

Electronic structure of ionic PbFCl-type compounds under pressure

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Abstract

The electronic structures of alkaline-earth fluoro-halides—SrFBr, SrFI, and CaFBr, which crystallize in the PbFCl-type structure—have been studied using the tight-binding linear muffin-tin orbital method within the local density approximation. The total energies were calculated using the atomic sphere approximation and were used to determine the ground state properties of these systems. The calculated ground state properties agree fairly well with the experimental results. These systems were found to be direct band gap insulators. The pressure dependence of the band gap was also studied. The band gap closes at high pressures leading to band overlap. A possible reason for the metallization in these compounds is discussed.

1. Introduction

The alkaline-earth fluoro-halides MF_X, where M = Ca, Sr, Ba, Pb, Eu and X = Cl, Br, I, form an important class of materials crystallizing in the PbFCl-type tetragonal structure ($P4/nmm$), which is also called the matlockite structure [1, 2]. These compounds when activated with divalent impurity, namely Eu²⁺, are used as x-ray phosphors for medical imaging via photo-stimulated luminescence processes (PSL) [3–5]. They also find application as *in situ* pressure gauges for experiments with diamond anvil cells at high temperatures [6, 7]. Also SrFCl:Sm²⁺ finds special application as a material that is more sensitive than the ruby sensor which is currently used for pressure measurements in diamond anvil cells [6, 8]. In addition to the photo-stimulated processes, the structural systematics of these compounds at ambient conditions and that of BaFCl in an extended pressure range have been studied [9–11]. Extensive high-pressure x-ray diffraction studies have been carried out by Shen *et al* [12] on MFCl compounds. In their studies, structural phase transitions were observed in BaFCl and BaFBr around 21 and 270 GPa, where the high-pressure phase is not identified. A similar work was reported by Subramanian *et al* [13] where the high-pressure phase was found to be of monoclinic structure

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($P2_1/m$) and the transition pressure is around 22 GPa. Molecular dynamics stimulations of the high-pressure phase transition in BaFCl were performed by Liu *et al* [14]. The thermal expansion coefficient of BaFX ($X = \text{Cl, Br}$) has been studied by Kurobori *et al* [15]. A first theoretical attempt has been made by Kalpana *et al* [16] to study the electronic structure of some of the PbFCl-type compounds using the tight-binding linear muffin-tin orbital (TB-LMTO) method. An extensive study has been made on BaFX ($X = \text{F, Cl, Br}$), SrFCl, and CaFCl, and the metallization pressures of these ionic compounds were also predicted [16]. With the same motivation, efforts have been made in the present work to study some of the remaining compounds of the above-mentioned series such as SrFBr, SrFI, CaFBr. Electronic band structure calculations for these mixed-halide systems, SrFBr, SrFI, and CaFBr, have been performed at ambient as well as high pressures. These compounds are ionic insulators with the excess two electrons of the metal atom being transferred to the halide anions, which have a deficit of a single electron. The bottoms of the conduction bands are formed by the 's'- and 'd'-like states of the metal atom, and the tops of the valence bands arise from the halogen 'p'-like states. The band gap values of these mixed-halide systems are not available for comparison.

2. Crystal structure and method of calculation

Alkaline-earth fluoro-halides crystallize in the primitive tetragonal structure with two molecules per unit cell (spacegroup = P_4/nmm). The atomic positions of these ternary MXY compounds are given below.

$$\begin{array}{l} \text{M: } 0 \quad 1/2 \quad Z(\text{M}) \\ \text{X: } 0 \quad 0 \quad 0 \\ \text{Y: } 0 \quad 1/2 \quad Z(\text{Y}). \end{array}$$

The internal parameters $Z(\text{M})$ and $Z(\text{Y})$ of these compounds have been taken from the literature [17, 18]. The electronic structure and total energies within the atomic sphere approximation (ASA) are obtained by the TB-LMTO method [19, 20]. The exchange–correlation potential within the local density approximation (LDA) is calculated using the parametrization scheme of von Barth and Hedin [21]. Combined correction terms are also included which account for the non-spherical shape of the atomic spheres, and effect the truncation of the higher partial waves inside the spheres to minimize the errors in the LMTO method. The tetrahedron method of Brillouin zone integration has been used to calculate the density of states [22]. The Wigner–Seitz sphere is chosen in such a way that the sphere boundary potential is minimum and the charge flow is in accordance with the electronegativity criteria.

The axial ratios of all the systems studied here are taken from the experimentally reported lattice constants and are 1.739, 2.077, and 2.073 respectively for SrFBr, SrFI, and CaFBr. The c/a ratio increases drastically as we move from SrFBr to SrFI. A similar trend is also observed in CaFBr as we move from CaFCl to CaFBr [9].

It is very well known that the TB-LMTO method gives accurate results for the close-packed structures. Hence empty spheres were added in the appropriate positions in the present study. Three empty spheres were added for SrFBr and SrFI and two in the case of CaFBr. For each of these compounds the following basis orbitals were used as the valence states:

$$\begin{array}{lll} \text{SrFBr:} & \text{Sr: } 5s^2, 4p^6, 4d^0; & \text{F: } 2s^2, 2p^5, 3d^0; & \text{Br: } 4s^2, 4p^5, 4d^0. \\ \text{SrFI:} & \text{Sr: } 5s^2, 4p^6, 4d^0; & \text{F: } 2s^2, 2p^5, 3d^0; & \text{I: } 5s^2, 5p^5, 5d^0. \\ \text{CaFBr:} & \text{Ca: } 4s^2, 3p^6, 3d^0; & \text{F: } 2s^2, 2p^5, 3d^0; & \text{Br: } 4s^2, 4p^5, 4d^0. \end{array}$$

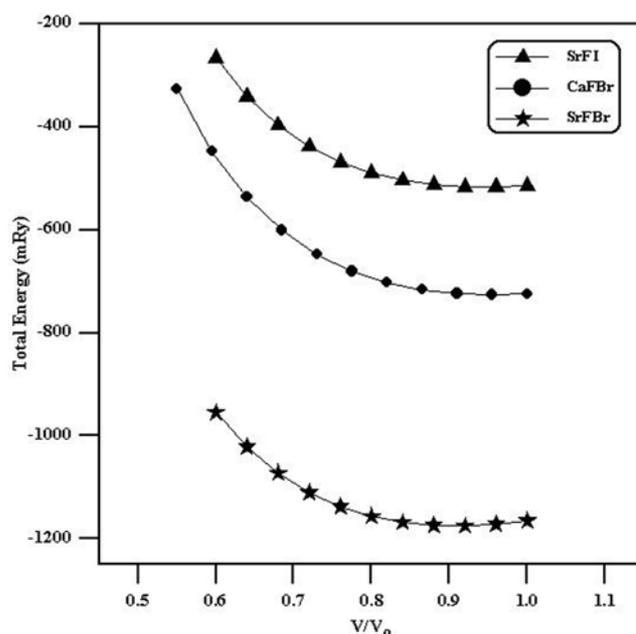


Figure 1. Calculated total energy ($-23\,520.00+$, $-41\,551.00+$, $-13\,530.00+$) versus relative volume for SrFBr, SrFI, and CaFBr.

3. Results and discussion

For each of these compounds the total energies were plotted as a function of reduced volume. The graph connecting the total energies and the relative volumes for these compounds is given as figure 1. The calculated total energies are fitted to the Birch equation of state [23] to obtain the equilibrium properties. The calculated ground state properties are tabulated in table 1. The calculated lattice parameter is in good agreement with the experimental results. The experimental value of the bulk modulus is available only for SrFBr. The calculated value overestimates the experimental value by around 28%, which may be due to the inherent limitation of the LDA. A similar trend is noticed for other fluoro-halides also [16]. In addition, the interatomic distances are also tabulated in table 1. The present calculation shows that the total energy calculations based on the density functional theory within the framework of the LDA are sufficiently accurate in predicting the ground state properties.

The self-consistent band structure along the symmetry directions was obtained at ambient conditions for these compounds. The band structure of SrFBr at ambient conditions is shown in figure 2(a). In order to study the effect of pressure on the band gap, the band structures were plotted at high pressure also. The overall band profiles of these compounds are all the same and similar to that of SrFBr. The lowest-lying band arises from the F '2s' states. The bands lying above this are mainly contributed by the 'p'-like states of the metal atom. Well above these are the bands arising from the Br '4s' states. The upper valence bands lying close to the Fermi level are due to the 'p'-like states of fluorine and bromine. The top of the valence band occurs at the Γ point. The conduction band arises from the 's'- and 'd'-like states of the metal atom. The bottom of the conduction band also occurs at the Γ point, making the compound a direct band gap insulator.

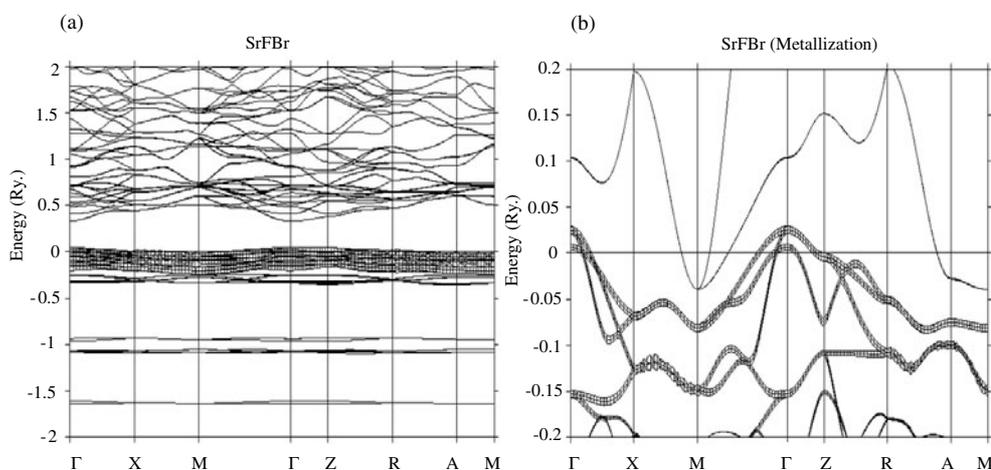


Figure 2. (a) The band structure of SrFBr at ambient conditions. (b) The band structure of SrFBr at metallization.

Table 1. Equilibrium ground state properties of SrFBr, SrFI, and CaFBr.

Properties	SrFBr		SrFI		CaFBr	
	Present	Experiment ^a	Present	Experiment ^b	Present	Experiment ^b
Lattice parameter, a (Å)	4.084	4.217	4.173	4.253	3.829	3.883
Lattice parameter, c (Å)	7.105	7.337	8.667	8.833	7.926	8.050
Bulk modulus (GPa)	79.98	51(10) 52 (6)	50.40	—	66.17	—
M–F (Å)	2.425	2.511	2.544	—	2.336	—
F–F (Å)	2.879	2.982	2.956	—	2.700	—

^a Reference [8, 17].

^b Reference [9].

The band structure of SrFBr at the metallization volume is shown in figure 2(b). In SrFBr and SrFI, the gap at the Γ point decreases upon compression and this leads to metallization. In CaFBr, the band gap initially increases and then decreases on further compression. This is similar to the scenarios for other alkaline-earth fluorides and fluoro-halides [16, 24]. The variation of band gap with pressure for all these compounds is shown in figure 3. The band gap closes as an indirect gap in SrFBr and CaFBr and as a direct gap in SrFI. The calculated values of the band gap at ambient conditions and the density of states at metallization pressures are tabulated in table 2. As there are no experimental values available for comparison, our calculated values of the band gap could not be compared. From the table, it can be clearly seen that the metallization pressure increases from SrFCl [16] to SrFBr and then decreases for SrFI, whereas there is a reduction in the metallization pressure when one goes from CaFCl to CaFBr. This can be well correlated with the interplanar distances. The interplanar distances for SrFBr, SrFI, and CaFBr were calculated using PARST [28] and are tabulated in table 3. As the M–F distance decreases, the metallization pressure decreases. A similar trend was also observed in other alkaline-earth fluorides by Kalpana *et al* [16]. In addition, the tremendous increase in the M–X distance may be due to the variation in c/a , which can again be explained using the charge density plots. The density of states at metallization for SrFBr is shown in

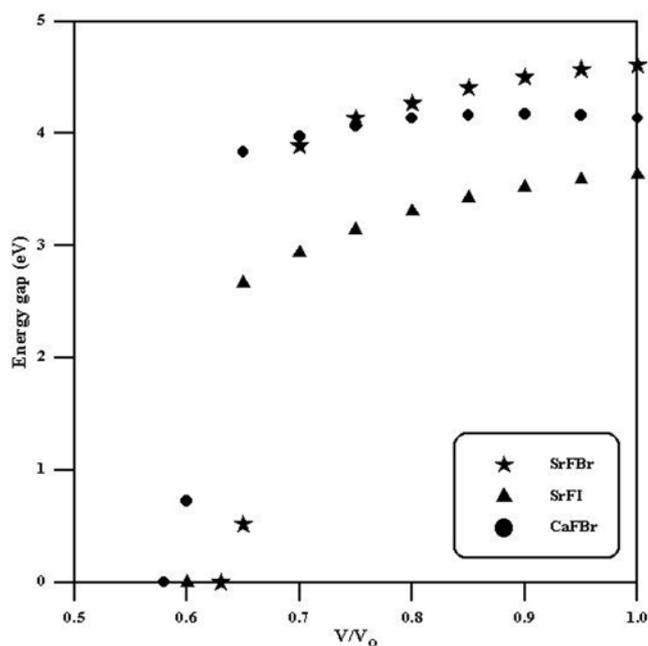


Figure 3. Variation of band gap as a function of relative volume for SrFBr, SrFI, and CaFBr.

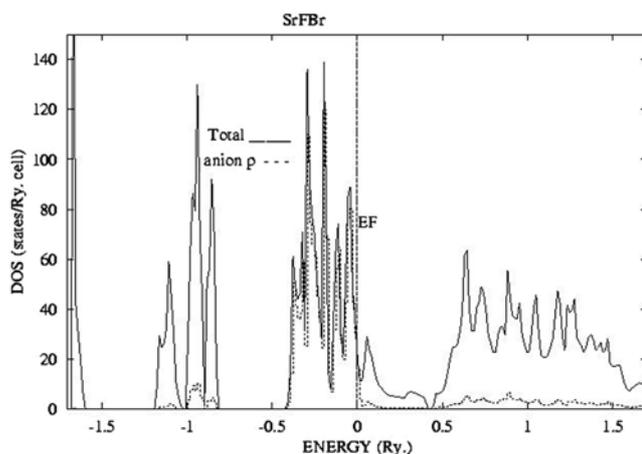


Figure 4. The density of states at metallization for SrFBr.

figure 4. From the band structure at the metallization volume, it can be clearly seen that the 'p'-like states of the halogen atom tend to move above the Fermi level and the 'sd'-like states of the metal atom drop down below the Fermi level, leading to band overlap metallization. The wide bands indicated in the band structure at metallization are the halogen 'p'-like states moving above the Fermi level. The density of states at metallization for all these compounds is given in table 2 along with the metallization pressures. The major contribution to the density of states arises from the anion 'p'-like states, which can be seen from figure 4.

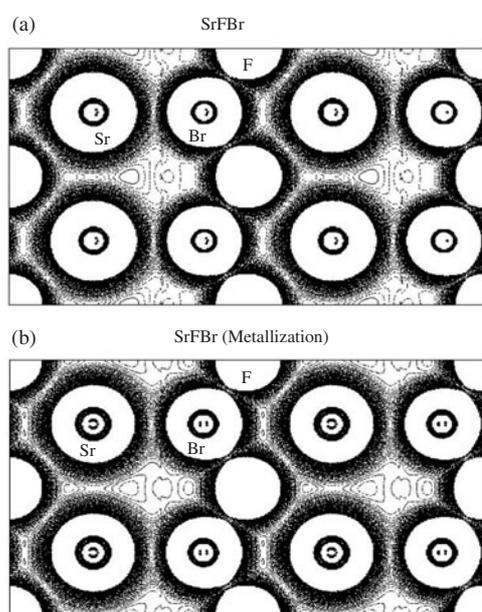


Figure 5. (a) The charge density plot for SrFBr in the [200] plane. (b) The charge density plot for SrFBr at the metallization volume in the [200] plane.

Table 2. The calculated band gap, metallization pressure, and density of states for SrFBr, SrFI, and CaFBr.

Properties	SrFBr	SrFI	CaFBr
Band gap (eV)	4.502	3.590	4.163
Metallization pressure (GPa)	63.33	58.75	91.26
$N(E_F)$ (states Ryd ⁻¹ /FU)	11	4.1	7.50

Table 3. Calculated interplanar distances of fluoro-halides.

Compounds	M–F plane (Å)	M–Y plane (Å)	Y–Y plane (Å)
CaFBr ^a	1.368	1.288	2.747
SrFBr ^a	1.364	1.219	2.170
SrFI ^a	1.475	1.555	2.774

^a Reference [28].

The bonding nature of the solids can be studied well using electronic structure calculations [25, 26]. An understanding of the bonding nature of these compounds is really lacking. A better way of understanding the bonding nature of these compounds is to produce charge density plots. The charge densities are plotted for SrFBr at ambient conditions in figure 5(a). The bonding nature of these compounds is mainly ionic, leading to the insulating behaviour of these compounds. The charge density of SrFBr at metallization is plotted and the covalent nature of the bonding is seen figure 5(b).

4. Conclusions

The structural and electronic properties of the mixed alkaline-earth fluoro-halides SrFBr, SrFI, and CaFBr have been calculated using the TB-LMTO method. From the total energy calculations, the ground state properties are calculated; the results are in fairly good agreement with the experimental ones. The band structures for these compounds are plotted at ambient as well as high pressures. The overall band profiles are found to be the same, with the direct gap occurring between the 'p'-like states of the halogen atom and the 'sd'-like states of the metal atom. The metallization pressures have been predicted for these compounds and are correlated with the interplanar distances. For these compounds, to our knowledge, these are the first band structure calculations to be reported. Because of the lack of experimental or theoretical results, it is not possible to make a comparison of the band structures obtained.

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