

Electronic properties of orthorhombic BaSn₂S₅ single crystal

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Abstract: A theoretical investigation of the electronic structure and linear optical properties of BaSn₂S₅ compound is performed using the full-potential linearized augmented plane wave based on the local density approximation (LDA), generalized gradient approximation (GGA), Engel–Vosko GGA and the modified Becke–Johnson (mBJ) to solve the exchange correlation potential. The calculated energy gaps obtained using these approximations are 1.42, 1.59, 2.03 and 2.32 eV respectively. The mBJ shows very close agreement with the experimental energy gap (2.35 eV). The bond lengths of Ba–S and Sn–S are calculated, which are in good agreement with the experimental values. Bonds between Ba and S atoms show ionic nature, while polar covalent bonds between Sn and S atoms are obtained. The optical properties are calculated and discussed in detail. Both calculated and experimental absorption coefficients are comparable to each other in the mid-IR region.

Keywords: Electronic structure; Electronic charge density; Linear optical properties; FPLAPW; DFT

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1. Introduction

From the last few decades, a substantial increase for energy harvesting and transparent electronics applications has been found [1–5]. By using the binary building blocks and cross substitute, different ternary and quaternary system semiconductors can be produced [6]. Luo et al. [7], have studied the novel ternary centric BaSn₂S₅ compound by ultraviolet to near infrared (UV-NIR) spectroscopy. They have observed that this compound exhibits wide IR transmission ranging from NIR to 25 μm, in which all the bands are lying between 3–5 and 8–14 μm of the ambience transparent windows, confirming that it has promising applications in optical devices in the spectral range from 3 to 8 μm (Mid-IR) [7]. They have found the compound to be stable up to 600 °C under N₂ atmosphere.

To the best of our knowledge, no comprehensive work either experimental data or first principles calculations on the structural, electronic, and optical properties of ternary centric BaSn₂S₅ compound have appeared in the literature.

Therefore as a natural extension to the experimental work presented above a detailed depiction of the electronic structural and optical properties of ternary centric BaSn₂S₅ compound using full potential method is timely and brings us deep insights to understand the origin of the electronic band structure and density of states. Hence it is very important to use a full potential method. Therefore we have addressed ourselves to perform first principle calculations based on the all-electron-full potential linearized augmented plane wave (FPLAPW) method, within the local density approximation (LDA), generalized gradient approximation (GGA), Engel–Vosko GGA (EVGGA) and the modified Becke–Johnson (mBJ) to solve the exchange correlation potentials for calculating the electronic structure, electronic charge density and linear optical properties for BaSn₂S₅. The crystal structure is illustrated in Fig. 1.

2. Computational method

We calculated the electronic band structure, density of states, electronic charge density distribution and linear optical susceptibilities of the orthorhombic centric BaSn₂S₅

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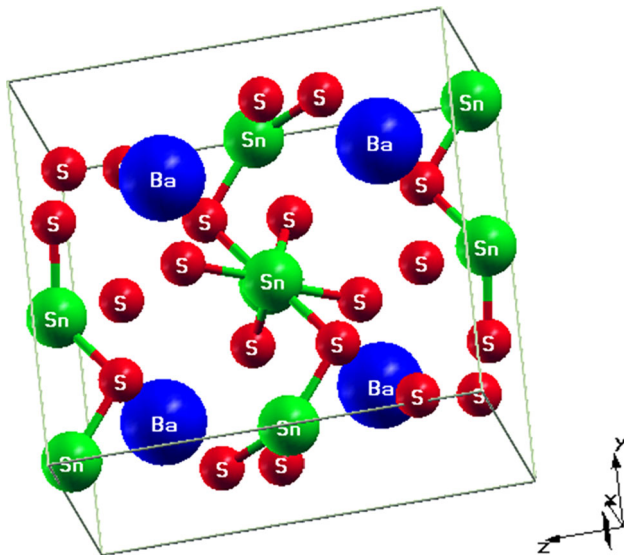


Fig. 1 (a) Crystal structure of BaSn_2S_5

compound with space group Pccn (no. 56). We employed the full-potential linearized augmented plane wave (FP-LAPW) technique as implemented in the WIEN2k package [8]. This was an implementation of the density functional theory (DFT) [9] with different possible approximations for the exchange–correlation (XC) potential. Exchange and correlation potentials were described by the LDA [10] and gradient approximation (GGA) [11], which was based on exchange–correlation energy optimization to calculate the total energy. In addition, we used Engel–Vosko GGA (EV-GGA) [12, 13] and the mBJ potential (mBJ) [14], which optimized the corresponding potential for electronic band structure calculations. In order to achieve energy eigenvalues convergence, the wavefunctions in the interstitial region were expanded in plane waves with a cutoff of $K_{\text{max}} = 7/R_{\text{MT}}$, where R_{MT} denoted the smallest atomic

sphere radius and K_{max} gave the magnitude of the largest K vector in the plane-wave expansion. The R_{MT} were taken to be 2.05 and 1.6 atomic units (a.u) for Ba, Sn and S atoms, respectively. The valence wavefunctions inside the spheres were expanded up to $l_{\text{max}} = 10$, while the charge density was Fourier expanded up to $G_{\text{max}} = 12 \text{ (a.u)}^{-1}$.

As starting point for our calculations, we used the X-ray diffraction data taken from Luo et al. [7] report. Using GGA approximation, we optimized the structure by minimization of the forces (1 mRy/au) acting on the atoms. From the relaxed geometry the electronic structure and chemical bonding were determined. Various spectroscopic features were calculated and compared with experimental data. Once the forces were minimized in this construction, one could then find the self-consistent density at these positions by turning off the relaxations and driving the system to self-consistency. The calculated lattice constants and the atomic positions exhibited very good agreement with the experimental data as listed in Table 1.

We used 40 k-points in the irreducible Brillouin zone for structural optimization. For calculating the total and the angular momentum decomposition of the atoms projected electronic density of states and the optical properties a denser mesh of 300 k-points was used. The convergence of the total energy in the self-consistent calculations was taken with respect to the total charge of the system with a tolerance 0.0001 electron charges.

3. Results and discussion

3.1. Electronic structure

The calculated electronic band structures along the high symmetry directions of the primitive Brillouin zone (BZ)

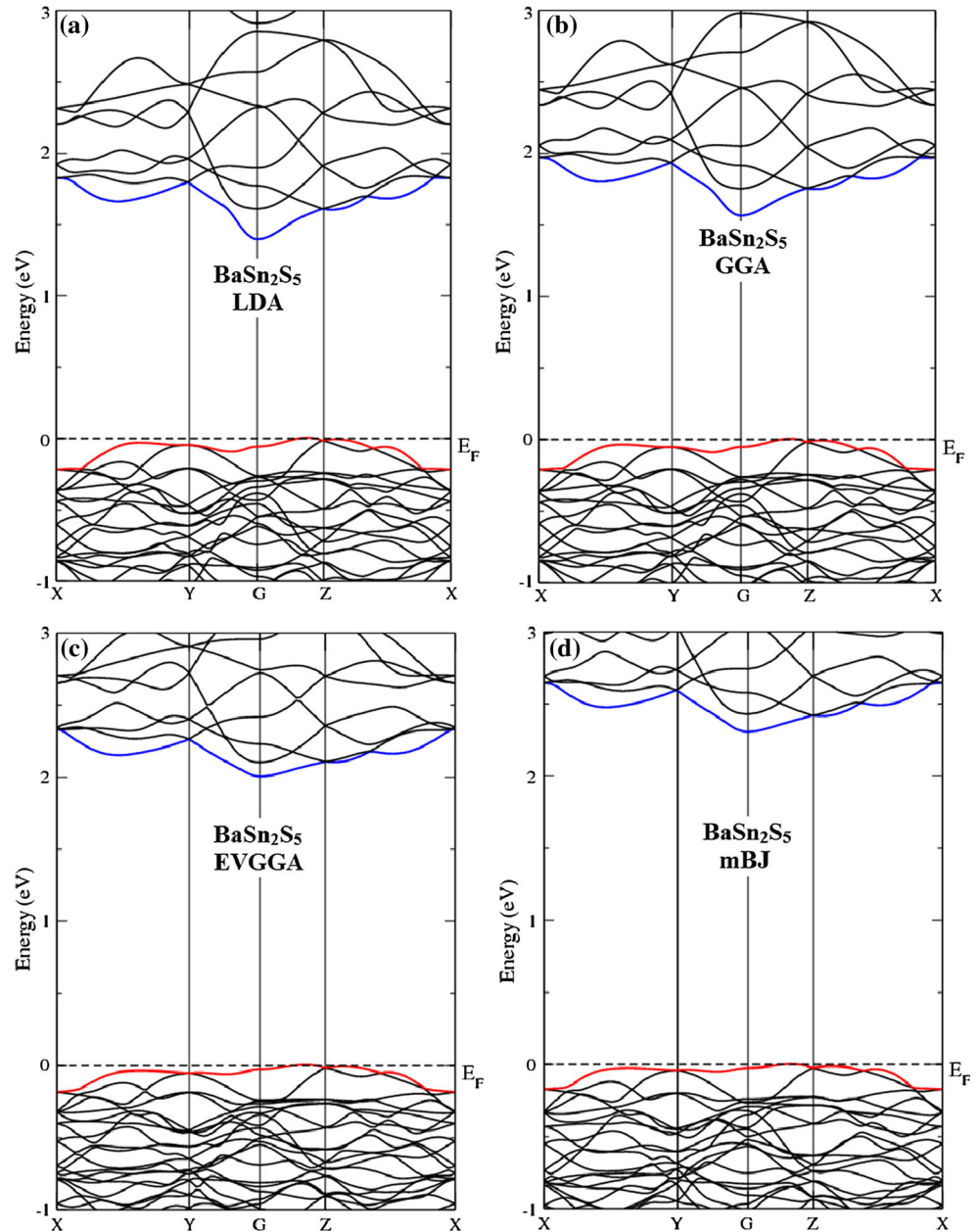
Table 1 Calculated and experimental lattice constant and atomic positions for BaSn_2S_5

Experimental data A^0				Calculated data A^0		
BaSn_2S_5						
a = 6.674				a = 6.627		
b = 10.607				b = 10.533		
c = 11.394				c = 11.314		
Atoms	x (exp.)	y (exp.)	z (exp.)	x	y	z
Ba	0.25000 ^a	0.25000 ^a	0.30200 ^a	0.25000 ^b	0.25000 ^b	0.30270 ^b
Sn	0.24653 ^a	−0.05958 ^a	0.02717 ^a	0.24604 ^b	0.93983 ^b	0.02853 ^b
S(1)	0.07020 ^a	0.36510 ^a	0.06508 ^a	0.07072 ^b	0.36176 ^b	0.06433 ^b
S(2)	0.0501 ^a	0.52920 ^a	0.35077 ^a	0.05009 ^b	0.52903 ^b	0.34833 ^b
S(3)	−0.2500 ^a	0.25000 ^a	0.34550 ^a	0.75000 ^b	0.25000 ^b	0.34058 ^b

^a Ref. [7]

^b This work

Fig. 2 (a) Calculated band structure of BaSn₂S₅ using LDA, (b) Calculated band structure of BaSn₂S₅ using GGA, (c) Calculated band structure of BaSn₂S₅ using EVGGA and (d) Calculated band structure of BaSn₂S₅ using mBJ

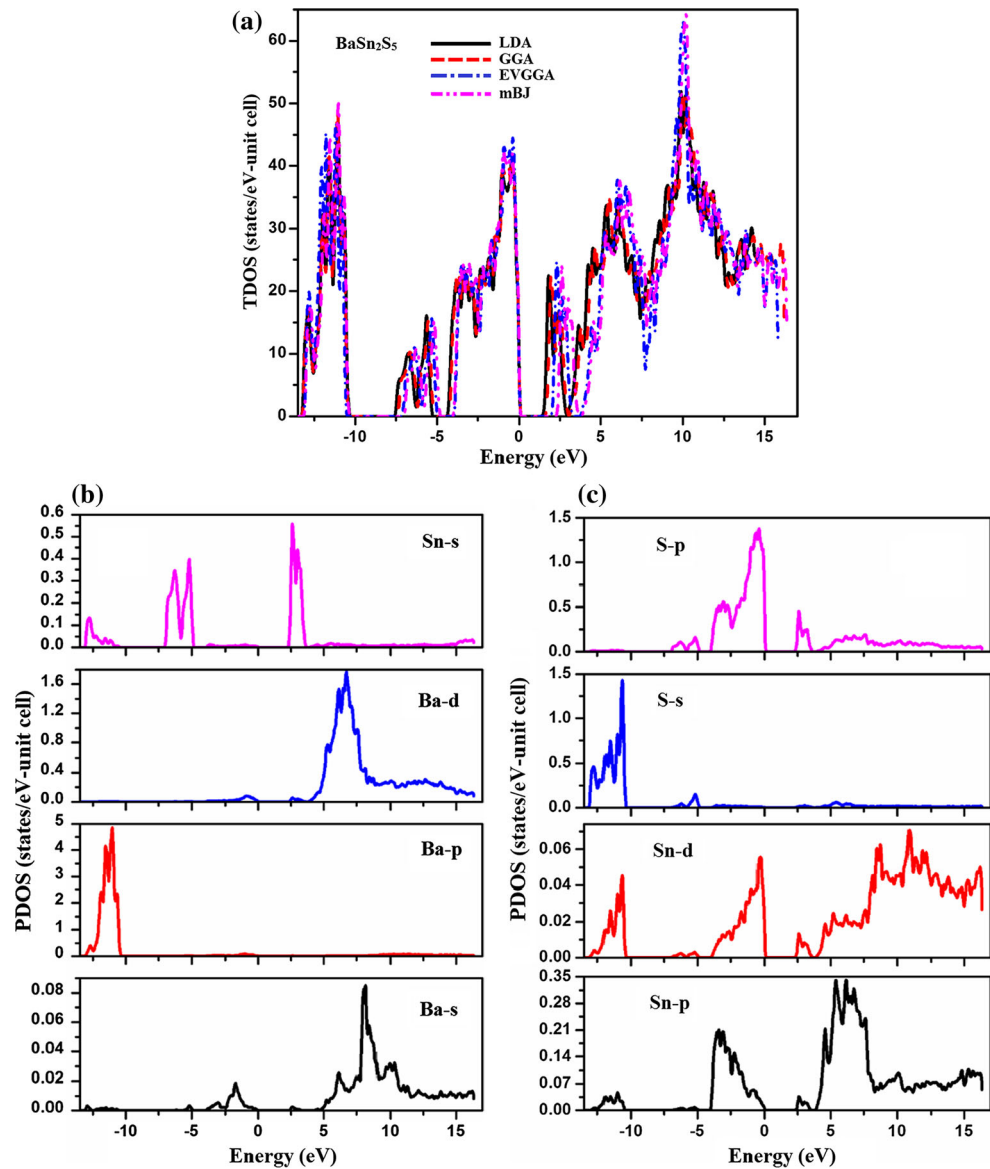


using LDA, GGA, EVGGA and mBJ are shown in Fig. 2(a)–2(d). Calculated Band structures show that the Fermi level is lying at zero eV. The valence band maximum (VBM) is located at Z point of BZ and the conduction band minimum (CBM) at Γ point of BZ, resulting an indirect band gap. The calculated energy band gaps are 1.42 eV, 1.59 eV, 2.03 eV and 2.32 eV respectively, using LDA, GGA, EVGGA and mBJ results, which are compared with 2.35 eV obtained experimentally [7].

The total density of states of BaSn₂S₅ have been calculated using LDA, GGA, EVGGA and mBJ as shown in Fig. 3(a), confirm that the mBJ approach gives better band splitting and

hence energy gap value closer to the experimental one. Therefore, we have selected to show the projected density of states of Ba, Sn and S using mBJ as shown in Fig. 3(b)–3(d). The lowest energy region of the projected DOS extended from -13.0 to -10.0 eV consist of Ba-p (5.0 states/eV), S/Sn-s (1.5/0.15 states/eV) and Sn-p (0.06 states/eV). Following Fig. 3(b), only *s* orbital of Sn atom is lying in the energy range between -10.0 and -5.0 eV. Near the Fermi level (E_F), density of states depict sharp peak due to flat bands, as shown in Fig. 3(c), originated mainly from S-*p* states (1.4 states/eV). The energy region extended from -5.0 to 0.0 eV is formed from Sn-*p* (0.21 states/eV) and Sn-*d* (0.06 states/eV).

Fig. 3 (a) Calculated total density state (TDOS) of BaSn_2S_5 using LDA, GGA, EVGGA and mBJ, (b) Calculated partial density of states (PDOS) of BaSn_2S_5 using mBJ, and (c) Calculated partial density of states (PDOS) of BaSn_2S_5 using mBJ



3.2. Electronic charge density

To obtain accurate results regarding the chemical bonding nature between the atoms of the investigated compound BaSn_2S_5 , we have calculated electronic charge density along (1 1 0) and (1 0 0) crystallographic planes, as illustrated in Fig. 4(a) and 4(b). According to the electronegativities of Ba (0.89), Sn (2.58) and S (1.96) atoms, our calculated results for the electronic charge density depict strong ionic bond between Ba and S atoms. Due to greater electronegativity of S atoms, it has the ability to attract electrons toward itself, as compared to Ba atoms as shown in Fig. 4(a). Following Fig. 4(b), one can observe that there exist polar covalent interactions between two Sn atoms and one S atom, which is attributed to the electronegativity difference (0.62). In Table 2, we have listed the calculated

bond lengths in comparison with the experimental data [7]. Good agreement was found supporting robustly the accuracy of the DFT-mBJ calculations.

3.3. Optical properties

Since BaSn_2S_5 compound crystallizes in the orthorhombic space group Pccn. This symmetry has three non-zero components of the optical dielectric tensor corresponding to the electric field \vec{E} being directed along a , b , and c -crystallographic axes. The compound possesses well pronounced structures of the three principal complex tensor components; $\epsilon^{xx}(\omega)$, $\epsilon^{yy}(\omega)$ and $\epsilon^{zz}(\omega)$. The imaginary part of the three principal complex tensor components completely defines the linear optical susceptibilities. The imaginary parts $\epsilon_2^{xx}(\omega)$, $\epsilon_2^{yy}(\omega)$ and $\epsilon_2^{zz}(\omega)$ of the optical

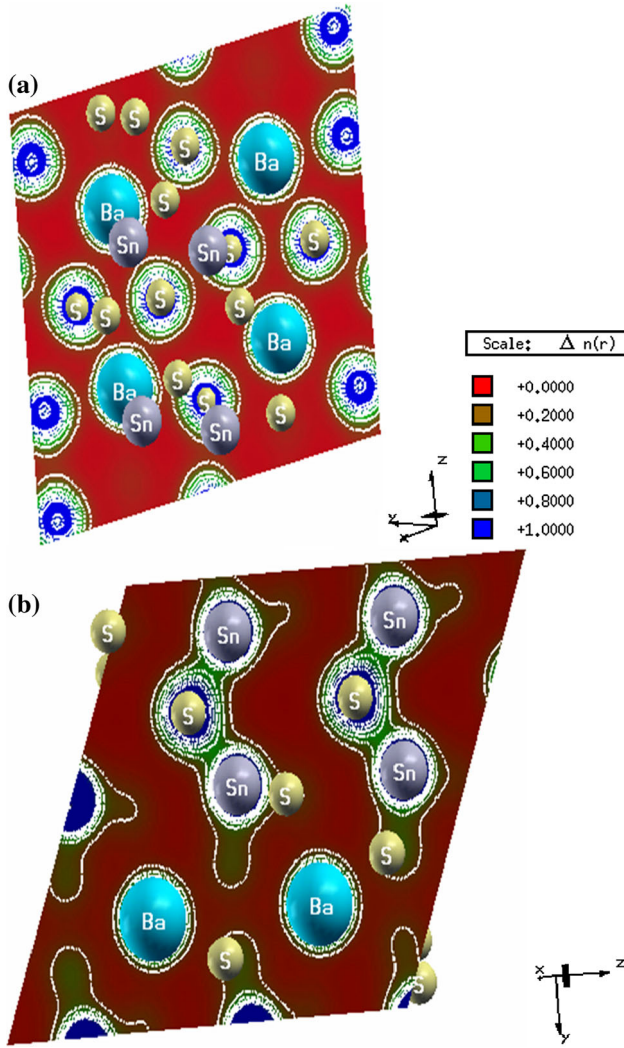


Fig. 4 Electronic space charge density distribution contour calculated with mBJ in (a) (110) and (b) (100) planes of BaSn₂S₅

Table 2 Calculated bond lengths in comparison with the experimental values [7] for BaSn₂S₅

Atoms	Bond length (exp) Å ⁰	Bond length (Caldt) Å ⁰
BaSn ₂ S ₅		
Ba(1)-S(1)	3.1964	3.1960
Ba(1)-S(1)	3.4520	3.4240
Ba(1)-S(2)	3.2952	3.2880
Ba(1)-S(2)	3.5393	3.5310
Ba(1)-S(3)	3.3735	3.3650
Sn(1)-S(2)	2.4210	2.4570
Sn(1)-S(1)	2.4368	2.4680
Sn(1)-S(3)	2.4869	2.5080
Sn(1)-S(1)	2.5316	2.5500
Sn(1)-S(2)	2.5962	2.6020

function's dispersion have been calculated using the following expression [15].

$$\epsilon_2^{ij}(\omega) = \frac{8\pi^2\hbar^2 e^2}{m^2 V} \sum_k \sum_{cv} (f_c - f_v) \frac{p_{cv}^i(k) p_{vc}^j(k)}{E_{vc}^2} \delta[E_c(k) - E_v(k) - \hbar\omega]. \quad (1)$$

where m , e and \hbar are the electron mass, charge and Planck's constant, respectively. f_c and f_v represent the Fermi distributions of the conduction and valence bands, respectively. The term $p_{cv}^i(k)$ denotes the momentum matrix element transition from the energy level c of the conduction band to the level v of the valence band at certain \mathbf{k} -point in the BZ and V is the unit cell volume.

The real part $\epsilon_1^{xx}(\omega)$, $\epsilon_1^{yy}(\omega)$ and $\epsilon_1^{zz}(\omega)$ are obtained from the imaginary part of these principal complex tensor components by means of Kramers–Kronig transformation [16].

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} p \int_0^{\infty} \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (2)$$

Figure 5(a) illustrates the imaginary parts $\epsilon_2^{xx}(\omega)$, $\epsilon_2^{yy}(\omega)$ and $\epsilon_2^{zz}(\omega)$ of the optical function's dispersion. The absorptive part $\epsilon_2^{xx}(\omega)$, $\epsilon_2^{yy}(\omega)$ and $\epsilon_2^{zz}(\omega)$ of the investigated compound depict that the absorption edge begins at 2.32 eV, corresponds to the energy band gap E_g . Following Fig. 5(a), one can see the maximum peaks at 5.8 eV [for $\epsilon^{xx}(\omega)$], 5.6 eV (for $\epsilon^{yy}(\omega)$) and 6.4 eV (for $\epsilon^{zz}(\omega)$), which is associated to the inter-band transitions from the p states of S atom to s states of Sn atom. In the visible region, $\epsilon^{yy}(\omega)$ shows greater dispersion in comparison to the remaining two spectral components.

The absorptive part $\epsilon_2^{xx}(\omega)$, $\epsilon_2^{yy}(\omega)$ and $\epsilon_2^{zz}(\omega)$ increase with the increasing of the incident photon energy $\hbar\omega$ to reach its maximum at around 6.38 eV. Beyond 7.5 eV it shows a rapid decrease as shown in Fig. 5(a).

The dispersive portion $\epsilon_1(\omega)$ of the complex dielectric tensor is illustrated in Fig. 5(b). The static values are 6.2 for both of $\epsilon_1^{xx}(\omega)$ and $\epsilon_1^{yy}(\omega)$, while it is 5.8 for $\epsilon_1^{zz}(\omega)$. The components of $\epsilon_1(\omega)$ are related to the energy band gap E_g , which is explained by Penn model [17]. Figure 5(b) displays two main peaks at around 2.5 and 5.2 eV. Beyond 5.2 eV, $\epsilon_1(\omega)$ tends to decrease and becomes negative. The negative values of $\epsilon_1(\omega)$ describe the reflectiveness of compounds for the incident electromagnetic radiation's giving metallic like nature within these energy ranges. In these specific energy ranges, the material can be used as a shielding materials.

Figure 5(c) displays the computed reflectivity $R(\omega)$ as a function of photon energy $\hbar\omega$. The higher value of the

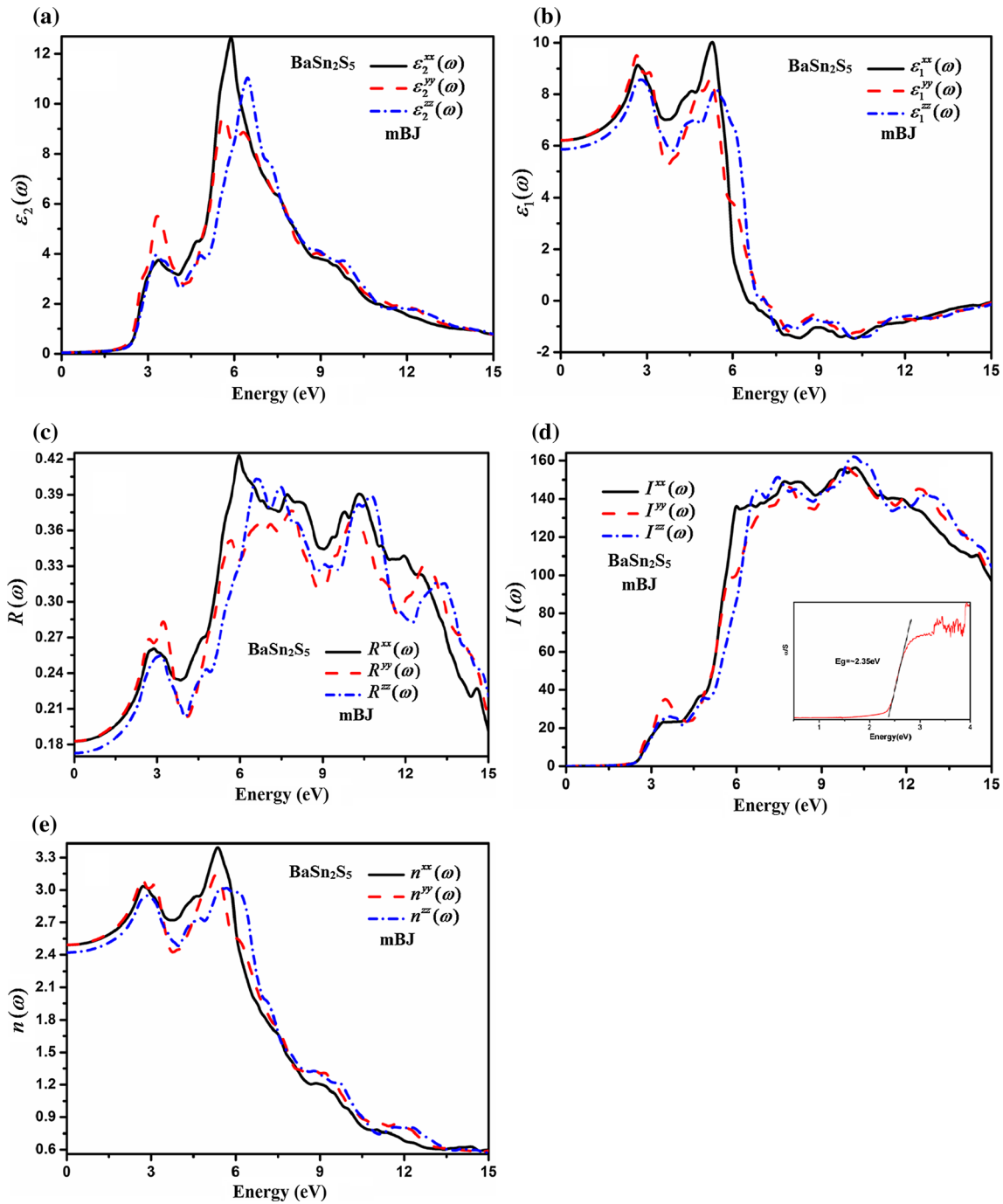


Fig. 5 (a) Calculated imaginary of dielectric function of BaSn₂S₅ using mBJ, (b) Calculated real parts of dielectric function of BaSn₂S₅ using mBJ, (c) Calculated reflectivity of BaSn₂S₅ using mBJ,

(d) Calculated absorption coefficient along with the experimental figure of BaSn₂S₅ using mBJ and (e) Calculated refractive index of BaSn₂S₅ using mBJ

reflectivity spectra corresponds to the negative value of the real part $\epsilon_1(\omega)$ of the dielectric tensor. In the highest UV portion at energy 15.0 eV, both incident photon frequency and plasma frequency become equal due to which $R(\omega)$ decreases dramatically (called plasma reflection edge).

The absorption coefficient $I(\omega)$ versus energy is plotted along with the experimental figure of Luo et al. [7] in Fig. 5(d). Both computed and experimental data for absorption coefficient of the investigated compound are in close agreement in the mid IR region. $I(\omega)$ exposes broad spectra in the energy range from 5.0 to 12.5 eV. These

peaks in $I(\omega)$ predict that we can also use the compound for optoelectronic devices such that LED, photodiode etc.

We have also computed the refractive index $n(\omega)$ for BaSn₂S₅ as shown in the Fig. 5(e). The static values are 2.49 for $n^{xx}(0)$ and $n^{yy}(0)$, and 2.42 for $n^{zz}(0)$. The spectral components of $n(\omega)$ gain its highest values of 3.39 at 5.4 eV, 3.13 at 5.3 eV and 3.01 at 5.6 eV for the three components, respectively. The three components of $n(\omega)$ show greater value than unity up to 9.8 eV, due to the reduction in the speed of photons during the interaction with the electrons inside the materials. $n(\omega)$ has inverse relation with the speed of photons (c) i.e. smaller is the speed of photon's greater is the $n(\omega)$ and vice versa. In general, $n(\omega)$ increases with the increase in electrons density because the electromagnetic radiations strike more electrons and slow down. The materials, where the atoms are bonded covalently, the probability of photons interaction with the electrons is greater than the ionic bonding materials resulting in an increase in $n(\omega)$.

4. Conclusions

We have calculated the energy band structure, density of states, electronic charge density and the linear optical properties of BaSn₂S₅. The computed band gaps of BaSn₂S₅ are 1.42, 1.59, 2.03 and 2.32 eV using LDA, GGA, EVGGA and mBJ. The band gap obtained from the mBJ exchange correlation energy is very close to the experimental value (2.35 eV), which confirms the accuracy of mBJ calculations. The calculated density of states depicts that the maximal of the valence band is mostly originated from S-p states. We have calculated the total electronic charge density along two (110) and (100) crystallographic planes demonstrating the ionic nature between Ba and S atoms and polar covalent bond between Sn and S atoms. The bond lengths of Ba–S and Sn–S atoms show

very close agreement with the experimental data. The entire optical properties are calculated based on the electronic band structure and density of states. In the mid IR region, the experimental and computed absorption coefficients are comparable.

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