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Exploring novel phase of tin sulfide for photon/energy harvesting materials

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ABSTRACT

Recently discovered novel π-SnS (cubic phase) has gained much attention due to suitable nature for several optoelectronic devices and thermoelectric applications. Local density approximation (LDA) and generalized gradient approximation (GGA) with ultra-soft pseudo-potential (UPP) technique within density functional theory (DFT) are used to study the structural, electronic, optical, and elastic properties of π-SnS. The structural properties show good consistency with previous results. The band structure study shows that its nature is indirect with bandgap 1.073/1.37 eV (LDA/GGA). The calculated elastic constants satisfy the Born stability criteria which are determined for the first time as per our knowledge. On the basis of Voigt-Reuss-Hill approximation, bulk modulus, shear modulus, Young's modulus, Poisson's ratio, Lame's coefficients, average sound velocity and Debye temperature are determined. In LDA/GGA the value of Bulk modulus is estimated 55.32/20.98 GPa, which is in good agreement to that calculated with Birch-Murnaghan equation of state (EOS). The 2D and 3D surface visualization of bulk, shear and Young's moduli suggest that π-SnS is elastically anisotropic. In LDA/GGA the value of Debye temperature (θ_D) is estimated as 361.01/299.39 K. The thermal conductivity of π-SnS could be high due to high Debye temperature (θ_D) relative to α-SnS ($\theta_D \sim 270$ K). Additionally, for the first time transversal and longitudinal wave velocities in [1 0 0], [1 1 0] and [1 1 1] directions are calculated. In the view of present studies π-SnS could be suitable candidate for exploitation in optoelectronic, thermoelectric and energy storage devices.

1. Introduction

In the last decade, mono-chalcogenide layered semiconductors belong to $A^{IV}B^{VI}$ group are considered very eminent candidates for technical application in optoelectronic devices, thermoelectric generators, temperature sensors (Gao et al., 2013; Han et al., 2013; Keshav and Mahesha, 2018; Pejjai et al., 2017; Santhosh et al., 2017). The narrow band-gap chalcogenides MX (M = Pb, Cd, Sn & X = S, Se, Te) have garnered much attraction due to extensive applications in near infrared (NIR) detectors, photovoltaic cells, solar cells and as biological imaging agents (Luther et al., 2008; Ning et al., 2011; Razykov et al., 2017; Semonin et al., 2011; Tang et al., 2011; Zafar et al., 2017). The PbS and PbSe nano-crystals, in the case of IV–VI chalcogenides have more focused and tuned band-gaps near infrared and visible spectrum (Fu and Tsang, 2012; Moreels et al., 2011; Xiao et al., 2013). These chalcogenides have also shown better performance and conversion efficiencies, when used in optoelectronic devices. But the toxicity of Cd and Pb materials are the major obstacle in their use (Butt et al., 2014).

In this scenario, the tin based chalcogenides (SnS, SnSe and SnTe) have received more attention and are assumed to play a vital role in switching the above technologies owing to their comparably non-toxic nature, chemical stability, easy controllability of stoichiometry, earth-abundance and are economical (Butt et al., 2017; Peter, 2011; Rehman et al., 2017). In this case, orthorhombic tin mono-sulfide (α-SnS)

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(Wiedemeier et al., 1978) opens many possibilities and becomes a suitable candidate for potential applications of SnS thin layered crystals (Clemen et al., 1978), solar cells (Antunez et al., 2011), effective thin-film thermo elements (Bashkirov et al., 2012) and photovoltaic detectors (Trbojevic et al., 1981). Recently, a new crystalline cubic phase π-SnS (cube shaped nano-particles) with lattice parameters $a_0 = 11.70$ Å of tin mono-sulfide has been synthesized. The experimental band-gap is 1.73 eV (indirect) which lies in the visible and near infrared region (Nair et al., 2016). Thus, the π-SnS (cubic) band-gap is much larger (~0.7 eV) relative to α-SnS (orthorhombic). This energy difference suggests that cubic π-SnS phase has an extra potential in both visible range and near infrared regions with some technological applications in photo catalysis, thermoelectric applications and solar cells (Barrios-Salgado et al., 2016; Nair et al., 2016; Rabkin et al., 2015). To the extent of our knowledge, there exist a few theoretical studies on the structural and electronic properties of π-SnS (Abutbul et al., 2016b; Segev et al., 2017b). It is important to explore the physical properties such as structural, electronic, optical, mechanical and thermodynamic properties of π-SnS for comprehensive understanding and applications of this new phase SnS in modern technology. In current work, we present a detailed study on the physical properties including structural, electronic, optical, elastic and thermodynamics of π-SnS for the first time. These studies provide a pathway to better understand the physical properties of π-SnS and their advancement in the designing and applications for various optoelectronic devices and clean energy systems.

2. Computational method

The geometry optimization of π-SnS was done by crystallographic information file (CIF). The experimental lattice parameter $a_0 = 11.70$ Å is used to generate this CIF (Rabkin et al., 2015). The crystal structure of π-SnS consists of 64 atoms as shown in Fig. 1. The 32 violet and 32 yellow balls represent Sn and S atoms, respectively. After the geometry optimization, the relax structure of cubic SnS is then used to calculate energy band structure, orbital density of state, optical properties, elastic constants, elastic anisotropy, sound velocity anisotropy and Debye temperature.

A plane-wave pseudo-potential (PW-PP) in context of density functional theory (DFT) has been employed using CASTEP (Clark et al., 2005) code. The pseudo-potential technique is more efficient and much faster due to no former shape estimation of the orbitals is required (Usman et al., 2013). The electronic configurations of Sn and S are $4d^{10}$ $5s^2$ $5p^2$ and $3s^2$ $3p^4$ respectively. To calculate the interaction of valence electrons, the Vanderbilt's ultra-soft pseudo-potentials (USPs) (Vanderbilt, 1990) has been executed with a cut off energy of 300 eV for the electron wave function expansion. We implied two different independent exchange correlation methods, for better reliability and compatibility of the obtained results to grasp electron– ion interactions. One is local density approximation (LDA) with the Ceperley-Alder-Perdew-Zunger (CA-PZ) functional (Ceperley and Alder, 1980; Perdew and Zunger, 1981) and second is generalized gradient approximations (GGA) with the Perdew-Burke-Ernzerhof functional (Perdew et al., 1996). All calculations were performed on primitive unit cell.

The 8 × 8 × 8 k points of Monkhorst-Pack (MP) grid are carried out for the Brillouin-zone (BZ) integration. The Broyden–Fletcher–Goldfarb–Shenno (BFGS) technique (Pfrommer et al., 1997) is implemented on primitive cell atoms for relaxation until total energy convergence and the force on each atom are set to be 0.05 eV/Å and 2.0×10^{-5} eV/atom. The value of maximum displacement and stress are also fixed to 2×10^{-3} Å and 0.1 GPa. The convergence tolerance in the calculation of elastic constants are slightly different such as maximum force, energy convergence and maximum displacement are 0.006 eV/Å, 2.0×10^{-6} eV/atom and 2×10^{-4} Å respectively. The elastic constants and Debye temperature were calculated at ambient pressure. The orbital density of states and optical properties like real and imaginary part of dielectric constants, complex refractive index, absorption spectrum, optical conductivity, reflectance and energy loss function were determined with more dense mesh (10 × 10 × 10).

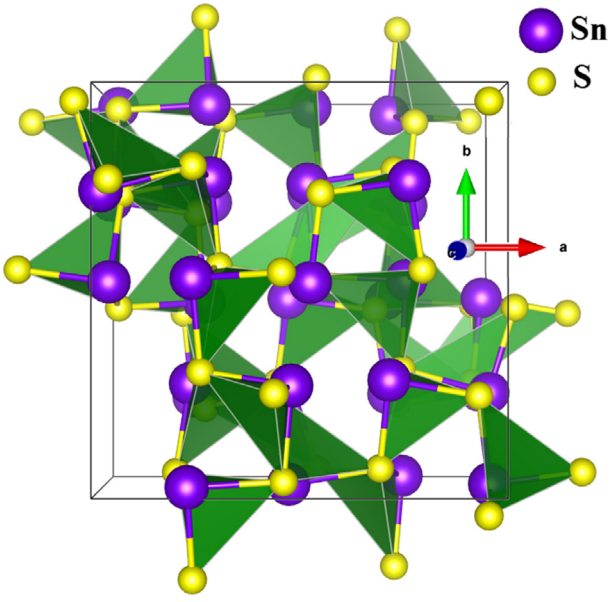

Fig. 1. Crystal structure of unit cell of cubic tin selenide (π-SnS). The violet and yellow balls represent Sn and S atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3. Result and discussion

3.1. Structural optimization

The electronic, elastic and thermodynamic properties of π-SnS are calculated using PW-PP (plane-wave pseudo-potential) technique using the two exchange correlation potentials i.e. LDA and GGA. The corresponding structural information is listed in Table s1 (see in supporting information), along with the available experimental and theoretical data for comparison. In present work the calculated results such as lattice parameter are well consistent with the available experimental (Abutbul et al., 2016a, 2016b; Barrios-Salgado et al., 2016; Rabkin et al., 2015) and theoretical (Segev et al., 2017a) data, which endorse the reliability of present work, also certify the obtained results are trustworthy.

In order to clearly understand the bonding mechanism in interatomic forces, it is necessary to determine the energy absorbed by stretching and bond breaking. In this respect, the calculation of cohesive energy (E_{coh}) of π-SnS crystal structure is considered. The cohesive energy is defined as the sum of total energy of each atom minus the total energy of crystal structure. The cohesive energy per atom of π-SnS was calculated from Eq. (1).

$$E_{coh} = \frac{1}{x+y}(xE_{atom}^{Sn} + yE_{atom}^{S} - E_{tot}^{SnS}) \quad (1)$$

where E_{atom}^{Sn}, E_{atom}^{S} and E_{tot}^{SnS} are the total energies of the pure free atoms of Sn, S and SnS respectively. The small value of cohesive energy (E_{coh}) indicates that the final compound is energetically more stable. The recorded cohesive energies with LDA and GGA of π-SnS are 5.173 and 4.449 eV/atom respectively. The results of GGA as compare to LDA shows more stability of π-SnS, because GGA additionally takes into account the spatial variation of the density in calculations.

Formation energy with negative sign indicates that the final compounds from the pure elements is possible and is defined as