Supporting Information

corresponding to the work “Synthesis and Spectral Properties of Nanocrystalline V-substituted In$_2$S$_3$, a Novel Material for More Efficient Use of Solar Radiation” by R. Lucena, I. Aguilera, P. Palacios, P. Wahnon, and J. C. Conesa

Experimental details

InCl$_3$ (Aldrich 99,999%), VCl$_3$ (Aldrich 99%), Na$_2$S (Aldrich 99%) and ethyleneglycol (Panreac 99%) were used as received. For the synthesis of In$_2$S$_3$, InCl$_3$ (6.14 mmol) and Na$_2$S (11.97 mmol) were dissolved in either deionized water or a mixture of ethyleneglycol and deionized water in 9:1 ratio by volume (70 cm$^3$), and introduced into a 125 cm$^3$ teflon-lined stainless steel autoclave. For the synthesis of V-doped material the same procedure was followed, except that InCl$_3$ (5.75 mmol) and VCl$_3$ (0.64 mmol) instead of only InCl$_3$ were used. In all cases the solutions were prepared under nitrogen in a glove bag, and the final pH value was adjusted to 3 with HCl (Panreac 35%). The closed autoclave was heated to 463 K in an oven for 72 h, after which it was cooled to ambient temperature and then its content was filtered and the solid product (orange-yellow in the case of both In$_2$S$_3$ preparations, greenish-brown in the case of the V-containing materials) was washed first 5 times in methanol and then 10-15 times in deionized water, and finally dried in air at 333 K. X-ray fluorescence chemical analysis gave In:S and V:In:S atomic ratios of 2.0:2.99 and 0.17:1.83:2.89 respectively for both products.

Powder X-ray diffraction diagrams in Bragg-Brentano geometry were obtained with a Philips X'Pert Pro PANalytical diffractometer using Cu Ka radiation. UV-Vis-NIR spectra were obtained in diffuse reflectance mode using a Varian Cary 5000 spectrophotometer and Spectralon® as reference material. Simulated patterns were obtained with program PowderCell (http://www.bam.de/de/service/publikationen/powder_cell.htm). To simulate the pattern of V$_2$S$_3$ (monoclinic according to ref. 13) the atomic positions used were those reported for V$_3$S$_4$ [C. Mujica, J. Llanos, O. Wittke, J. All. Compd. 1995, 226, 136], setting an occupation of 2/3 for the inter-layer V site.

Transmission electron microscopy (TEM) data were obtained with a JEOL 2100-F system, having 0.19 nm point resolution and equipped with X-ray energy-dispersive spectroscopy (EDS) analyzer.

X-band EPR spectra (in the standard form of first derivative of the absorption spectra) were taken on weighted portions of powder held in a closed and evacuated quartz tube at 77 K or ambient temperature with a Bruker ER 200 D instrument interfaced to a digital data acquisition system. The number of EPR-detectable spins was determined from them through double integration and comparison with the result obtained similarly for a weighted CuSO$_4$.5H$_2$O standard (Aldrich 99,99%), measured at the same temperature. The known dependence between integrated value and g factor (R. Aasa and T. Vangard, J. Magn. Reson. 1975, 19, 308) was taken into account.

Models and methods used in the DFT calculations

DFT calculations were made in first place for the most stable structure (beta) of In$_2$S$_3$, then also for the metastable phase gamma (see Figures S1a and S1b in this Supporting information), in which respectively one sixth or one eighth of the octahedral In atoms were substituted by V. The calculations were carried out at the spin polarized GGA-PBE level using the VASP program [G. Kresse and J. Hafner, Phys. Rev. B 1993, 47, 558], the core region being described with the PAW method [G. Kresse and D. Joubert, Phys. Rev. B 1999, 59, 1758]. Convergence tests were carried out for both the kinetic energy cutoff of the planewave expansion and the k-points sampling (according to a Monkhorst-Pack, MP, scheme) of the Brillouin zone corresponding to the primitive cell. The final energy cutoff was 280 eV, and the MP grids were gamma-centred meshes of 4x4x4 and 8x8x8 k-points for the $\beta$ and $\gamma$ structures respectively. Density of states (DOS) curves and optical properties [B. Adolph, J. Furthmüller and F. Bechstedt, Phys. Rev. B 2001, 63, 125108; M. Gajdoš, K. Hummer, G. Kresse, J. Furthmüller and F. Bechstedt, Phys. Rev. B 2006, 73, 045112], the latter considering only direct transitions, were obtained from the converged wavefunctions after full relaxation of ion positions and cell parameters. The optical properties were computed after the bandgap underestimation typical of DFT was corrected by applying, as is usually done, a shift increasing the energy of the unoccupied CB levels. As shown by exact exchange (EXX) calculations on other proposed IB materials [P. Palacios, J.J. Fernández, K. Sánchez, J.C. Conesa and P. Wahnon, Phys. Rev. B 2006, 73, 085206], such shift does not need to be applied to the IB. For both V-substituted and pure $\beta$-In$_2$S$_3$ we have used here a shift of 1.2 eV, which is the difference between the experimental (ref. 6) and DFT-derived bandgaps of $\beta$-In$_2$S$_3$. 
Figure S1. a) Body-centred tetragonal unit cell of the β-In$_2$S$_3$ lattice (S in yellow, In in brown or grey), containing 48 S and 32 In atoms (i.e. the primitive cell has 24 S and 16 In atoms; of the latter, 12 are octahedrally coordinated). b) Structure of the γ-In$_2$S$_3$ phase (same color coding) according to ref. 12. Note that in that latter work the structure could be determined only for the material stabilized at room temperature through doping with As or Sb atoms, that after replacing In do not remain at the octahedral site but migrate to an inter-layer interstitial tetrahedral site; but DFT calculations in the present work have verified that for In itself such migration, that according to these calculations would not affect significantly the unit cell dimensions, is energetically disfavored (by ca. 0.20 eV per displaced In atom). For the DFT calculations on V:In$_2$S$_3$, two octahedral In atoms (marked in grey) in each primitive cell of β-In$_2$S$_3$, or 1/8 of the In atoms in γ-In$_2$S$_3$ (one atom in a 2x2x1 supercell) were substituted by V atoms, leading respectively to a centred monoclinic lattice (space group C2/c) where the primitive cell formula is V$_3$In$_{12}$S$_{24}$ and the shortest V-V distance is 7.85 Å, and to a larger hexagonal cell (space group P$\bar{3}$m1) where the primitive cell formula is VIn$_{12}$S$_{12}$ and the shortest V-V distance is 7.6 Å.
Figure S2. Diffuse reflectance UV-Vis-NIR spectra of well crystallized In$_2$S$_3$ and V:In$_2$S$_3$ powder materials.
Figure S3. Representative TEM micrographs taken from different portions of the V:In$_2$S$_3$ material, showing the varying degrees of crystallinity achieved in it. The pictures display the metal atomic ratios obtained from EDS analyses in the regions indicated (circles represent the positions and approximate sizes of the areas analyzed); they indicate a moderate degree of composition deviation from the chemical analysis value (V:In = 0.093). Particularly meaningful is the result indicated in region (a) of image C, where an isolated In$_2$S$_3$ nanocrystal is clearly discerned (the observed lattice spacing corresponds to the (111) planes of its spinel structure); the V:In ratio in it indicates that the In$_2$S$_3$ phase has been indeed able to incorporate vanadium in its structure at the levels given by the chemical analysis.
Figure S4- EPR spectrum (at 77 K) of the synthesized V:In$_2$S$_3$ material. The spectrum at room temperature (not shown) is similar, with an integrated intensity ca. 4 times lower as corresponds to a nearly Curie-type paramagnetic behaviour.
Figure S5. Spin polarized total DOS curves obtained with DFT for the V$_2$In$_{14}$S$_{24}$ primitive cell of Figure S1 and for the undoped structure (In$_{16}$S$_{24}$). For V$_2$In$_{14}$S$_{24}$ the zero of energy is set at the Fermi level, while for In$_{16}$S$_{24}$ the energy zero is set by aligning the valence band edge of both systems.