

## Supporting Information

### **Layered Mixed-Anion Chalcogenides $\text{Pb}_4\text{Sb}_4\text{Q}_9\text{Cl}_2$ (Q = S, Se): Puckered 2D Frameworks, Indirect Band Gaps, and Low Thermal Conductivity**

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**Table S1.** Atomic coordinates, site occupancies, and equivalent isotropic displacementparameters for (a)  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and (b)  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ .a)  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$ 

| Atom | W.P. | x/a        | y/b         | z/c        | U <sub>eq</sub> <sup>a</sup> | Site occ. |           |
|------|------|------------|-------------|------------|------------------------------|-----------|-----------|
| Pb1  | 4h   | 0.87258(5) | 0.06986(4)  | 0.5        | 0.0220(3)                    | Pb        | 1         |
| Pb2  | 4h   | 0.75966(4) | 0.31819(4)  | 0.5        | 0.0193(3)                    | Pb        | 1         |
| Sb1  | 8i   | 0.00491(9) | 0.27249(9)  | 0.0559(10) | 0.0276(12)                   | Sb        | 0.5       |
| Sb2  | 8i   | 0.87681(9) | 0.51828(10) | 0.0584(8)  | 0.0267(10)                   | Sb        | 0.5       |
| S1   | 4g   | 0.7307(2)  | 0.4497(2)   | 0.0        | 0.0140(7)                    | S         | 1         |
| S2   | 4g   | 0.8557(3)  | 0.2078(2)   | 0.0        | 0.0131(7)                    | S         | 1         |
| X1   | 4h   | 0.9299(3)  | 0.3957(3)   | 0.5        | 0.0235(9)                    | S/Cl      | 0.93/0.07 |
| X2   | 4h   | 0.6809(3)  | 0.1218(3)   | 0.5        | 0.0222(8)                    | S/Cl      | 0.87/0.13 |
| X3   | 4h   | 0.5496(3)  | 0.3298(3)   | 0.5        | 0.0275(10)                   | S/Cl      | 0.75/0.25 |
| Cl1  | 2a   | 0.0        | 0.0         | 0.0        | 0.0224(12)                   | Cl        | 1         |

b)  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ 

| Atom | W.P. | x/a        | y/b         | z/c        | U <sub>eq</sub> <sup>a</sup> | Site occ. |           |
|------|------|------------|-------------|------------|------------------------------|-----------|-----------|
| Pb1  | 4h   | 0.75966(4) | 0.31819(4)  | 0.5        | 0.0193(3)                    | Pb        | 1         |
| Pb2  | 4h   | 0.87258(5) | 0.06986(4)  | 0.5        | 0.0220(3)                    | Pb        | 1         |
| Sb1  | 8i   | 0.87681(9) | 0.51828(10) | 0.0584(8)  | 0.0267(10)                   | Sb        | 0.5       |
| Sb2  | 8i   | 0.00491(9) | 0.27249(9)  | 0.0559(10) | 0.0276(12)                   | Sb        | 0.5       |
| Se1  | 4g   | 0.7307(2)  | 0.4497(2)   | 0.0        | 0.0140(7)                    | Se        | 1         |
| Se2  | 4g   | 0.8557(3)  | 0.2078(2)   | 0.0        | 0.0131(7)                    | Se        | 1         |
| X1   | 4h   | 0.9299(3)  | 0.3958(3)   | 0.5        | 0.0235(9)                    | Se/Cl     | 0.93/0.07 |
| X2   | 4h   | 0.5496(3)  | 0.3298(3)   | 0.5        | 0.0272(10)                   | Se/Cl     | 0.87/0.13 |
| X3   | 4h   | 0.6809(3)  | 0.1218(3)   | 0.5        | 0.0225(8)                    | Se/Cl     | 0.75/0.25 |
| Cl1  | 2a   | 0.0        | 0.0         | 0.0        | 0.0224(12)                   | Cl        | 1         |

**Tables S2.** Selected interatomic distances (Å) for  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ .

| $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$ |          |             | $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ |          |             |
|---|----------|-------------|--|----------|-------------|
| (x=S)   | Contacts | Distance(Å) | (x=Se)   | Contacts | Distance(Å) |
| Pb1   | S1x2     | 2.918(3)    | Pb1  | Se1x2    | 2.9828(18)  |
| Pb1   | S2x2     | 3.030(3)    | Pb1  | Se2x2    | 3.1245(18)  |
| Pb1   | X1       | 2.829(4)    | Pb1  | X1       | 2.911(3)    |
| Pb2   | Cl1x2    | 3.0003(5)   | Pb2  | Cl1x2    | 3.0402(11)  |
| Pb2   | S2x2     | 2.969(3)    | Pb2  | Se2x2    | 3.0416(18)  |
| Pb2   | X2x2     | 3.085(4)    | Pb2  | X2x2     | 3.169(3)    |
| Pb2   | X3       | 2.992(4)    | Pb2  | X3       | 3.088(3)    |
| Sb1   | S1       | 2.453(4)    | Sb1  | Se1      | 2.607(3)    |
| Sb1   | X1       | 2.739(4)    | Sb1  | X1x2     | 2.889(9)    |
| Sb1   | X3       | 2.920(4)    | Sb1  | X3       | 2.971(10)   |
| Sb1   | X3x2     | 2.566(4)    | Sb1  | X3x2     | 2.690(10)   |
| Sb2   | S2       | 2.468(4)    | Sb2  | Se2      | 2.609(3)    |
| Sb2   | X1       | 2.866(5)    | Sb2  | X1       | 3.042(10)   |
| Sb2   | X2x2     | 2.501(4)    | Sb2  | X2x2     | 2.896(13)   |
| Sb2   | X2x2     | 2.848(4)    | Sb2  | X2x2     | 2.636(12)   |

**Table S3.** Details of Rietveld refinements for  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ .

| Chemical formula                                | $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$ | $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ |
|---|---|--|
| Formula weight                                  | 1674.2  | 2097.30  |
| Temperature, K                                  | 296(2)  |  |
| Wavelength, Å                                   | 0.6199  |  |
| Crystal system                                  | Orthorhombic                                  |  |
| Space group, Z                                  | <i>Pbam</i> (No 55), 2                        |  |
| <i>a</i> (Å)                                    | 15.031(1)                                     | 15.4645(8)                                     |
| <i>b</i> (Å)                                    | 15.525(1)                                     | 16.0721(1)                                     |
| <i>c</i> (Å)                                    | 4.0872(3)                                     | 4.18268(3)                                     |
| Volume, Å <sup>3</sup>                          | 953.78(1)                                     | 1039.60(1)                                     |
| Density (calculated), g/cm <sup>3</sup>         | 5.8323 (8)                                    | 6.71404(7)                                     |
| 2 $\theta$ Range                                | 2-35  |  |
| Linear Absorption coefficient, cm <sup>-1</sup> | 296.321(4)                                    | 376.196(4)                                     |
| $R_p$   | 2.90  | 2.28   |
| $R_{wp}$  | 4.85  | 3.47   |
| $R_{exp}$                                       | 1.01  | 1.05   |
| <i>GOF</i>                                      | 4.80  | 3.30   |

**Table S4.** SEM-EDS elemental analysis of  $\text{Pb}_4\text{Sb}_4\text{Q}_9\text{Cl}_2$  ( $\text{X} = \text{S}, \text{Se}$ ) from SEM-EDS

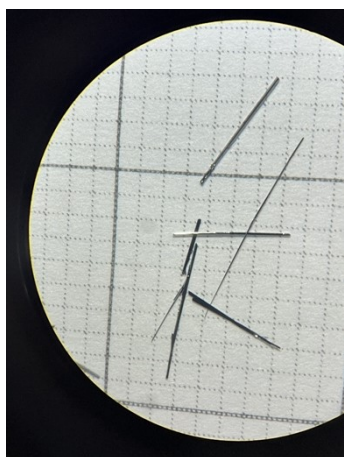
| $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$ |           |            | $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ |           |            |
|---|-----------|------------|--|-----------|------------|
|   | EXP. Mol% | Ideal Mol% |  | EXP. Mol% | Ideal Mol% |
| Pb  | 19.03     | 21.05      | Pb   | 20.52     | 21.05      |
| Sb  | 21.44     | 21.05      | Sb   | 20.78     | 21.05      |
| S   | 48.75     | 47.37      | Se   | 49.29     | 47.37      |
| Cl  | 10.78     | 10.53      | Cl   | 9.40      | 10.53      |

**Table S5.** Binding energies (in eV) of constituent element core levels in  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ .

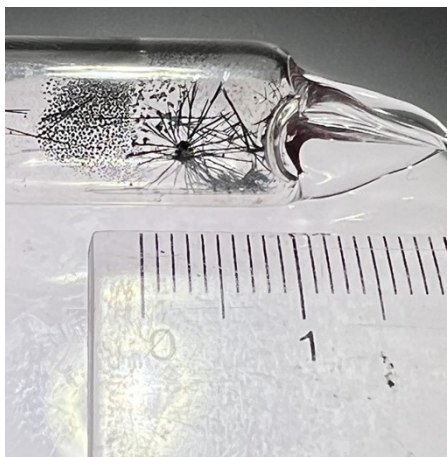
|                   | $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$ | $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ |
|-------------------|---|--|
| Pb                |   |  |
| 4f <sub>7/2</sub> | 138.2   | 138.0  |
| 4f <sub>5/2</sub> | 143.0   | 142.8  |
| Sb                |   |  |
| 3d <sub>5/2</sub> | 529.6   | 529.6  |
| 3d <sub>3/2</sub> | 538.8   | 538.8  |
| S                 |   |  |
| 2p <sub>3/2</sub> | 161.4   |  |
| 2p <sub>1/2</sub> | 162.5   |  |
| Se                |   |  |
| 3d <sub>5/2</sub> |   | 53.7   |
| 3d <sub>3/2</sub> |   | 54.4   |
| Cl                |   |  |
| 2p <sub>3/2</sub> | 197.8   | 197.8  |
| 2p <sub>1/2</sub> | 199.3   | 199.3  |

**Table S6.** Bond-valence sums (BVS) for  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ .

| Site   | Elements | Occupancy | $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$ | $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ |
|--------|----------|-----------|---|--|
| Pb1    | Pb       | 1         | 2.24  | 2.44   |
| Pb2    | Pb       | 1         | 2.17  | 2.24   |
| Sb1    | Sb       | 1         | 2.46  | 2.57   |
| Sb2    | Sb       | 1         | 2.52  | 2.65   |
| S1/Se1 | S/Se     | 1         | 2.08  | 2.29   |
| S2/Se2 | S/Se     | 1         | 2.12  | 2.38   |
| X1a    | S/Se     | 0.93      | 1.70  | 1.63   |
| X1b    | Cl       | 0.07      | 1.22  | 0.91   |
| X2a    | S/Se     | 0.87      | 1.48  | 1.84   |
| X2b    | Cl       | 0.13      | 1.13  | 1.01   |
| X3a    | S/Se     | 0.75      | 1.63  | 1.58   |
| X3b    | Cl       | 0.25      | 1.26  | 0.87   |
| Cl1    | Cl       | 1         | 1.12  | 1.01   |

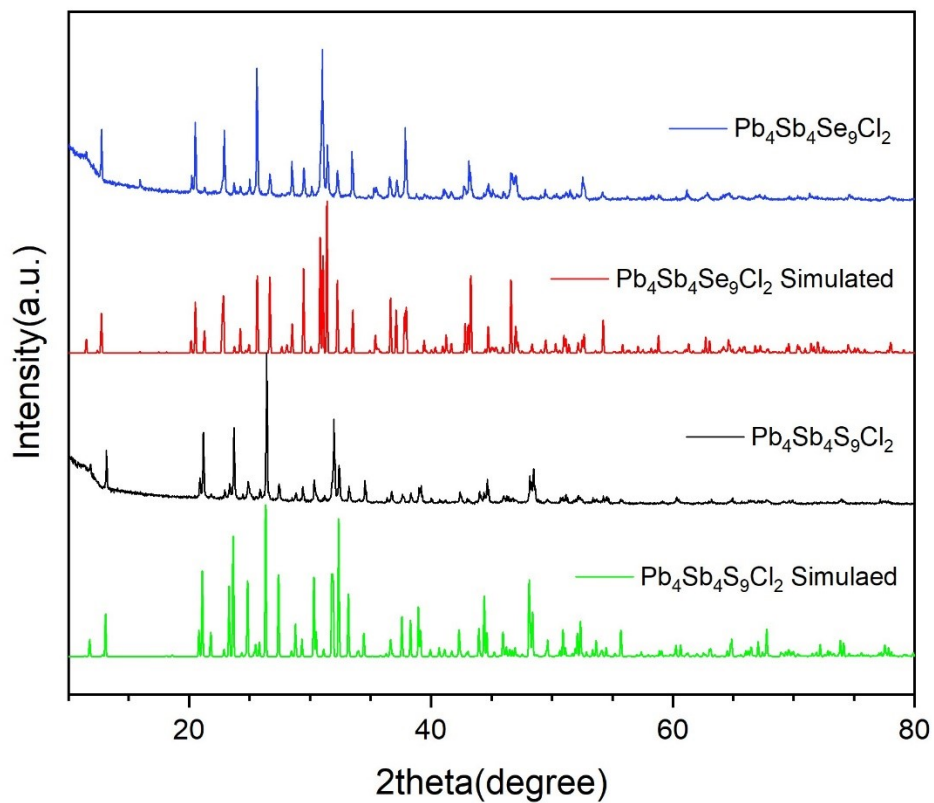


a)  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$

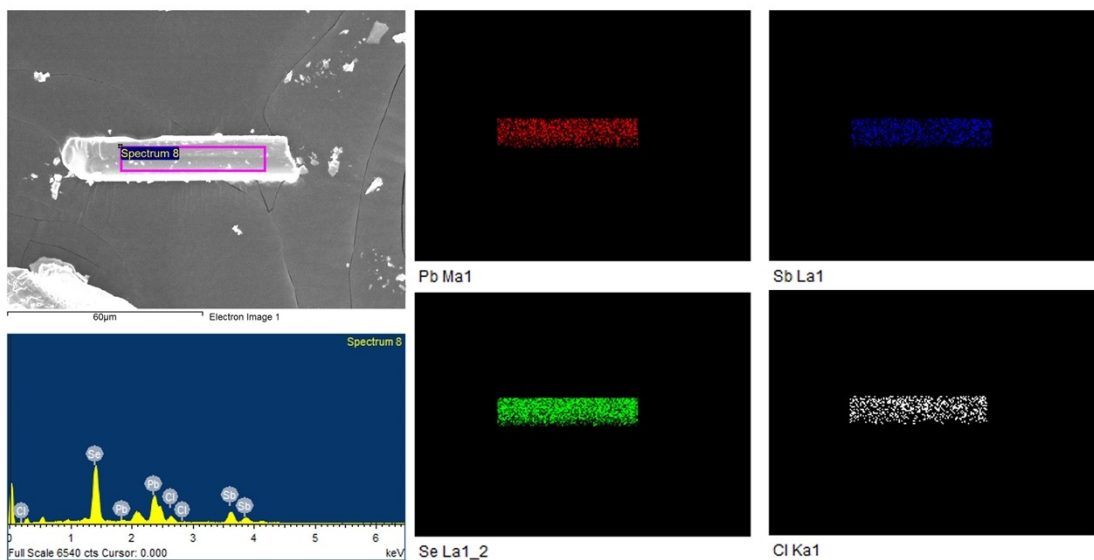


b)  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$

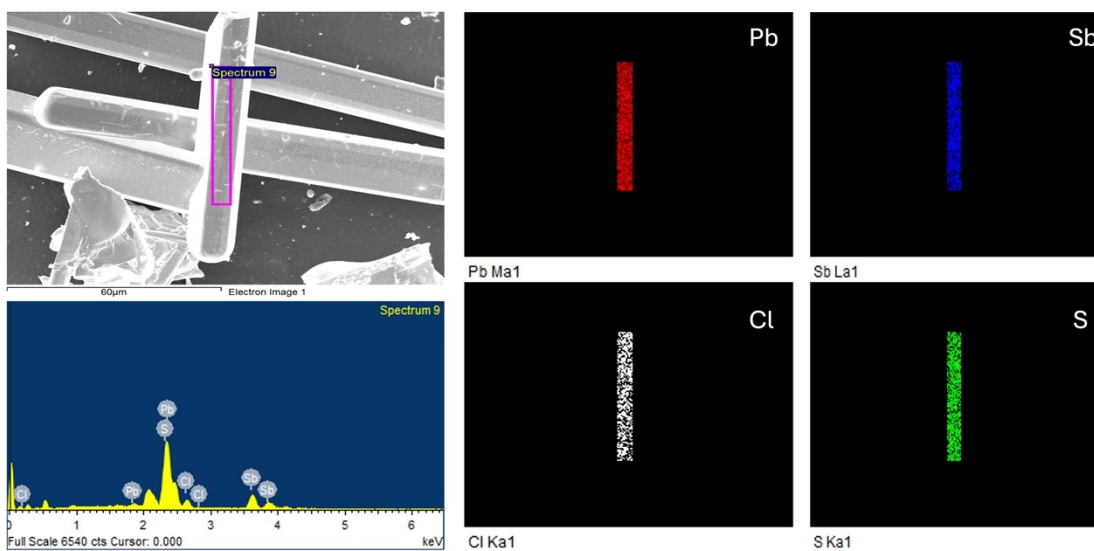
**Figure S1.** Optical photographs of  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$  crystals.



**Figure S2.** Experimental and simulated powder X-ray diffraction patterns of  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ .

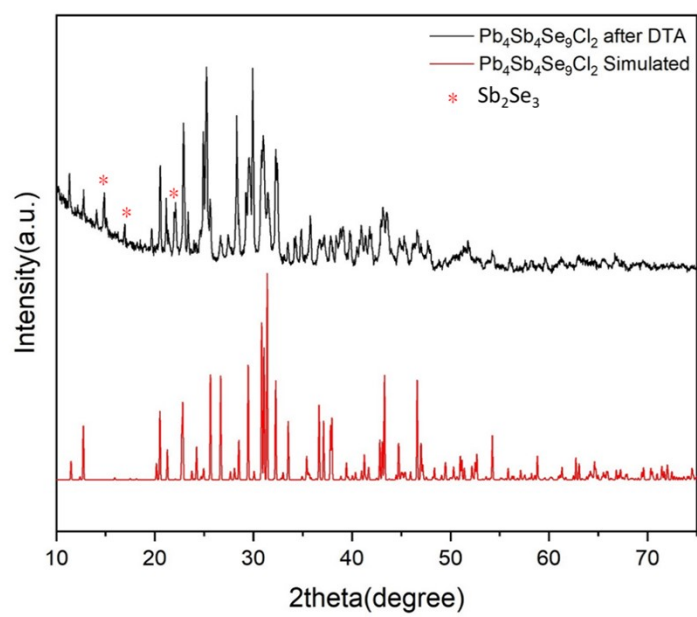
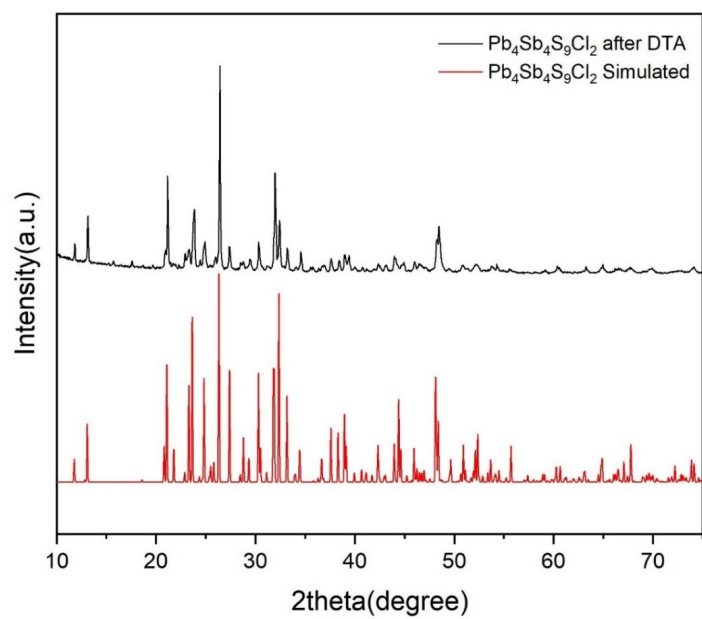


a)  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$

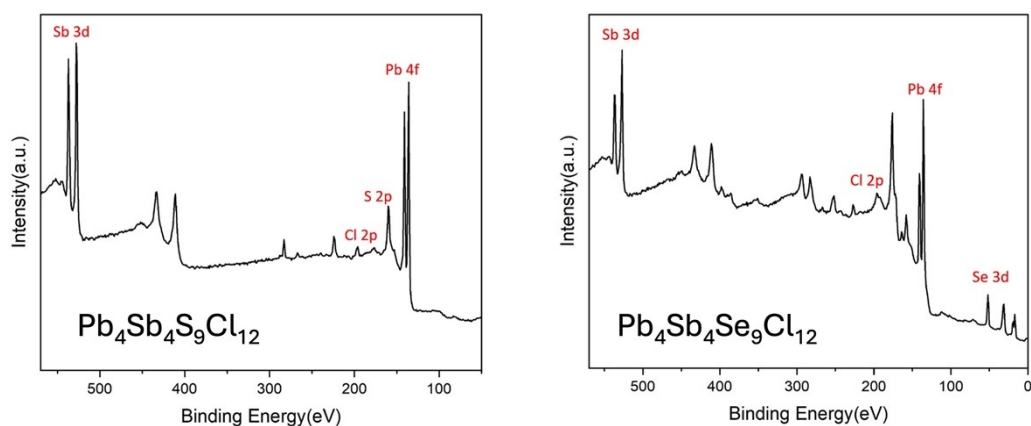


b)  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$

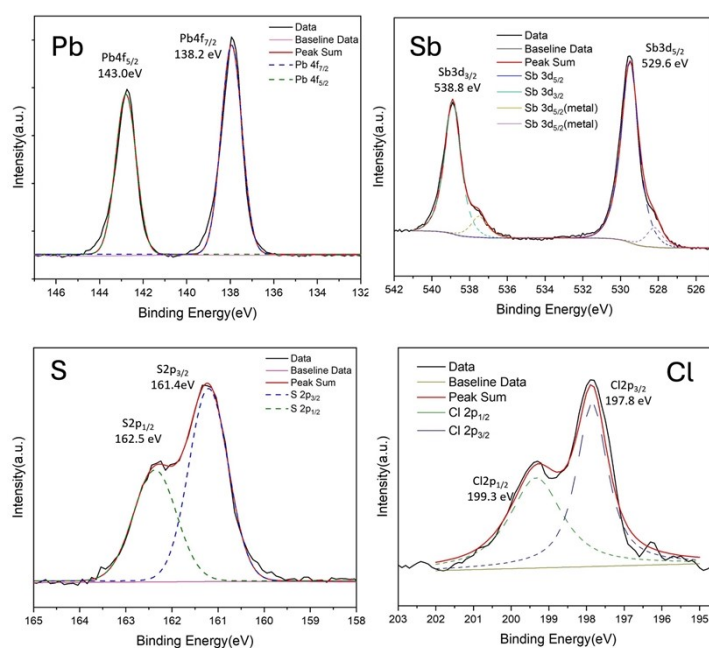
**Figure S3.** SEM images and EDS elemental maps of a)  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and b)  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ .



**Figure S4.** Powder X-ray diffraction patterns of a)  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$ , b)  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$  before and after DTA measurements.

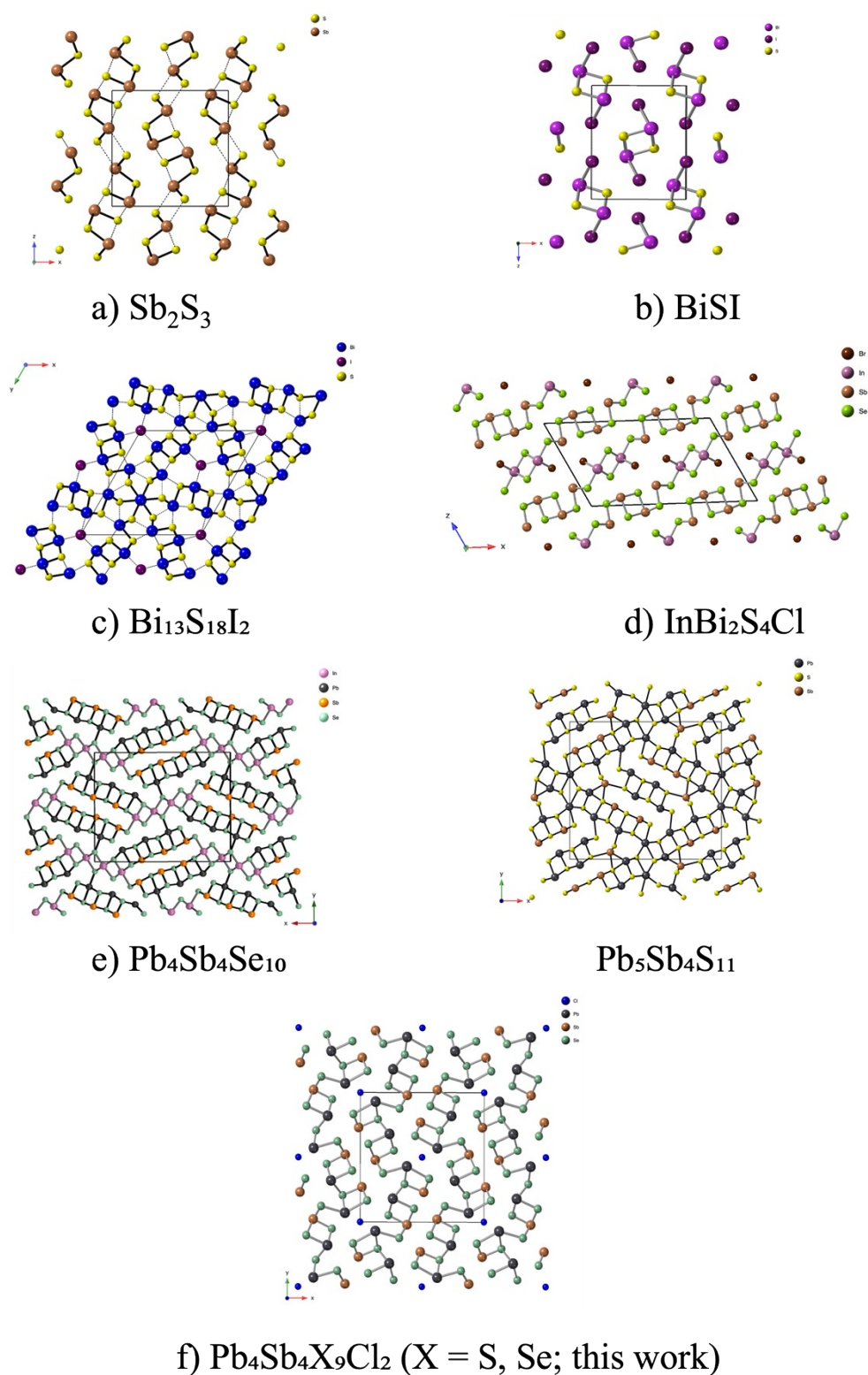


a) Broad scan of  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$

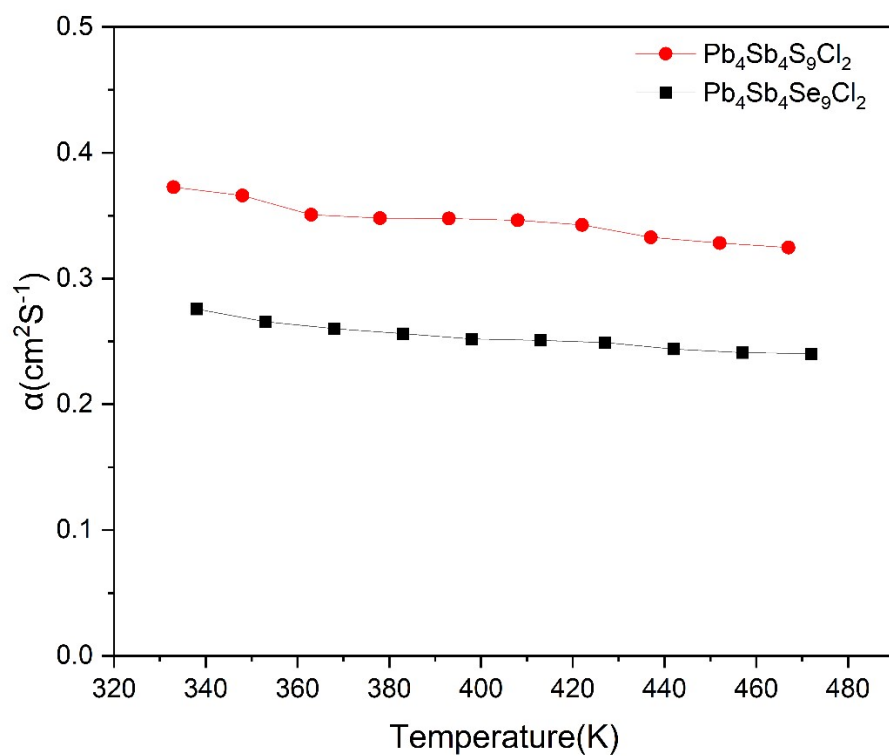


b) High resolution spectra for  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$

**Figure S5.** XPS data for  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ : (a) survey spectra; (b) high-resolution spectra of  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$ . Note: XPS measurements on  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  confirm a chemical environment closely analogous to that of  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$ . High-resolution spectra exhibit Pb 4f peaks at 138.4 eV ( $4f_{7/2}$ ) and 143.3 eV ( $4f_{5/2}$ ) characteristic of  $\text{Pb}^{2+}$ , and Sb 3d peaks at 529.6 eV ( $3d_{5/2}$ ) and 539.0 eV ( $3d_{3/2}$ ) consistent with  $\text{Sb}^{3+}$ .<sup>1, 2</sup> The S 2p doublet appears at 162.3 eV ( $2p_{3/2}$ ) and 163.5 eV ( $2p_{1/2}$ ), confirming the presence of sulfide anions ( $\text{S}^{2-}$ ).<sup>3, 4</sup> Chlorine 2p features at 198.0 eV ( $2p_{3/2}$ ) and 200.0 eV ( $2p_{1/2}$ ) correspond to chloride ions ( $\text{Cl}^-$ ).<sup>5</sup> The close similarity in the spectral profiles of the S- and Se-based analogues confirms that substitution of Se for S does not alter the fundamental chemical environments within the lattice.



**Figure S6.** Comparison of representative ribbon- and layer-related motifs in selected chalcogenide and chalcogenide structures: (a)  $\text{Bi}_2\text{S}_3$ <sup>6</sup>, (b)  $\text{BiSI}$ <sup>7</sup>, (c)  $\text{Bi}_{13}\text{S}_{18}\text{I}_2$ <sup>8,9</sup>, (d)  $\text{InBi}_2\text{S}_4\text{Cl}$ <sup>10</sup>, (e)  $\text{Pb}_4\text{Sb}_4\text{Se}_{10}$ <sup>11</sup> and  $\text{Pb}_5\text{Sb}_4\text{S}_{11}$ <sup>12</sup>, (f)  $\text{Pb}_4\text{Sb}_4\text{Q}_9\text{Cl}_2$  (X = S, Se; this work).



**Figure S7.** Temperature-dependent thermal diffusivity of  $\text{Pb}_4\text{Sb}_4\text{S}_9\text{Cl}_2$  (black) and  $\text{Pb}_4\text{Sb}_4\text{Se}_9\text{Cl}_2$  (Red).

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