

a)

b)

Supporting Information

Electronic Structure and Defect States in Bismuth and Antimony Sulphides Identified by Energy-Resolved Electrochemical Impedance Spectroscopy

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Structural Characterisation

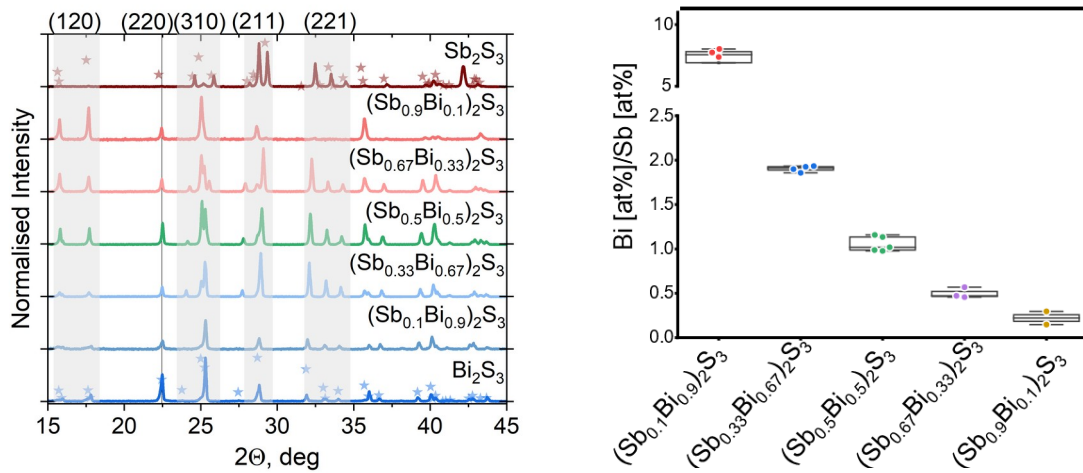
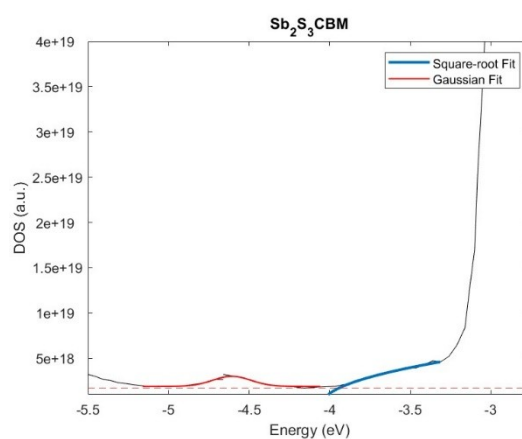
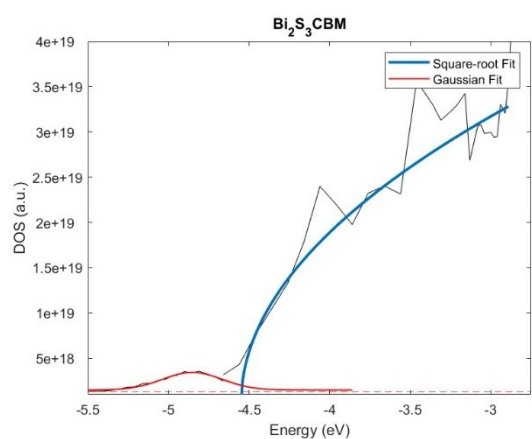
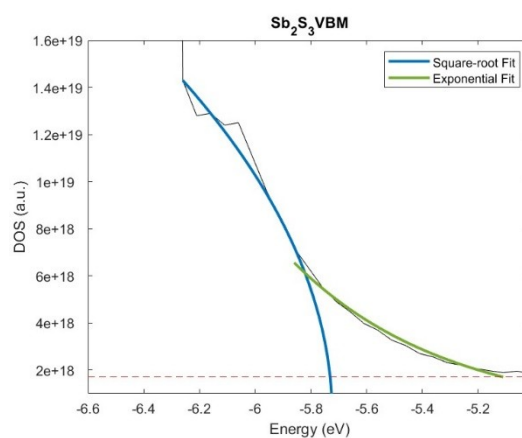
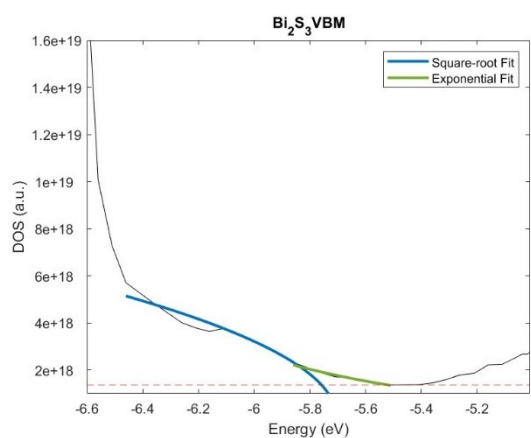
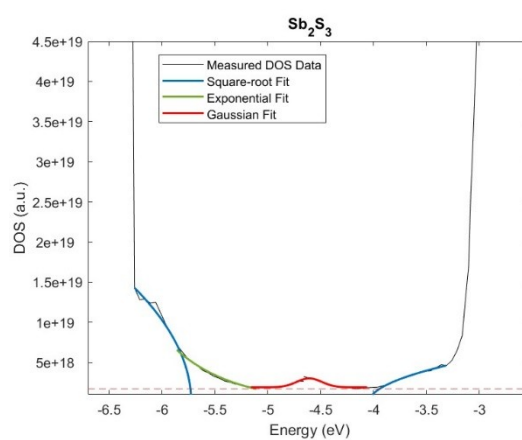
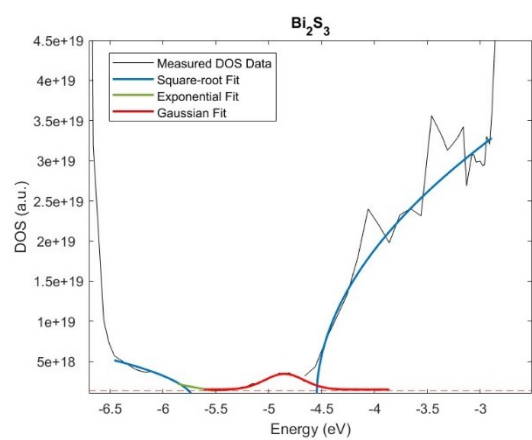
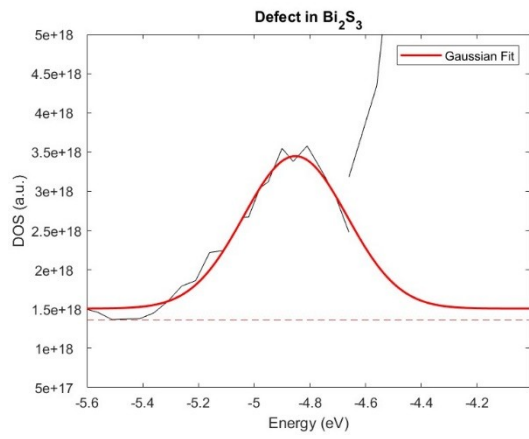


Figure S1. a) XRD patterns of $(Sb_xBi_{1-x})_2S_3$ thin films deposited by CSS. b) Ratio of Bi[at%]/Sb[at%] by EDX to confirm the alloy composition.

ER-EIS DOS Fitting of Bi_2S_3 and Sb_2S_3 

g)



h)

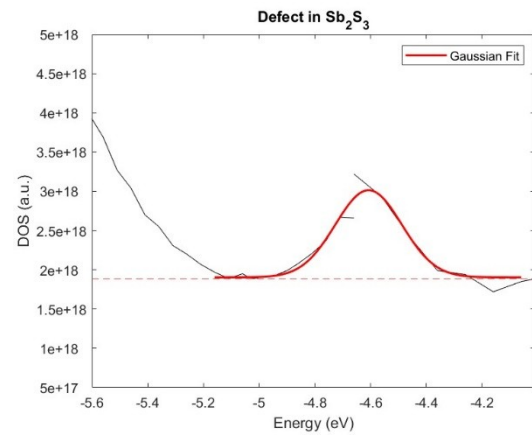
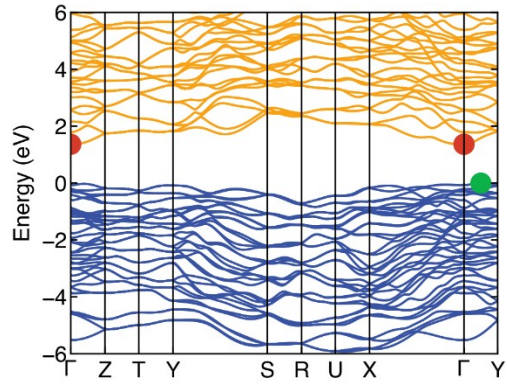


Figure S2. Fitting of full range DOS spectra (a, b), with further zooming-in of VBM (c, d), and CBM (e, f) regions and the defect states (g, h) in Bi_2S_3 and Sb_2S_3 by square root and Gaussian functions, respectively.

a)



b)

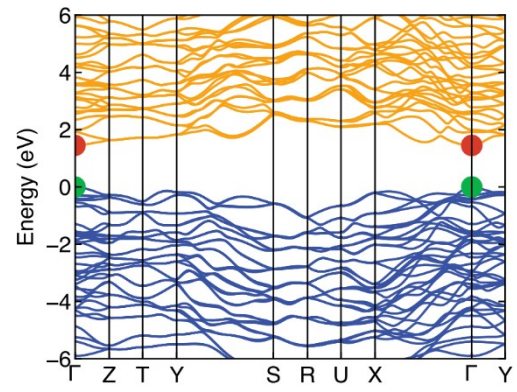


Figure S3. Electronic band structure calculated by DFT showing indirect bandgap for a) Bi_2S_3 and direct bandgap for b) Sb_2S_3 .

Table S1. Bandgap (E_g), mean defect energy (E_D) vs VBM, and E_D as a fraction of E_g from DFT calculations and ER-EIS experiments.

Material	Method	E_g , eV	E_D -VBM, eV		$(E_D$ -VBM) / E_g , %
Bi_2S_3	DFT theory	1.33 (indirect)	0.92 (neutral V_S)	0.75 (charged V_S)	69.17
	ER-EIS experiment	1.20	0.92		75.83
Sb_2S_3	DFT theory	1.45 (direct)	0.66 (neutral V_S)	0.37, 1.25 (charged V_S)	45.52
	ER-EIS experiment	1.80	1.11		61.67

a)
c)

e)

b)
d)

ER-EIS DOS Fitting of $(\text{Sb}_x\text{Bi}_{(1-x)})_2\text{S}_3$ alloys

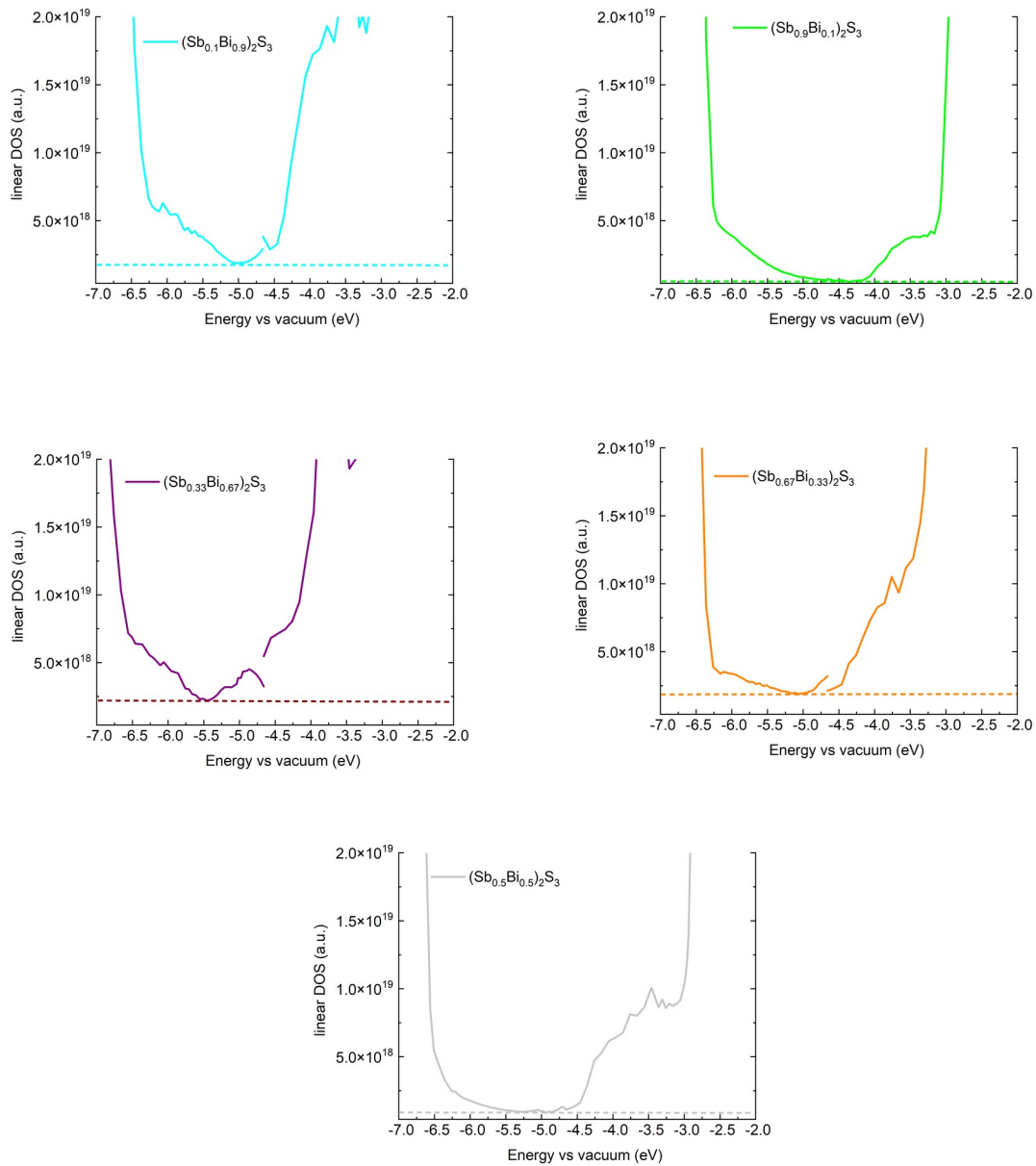


Figure S4. DOS measured by ER-EIS of $(\text{Sb}_x\text{Bi}_{(1-x)})_2\text{S}_3$ alloys.