

# First-principles study of electronic and optical properties of BaS, BaSe and BaTe

Research Article

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**Abstract:** The optimized crystal structure, energy band structures, density of states (DOS) and optical properties of BaX (X=S, Se and Te) were investigated by the full potential linearized augmented plane wave plus local orbitals method (FP-LAPW+lo). The exchange-correlation potential was treated using the generalized gradient approximation (GGA). We have used also Engel and Vosko GGA (EV-GGA) formalism to improve the band gap results. The calculated results such as band gaps, dielectric constants and reflectivity spectra showed good agreement with the experimental data. The effect of the spin-orbit coupling (SOC) on the optical properties was also studied and found to be very small, especially in the low-energy region.

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## 1. Introduction

II-VI chalcogenide compounds have attracted increasing attention because of their potential applications in light-emitting diodes (LEDs) and laser diodes (LDs). Since the first demonstration of a blue-green-emitting laser using ZnSe by M. A. Haase *et al.* [1], many experimental and theoretical works have been reported on II-VI chalcogenide, such as zinc chalcogenides [2–4], calcium chalcogenides [5], and beryllium chalcogenides [6, 7]. Scientists expect that chalcogenides may provide new II-VI candidates, complementing the well-known IV and III-V semiconductors, for the fabrication of various electrical and optical devices.

Among II-VI chalcogenide compounds, the compounds BaX (X=S, Se and Te) have been widely researched because of their interesting structural and electronic properties [8–11]. For example, the researches of T. A. Grzybowski and G. Kalpana show that under normal conditions these compounds crystallize in the NaCl-type structure with a closed-shell ionic system, and under pressure they undergo a first-order structural phase transition to CsCl-type structure [12, 13]. K. Syassen *et al.* have obtained the optical and absorption spectra of BaTe in the pressure range of 0 to 400 kbar at 300 K [14]. Y. Kaneko *et al.* have measured the reflectivity spectra of BaS and BaSe in the synchrotron radiation region of 4–40 eV [15, 16]. To our knowledge, most of the available results on the reflectivity and absorption of these compounds are limited to excitonic transitions, and there are not yet any experimental results on such quantities for BaTe in the optical frequency range. Pourghazi *et al.* calculated optical properties of BaX com-

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pounds using the FP-LAPW [8]. However, while their results were in fair agreement with the experimental data in the low-energy range below 15 eV, the results above 15 eV were not good. Recently, G. Q. Lin *et al.* studied barium chalcogenides using plane wave pseudopotential (PWP) scheme based on the density functional theory (DFT) [17]. They showed that all the three compounds are direct band-gap semiconductors with a minimum gap at the  $\Gamma$  point. Lin's results were in contradiction to those of the previous researches [8, 15].

It is very interesting to obtain the optical response, such as the reflectivity and absorption in the optical frequency range, and inspect the available band gaps data for these compounds in detail. In this work, we investigated the crystal structures, and the electronic and optical properties of barium chalcogenides in the NaCl structure using the full potential linearized augmented plane wave plus local orbital method (FP-LAPW+lo), based on density functional theory and implemented in WIEN2K code [18]. This paper is organized as follows. A brief description of the calculation method is given in Sec. 2. In Sec. 3, the results of calculations as well as the discussions are presented and compared with available experimental data. Finally, conclusions are given in Sec. 4.

## 2. Calculation method

The calculations presented in this work were performed using the FP-LAPW+lo method. In this method no shape approximation on the potential or on the electronic charge density is made. It divides space into an interstitial region and non-overlapping spheres centred at the atomic sites. In the atomic sphere, a linear combination of radial functions times spherical harmonics is used; in the interstitial region, the basis set consists of plane waves. The exchange correlation potential within the GGA is calculated using the scheme of Perdew-Burke-Ernzerhof [19]. The calculations of the electronic and optical properties have been done relativistically with and without the spin-orbit coupling (SOC). The convergence parameter  $RK_{\max}$ , which controls the size of the basis set in these calculations, was set to 9.0. The cut-off energy, which defines the separation between the core and valence states, was set to -7.0 Ry. In the following calculations, we have chosen 10 local orbits for BaS, and 15 local orbits for BaSe and BaTe. The atomic sphere radii were set to 2.5 a.u. for each of the four elements. Brillouin zone (BZ) integrations within the self-consistency cycles were performed *via* a tetrahedron method, using 47  $k$ -points in the irreducible BZ. The charge convergence was selected as 0.0001 e.

For the calculation of the optical properties (for the imag-

inary part of the dielectric tensor) a denser sampling of the BZ was needed, where we used 816  $k$ -points. The dielectric function:

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (1)$$

is known to describe the optical properties of the compounds. In this study, the imaginary part of the dielectric function is given by:

$$\epsilon_2(\omega) = \frac{Ve^2}{2\pi\hbar m^2 \omega^2} \int d^3k \sum_{nn'} \left| \langle \vec{k}n | \vec{p} | \vec{k}n' \rangle \right|^2 f(\vec{k}n) \left( 1 - f(\vec{k}n') \right) \delta(E_{\vec{k}n} - E_{\vec{k}n'} - \hbar\omega), \quad (2)$$

where  $\vec{p}$  is the momentum operator,  $|\vec{k}n\rangle$  is the eigenfunction with eigenvalue  $E_{\vec{k}n}$ , and  $f(\vec{k}n)$  is the Fermi distribution function. The evaluation of the matrix elements of the momentum operator in Eq. (2) is done over the muffin tin and the interstitial regions separately. Further, the details about the evaluation of matrix elements can be found in Ref. [20] and Ref. [21].

The real part of the dielectric function was computed from  $\epsilon_2(\omega)$  using the Kramers-Kronig relation in the form:

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\epsilon_2(\omega') \omega' d\omega'}{\omega'^2 - \omega^2}. \quad (3)$$

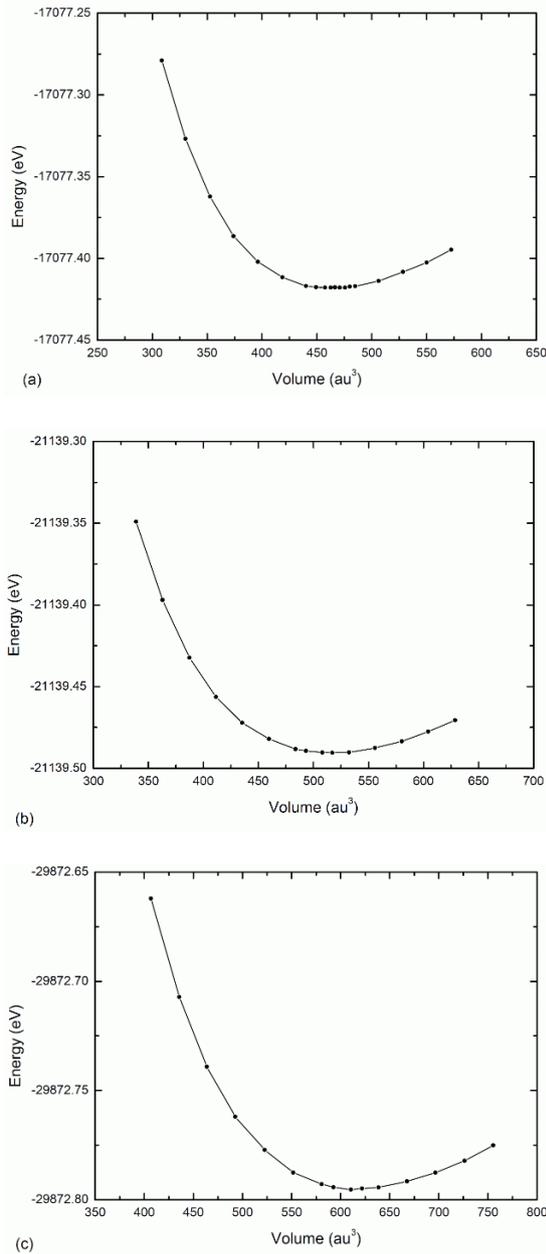
The knowledge of both the real and imaginary parts of the dielectric function allows the calculation of important optical functions. The reflectivity spectrum can be calculated with the use of the dielectric function by way of the following relationship:

$$R(\omega) = \left| \frac{\sqrt{\epsilon(\omega)} - 1}{\sqrt{\epsilon(\omega)} + 1} \right|^2. \quad (4)$$

## 3. Results and discussion

### 3.1. Geometric and electronic structure

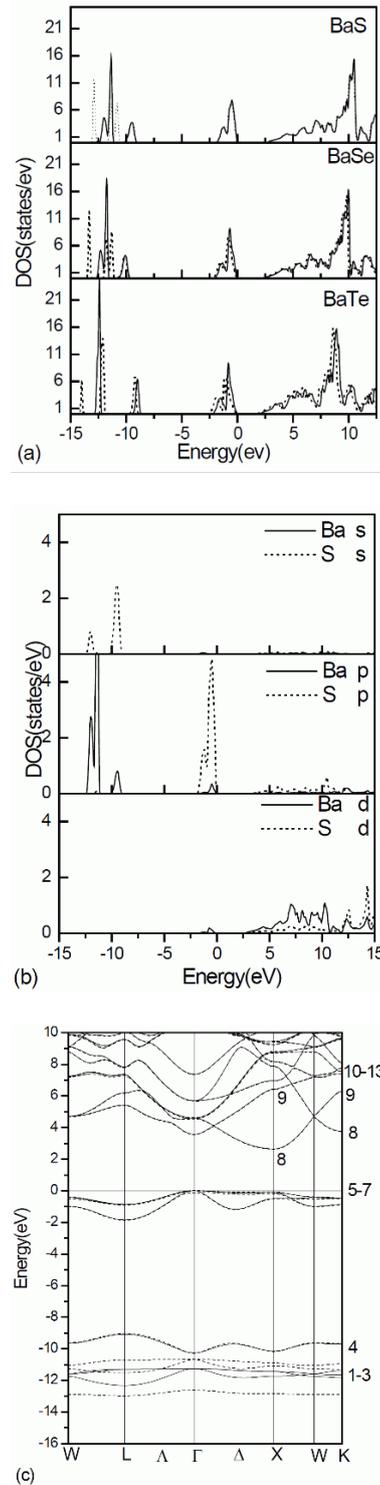
The calculations for optimized crystal structures have been performed. Fig. 1 represents our calculated total energy of BaX (X=S, Se and Te) as a function of cell volumes. The theoretical lattice parameters are 12.283 a.u., 12.735 a.u. and 13.524 a.u. for BaS, BaSe and BaTe, respectively. The corresponding experimental lattice parameters are 12.074 a.u., 12.463 a.u. and 13.242 a.u. for BaS, BaSe and BaTe, respectively. Our theoretical parameters are very close to the experimental values for all of the three



**Figure 1.** Total energy of (a) BaS, (b) BaSe and (c) BaTe with the NaCl-type structure as a function of the cell volumes.

compounds, so in the next calculations the experimental lattice constants have been used [13].

Our calculated total density of states (DOS) for BaS, BaSe and BaTe are shown in part (a) of Fig. 2. In parts (b) and (c), we show only the partial DOS and the electronic band structure for BaS, because they are very similar to those obtained for BaSe and BaTe. The results are given both with and without SOC. From the calculated partial



**Figure 2.** (a) Total density of states without (solid line) and with (dotted line) SOC for three compounds; (b) partial density of states without SOC for BaS; (c) band structure without (solid line) and with (dotted line) SOC for BaS.

DOS for our binary compounds, we find that the major contributions to the occupied parts come from the Ba 5p and 5d states and the chalcogen s and p states.

There are four main regions in the DOS. The first region is dominated by 5p-Ba character, while in the next region is the s-chalcogens character. The region just below the Fermi level  $E_F$  is predominantly p states of chalcogens (S, Se, Te) with only a small contribution for d-Ba. Just above the Fermi level the 5d-Ba state dominates. The structure of spin-orbit splitting and its values (nearly 1.0 eV) are considerable in the first region. Spin-orbit coupling removes the degeneracy between two of the three bands in the electronic band structure.

One can see that the band-structure is composed of the p-orbital-like valence bands due to the chalcogen and the

d-orbital-like conduction bands due to Ba in all of the three compounds. The direct gap at the Xpoint is smaller than that at the  $\Gamma$ -point and the top of the valence band is located at the  $\Gamma$ -point. There is an indirect energy gap between the top of the chalcogen p valence bands occurring at the  $\Gamma$  point and the bottom of the Ba 5d bands occurring at the X point. These theoretical results have been confirmed by the detailed analysis of the exciton reflection spectra observed on a series of IIa-VIb crystals [22]. It is noted that Lin *et al.* find a direct band gap for all three compounds using plane-wave pseudopotential (PWP) method [17]. This could be interpreted as being due to the energy difference at  $\Gamma$  and X points in the bottom of the conduction band, which is very small.

**Table 1.** The calculated and experimental values of band gap energies,  $E_g$ (eV).

	Present work							Exp [23]
	GGA [19]		EV-GGA [30]	LAPW [8]	LMTO [13]	PWP [17]	ASW [24]	
	without soc	with soc	without soc					
BaS	2.652	2.605	3.537	2.33	2.30	2.17	2.10	3.88
BaSe	2.405	2.269	3.243	2.08	2.01	2.02	1.80	3.58
BaTe	1.995	1.733	2.788	1.61	1.58	1.65	1.40	3.08

The calculated band gaps are shown in Tab. 1, in which experimental data [23] and other calculated results [8, 13, 17, 24] are also listed. Our calculated band gaps are in fair agreement with experiments and much closer than other theoretical studies. Though the theoretical band gaps are on the whole smaller than the experimental results due to the GGA approximation, our calculated results are very close to the experimental values for using available local orbitals to better describe unoccupied states. The calculated energy gaps decrease with the increase of the chalcogen atom size. Similar behaviour was observed in Ca and Sr chalcogenides [25, 26]. The SOC reduces the band gap, similar to what has been found for HgI<sub>2</sub> and SnI<sub>2</sub> [27, 28].

It is well known that the LDA and the GGA usually underestimate the energy gap [29]. This is mainly due to the fact that they have simple forms that are not sufficiently flexible for accurately reproducing both exchange-correlation energy and its charge derivative. Engel and Vosko [30] constructed a new functional form of the GGA by considering this shortcoming which has been proven to improve the results for quantities that depend on the energy eigenvalues, including the band gap [29]. By us-

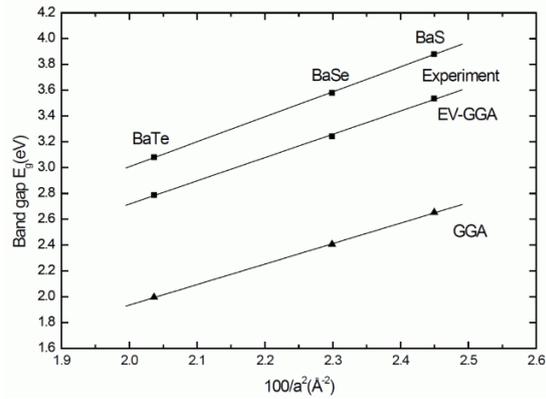
ing Engel and Vosko's generalized gradient approximation (EV-GGA), we were able to improve our band gap results as shown in Tab. 1. One can see that the values of calculated band gaps with EV-GGA are a significant improvement over the earlier results based on GGA and much closer to the experimental values.

Using experimental data, Dalven summarized an empirical relationship that band gaps of semiconductors with the cubic NaCl structure were linear with  $1/a^2$ , where  $a$  was the lattice constant of the crystal [31]. As shown in Fig. 3, our calculated band gaps for BaS, BaSe and BaTe using GGA and EV-GGA methods are linear with  $1/a^2$

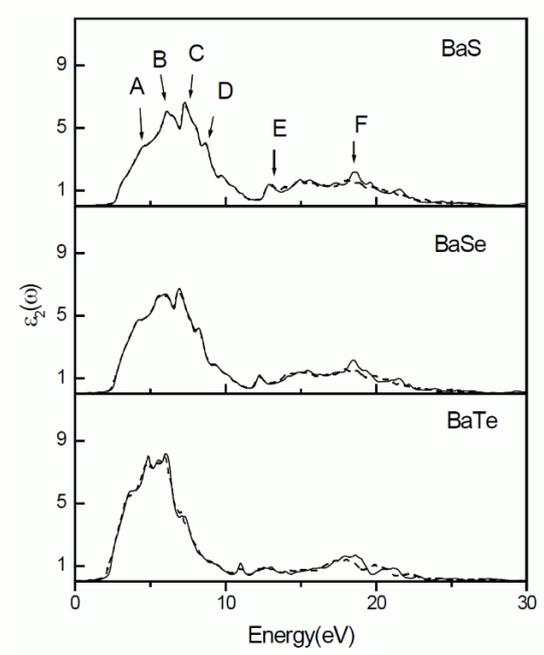
### 3.2. Optical properties

The calculated  $\epsilon_2(\omega)$  for BaS, BaSe and BaTe are shown in Fig. 4 with and without SOC. One can find that the behaviour of the imaginary part of the dielectric function is rather similar for all of the three compounds with some differences in details. All the structures in  $\epsilon_2(\omega)$  are shifted towards lower energies as we go from S to Te. This trend can be directly inferred from the band structure results.

The major peak positions of  $\epsilon_2(\omega)$  together with the dom-



**Figure 3.** The experimental and calculated band gap *versus*  $100/a^2$  (where  $a$  is the equilibrium lattice constant) for rock-salt barium chalcogenides BaS, BaSe and BaTe.

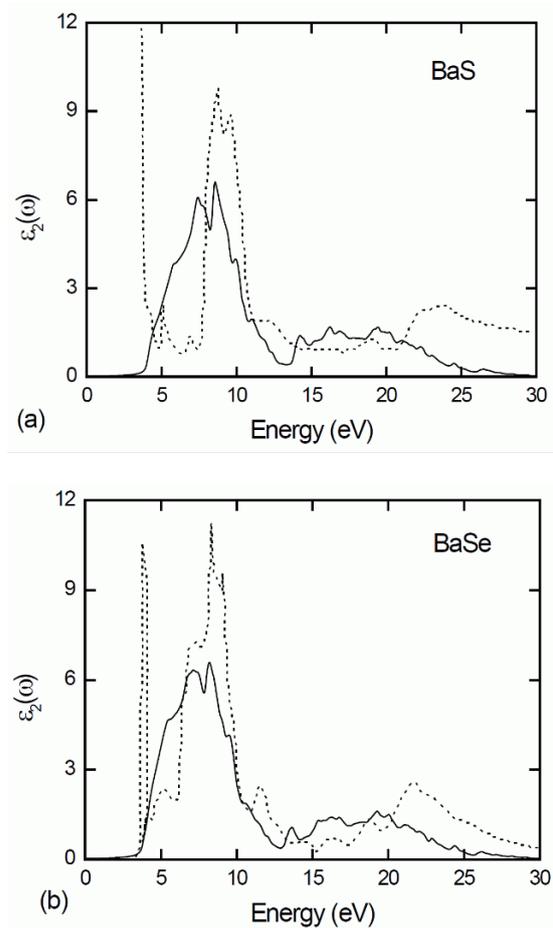


**Figure 4.** Calculated imaginary part of the dielectric function without (solid line) and with (dotted line) SOC for BaS, BaSe and BaTe.

inant contributions of interband transitions to each peak are tabulated in Tab. 2. It is clear that the chalcogen p states and the Ba 5d states play major roles in these optical transitions as initial and final states, respectively. The effect of SOC on the structures of  $\epsilon_2(\omega)$  is more significant in high-energy regions than that in low-energy regions. The imaginary parts of the dielectric function for BaS and BaSe are compared with experimental data in Figs. 5(a) and (b) [16] respectively. The calculated spectra have

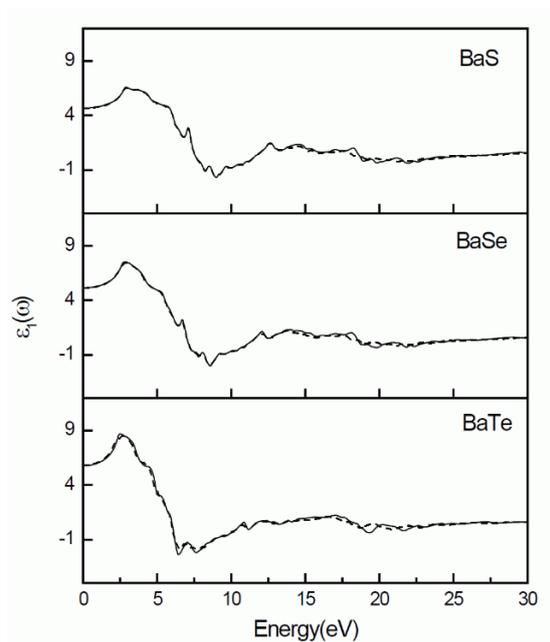
**Table 2.** Peak position of  $\epsilon_2(\omega)$  together with the dominant contributions to every peak.

Peak	Peak position(eV)			The dominant transition(s)		Transition Location in BZ
	BaS	BaSe	BaTe	From band(s)	To band(s)	
A	4.55	4.26	3.65	5,6 and 7	9 and 10	$\Gamma$
B	6.19	5.65	4.92	6 and 7	11	$\Lambda$
C	7.31	6.95	6.19	6 and 7	10	W
D	8.66	8.20	6.94	6 and 7	10 and 11	L
E	12.92	12.26	10.98	4	8	X
F	18.60	18.49	17.90	2 and 3	11	W



**Figure 5.** Calculated (solid line)  $\epsilon_2(\omega)$  (with SOC) compared with experimental data (dotted line) [16] for (a) BaS and (b) BaSe.

been scissors shifted by an amount equal to the difference between the calculated and the experimental band gaps (1.20 eV for BaS and 1.15 eV for BaSe). From figures, we see that our calculations reproduce qualitatively well the features observed experimentally. However, the



**Figure 6.** Calculated real part of the dielectric function without (solid line) and with (dotted line) SOC.

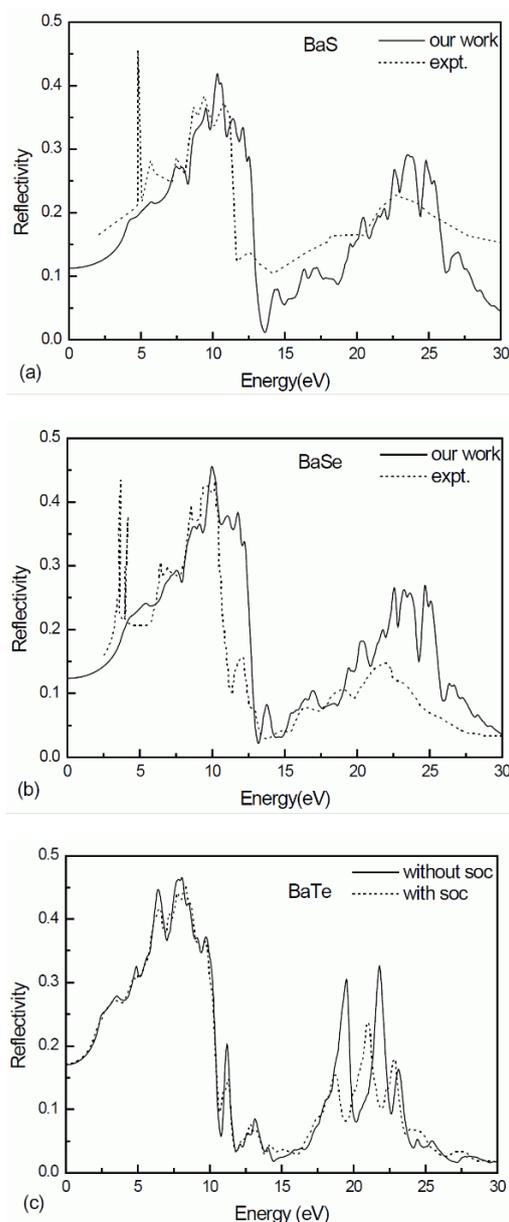
**Table 3.** The calculated (with SOC) and experimental static dielectric constant.

	our work		TDDTT [32]	Exp [33]
	Without shift	With shift		
BaS	4.67	4.08	4.07	4.26
BaSe	5.13	4.43	4.50	4.48
BaTe	5.82	5.09	4.94	4.71

experimental peaks at around 3.6 eV for BaS and 3.8 eV for BaSe are not present in our results. This could be interpreted as being due to the neglect of excitonic and local field effects in our calculations.

The results for the real part of the dielectric function  $\epsilon_1(\omega)$ , for the three compounds are given in Fig. 6. One can see that these curves have a main peak around 2.7 eV, and a minimum between 5.0 and 10.0 eV. The static dielectric constant  $\epsilon_1(0)$  has been calculated for BaS, BaSe and BaTe respectively, and the values are shown in Tab. 3, in which other calculated results [32] and experimental data [33] are also listed. We note that a smaller energy gap yields a larger  $\epsilon_1(0)$  value. This could be explained on the basis of the Penn model [34].

The calculated reflectivity spectra for the three compounds, along with the available experimental data [16] are given in Fig. 7. There is a close resemblance between



**Figure 7.** Calculated reflectivity with SOC (solid line) compared with the experimental data (dotted line) [16] for (a) BaS and (b) BaSe; (c) Calculated reflectivity with and without SOC for BaTe.

the three compounds. The reflectivity spectra can be divided into two regions: regions below and above 14 eV. As can be seen in Fig. 7 there is a close match between our calculated results and the experiment, especially for BaSe. Our calculated reflectivity starts at around 15% for BaS and BaSe, irrespective of whether SOC is included or not, which is in good agreement with the experimental value.

Just as pointed out above, there are no experimental results so far on optical quantities for BaTe in the optical frequency range, so our calculated result can serve as an important reference for future work on BaTe. From Fig. 7(c) one can see the reflectivity reaches about 0.46 at around 8.0 eV for BaTe and 0.23 at around 21.8 eV for BaTe after considering SOC.

It should be mentioned that the experimentally observed peaks at around 5eV for BaS and 3 eV for BaSe are not present in our calculations. Kaneko *et al.* interpreted that the origin of these peaks is an excitonic effect [22], which explains their absence in our results.

## 4. Conclusions

The optimized structure, electronic structure and optical properties of BaX (X=S, Se and Te) have been studied by the FP-LAPW+lo method with and without SOC. All three compounds have indirect band structures, and the obtained energy band gaps are very close to the experimental values. The values of  $\epsilon_1(0)$  increase as the energy gap decreases, and the calculated results coincide very well with the available experimental data. Our calculated optical spectra reproduce qualitatively well the features observed in experiments for BaS and BaSe. Since there is no experimental optical quantity data for BaTe available, our result can serve as a reference for future work.

The effect of SOC on the optical properties such as the real and imaginary parts of the dielectric function, and reflectivity has also been investigated for these compounds. The results show that the effect is significant in the high-energy region, and weak in the low-energy region.

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