Structural phase stability of CaF$_2$ and SrF$_2$ under pressure

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Abstract

The electronic band structure of CaF$_2$ and SrF$_2$ was calculated in the fluorite and orthorhombic phases. The calculations were performed using tight binding linear muffin tin orbital method. The calculated ground state properties are in fairly good agreement with the experimental results. The transition pressure of CaF$_2$ and SrF$_2$ was found to be 9.1 and 7 GPa, respectively. The calculated transition pressures of CaF$_2$ are in good agreement with the experimental results. These systems were found to be wide band gap insulators with the band gap initially increasing with pressure, which decreases upon further compression. CaF$_2$ and SrF$_2$ are predicted to undergo metallization around 210 and 92 GPa, respectively. The possible reason for the metallization was also discussed.
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1. Introduction

The alkaline-earth fluorides CaF$_2$, SrF$_2$ and BaF$_2$ crystallize in the cubic fluorite structure and constitute an important class of relatively simple ionic crystals whose optical and lattice-dynamical properties are of much theoretical and experimental interest [1,2]. Calcium fluoride is a well-known face centered cubic mineral. The structure of fluorite has eight fluorine atoms arranged in a cube around the calcium atom, with the cubes of fluorine edge-connected in a face centered cubic array. Conversely, the fluorine atom is surrounded

by four calcium atoms arranged in an ideal tetrahedron with the tetrahedral also edge-connected [3]. Synchrotron-radiation studies of CaF$_2$ at high pressures have been performed on a powder sample up to 45 GPa and on a single crystal sample up to 9.4 GPa. A phase transition is observed around 9.5 GPa and the high-pressure phase is of orthorhombic PbCl$_2$-type structure [4]. First principle pair wise simulations and quantum-mechanical ab initio perturbed ion (AIPI) calculations have been extensively carried out to obtain the static equation of state (EOS) of the cubic fluorite-type structure and orthorhombic PbCl$_2$-type structure of CaF$_2$ by Pendas et al. [5]. As far as SrF$_2$ is concerned, no experimental studies are available to the best of our knowledge regarding the high-pressure structural phase transitions. Recently, atomic simulation work was done by

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Francisco et al. [6] wherein, the high-pressure phase is reported to be of orthorhombic structure. They have determined the EOS of SrF_2 in fluorite and orthorhombic phases (Pbnm) using electron gas interionic potential (EGPI) and reported the transition pressure to be 5 GPa. As stated already CaF_2 undergoes a transition to α-$PbCl_2$-type structure and BaF_2 is also reported to undergo a transition to orthorhombic structure both experimentally and theoretically [7,8]. Tight binding linear muffin tin orbital (TB-LMTO) method was used to study the above-mentioned transition is BaF_2 [9]. SrF_2 is also expected to undergo a transition to the orthorhombic structure. In the present work, TB-LMTO method was used to verify the structural phase transition of CaF_2 and SrF_2. These compounds are wide band gap insulators. Since there is no band structure available even at ambient conditions efforts have been taken in the present study to obtain the electronic structure of these compounds using the TB-LMTO method. In addition, the metallization pressures of these compounds are also calculated. The rest of the paper is organized as follows: Section II gives the computational details and the structural aspects of these compounds. Results are elaborated in Section 3. Finally, Section 4 reports the conclusions of this paper.

2. Computational details and structural aspects

To obtain the electronic structure and the ground state properties of alkaline-earth fluorides, TB-LMTO method has been used [10,11]. von Barth and Hedin parameterization scheme has been used for the exchange correlation potential [12] within the local density approximation (LDA). The accuracy of the total energies obtained with in the density-functional theory, often even using the LDA, is in many cases sufficient to predict which structure at a given pressure has the lowest free energy [13]. Atomic sphere approximation (ASA) has been used in the present work [14]. In this approximation, the crystal is divided into space filling spheres centered on each of the atomic site. Combined correction terms are also included, which account for the

non-spherical shape of the atomic cell and the truncation of the higher partial waves inside the sphere to minimize the errors in the LMTO method. The wigner-seitz sphere is chosen in such a way that the difference in the potential at the sphere boundaries is minimum and the charge flow between the atoms is in accordance with the electro-negativity criteria. 's', 'p' and 'd' partial waves are included. The tetrahedron method of brillouin zone integration has been used to calculate the density of states [15]. The '3p' states of Ca,'4p' states of Sr and '2s' states of fluorine are treated as the valence states.

Both CaF_2 and SrF_2 crystallize in the cubic fluorite structure with the space group (Fm-3m) at ambient conditions. Metal and fluorine occupy the positions (0 0 0) and (0.25 0.25 0.25), respectively. The high-pressure phase of CaF_2 is of orthorhombic structure with the space group Pbnm ($Z = 4$). The Ca and F ions occupy the positions (0.113 0.246 0.250), (0.425 0.428 0.250), (0.667 0.979 0.250), respectively [4,5]. The high-pressure phase of SrF_2 is predicted to be of orthorhombic type with the space group *Pnam* ($Z = 4$). This is similar to that of BaF_2. Sr and F ion are positioned at (0.259 0.112 0.250), (0.361 0.433 0.250) and (0.039 0.320 0.750).

The axial ratios b/a and c/a are minimized as a function of total energy at a fixed volume in the orthorhombic phase of SrF_2 and the minimized values are used in the calculations. Though LMTO method is not accurate in the case of axial ratio minimization, calculations were performed within the limitation of LMTO-ASA. One empty sphere is added in the fluorite-type phase of both the compounds. Five and seven empty spheres are added in the high-pressure phase of CaF_2 and SrF_2, respectively.

3. Results

3.1. Total energy calculations and high-pressure structural transformations

In order to study the structural phase stability for each of these compounds, the total energies are calculated in a manner similar to our earlier works

[16–18] for the fluorite and the orthorhombic structures by reducing the volume from $1.05V_o$ to $0.6V_o$, where V_o is the equilibrium volume. The variations of total energies with relative volume for these compounds are given in Figs. 1 and 2. From the graphs, it can be clearly seen that the fluorite-type structure is stable in both the compounds. The orthorhombic-type structure is positioned above fluorite structure in these compounds. The calculated total energies are fitted to the Birch EOS [19] to obtain the pressure volume relation. The graph connecting the pressure and relative volume in both the phases for these compounds is shown in Figs. 3 and 4. The pressure is obtained by taking the volume derivative of the total energy. The bulk modulus

$$B = -V_o \, dP/dV \tag{1}$$

is also calculated from the $P-V$ relation. The structural phase stability is determined by calculating Gibbs free energy [20] for both the phases which is

$$G = E_{tot} + PV - TS. \tag{2}$$

Since the theoretical calculations are performed at $0\,K$, Gibbs free energy becomes equal to enthalpy (H):
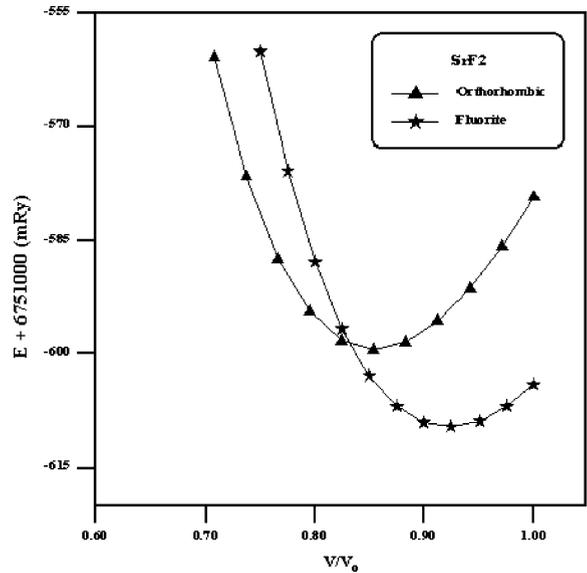
$$H = E_{tot} + PV. \tag{3}$$

At a given pressure, a stable structure is one for which enthalpy has its lowest value and the transition pressures are calculated at which the enthalpies for the two phases are equal. In the case of CaF_2, high-pressure structural phase transition is reported by Gerward et al. [4] using synchrotron-radiation studies. According to them a phase transition is observed at about 9.5 GPa wherein the high-pressure phase is of orthorhombic-type structure with the space group Pbnm. A similar transition is also observed in the present study at about 9.1 GPa, and the volume collapse is around 7%. This is lesser than the value reported by Gerward et al. [4] and Dandekar et al. [21], which are 11% and 10%, respectively. But the present value is comparable with the other reported value of 8.1% by Seifert [22]. The bulk modulus of CaF_2 at ambient conditions is 103 GPa, which overestimates the experimental value by 22% [1,23]. As CaF_2, and BaF_2 is reported to undergo a transition to the orthorhombic phase, SrF_2 is also expected to follow the

Fig. 2. Calculated total energy vs. relative volume in the fluorite and orthorhombic phases of SrF_2.
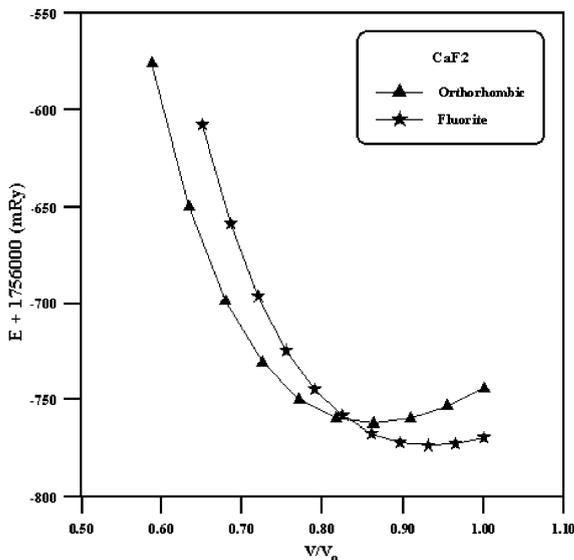
Fig. 1. Calculated total energy vs. relative volume in the fluorite and orthorhombic phases of CaF_2.
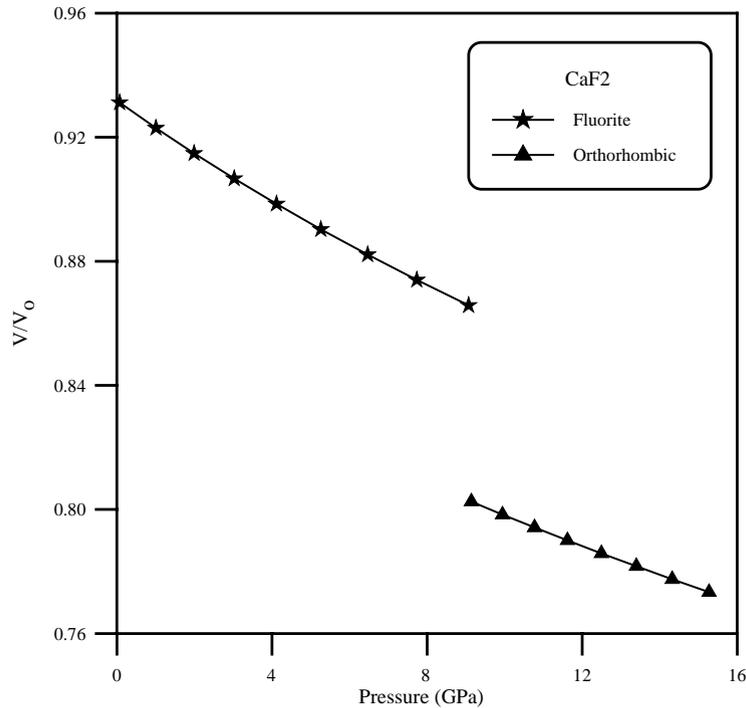
Fig. 3. Calculated pressure volume relation in the fluorite and orthorhombic phases of CaF_2.

same trend and the transition pressure is predicted to be around 7 GPa. Recently, Francisco et al. using atomic simulation method reported a similar reversible transition and the transition pressure is found to be around 5 GPa. The bulk modulus of SrF_2 is found to be 90.35 GPa. The calculated value of bulk modulus of CaF_2 and SrF_2 overestimates the experimental value by 22%. This is similar to that of BaF_2 and other alkaline-earth fluoro-halides [9,24], which is due to the inherent limitation of LDA. The calculated ground state properties of CaF_2 and SrF_2 are tabulated in Table 1. The calculated transition pressures are tabulated in Table 2 along with the volume collapse associated with the transitions.

3.2. Band structure and density of states

The self-consistent band structures for CaF_2 and SrF_2 are obtained at ambient as well as at high-pressures. In both the compounds the lowest lying bands are mainly fluorine 's' like states. The bands lying above these are the 'p' like states of the metal

atom. The slight difference between the band structures of both these compounds is that the 'p' like states of the metal atom lies well separated from the anion 's' like states in SrF_2 while it lies close in CaF_2. In both these compounds, the bands lying close to the Fermi level are contributed by the anion 'p' like states. The conduction band arises mainly from the 's' and 'd' like states of the metal atom. These compounds are wide band gap insulators with the gap occurring between the Fluorine 'p' like states and the 'sd' like states of the metal atom. The band gap is indirect and it is 7.24 eV for CaF_2 lying between $(0\,0\,0)\,\pi/a$ and $(0\,0\,1)\,\pi/a$. This value of the band gap under estimates the experimental values by 21% [25]. This is similar to that observed in other semi-conductors, insulators and other alkaline-earth halides [24,26–28]. In SrF_2, the gap is around 7.5 eV and lies between $(0\,0\,0)\,\pi/a$ and $(-0.5\,0.5\,1)\,\pi/a$ is similar to that of BaF_2 [9]. The band structures at ambient conditions are shown in Fig. 5a and b. The fat bands indicated in these figures denote the 'd' like states of the metal atom.
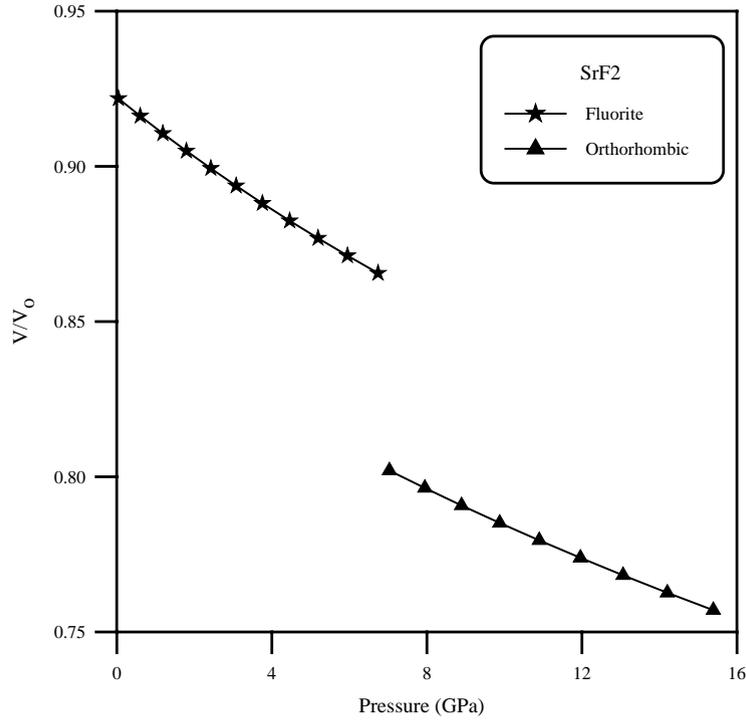
Fig. 4. Calculated pressure volume relation in the fluorite, and orthorhombic phases of SrF_2.

Table 1
Calculated equilibrium properties of CaF_2 and SrF_2

Properties	CaF₂			SrF₂		
	Fluorite		Orthorhombic	Fluorite		Orthorhombic
	Theory	Experiment	Theory	Theory	Experiment	Theory
Lattice parameter (a.u.)	$a = 10.087$	10.327^a 10.291^b	$a = 13.207$ $b = 10.399$ $c = 6.446$	$a = 10.671$	10.963^a	$a = 10.936$ $b = 13.561$ $c = 7.108$
Bulk modulus (GPa)	103	90^c 82.7^d	153.8	90.35	69^e	127
$M-F$ (a.u.)	4.396	—	4.107	4.667	—	4.389
$F-F$ (a.u.)	5.076	—	4.851	5.389	—	5.018
Energy gap (eV)	7.24	10.0^f	7.88	7.55	—	8.24

[a] Ref. [29].
[b] Ref. [30].
[c] Ref. [23].
[d] Ref. [5].
[e] Ref. [1].
[f] Ref. [25].

In both these compounds the 's' and 'd' like states of the cation are hybridized and lie above the Fermi level as shown in the band structures.

In the case of CaF_2, the gap increases from the fluorite phase to the orthorhombic-type structure and it becomes a direct gap of 7.88 eV. The gap

Table 2
Calculated transition pressures of CaF_2 and SrF_2

Properties	CaF_2		SrF_2	
	Theory	Experiment	Theory	Other works
Transition pressure (GPa)	9.1	9.5[a]	7	5[b]
Volume collapse (%)	7	10[c]	7	—
		8.1[d]		—
Metallisation pressure (GPa)	210	—	91	—

[a] Ref. [4].
[b] Ref. [6].
[c] Ref. [21].
[d] Ref. [22].
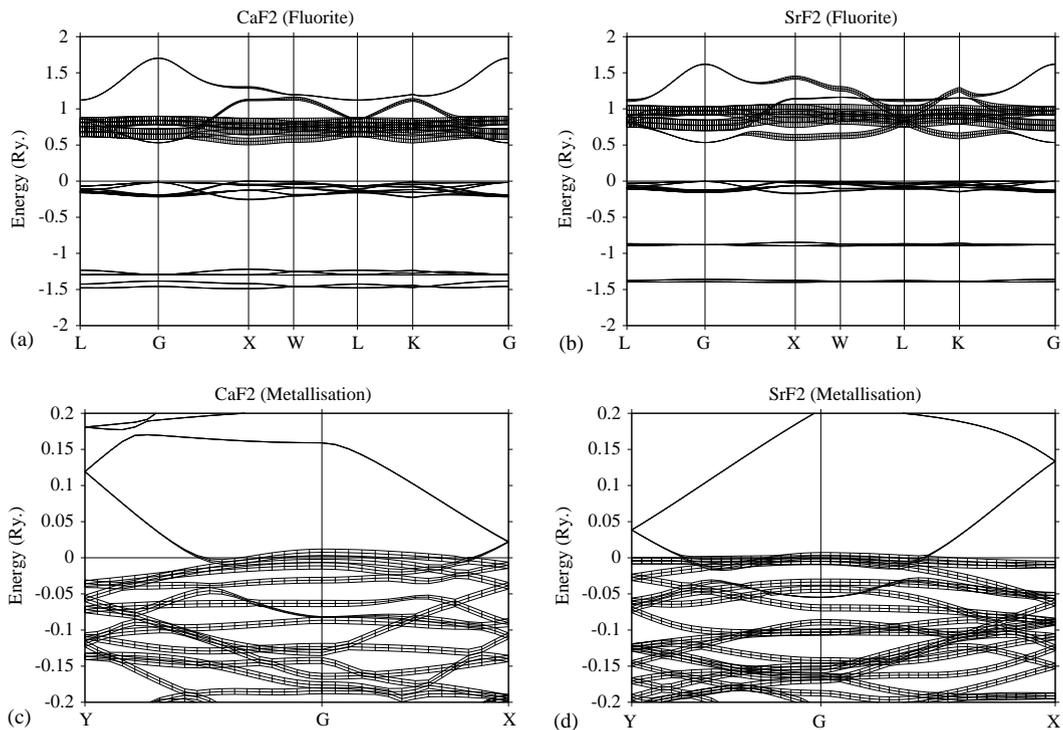
Fig. 5. (a) Band structure of CaF_2 in the fluorite phase, (b) band structure of SrF_2 in the fluorite phase, (c) band structure of CaF_2 at the metallization in the orthorhombic phase, and (d) band structure of SrF_2 at the metallization in the orthorhombic phase.

keeps on increasing in this phase and started decreasing around $V/V_o = 0.55$ with the gap value as 4.25 eV. On further compression, the gap closes and band overlap metallization occurs around 210 GPa. The band structure at the metallization is shown in Fig. 5c. From the band structure also, it

can be clearly seen that the Ca 's' and 'd' like states drops down below the Fermi level along the $Y-G$ direction and the anion 'p' like states shifts above the Fermi level leading to the band overlap metallization. The 'p' like states are indicated as the fat bands in the high-pressure phase (Fig. 5c).

A similar behavior is also observed in SrF_2. The gap increases in the high-pressure phase and begins to decrease around $V/V_o = 0.65$, which is around 6.98 eV. It further decreases on application of pressure and leads to metallization around 91 GPa. As mentioned above the 'sd' like states of the cation drops down below the Fermi level leading to the band overlap metallization. The band structure at the metallization is shown in Fig. 5d. Generally, the transition pressure and the metallization pressure decreases as one moves down the column in the periodic table. A similar trend is also observed in the present work and the metallization pressure decreases from 210 to 33 GPa as one moves from CaF_2 to BaF_2. The metallization pressure of BaF_2 is predicted to be 33 GPa in our earlier work [9]. This is the first ever-reported band structure at ambient as well as high pressures. As there are no other reports available, these results could not be compared. The metallization pressures of these compounds are tabulated in Table 2.

4. Conclusions

The structural and electronic properties of CaF_2 and SrF_2 have been calculated using the TB-LMTO method. From the total energy calculations it can be clearly seen that the fluorite-type structure is stable at ambient conditions. CaF_2 undergoes a structural phase transition to the orthorhombic structure (Pbnm) at a pressure of around 9.1 GPa. The calculated transition pressure of CaF_2 agrees fairly well with the reported experimental value of 9.5 GPa [4]. The high-pressure phase of SrF_2 is also of orthorhombic type (*Pnam*) and the transition pressure is found to be 7 GPa. Both of these compounds are wide band gap insulators with the gap occurring between the Fluorine 'p' like states and the 'sd' like states of the metal atom. The band gap of CaF_2 is indirect and it is 7.24 eV lying between $(0\,0\,0)$ π/a and $(0\,0\,1)$ π/a. In SrF_2, the gap is around 7.5 eV and lies between $(0\,0\,0)$ π/a and $(-0.5\,0.5\,1)$ π/a is similar to that of BaF_2. The calculated band gap underestimates the reported values, which may be due to the inherent limitation of LDA. Upon compres-

sion these compounds are predicted to undergo insulator to metal transition. The metallization pressures are predicted to be around 210 and 91 GPa for CaF_2 and SrF_2, respectively. The calculated transition pressures and the metallization pressures follow the expected trend of reduction in pressure as one moves down the column of alkaline-earth fluorides. The band structures are plotted at ambient and at high-pressures. The possible reason for the metallization could be that the 'sd' like states of the metal atom drops down and the 'p' like states of the anion tends to move up under pressure leading to the band overlap metallization. To our knowledge this is the first band structure calculation reported. Due to the non-availability of the experimental or theoretical results, it is not possible to compare the calculated band structure results.

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