Computational Materials Science 101 (2015) 301–312

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

DFT study of structural, elastic properties and thermodynamic parameters of Bi_2S_3 under hydrostatic pressures

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ARTICLE INFO

Article history:
Received 18 November 2014
Received in revised form 29 January 2015
Accepted 1 February 2015
Available online 24 February 2015

Keywords:
DFT
Bi_2S_3 crystal
Birch–Murnaghan equation of state
Elastic properties
Anisotropy
Thermal conductivity
Thermal expansion coefficient

ABSTRACT

The pressure dependencies of structural properties, stability, mechanical properties, mechanical anisotropic, linear compressibility, Debye temperature, minimum thermal conductivity and thermal expansion coefficient of the orthorhombic Bi_2S_3 in the *Pnma* structure have been investigated using density functional theory. All calculated properties are in excellent agreement with experimental results, which imply the reliability of the present calculation method. The obtained elastic constants satisfying that the Bi_2S_3 crystals are mechanically stable up to 9.18 GPa and its hardness is improved under compression. The surface constructions and planar contours of bulk and Young's moduli at (100), (010) and (001) crystal planes indicate that bulk modulus is more isotropic than Young's modulus, and anisotropies in both moduli decrease under compression. Furthermore sound velocity, Debye temperature and minimum thermal conductivity are found to be increasing with pressure. The thermal expansion coefficient of Bi_2S_3 has a strong pressure dependence and its thermal conductivities are extraordinary low which demonstrate its technological application as novel thermal barrier coating materials. Unfortunately, there is currently no experimental measurements of elastic constants and other related properties for comparison.

1. Introduction

Inorganic one-dimensional (1D) semiconductors have attracted increasing interest in both academic and industrial research because of their novel electronic, magnetic, catalytic, optical and mechanical properties [1,2]. Among 1D semiconductors, nanoribbons have a rectangular cross-section which represent a special geometrical shape [3]. Main group metal chalcogenides $A_2^{V}B_3^{IV}$ (A = As, Sb, Bi; B = S, Se, Te) are one of the most important nanoribbons and have applications in television cameras with photoconducting targets, thermoelectric devices, opto-electronic devices, hydrogen storage materials, sensors, and infrared spectroscopy [3–6]. Important member of these semiconductors is Bi_2S_3 because of its low toxicity [7]. Bi_2S_3 has a strongly anisotropic orthorhombic structure in the *Pnma* space group with 4 stoichiometric Bi_2S_3 units per unit cell. Each molecule contains two bismuth atoms and 3 sulfide atoms which add up to 20 atoms per unit cell [8]. In each unit cell two Bi_4S_6 ribbons are extended by ionic/covalent bonds along the crystallographic direction [010] (*b*-axis) [9]. The space between ribbons is depleted of electrons, and bonding between neighbor ribbons are much weaker than Bi–S bonds within the ribbons [9,10]. Bi_2S_3 is a semiconductor [11] with a narrow and direct band gap 1.30–1.70 eV [1–5,9,12–18], and unique band edge [13] which has been widely used in solar cells, photodiode arrays, photovoltaic convertors, and photodetectors in visible wavelength region [2,3,5,13,14,19]. Several techniques such as solvothermal process [3,5], hydrothermal technique [20] and low temperature synthesis method [21] have been reported for preparation of Bi_2S_3 nanoribbons. Several experimental [1,2,4,6,11,12,16,19,22] and theoretical [9,10,23,24] investigations have been reported for the chemical and physical properties of Bi_2S_3. Understanding the behavior of materials under compression based on theoretical or measurements is the object of increasing scientific interest. To the best of the author's knowledge, only two high-pressure studies on Bi_2S_3 can be found in the literature. Historically, first pressure effect on Bi_2S_3 has been studied by Lundegaard et al. [25]. They have investigated equation of state (EOS) and crystal structure of Bi_2S_3 at nine distinct hydrostatic pressures in the range 0–9.18 GPa. Furthermore, they showed that the *Pnma* phase of Bi_2S_3 is stable up to 9.18 GPa, and lone-electron pairs of Bi moves to the parent atom with increasing in the applied pressure. Next high-pressure study on Bi_2S_3 has been performed by Efthimiopoulos et al. [26], applying hydrostatic pressures up to 65 GPa. They studied the high-pressure structural properties and

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http://dx.doi.org/10.1016/j.commatsci.2015.02.005
0927-0256/

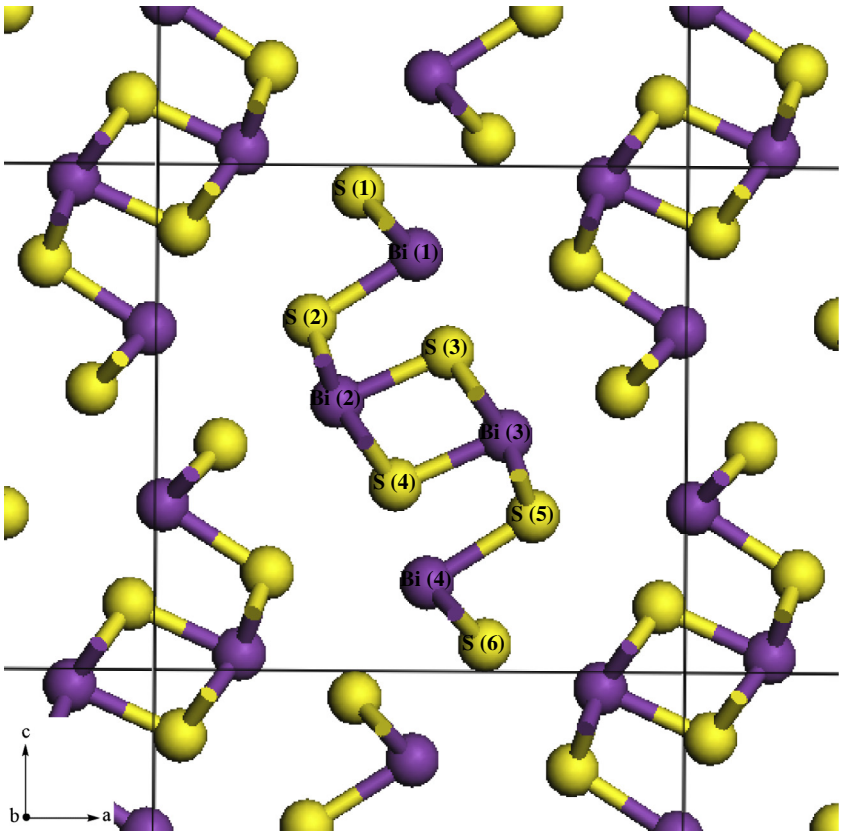

Fig. 1. Crystal structure of Bi_2S_3 at zero pressure.

Table 1
The crystal structure data of Bi_2S_3 at different applied external hydrostatic pressures.

Pressure (GPa)		Zero	0.0001	0.97	2.43	3.53	5.92	7.22	8.3	9.18
a (Å)	Exp.	11.282	11.269	11.136	10.987	10.907	10.758	10.701	10.659	10.634
	Calc.	**11.578**	**11.577**	**11.384**	**11.177**	**11.024**	**10.799**	**10.752**	**10.711**	**10.682**
	%Dev.	2.62	2.73	2.22	1.72	1.07	0.38	0.47	0.48	0.45
b (Å)	Exp.	3.972	3.971	3.957	3.935	3.919	3.883	3.865	3.852	3.842
	Calc.	**3.986**	**3.985**	**3.964**	**3.937**	**3.924**	**3.891**	**3.879**	**3.862**	**3.850**
	%Dev.	0.35	0.35	0.17	0.05	0.12	0.20	0.36	0.25	0.20
c (Å)	Exp.	11.131	11.129	11.035	10.903	10.822	10.650	10.565	10.510	10.463
	Calc.	**11.054**	**11.053**	**10.984**	**10.928**	**10.854**	**10.706**	**10.608**	**10.549**	**10.503**
	%Dev.	−0.69	−0.68	−0.46	0.22	0.29	0.52	0.40	0.37	0.38
V_{uc} (Å^3)	Exp.	498.40	498.08	486.32	471.41	462.58	444.89	437.03	431.56	427.56
	Calc.	**510.09**	**509.96**	**495.66**	**480.87**	**469.52**	**449.85**	**442.42**	**436.36**	**431.94**
	%Dev.	2.34	2.38	1.92	2.00	1.5	1.11	1.23	1.11	1.02
ρ (g/cm^3)	Exp.	6.852	6.856	7.022	7.244	7.383	7.676	7.814	7.913	7.987
	Calc.	**6.695**	**6.696**	**6.889**	**7.101**	**7.273**	**7.591**	**7.719**	**7.826**	**7.906**
	%Dev.	−2.29	−2.33	−1.89	−1.97	−1.48	−1.10	−1.21	−1.09	−1.01

$\alpha = \beta = \gamma = 90$.
The calculated values of this work (GGA-PBE) are in bold for more clarity.

Raman frequencies of layered Bi_2S_3 with a combination of experimental and theoretical methods. The main outcome of this investigation was the stability of the *Pnma* phase of layered Bi_2S_3 up to 50 GPa and appearing of structural disorder at higher pressures. Under pressure, atoms and molecules get closer together, elements become denser, occupied volume decreases and mechanical properties such as bulk modulus and elastic constants can be greatly changed [27]. The knowledge of elastic constants is necessary for many practical applications depending to the mechanical properties of solids such as load deflection, thermoelastic stress, internal strain, sound velocities, fracture toughness, Debye temperature and thermal expansion coefficient [28–30]. Up to now, there are no experimental and theoretical reports on the elastic properties of Bi_2S_3 under hydrostatic pressure. In this case, we focused in detail on structure, equation of state (EOS), elastic properties and thermodynamic parameters of Bi_2S_3 in the range 0–9.18 GPa using the first principles calculations.

2. Computational details

The experimental crystal structural data reported by Lundegaard et al. [25] were taken as initial geometries. All calculations are performed using plane wave pseudo-potential method in the Cambridge Serial Total Energy Package (CASTEP) code [31]. The electronic exchange–correlation interactions were treated