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# **Support Information**

## Band Structure Engineering in Highly Degenerate Tetrahedrites Through

### **Isovalent Doping**

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#### **Figure captions**

Figure S1: The XRD patterns of  $Cu_{12}Sb_4S_{13-x}Se_x$  solid solutions (x = 0, 0.5, 1,

2).

Figure S2: The zoom-in images of band structure of  $Cu_{12}Sb_4S_{13-x}Se_x$  (a: x =

0; b: x = 1; c: x = 2).



Figure S1

The powder XRD patterns of  $Cu_{12}Sb_4S_{13-x}Se_x$  solid solutions (x = 0, 0.5, 1, 2) were obtained using a Rigaku Miniflex II bench-top X-ray diffractometer and analyzed by a JADE 5.0 software. The results indicated that the tetrahedrite structure is well kept until x = 2 in spite of a tiny portion of second phase is observed for x = 2 sample.



Figure S2

From the enlarged images, we clearly see the evolution of the top of valence band upon Se doping that more bands take part in the electrical transport.