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High-pressure structural phase transitions, electronic properties and intermediate states of the CaSe

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In this study, ab initio calculations have been carried out in order to understand the effect of extreme external pressure on the crystal structure of CaSe. The crystal structure of the CaSe, one of the calcium chalcogen, is studied using the density functional theory (DFT) with the generalized gradient approximation (GGA) up to 250 GPa under high hydrostatic pressure. Structurally CaSe crystallizes in cubic NaCl-type (B1) structure (space group: $Fm\bar{3}m$) at ambient conditions. The results indicated that CaSe undergoes a structural phase transition from this cubic structure to another cubic CsCl-type (B2) structure (space group: $Pm\bar{3}m$) at high pressure. This transformation is based on two intermediate states with space group $R\bar{3}m$ and $C2/m$. Additionally, the electronic band structures and density of states for the obtained B1 and B2 structures of CaSe have been calculated. According to these calculations, obtained band gap values are in a good agreement with the values reported in the literature.

Keywords: Ab-initio, Intermediate state, Phase transition, Enthalpy, Electronic structure

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1. Introduction

Under high pressure, alkaline earth chalcogenides such as CaO, CaS, CaSe and CaTe are closed-shell ionic systems that crystallize in B1-type structure at ambient conditions and have technological importance in many applications, from catalysis to microelectronics [1-5]. There are also applications in the field of Luminescent devices [6-8].

Boucenna et al. used the pseudo-potential plane-waves (PP-PWs) approach to determine the phase transition from B1 to B2 phase and obtained this transition at 32.7 GPa. They also studied the electronic properties of CaSe and obtained bandgaps of 2.859 eV and 0.407 eV for B1 and B2 phases, respectively [2]. Charifi et al. studied the mechanism of transform of CaSe using the scalar relativistic full potential linearized augmented plane-wave (FP-LAPW) method. They obtained transition pressure of 34.38 GPa using GGA and 40.65 GPa using LDA. Besides, they studied the electronic properties of CaSe and observed a band gap of 2.10 eV for the B1 phase and 0.79 eV for the B2 phase [3]. Cortona et al. found the transition pressure at 45 GPa from B1 to B2 [9]. Jha et al. found the transition pressure at 37 GPa from B1 to B2 using a three-body potential approach [4].

Some basic properties of CaSe, such as changes in band gap under increasing pressure, are still unknown. Therefore, in order to understand some physical properties of this compound, it is necessary to study the electronic structure in detail. A characteristic feature of the electronic band structure of CaSe compound is the absence of d electrons in the valence band. There is a lack of knowledge in the literature for calcium chalcogens among the alkaline earth chalcogenides. Therefore, in order to fully utilize these materials for new devices, the structural and electronic properties of these compounds should be investigated in more detail. For this reason, the aim of this study is to provide a comparative study of structural and electronic properties under high pressure using Siesta method, which completes existing experimental and theoretical studies on CaSe. For this material, obtained results yield the following sequence Fm

$\bar{3}m \rightarrow Pm\bar{3}m$ which is compatible with the other studies. Additionally it is also suggested that the $Pm\bar{3}m$ phase of this material proceeds through two intermediate states with space groups $R\bar{3}m$ and $C2/m$ expressed as CaSe-(a) and CaSe-(b), respectively. In addition, as a result of rigorous research, it is thought that the intermediate states obtained for the $Pm\bar{3}m$ phase of CaSe are first obtained in this study.

2. Method of computation

The structural and electronic properties of the cubic NaCl-type structure of CaSe are investigated using the *ab initio* method in the framework of density functional theory. The SIESTA [10] package program is used as the *ab-initio* code in the study. Approach GGA [11] is applied and parameters of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation function are entered into the calculations with "double ζ (DZ) basis set". Troullier-Martins' norm-conserving pseudo-potential [12] is used for electronic band structure, total and partial density of state calculations. Cut off energy in this work is sufficient as 300 Ryd. In order to calculate the relation between the energy- volumes, the unit cells of the crystal structures are utilized for B1 and B2 structures. For Brillouin region integration, 8x8x8 Monkhorst-Pack (MP) mesh [13] were used for both $Fm\bar{3}m$ and $Pm\bar{3}m$ phases.

Simulation cells are constructed from 64 atoms under periodic bond conditions using a 2x2x2 supercell. Pressure is gradually increased by 10 GPa by applying Parrinello-Rahman technique to the system. The KPLOT [14] program and the RGS [15] algorithm are used to analyze each simulation step. They give detailed information about the space group, atomic positions and lattice parameters of an analyzed structure. 1.0 femtosecond is used for each MD time step. In addition, the Crystallmaker program is used to visualize phase transformation and its mechanism.

3. Results and Discussion

Using the KPLLOT program, the structure of CaSe at each applied pressure value is analyzed and it is observed that the cubic structure is preserved up to 220 GPa. The transform is predicted from cubic B1 structure to another cubic B2 structure at 220 GPa. The obtained main structures are shown in Figure 1 and the transition pressures, lattice parameters, bulk modulus and derivate of bulk modulus of these main structures are given in Table-1 with other results obtained from theoretical and experimental studies.

In the case of constant pressure simulations, the predicted transition pressure value is generally overestimated in a similar way to superheating molecular dynamic simulations. This implies a high intrinsic activation barrier for transforming one solid phase into another in simulations. This overestimated transition pressure are anticipated when the special conditions such as the finite size of the simulation cells and the lack of any defect in the simulated structures are considered. Structural phase transformations in simulations do not occur with nucleation and growth, but instead occur in all simulation cells. Consequently, the systems must pass an important energy barrier to transform from one phase to another, and therefore, simulated structures must be over-pressurized to achieve a phase transition. In addition, in our simulations, the absence of thermal motion (the structure is relaxed at constant pressure) shifts the transitions to higher pressures. On the other hand, thermodynamic theorem does not take into account the possible presence of such an activation barrier that separates the two structural phases and the thermal movement [16-18]. So the next step is to take energy-volume calculations to study the stability of CaSe's high-pressure phases. The calculated total energy-volume relations are fitted to the 3rd degree Birch-Murnaghan state equation given in Equation 1 and shown in Figure 2.

$$P = 1.5 B_0 \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \times \left\{ 1 + 0.75 (B'_0 - 4) \left[\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\} \quad (1)$$

Where P is the pressure, V is the volume, V_0 , B_0 and B'_0 are the volume, bulk modulus and derivate of bulk modulus at zero pressure, respectively [19, 20].

We used Gibbs free energy to determine which phase is thermodynamically stable at the given pressure and temperature. Gibbs free energy is as given in Equation 2.

$$G = E_{\text{tot}} + PV - TS \quad (2)$$

Where E , P , V and S are total energy, pressure, volume and entropy, respectively. The theoretical work we have done was achieved at 0 K temperature. So the "TS" term was neglected. Thus, the Gibbs free energy G equals the enthalpy given in Equation 3.

$$H = E_{\text{tot}} + PV \quad (3)$$

Where $P = -\partial E_{\text{tot}}/\partial V$. Enthalpy calculations usually give transition pressures that are consistent with experimental results. The intersection of two enthalpy curves shows the phase transition involving the pressure between these two phases. The enthalpy curve is plotted in Figure 3 for the obtained phases of CaSe as a function of the pressure to determine the transition pressure. Energy-volume datas are used for drawing the enthalpy curve. As can be seen from Figure 3, the transition pressure between the B1 and B2 structures of the CaSe was obtained about 38 GPa.

In order to explain the mechanism of the phase transitions, the lengths of the lattice vectors of the simulation cell and the changes in the angles between these vectors according to the simulation steps are examined. These vectors are denoted A, B and C along the [100], [010] and [001] directions, respectively. The angle between A and B vectors, the angle between A and C vectors and the angle between B and C vectors are expressed by γ , β and α , respectively.

The lengths of the lattice vectors and the variation of the angles between these vectors according to the simulation steps are shown in Figure 4 for 220 GPa.

As shown in Figure 4, the A, B and C lengths remain constant up to about 100 fs. The A, B and C lengths start to increase at around 100 fs and after reaching 10.2 Å, they remain unchanged through the simulation. The α , β and γ angles also experience small changes up to about 100 fs. As the α and γ angles decrease at about 70° , β angle reaches 112° and after 100 fs, they remain constant throughout the simulation.

To determine the thermodynamic nature of the phase transition of B1→B2 in CaSe, pressure-volume and pressure-lattice constants relations are plotted in Figure 5. At 220 GPa the B2 type structure is characterized. This finding suggests that the first-order phase transition from B1 to B2-type structure is between 210 GPa and 220 GPa. After that pressure is increased up to 250 GPa to see how the B2 structure would respond to the applied pressure, but we could not find any other phase transition. As can be seen from Figure 5, the volume and lattice constants have significantly changed when the pressure is increased from 210 GPa to 220 GPa. The reason for this change is that at 220 GPa, the $Fm\bar{3}m$ phase of the material turns into the $Pm\bar{3}m$ phase. The collapse in the value of volume during this transformation shows us that the phase transition is first order.

Each MD time step of the B2 structure is analyzed in detail by the KPLOT program to determine whether there are any intermediate states during this phase change at 220 GPa. As a result of the analysis, the $Fm\bar{3}m$ phase of CaSe is transformed into the rhombohedral structure with space group $R\bar{3}m$ at 25th step, the monoclinic structure with space group $C2/m$ at 94th step and then the cubic structure with space group $Pm\bar{3}m$ at 108th step. The lattice constants of these obtained intermediate states are $a = 3.6583$, $b = 3.6583$, $c = 3.6583$ and $a = 5.1614$, $b = 3.2208$, $c = 3.5283$ for $R\bar{3}m$ and $C2/m$, respectively. The formation of the this cubic B2 structure is shown in Figure 6.

The calculated electronic band structures of CaSe are given in Figures 7 and 8 for B1 and B2 structures, respectively. The density of state curves calculated for structures B1 and B2 are given in Figure 9 and 10, respectively, along high symmetry directions and shown at the level of Fermi energy as a function of the energy. The Fermi energy level is set to 0 eV. The symmetry points are chosen as $W - L - \Gamma - X - W - K$ for the B1 phase and $X - R - M - \Gamma - R$ for the B2 phase. As seen from the electronic band structure graphs, the valence band is located below the Fermi Energy level and the transmission band is located on the top. The obtained results show that both phase of CaSe corresponds to a direct band transition with a band gap of about 2.65 eV [2,3,5] and 0.49 eV [2,3] for $Fm\bar{3}m$ and $Pm\bar{3}m$, respectively. Because the maximum of the valence band and the minimum of the conduction band are at the same symmetry points [Γ] for $Fm\bar{3}m$ and [M] for $Pm\bar{3}m$. CaSe has semiconductor character due to the band gap at Fermi energy levels in all phases.

It is also calculated the partial density of states (PDOS) to obtain further information about the electronic nature of CaSe and depicted in Figure 9 and 10. It can be seen from Figure 9 and 10 that the largest contribution came from Se-4p states between 0 eV and -5 eV and from Ca-4s between 0 eV and 10 eV for all phases of CaSe.

CONCLUSION

In the present study, the structural characterization, the electronic properties and high pressure induced phase transition in CaSe is investigated using an ab initio molecular dynamics simulations. The most relevant conclusions are summarized as follows:

- (i) The calculated ground state properties of this compound at ambient pressure are comparable with the available results.
- (ii) First-order phase transition for CaSe is proposed.
- (iii) The intermediate states with space group $R\bar{3}m$ and $C2/m$ are obtained for the $Pm\bar{3}m$ phase.

(iv) The band structure calculations reveal that both cubic B1 structure (space group: $Fm\bar{3}m$) and another cubic structure (space group: $Pm\bar{3}m$) of CaSe is a semiconductor.

REFERENCES

1. K. Kholiya, S. Verma, K. Pandey and B.R.K. Gupta. *Physica B: Condensed Matter* **405** (12), 2683 (2010).
2. S. Boucenna, Y. Medkour, L. Louail, M. Boucenna, A. Hachemi and A. Roumili. *Computational Materials Science* **68**, 325 (2013).
3. Z. Charifi, H. Baaziz, F. El Haj Hassan and N. Bouarissa. *Journal of Physics: Condensed Matter* **17** (26), 4083 (2005).
4. P.K. Jha and S.P. Sanyal. *Physica status solidi (b)* **212** (2), 241 (1999).
5. H. Khachai, R. Khenata, A. Haddou, A. Bouhemadou, A. Boukortt, B. Soudini, F. Boukabrine and H. Abid. *Physics Procedia* **2** (3), 921 (2009).
6. S. Asano, N. Yamashita and Y. Nakao. *Physica status solidi (b)* **89** (2), 663 (1978).
7. Y. Nakanishi, T. Ito, Y. Hatanaka and G. Shimaoka. *Applied surface science* **65**, 515 (1993).
8. R. Pandey and S. Sivaraman. *Journal of Physics and Chemistry of Solids* **52** (1), 211 (1991).
9. P. Cortona and P. Masri. *Journal of Physics: Condensed Matter* **10** (40), 8947 (1998).
10. P. Ordejón, E. Artacho and J.M. Soler. *Physical Review B* **53** (16), R10441 (1996).
11. J.P. Perdew, K. Burke and M. Ernzerhof. *Physical review letters* **77** (18), 3865 (1996).
12. N. Troullier and J.L. Martins. *Physical review B* **43** (3), 1993 (1991).
13. H.J. Monkhorst and J.D. Pack. *Physical review B* **13** (12), 5188 (1976).
14. R. Hundt, J.C. Schön, A. Hannemann and M. Jansen. *Journal of Applied Crystallography* **32** (3), 413 (1999).
15. A. Hannemann, R. Hundt, J.C. Schön and M. Jansen. *Journal of Applied Crystallography* **31** (6), 922 (1998).

16. H. Öztürk and M. Durandurdu. *Physical Review B* **79** (13), 134111 (2009).
17. M. Canpolat, C. Kürkçü, Ç. Yamçıçier and Ziya Merdan. *Solid State Communications* **288**, 33 (2019).
18. C. Yamcicier, Z. Merdan and C. Kurkcu. *Canadian Journal of Physics* **96** (2), 216 (2017).
19. F. Birch. *Physical review* **71** (11), 809 (1947).
20. F.D. Murnaghan. *Proceedings of the National Academy of Sciences* **30** (9), 244 (1944).
21. A.M. Hao, X.C. Yang, Z.M. Gao, X. Liu, Y. Zhu and R.P. Liu. *High Pressure Research* **30** (2), 310 (2010).
22. M. Bayrakci, K. Colakoglu, E. Deligoz and Y.O. Ciftci. *High Pressure Research* **29** (2), 187 (2009).
23. R. Khenata, M. Sahnoun, H. Baltache, M. Rérat, D. Rached, M. Driz and B. Bouhafs. *Physica B: Condensed Matter* **371** (1), 12 (2006).
24. P. Rodríguez-Hernández, S. Radescu and A. Muñoz. *High Pressure Research* **22** (2), 459 (2002).

Table I: Transition pressures (P_T), lattice lengths (a , b and c), bulk modulus (B_0) and derivative values of bulk modulus (B'_0) for $Fm\bar{3}m$ and $Pm\bar{3}m$ phases of CaSe.

Phases	P_T (GPa)	$a=b=c$ (Å)	B_0 (GPa)	B'_0	References
$Fm\bar{3}m$	0	5.9697	62.67	4.03	This Study
		5.9160	51.00	4.20	[9]
		5.9680	48.75	3.40	[3]
		5.9200	48.56		[21]
		5.8510	63.94	4.39	[5]
		5.9100	60.88	4.84	[22]
		5.9680	52.28	3.34	[23]
		5.8990	66.00	4.10	[24]
$Pm\bar{3}m$	38.00	3.6189	60.75	4.10	This Study
	34.38	3.6530	51.41	3.80	[3]
		3.6200	53.91		[21]
		3.6210	64.49	4.26	[5]
	35.20	3.6580	58.29	4.12	[23]
	38.40		61.03	3.96	[1]
	37.30	3.6100	58.65	4.41	[22]
	38.00	3.5800	64.00	3.60	[24]

FIGURE CAPTIONS:

Figure 1. Crystal structures of CaSe: B1 structure (left) at zero pressure and B2 structure (right) at 220 GPa.

Figure 2. Energy-volume graph of the main structural phases of the CaSe compound.

Figure 3. Enthalpy graph for the stable phases of CaSe as the function of the pressure.

Figure 4. Lattice vector lengths and the variation of the angles between these vectors of CaSe at 220 GPa.

Figure 5. The graph of the change of simulation cell volume and lattice constant as function of the pressure.

Figure 6. Formation of CsCl (B2) structure at 220 GPa. a) $Fm\bar{3}m$, b) $R\bar{3}m$, c) $C2/m$ and d) $Pm\bar{3}m$.

Figure 7. Band structure for NaCl (B1) structure.

Figure 8. Band structure for CsCl (B2) structure.

Figure 9. Density of states in NaCl (B1) structure

Figure 10. Density of states in CsCl (B2) structure.

FIGURE 1.

FIGURE 2.

FIGURE 3.

FIGURE 4.

FIGURE 5.

FIGURE 6.

FIGURE 7.

FIGURE 8.

FIGURE 9.

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