_4\text{In}_2\text{Se}_3\text{Cl}_8$ (c) $\text{Hg}_4\text{In}_2\text{Te}_3\text{Cl}_8$

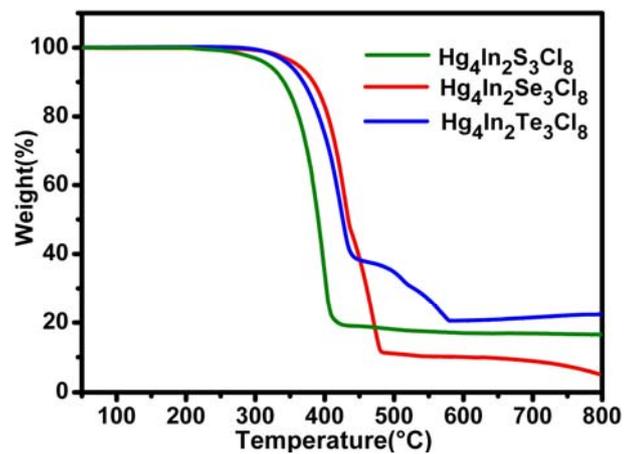


Fig. S3 TGA analysis of $\text{Hg}_4\text{In}_2\text{Q}_3\text{Cl}_8$ (Q = S, Se, Te).

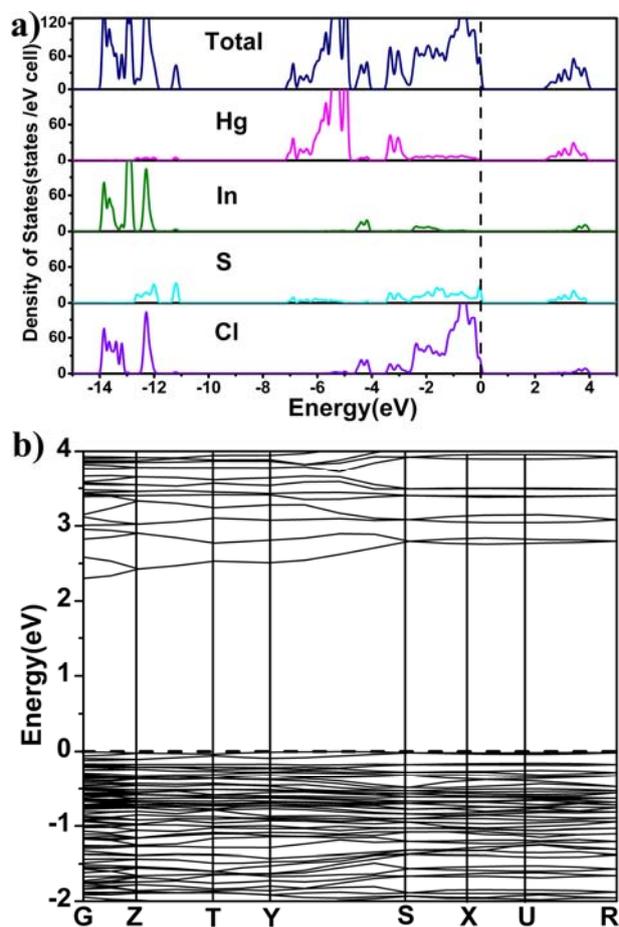


Fig. S4 Total and partial density of states (DOS) and band structure of $\text{Hg}_4\text{In}_2\text{S}_3\text{Cl}_8$.

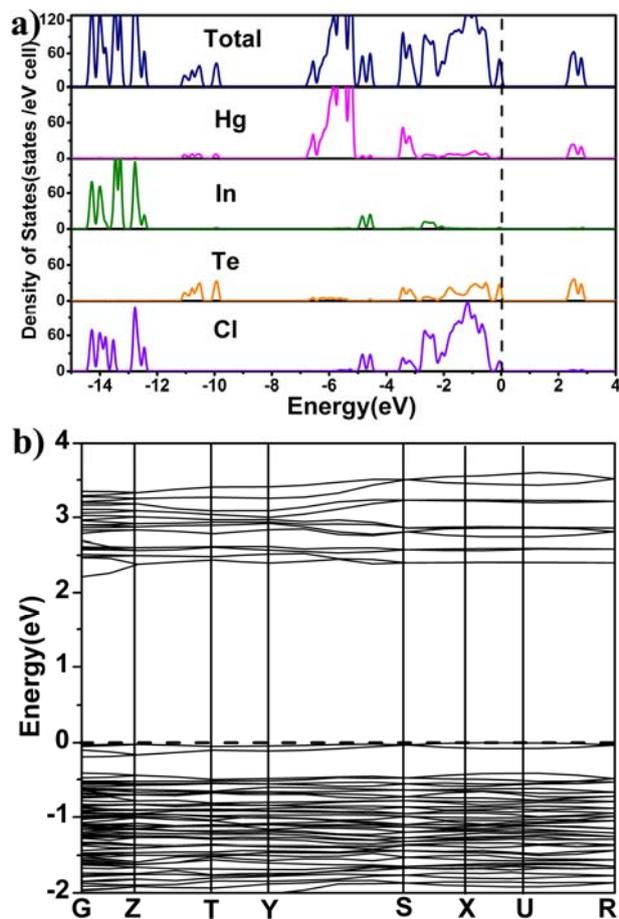


Fig. S5 Total and partial density of states (DOS) and band structure of $\text{Hg}_4\text{In}_2\text{Te}_3\text{Cl}_8$.

References

- 1 G. Kortüm, *Reflectance Spectroscopy*, Springer, New York, 1969.
- 2 G. M. Sheldrick, *Program for Structure Refinement*, University of Göttingen, Germany, 1997.
- 3 A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.