

Bi doped Sb₂S₃ for low effective mass and optimized optical property

Ming-Hui Shang*

Institute of Material, Ningbo University of Technology,

89 Cuibai Rd., Haishu, Ningbo 315016, China and

Graduate School of Advanced Integration Science, Chiba University,

1-33 Yayoi-cho, Inage, Chiba 263-8522, Japan

Jing Zhang, Shihao Wei, and Yuejin Zhu

Faculty of Science, Ningbo University, 818 Fenghua Rd.,

Jiangbei, Ningbo 315211, China

Lin Wang, Huilin Hou, and Yulian Wu

Institute of Material, Ningbo University of Technology,

89 Cuibai Rd., Haishu, Ningbo 315016, China

Takashi Fujikawa and Nobuo Ueno

Graduate School of Advanced Integration Science, Chiba University,

1-33 Yayoi-cho, Inage, Chiba 263-8522, Japan

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1 I. SUPPLEMENTARY

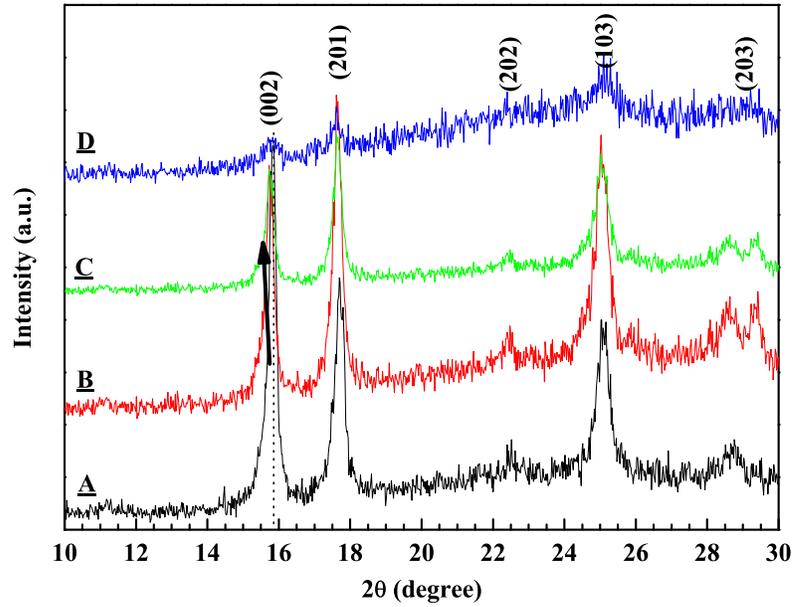


FIG. 1. (Color on line) X-ray diffraction patterns (XRD) of Bi-doped Sb_2S_3 . The diffraction peak at 15.82° moves to lower degree as indicated by arrow.

TABLE I. Stoichiometry of Sb, Bi, S and the impurity (like C, N). The error band of the data is 5.0at.%.

sample	Sb at. %	Bi at. %	S at. %	Sb at. %
A	39.5	0.0	59.0	1.5
B	39.0	0.5	59.0	1.5
C	38.6	0.96	58.6	1.8
D	37.5	2.0	58.4	1.9

2 X-ray diffraction patterns (XRD) were collected using a Bruker instrument (D8 advance, Ger-
 3 many) applying Cu $K\alpha$ radiation at scan rate 4° per min. The pure sample exhibits conventional
 4 Sb_2S_3 diffraction peaks with the Miller indices noted in Fig. 1. With Bi-incorporation, the doped
 5 Sb_2S_3 crystal shows no peak related to new phase, implying Bi is doped via substituting Sb-sites.
 6 It is noticed that the diffraction peak at 15.82° moves to lower degree as the arrow indicated. The
 7 lattice parameters calculated from the XRD pattern is enlarged from 11.18 \AA of pure Sb_2S_3 to

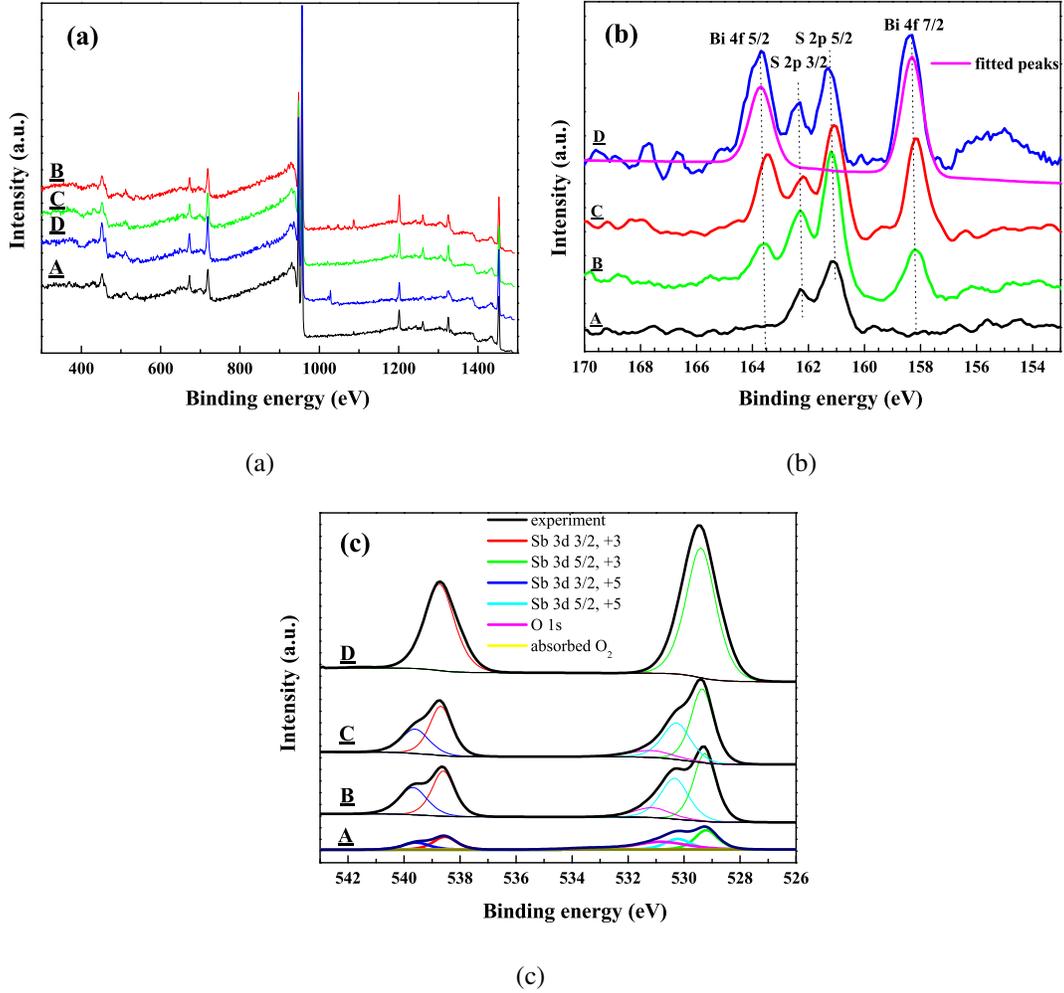


FIG. 2. (Color on line) XPS whole energy spectra (a), core level spectra of Sb and Bi (b) and spectra of S 2p (c).

11.25 Å of 1.25 at.% Bi doped Sb₂S₃. It suggests the lattice is expanded by Bi, radius of which is larger than that of Sb atoms. *From the XRD, there is no phase of Bi₂S₃ can be found. But Bi is indeed doped in the sample as reflected by XPS spectra (Fig. 2). The whole energy spectra (Fig. 2(a)) and core level XPS (Fig. 2(b)) indicate that Bi is incorporated in. And XPS of S 2p (Fig. 2(c)) show that chemical environment of S atoms in the hosts is kept with Bi-incorporation. And the sample kept the crystal structure of Sb₂S₃ with Bi doped in Sb sites.*

From the XPS spectra, the stoichiometry of Sb, Bi, S and the impurity (like C, N) can be determined as shown in Table I. The impurity in these doped samples approximately keeps with no significant variation. We thus believe the experiment data in the manuscript can reflect the Bi doping property.

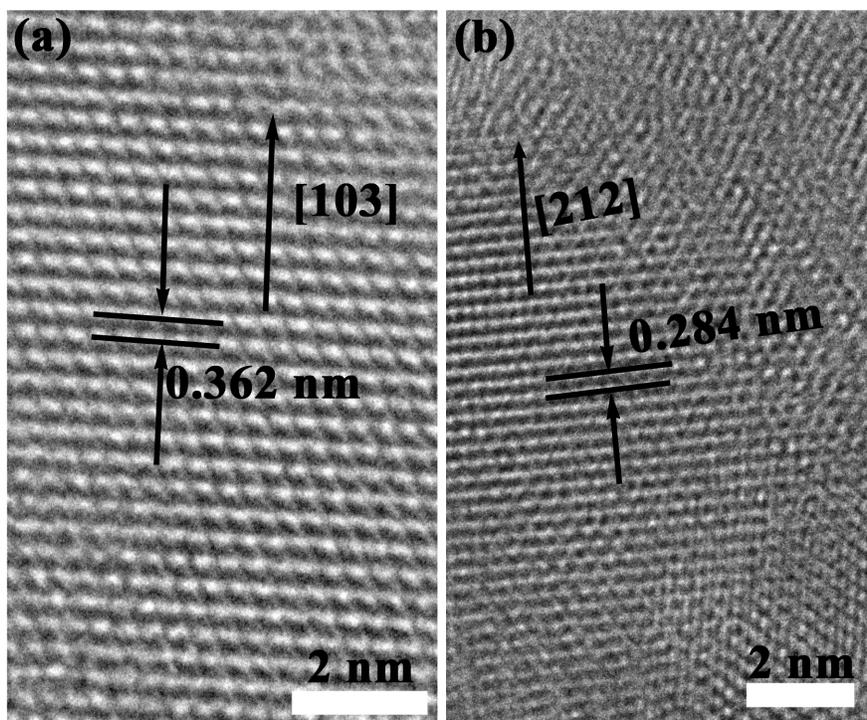


FIG. 3. (Color on line) HRTEM images of as synthesized sample of A (a) and B (b) with Bi-density of 0.00at.% and 1.25at.%, respectively.

1 The obtained products (A and B) were characterized using high-resolution transmission elec-
2 tron microscopy (HRTEM, JEM-2100F). The HRTEM images are displayed in Fig. 3.

TABLE II. Calculated total energy of structures with different Bi-density by considering the inequivalent Sb sites *using HSE functional*.

Etot(eV)	1.25 at. %	2.50 at. %	5.00 at. %
site1	-350.455	-175.203	-76.357
site2	-328.347	-164.266	-82.216

Total energy of Sb_2S_3 systems doped Bi by substituting Sb on site1 and site2 are calculated and shown in Table II *using HSE functional*.

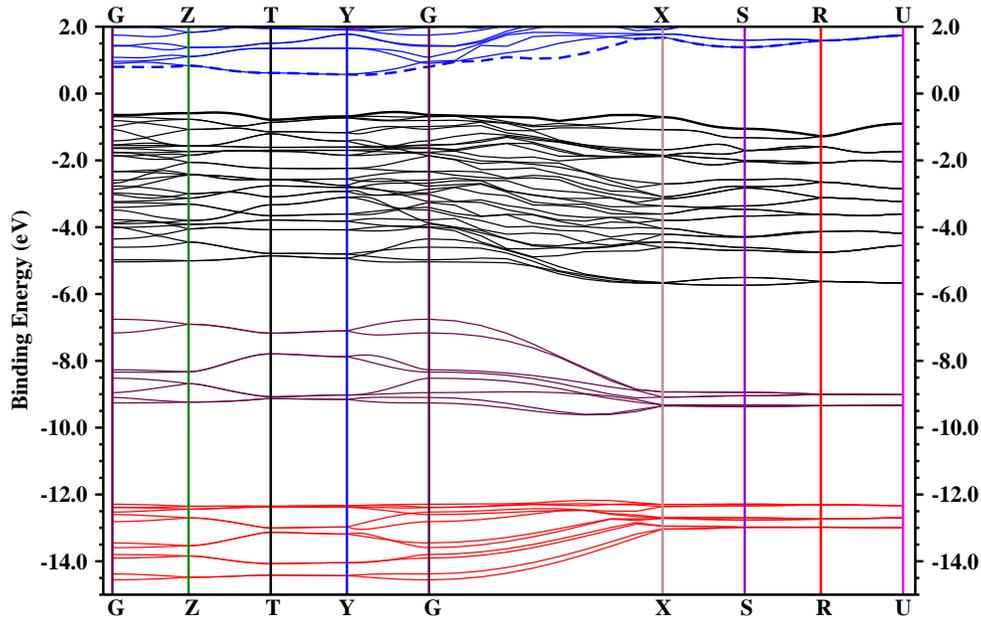


FIG. 4. (Color on line) Electron band structure of pure antimony trisulphide, where we use *standard PBE functional and* the same K-points path within the first BZ investigated by Haijun Zhang.¹

Fig.4 exhibits band structure of pure Sb_2S_3 system calculated *with standard PBE functional* along the K-points path through the first BZ following the high-symmetry line which edging $\Gamma(0\ 0\ 0)$ - $Z(0\ 0\ \frac{1}{2})$ - $T(0\ \frac{1}{2}\ \frac{1}{2})$ - $Y(0\ \frac{1}{2}\ 0)$ - $\Gamma-X(\frac{1}{2}\ 0\ 0)$ - $S(\frac{1}{2}\ \frac{1}{2}\ 0)$ - $R(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ - $U(\frac{1}{2}\ 0\ \frac{1}{2})$ previously investigated by Haijun Zhang.¹

1 Calculated electron band of pure Sb_2S_3 system *using standard PBE functional* by following
 2 following K-points path through the first BZ following the high-symmetry lines edging $\Gamma(0\ 0\ 0)$ -
 3 $X(\frac{1}{2}\ 0\ 0)$ - $S(\frac{1}{2}\ \frac{1}{2}\ 0)$ - $Y(0\ \frac{1}{2}\ 0)$ - Γ - S - $R(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ - $T(0\ \frac{1}{2}\ \frac{1}{2})$ - $Z(0\ 0\ \frac{1}{2})$ - $U(\frac{1}{2}\ 0\ \frac{1}{2})$ - R - Z - Γ , which is the same as
 4 which investigated by R. Caracas and X. Gonze² (Fig. 5).

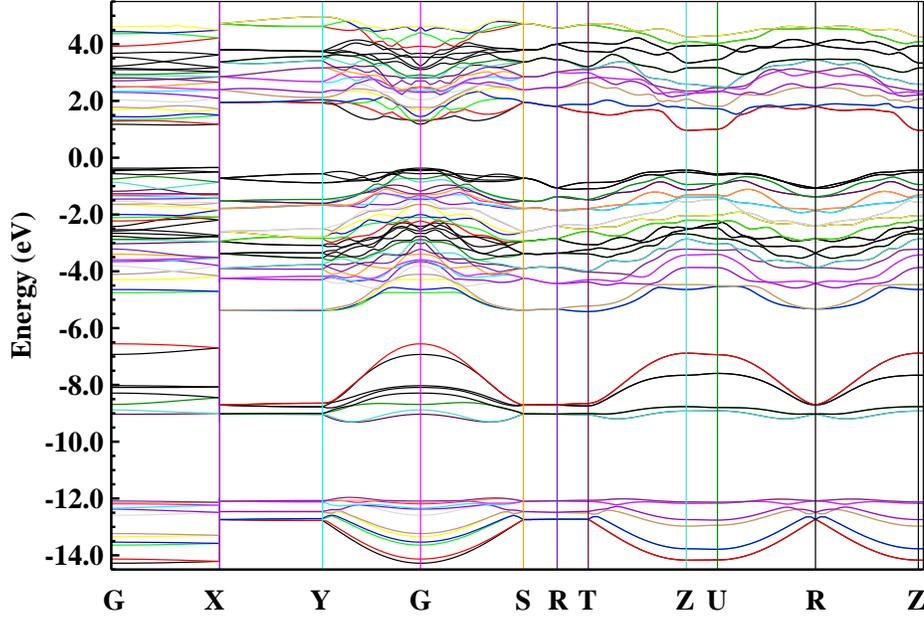


FIG. 5. (Color on line) Electron band structure of pure antimony trisulphide, where we use the same K-points path within the first BZ investigated by R. Caracas and X. Gonze² *using PBE functional*.

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7 Bi-doped Sb_2S_3 band structures are all recalculated by following high symmetry K-points path
 8 edging $\Gamma(0\ 0\ 0)$ - $X(\frac{1}{2}\ 0\ 0)$ - $S(\frac{1}{2}\ \frac{1}{2}\ 0)$ - $Y(0\ \frac{1}{2}\ 0)$ - Γ - S - $R(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ - $T(0\ \frac{1}{2}\ \frac{1}{2})$ - $Z(0\ 0\ \frac{1}{2})$ - $U(\frac{1}{2}\ 0\ \frac{1}{2})$ - R - Z - Γ ,
 9 investigated by R. Caracas et. al.² as summarized in Table III.

10 Calculated effective mass of electron (m_e^*) and hole (m_h^*) along different direction are exhibited
 12 in Table IV, *where the HSE functional was used for obtaining more accurate results*.

TABLE III. The detailed information of calculated band structures for antimony trisulphide doped by Bi with five concentration levles, where we use *standard PBE functional and* the same K-points path within the first BZ investigated by R. Caracas and X. Gonze. The E_f indicates the calculated the Fermi level, while the direct and indirect energy band gap are shown as E_g^d and E_g , respectively.

(eV)	0.00 at.%	1.25 at.%	2.50 at.%	5.00 at.%
BCB	5.5756 $_{Z \rightarrow \Gamma}$	5.5754 $_{Z \rightarrow \Gamma}$	5.5698 $_{Z \rightarrow \Gamma}$	5.5601 $_{Z \rightarrow \Gamma}$
TVB	4.2900 $_{X \rightarrow S}$	4.3048 $_{Y \rightarrow \Gamma}$	4.3166 $_{X \rightarrow S}$	4.3313 $_{X \rightarrow S}$
E_F	4.5241	4.5349	4.5593	4.6276
E_g	1.2856	1.2706	1.2532	1.2288
$BCB-E_F$	1.0515	1.0405	1.0105	0.9325
E_F-TVB	0.2341	0.2301	0.2427	0.2963
E_g^d	1.6362	1.6316	1.5609	1.5262

TABLE IV. Calculated effective mass (relative to the statistic mass of electron, m_0) of electron and hole with respect to Bi-density within ground states of corresponding supercells. m_e^* and m_h^* indicates the effective mass of electron and hole, respectively. m_e^{*i} , $i=x,y,z$, denotes to the effective mass along x, y, z directions. *HSE functional was applied for more accurate results.*

Bi- density	m_e^*			m_h^*		
	m_e^{*x}	m_e^{*y}	m_e^{*z}	m_h^{*x}	m_h^{*y}	m_h^{*z}
0.00at.%	0.092	0.111	1.007	0.616	1.101	0.046
1.25at.%	0.008	0.007	0.005	0.005	0.025	0.210
2.50at.%	0.078	1.160	0.150	13.895	6.799	0.267
5.00at.%	0.048	0.075	0.405	2.062	0.135	0.049

II. REFERENCES

* smh2875@hotmail.com, (M.-H. S.)

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