Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary information:

New insights on the nature of impurity levels in V-doped In_2S_3: Why is it impossible to obtain a metallic intermediate band?

Elaheh Ghorbani,[*,†] Paul Erhart,[‡] and Karsten Albe[†]

†*Fachgebiet Materialmodellierung, Institut für Materialwissenschaft, TU Darmstadt, Otto-Berndt-Straße 3, D-64287 Darmstadt, Germany*

‡*Department of Physics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden*

E-mail: ghorbani@mm.tu-darmstadt.de

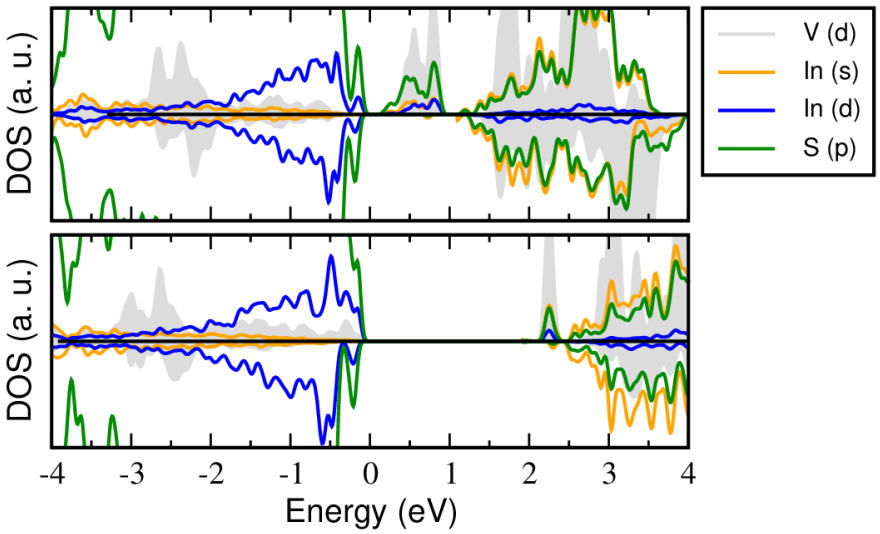

Figure S1: Spin-polarized local densities of states of In_2S_3:V calculated with PBE (top panel) and HSE functionals (bottom panel). Four V atoms are added into four well-separated In^{8c} sites, creating isoelectronic V^0_{In} centers.

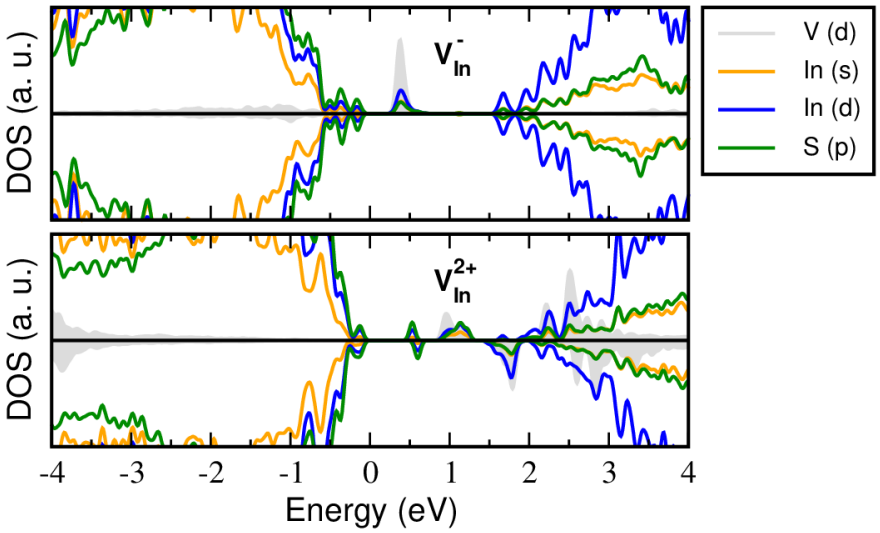

Figure S2: Spin-polarized densities of states of In_2S_3:V, when the incorporated V forms an acceptor (V^-_{In}; top panel) or a double-donor center (V^{2+}_{In}; bottom panel).

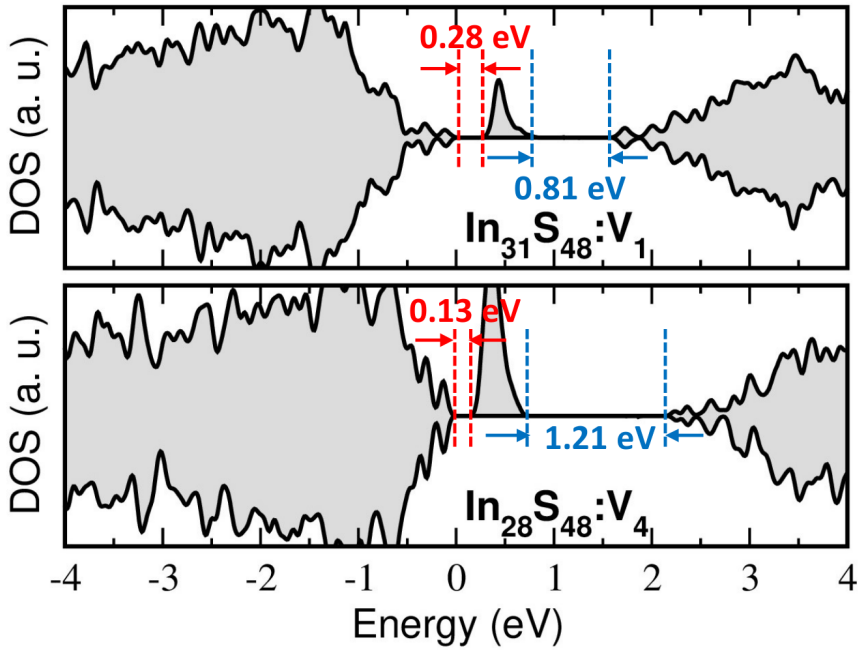

Figure S3: THe HSE calculated spin-polarized total density of states of $In_{31}S_{48}$:V_1^{16h} (top pannel) and $In_{28}S_{48}$:V_4^{16h} (bottom panel), when the incorporated V is on +II oxidation state. The zero of energy is set to the energy of the VBM obtained for each compound. For 1.25 at.% and 5 at.% vanadium, width of IB is 0.53 and 0.61 eV, respectively.

Table S1: Lattice parameters a, b, c and average (V-S) bond length (in Å) for various charge states of V on In^{16h} sites as calculated with HSE functional. The V concentration is 1.25 at.%.

Charge state	a	b	c	$d(V^{16h}$-$S)$
q=+2	7.59	7.62	32.43	2.43
q=+1	7.64	7.63	32.49	2.44
q=0	7.67	7.66	32.75	2.50
q=-1	7.71	7.71	32.83	2.55