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First-principles study of structural, electronic and elastic properties under pressure of calcium chalcogenides

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Abstract

We present ab initio calculations for CaS, CaSe and CaTe, in the B1 (NaCl) and B2 (CsCl) phase, by means of accurate first principle total energy calculations using the all-electron full-potential linear muffin-tin orbital method FP-LMTO. The calculations are presented within the local density approximation (LDA). Results are given for structural, electronic and elastic. Good agreement is found with experimental data. The efficiency and the accuracy of this method are so appreciated to predict some properties of this kind of materials

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1. Introduction

The structural phase transformations under high pressure in alkaline earth chalcogenides, have attracted considerable interest in the last decade [1]. These compounds form a closed-shell ionic system crystallized in the NaCl-type (B1) structure at ambient conditions. With the application of pressure the NaCl structure of the alkaline-earth chalcogenides undergoes a structural phase transition to CsCl-type (B2) structure. CaS, CaSe and CaTe are found to exhibit a structural phase transition with the application of pressures of 40, 38 and 33 GPa, respectively [2]. Several experimental and theoretical studies of CaX compounds have been published during the last few years. Structural studies of CaS, CaSe and CaTe, under high pressure up to 52 GPa, have been carried out experimentally using x-ray diffraction to observe a first order phase transformation from the NaCl phase to the CsCl phase [2].

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Pressure–volume relationships and structural transitions in CaTe are investigated at high pressure using also x-ray diffraction [3]. The cohesive properties under pressure of CaX compounds have been calculated by using ab initio calculations [4]. The elastic constants are investigated using pseudo potential [5] and tight binding theory [6]. Despite these studies a number of basic properties are still unknown, e.g. the pressure behavior of the band gaps. To understand some of the physical properties of these compounds, a detailed description of electronic structure of these compounds is needed. In our study we investigate the atomic structure in the B1 phase of the CaS, CaSe and CaTe materials by means of density-functional calculations. We use the (FP-LMTO) method [7]. The (LDA) has been chosen for treating the correlation term [9]. To obtain a deeper understanding of elastic properties of these compounds, we need to have a clear idea of the bonding properties. The band structure, electronic charge densities, elastic constants and density of states are analyzed in this compound. Comparison of our results with other available experimental and theoretical data shows a good agreement

2. Calculations

In this work, the all-electron full-potential linear muffin-tin orbital method FP-LMTO [7],[13], is used to calculate the total energies as well as the basic ground state properties, such as equilibrium lattice constant, bulk modulus and its pressure derivative, elastic constants, also the band structure, and density of states. For mathematical convenience, the crystal is divided into two regions: non-overlapping muffin-tin spheres surrounding every atom and the interstitial region between the spheres. Within the spheres, the potential is expanded in spherical harmonics, while in the interstitial region it is expanded Fourier series. In the literature, there have been several FP-LMTO implementations [8], [13]. The exchange correlation potential energy of the electrons was calculated by the local density approximation LDA using the scheme of Perdew et al. [9]. In the calculations, 3942 planes waves have been used for CaS, CaSe and CaTe respectively in B1 (NaCl) phase and 4168 in B2 (CsCl) structure. The maximum l for the wave function expansion inside the atomic spheres was confined to $l_{max}=6$, with 16 and 20 k points in the irreducible Brillouin zone (IBZ) for B1 and B2 structures respectively. The k integration over Brillouin zone is performed up to (4, 4, 4) grid by means of improved tetrahedron method [14]. The muffin-tin radii in B1 (NaCl) structure were chosen to be in a.u. for Ca (2.793, 2.819, 2.954 and for S, Se, Te to be (2.578, 2.819, 2.954) respectively. For B2 CsCl structure the R_{MT} were chosen to be for Ca (3.044, 3.081, 3.148) and for S, Se Te (2.707, 2.862, 3.147) respectively.

3. Results

3-1. Structural properties

The fitting of the Murnaghan equation of state [15] to the total energies versus lattice parameters, yields the equilibrium lattice parameter (a_0), bulk modulus B_0 , and the pressure derivative of the bulk modulus B_0' for both structures B1 and B2. In Table 1, we summarize our calculated structural properties (lattice constant, bulk modulus and its pressure derivative) of CaS, CaSe and CaTe compounds at ambient pressure. When we analyzed these results we found that B1 is the stable structure at ambient pressure which is consistent with experimental results and other theoretical works. Our results are closed with just 1% with the experimental results [2], and for theoretical results we compare our outputs with the work to Zimmer [3] and Cortona [4]. It's clear that's LDA underestimate the lattice parameter and the method is very recommended for this kind of materials.

We have also calculate the elastic constants C_{11} , C_{12} and C_{44} for both structures (B1) and (B2) at the calculate equilibrium lattice parameter for CaS, CaSe and CaTe, using the method discussed in detail in Ref. [16-17], which is also used in our previous papers for the alkali metal sulfides the M_2X compounds [20] the results are also presented in the table I. Our calculated positive value of the elastic constants is indicative of the stability of these compounds in both NaCl (B1) and CsCl (B2) structure there are no experimental results for these compounds We consider the present results of elastic constants as a prediction study

3-2. Electronic structure

The calculated band structures of CaS, CaSe and CaTe compounds in the B1 phase at equilibrium volume are presented in Fig. 1 (left panel). The total densities of states (DOS) calculated by tetrahedral method [27] using LDA approximation for all compounds are displayed also in Fig. 1 (right panel) The features of the band structure is the same for all the three compounds, the electronic configuration of Ca is (4s,4p, 3d), for S (3s,3p,3d), for Se (4s,4p,4d), and for Te(4s,5p,5d). The energy bands are displayed along several symmetries. We notice the influence of d shells in the all elements and in the valence band in dotted lines from respectively from the (3p,4p,5p) states of S, Se and Te. For both compounds B1 and B2 structures we found that the dominance of the 4s-states of (S, Se and Te) which is the origin of the first band in all the three compounds. A few contribution of the s-state of Ca in the valence bands, and 4p states are showed in the figures b for all the phases, in comparison with the results of Cervantes et al [10] and the results of Kalpana et al [18] we found a closed similarity of our results with Von Barth and al [19]. The calculate band values at high symmetry points in the NaCl-B1 structure are given in table 2 and fig.2, we notice the minimum direct gap occurs at X for all the compounds, the results of the valence gap are in good agreement with the results of TB-LMTO calculations for the valence and the conduction band, at Γ point the valence band is maximum at X the minimum conduction band, for all the compounds which is illustrated in fig 1. The indirect gaps materials are around to 2.11, 1.750, and 1.213 respectively for CaS, CaSe and CaTe.

Table 1: Calculated lattice constant a_0 (in Å), bulk modulus B (in GPa), pressure derivative (B') and elastic constants C_{ij} (in GPa) of CaS, CaSe and CaTe for (B1) and (B2) phases, and compared to experiment and other works

	a_0 (Å)	B	B'	C_{11}	C_{12}	C_{44}
CaS(B1)						
Present	5.685	64.85	4.24	131.66	31.45	53.94
Expt. ¹²	5.689	64	4.2			
Other ¹³	5.598	65.2	4.1			
CaS(B2)						
Present	3.519	77.83	4.23	221.49	5.999	103.03
Expt. ¹²	3.460	64	4.2			
Other ¹³	3.410	71.2	4.2			
CaSe(B1)						
Present	5.851	63.94	4.39	135.06	28.38	57.96
Expt. ¹²	5.916	51	4.2			
Other ¹³⁻¹⁵	5.829	56.2	4.1	112.6	22	34.43
CaSe(B2)						
Present	3.621	64.49	4.26	181.82	5.825	92.5
Expt. ¹²	3.612	51	4.2			
Other ¹³⁻¹⁵	3.560	61	4.2	160	7.41	68.62
CaTe(B1)						
Present	6.255	50.69	4.36	117.9	17.09	54.8
Expt. ¹²⁻¹⁴	6.350	42	4.3, 5.0			
Other ¹³	6.231	45.4	4.2	92.9	18.4	36.64
CaTe(B2)						
Present	3.847	58.18	4.2	121.87	26.33	65.5
Expt. ¹²	3.931	41.8	4.3			
Other ¹³	3.780	50.2	4.2	117.1	5.33	55.68

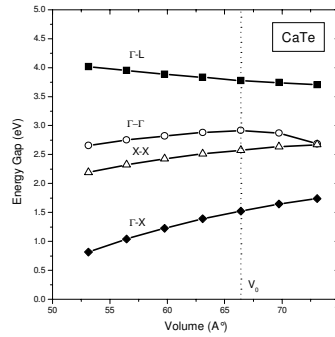
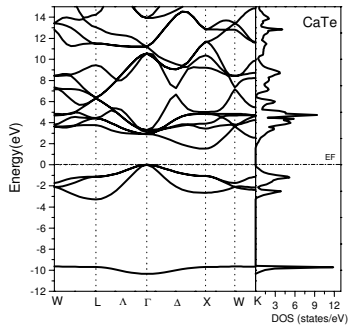
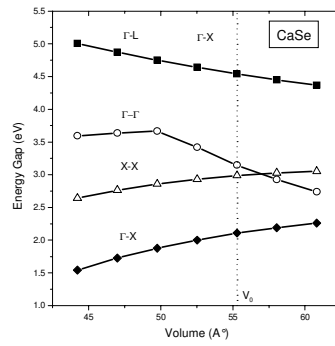
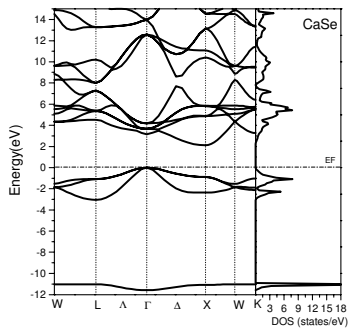
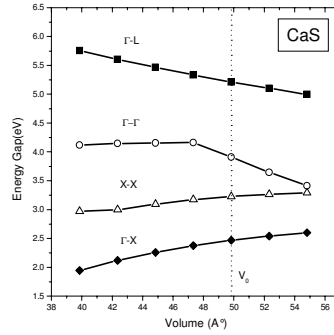
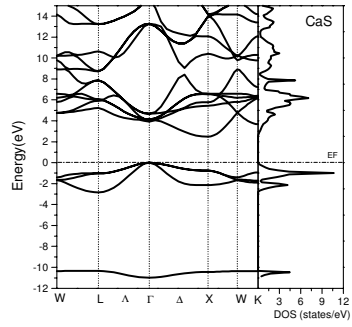


Fig. 1. The band structures (left panel) and density of states (right panel) in B1 phase of CaS, CaSe and CaTe

Fig. 2. Plots of the calculated band gaps of CaS, CaSe and CaTe versus the volume in the B1 structure

Table 2: Electron band eigenvalues for the lowest conduction bands and the upper valence band widths for CaS, CaSe and CaTe in (B1) phase. The energy values are (in eV)

	Γ - Γ	X-X	L-L	Γ -X	Γ -L
CaS					
Present work	3.969	2.942	6.42	2.111	5.201
CaSe					
Present work	3.451	2.729	5.904	1.75	4.587
Other ^b	3.539	2.889	6.159	1.98	4.685
CaTe					
Present work	2.743	2.378	5.114	1.213	3.779
Other ^b	3.086	2.467	5.794	1.35	3.816

4. Conclusion

In summary we report an ab initio study of structural, elastic and electronic properties of the CaS, CaSe, and CaTe. We used FP-LMTO method to perform a set of first-principles, self-consistent, total-energy calculations to determine the equations of state, and electronic structure, in the B1 (NaCl) and CsCl structures. The lattice constants and the bulk moduli are in excellent agreement with available experimental data and other calculations.

Good agreement is found. We prove that B1 structure is more stable than B2.

In the other hand, we find a very good agreement between our results of band structure, and earlier theoretical and experimental results. The calculate band gap is closed with experimental data, our results is new prediction of a novel properties such as elastic.

Finally, we can say that the present results demonstrate that FP-LMTO have actually reached a level of accuracy for certain fundamental material properties.

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