

FP-LAPW calculations of electronic and optical properties of calcium chalcogenides

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Abstract— First-principles calculations have been used to study the electronic and optical properties of calcium chalcogenides compounds CaS, CaSe and CaTe using a full potential linearized augmented plane-wave method (FP-LAPW) within density functional theory (DFT). The Perdew, Burke and Ernzerhof (PBE-GGA) as well as the Engel-Vosko (EV-GGA) generalized gradient approximations were used for the exchange and correlation energy density functional. First we present the main features of the electronic properties of these compounds, where the electronic band structure shows that the fundamental energy gap is indirect (Γ -X) for all compounds. The different interband transitions have been determined from the imaginary part of the dielectric function. The real and imaginary parts of the dielectric function are calculated. We have presented the assignment of the different optical transitions existing in these compounds from the imaginary part of the dielectric function spectra with respect to their correspondence in the electronic band. Results are discussed and compared with experimental and other theoretical data.

Keywords- calcium chalcogenides, FP-LAPW, band gap, optical transitions

1. INTRODUCTION

Alkaline-earth chalcogenides (AX: A = Be, Ca, Mg, Sr, Ba; X = O, S, Se, Te) have been objects a long time of investigation on account of a number of interesting properties like their diverse bond characteristics and simple crystal structure. They form a very important closed shell ionic system crystallizing in NaCl-type structure at room conditions except for the MgTe and the beryllium chalcogenides. These compounds are technologically important materials having many applications ranging from catalysis to microelectronics. They have also application in the area of luminescent devices [1-4].

Among these alkaline-earth chalcogenides a little information is available for calcium chalcogenides CaX (X = S, Se, Te) that have been found to undergo first-order phase transition from six-fold-coordinated B1 structure to eight-fold-coordinated CsCl-type B2 structure, at pressures of 40, 38 and 33 GPa, respectively [5].

There are several theoretical and experimental works on these compounds. Structural studies of CaX, under pressure up to 52 GPa, have been carried out experimentally using X-ray diffraction to observe a first-order transformation from the NaCl phase to the CsCl phase [5]. The cohesive properties of CaX under pressure have been found by ab-initio calculations [6]. The elastic constants have been investigated using pseudo-potential [7] and tight binding theory [8]. Recently, the linear optical properties of these compounds have been reported using FP-LAPW method [9]. Hence, in order to exploit fully these materials for new optical devices, the structural, electronic and optical properties of these compounds need to be investigated in more detail. Therefore, the purpose of this paper is to study the structural, electronic and optical properties by using full-potential linearized augmented plane wave (FP-LAPW) method.

This paper is organized as follows. In section 2 we give a brief description of the computational approach used in this work. Results of the present calculations as well as the discussions are given in section 3. Finally we present a brief conclusion.

2. CALCULATION METHOD

In order to calculate the structural, electronic and optical properties of CaS, CaSe and CaTe compounds, the FP-LAPW method [10] is employed to solve the Kohn-Sham equations. Calculations were performed by Wien2k code [11] within the

framework of DFT [12, 13] that has been shown to yield reliable results for the electronic and structural properties of various solids. The exchange-correlation contribution was described within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) [14] to calculate the total energy, while for the electronic properties in addition to that the Engel-Vosko (EV-GGA) formalism [15] was also applied. In this method the space is divided into an interstitial region (IR) and non overlapping muffin tin (MT) spheres centered at the atomic sites.

In the IR region, the basis set consists of plane waves. Inside the MT spheres, the basis sets is described by radial solutions of the one particle Schrödinger equation (at fixed energy) and their energy derivatives multiplied by spherical harmonics. In the calculations reported here we use a parameter $R_{MT}K_{max} = 8$, which determines the matrix size, where K_{max} is the plane wave cut-off and R_{MT} is the smallest of all atomic sphere radii. We choose the muffin-tin radii of Ca, S, Se, and Te to be 2.3, 2.2, 2.4 and 2.5 a.u., respectively. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-5} Ry. The integrals over the Brillouin zone are performed up to 47 k -points in the irreducible Brillouin zone (IBZ), using the Monkhorst Pack special k -points approach [16].

The optical properties of a solid are usually described in terms of the complex dielectric function :

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

which is known to describe the optical response of the medium at all photon energies $E = \hbar\omega$. In this study, the imaginary part of the dielectric function is given as in reference [17] by

$$\epsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{i,j} |M_{ij}|^2 f_i(1-f_j) \times \delta(E_j - E_i - \omega) d^3k \quad (2)$$

where M is the dipole matrix, i and j are the initial and final states respectively, f_i is the Fermi distribution function for the i the state, and E_i is the energy of electron in the i th state.

The real part ($\epsilon_1(\omega)$) of the dielectric function can be extracted from the imaginary part using the Kramers-Kronig relations [18]:

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

where P implies the principal value of integral.

Also the optical spectra such as the refractive index, $n(\omega)$ and the extinction coefficient, $k(\omega)$ and the reflectivity spectra $R(\omega)$ are calculated in terms of the components of the complex dielectric function as follows [19, 20]:

$$n(\omega) = \left\{ \frac{\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega)}{2} \right\}^{1/2} \quad (4)$$

3. RESULTS AND DISCUSSION

3.1. Structural properties

The fitting of the Murnaghan equation of state [21] to the total energies versus unit cell volumes, yields to the equilibrium lattice parameter (a_0), bulk modulus B_0 and the pressure derivative of the bulk modulus B' . In Table 1 we summarize our calculated structural properties of CaS, CaSe and CaTe at

ambient pressure. For comparison this table contains also previously published theoretical and experimental values. When we analyse these results we find that there is a good agreement between our results and the reported theoretical investigations. In comparison with the experimental data we find that the lattice parameters are overestimated whereas the bulk modulus are underestimated; these findings are consistent with the general trends of this approximation.

TABLE I: Calculated lattice constant (in Å), bulk modulus (in GPa) and its pressure derivative of CaS, CaSe and CaTe compounds.

	Present	Theoretical	Experimental
CaS			
a (Å)	5.72	5.598 ^a , 5.717 ^b	5.689 ^d
B (GPa)	57.10	65.2 ^a , 57.42 ^b	64
B'	4.34	4.1 ^a , 3.8 ^b	
CaSe			
a (Å)	5.96	5.829 ^a , 5.968 ^b , 5.753 ^c	5.616 ^d
B (GPa)	47.95	56.2 ^a , 48.75 ^b , 62.34 ^c	51 ^d
B'	4.17	4.1 ^a , 3.4 ^b	
CaTe			
a (Å)	6.39	6.231 ^a , 6.396 ^b , 6.074 ^c	6.348 ^d
B (GPa)	38.72	45.4 ^a , 39.6 ^b , 46.95 ^c	41.8 ^d
B'	3.52	4.2 ^a , 3.3 ^b	

^a Ref[6], ^b Ref[22], ^c Ref[8], ^d Ref[5]

3.2. Electronic properties

We have calculated the band structures for CaS, CaSe and CaTe compounds along the high directions in the first

Brillouin zone at the calculated equilibrium lattice constants. Fig.1 shows the band structure for CaS as a prototype since the band profiles are quit similar for all three compounds, with a small difference. The band structure calculations give an indirect band gap Γ -X for these compounds. The calculated values of the band gaps are compared with the experimental data and other calculated results in Table 2. It is seen that our calculated results are in good agreement with previous studies. However, the band gaps are on the whole underestimated in comparison with the experimental results. This is a typical error arising in the GGA approximation, which is assumed to arise due to the lack of non-locality and the energy dependence in the exchange correlation functionals used in the density functional formalism [26]. The values obtained for the band gap of these compounds within EVGGA are in better agreement with available experimental results in comparison with the values calculated by GGA. It is noticeable that the Engel and Vosko scheme [15], which is based on potential optimisation is capable of giving a more reliable band structure.

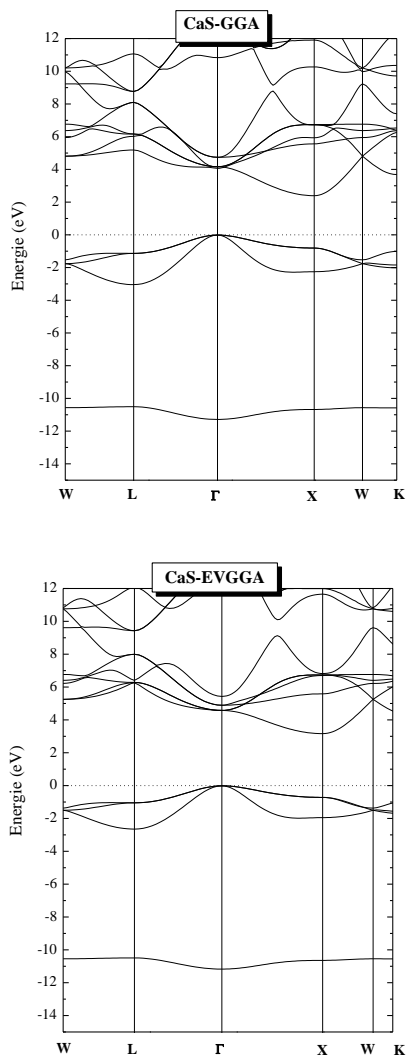


Figure 1: Band structure of CaS

TABLE II: Calculated band gap energy in (eV) compared to experimental data and other works of CaS, CaSe and CaTe compounds.

	Present		Other calculations	Experiment
	GGA	EVGGA		
CaS	2.405	3.176	2.39 ^a , 2.10 ^a , 2.08 ^b , 1.98 ^c ,	4.134
CaSe	2.105	2.815	2.81 ^d	3.85
CaTe	1.578	2.227	1.57 ^a , 1.53 ^b , 1.35 ^c	

^aRef[22], ^bRef[23], ^cRef[24], ^dRef[25]

3.3. Optical properties

To give an overview of the optical properties of CaS, CaSe and CaTe compounds and in particular to show the different optical interband transitions, the calculated dielectric function is shown in Fig.2 and 3. The results for the dispersive part of the dielectric function $\epsilon_1(\omega)$ for the CaS compound are given in Fig.2. It is interesting to note that the first peak in $\epsilon_1(\omega)$ coincides with the transition at the Γ point between the top of valence band and the bottom of conduction band. The main features in these curves are: a peak around 3.56 eV (CaS), 3.39eV (CaSe) and 2.99 eV (CaTe) , a rather steep decrease between 4 and 7 eV for CaS, between 5 and 6 eV for CaSe and between 4 and 5 eV for CaTe after which $\epsilon_1(\omega)$ becomes negative; a minimum, followed by a slow increase toward zero; a minimum at around the energies of 27.18 eV (CaS), 26.94 eV(CaSe) and 26.67 eV (CaTe) and then again a slow increase toward zero at higher energies.

The imaginary part of the dielectric function $\epsilon_2(\omega)$ for CaSe compound is shown in Fig. 3. The behaviour of $\epsilon_2(\omega)$ is rather similar for all these compounds with some differences in details. The first critical points of the dielectric function occur at 2.39, 2.11 and 1.58 eV for the compounds CaS, CaSe and CaTe respectively. This is known as the fundamental absorption edge. Beyond these points, the curve increase rapidly. This is due to the fact that the number of points contributing towards $\epsilon_2(\omega)$ increases abruptly. The main peaks in the spectra $\epsilon_2(\omega)$ of CaS, CaSe and CaTe are situated at 5.87 eV, 5.53 eV and 4.79 eV, respectively. These peaks are mainly due to the direct transitions (L - L). The main peaks are followed by a small structures localized at 6.8 eV (CaS), 6.2 eV (CaSe) and 5.30 eV (CaTe), they are related to the direct transitions(W-W).

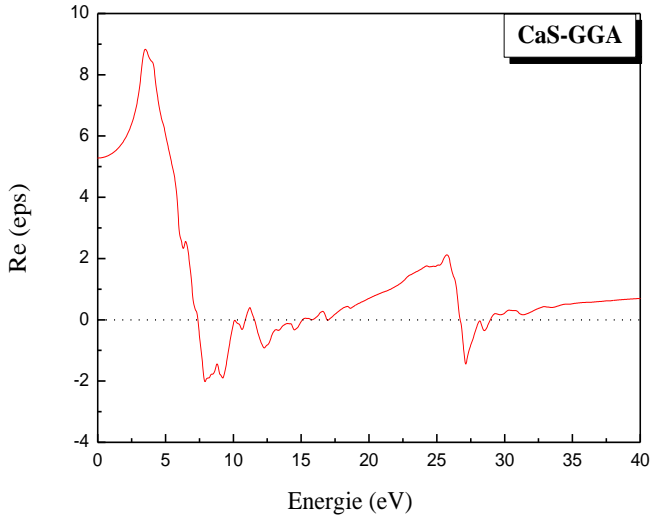


Figure 2: Calculated real part of the dielectric function for CaS compound

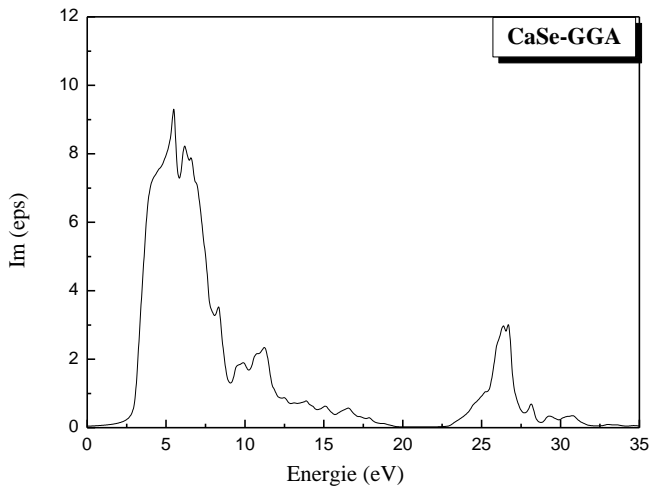


Figure 3: Calculated imaginary part of the dielectric function for CaSe compound

Particular attention has been devoted to the static values of dielectric function $\epsilon(0)$ and the refractive index $n(0)$ which are given in Table III. For comparison this table contains also previously published theoretical and experimental values.

Our results concerning the static dielectric constant are higher than those given in experiments while the obtained values for the refractive index are in good agreement with the experimental ones. From this table, we can also notice that the calculated dielectric constant and the refractive increase with the increase of the size of the chalcogen atoms.

TABLE III: Static values of dielectric function and refractive index of CaS, CaSe and CaTe compounds compared to theoretical and experimental works.

	$\epsilon(0)$		$n(0)$		
	Present	Exp	Other calculations	Present	
CaS	5.25	4.24 ^a	4.30 ^b , 4.47 ^c , 5.38 ^d	2.29	2.07 ^e
CaSe	5.40	4.58 ^a	4.81 ^b 5.99 ^d	2.31	2.09 ^e
CaTe	6.56		7.05 ^d	2.56	2.17 ^e

^a Ref [27], ^b Ref[28], ^c Ref[29], ^d Ref[9], Ref[30]

4. CONCLUSION

In this work, we have performed first principle study of CaS, CaSe and CaTe compounds in cubic phase, predicting their structural, electronic and optical properties using the full-potential linearized augmented plane wave method. A summary of our results follows:

- 1- Our calculated band gaps, using GGA, are in a reasonable agreement with the other computational works, but lower than the experimental results.
- 2-The interband transitions responsible for the structures seen in the imaginary part of dielectric function spectra are specified.
- 3-The obtained values for the static dielectric constant are higher than those given in experiments and are in reasonable agreement with some theoretical results.

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