A structural study on MFCl (M = Ca, Sr, Ba) and BaFX (X = Br, I)

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Abstract. Here we present the electronic band structure calculations of CaFCl, SrFCl, BaFCl, BaFBr and BaFI performed using tight binding linear muffin–tin orbital method. The calculated ground state properties namely the lattice parameters, bulk moduli and the pressure–volume relations were found to be in good agreement with the experimental values. The electronic band structure of these compounds were calculated at ambient as well as in the high pressure region. The band gap values of these insulating systems were calculated and compared with available experimental values. At high pressure these compounds exhibit the interesting phenomenon of band overlap metallization.

Keywords. Electronic structure; high pressure; metallization; insulator; alkaline-earth fluoro halides.

1. Introduction

Alkaline-earth fluoro halides are interesting host materials for divalent impurities (Eu^{2+} and Sm^{2+}). These materials doped with divalent impurities exhibit the excellent properties of photo-stimulated luminescence and thermostimulated luminescence (Inabe *et al* 1988; Crawford *et al* 1989). Because of this property they are used as X-ray phosphors in image plates. The characteristic properties of X-ray imaging depends strongly on the two types of F -centres $F(F^-)$ and $F(X^-)$ formed in these materials during irradiation. For a basic understanding of the physical properties of the title compounds, we have performed a detailed electronic band structure calculations. These compounds can be grouped into those with alkaline-earth metal varying and those with halogen varying.

2. Method of calculation

Alkaline-earth fluoro halides are known to crystallize in the tetragonal PbFCl-type (Wyckoff 1963) structure (space group $P4/nm$). The structure is characterized by packing of layers along the c -axis as shown in figure 1. The stacking of the layers is of the type $X-M-Y-Y-M$, where $X = F^-$, $M = \text{Ca}^{2+}$, Sr^{2+} , Br^{2+} and $Y = \text{Cl}^-$, Br^- and I^- .

The electronic band structure and the total energies within the atomic sphere approximation were obtained by means of TBLMTO method (Andersen and Jepsen 1984), whose short ranged basis are an exact transformation of the long ranged linear muffin–tin orbitals. The exchange–correlation part of the potential within the local density approximation (LDA) is calculated using the parametrization scheme of von Barth and Hedin. For all the compounds, the calculations were performed for 91 k

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Figure 1. Unit cell of PbFCl-type structure.

Table 1. Lattice parameter, bulk modulus (K_0), energy gap, metallization volume and pressure for the title compounds.

		CaFCl	SrFCl	BaFCl	BaFBr	BaFI
$a(\text{\AA})$	Expt.	3.894 ^{††}	4.129 ^{†††}	4.394 [†]	4.508 ^{††}	4.654 ^{††}
	Theory	3.886	4.118	4.392	4.509	4.662
c/a	Expt.	1.749	1.687	1.646	1.65	1.71
	Theory	1.742	1.68	1.65	1.652	1.718
K_0 (kbar)	Expt. ^{†††}	970	610	620	440	—
	Theory	718	609	516	477	412
E_g (eV)	Expt. ^{††††}	—	—	—	8.2	—
	Theory	6.473	8.218	7.07	6.106	5.101
V_m/V_0		0.6	0.678	0.79	0.701	0.67
P_m (kbar)		1096	541	209	409	435

[†] Sauvage 1974; ^{††} Liebich and Nicollin 1977; ^{†††} Shen *et al* 1994; ^{††††} von Seggern and Voigt 1988.

points within the irreducible wedge of the Brillouin zone. The density of states were calculated by the method of tetrahedra. The combined correction terms which account for the non-spherical shape of the potential and the truncation of the higher partial waves ($l > 2$) were included, so that the errors in the LMTO method is minimum. For each of the compound the following orbitals of the alkaline-earth metals namely, Ca: 4s, 3p, 3d, Sr: 5s, 4p, 4d, and Ba: 6s, 5p, 5d were used as valence states.

3. Results and discussion

For each of these compounds the total energies were calculated by varying the c/a ratio to determine the minimum c/a value. Then keeping the c/a value to be constant, the

Figure 2. Band structure of BaFCl at equilibrium volume.

total energies were calculated by changing the volume from $1.2 V_0$ to $0.6 V_0$, where V_0 is the equilibrium volume. The total energies were fitted to the Birch–Murunaghan equation of state, to obtain the ground state properties. The calculated value of the lattice parameters, c/a values and the bulk moduli are given in table 1 along with the experimental values. From the table it can be seen that there is a good agreement with the experimental values.

The self-consistent scalar relativistic band structure for all the compounds were obtained in the primitive tetragonal lattice. The band structure at ambient condition for BaFCl is shown in figure 2. The overall band profile is same for all the other compounds. The top of the valence band arises from the $\text{Cl } 3p$ states and the bottom of the conduction bands is from the $\text{Ba } 6s$ and $5d$ states. The fundamental band gap is found to be a direct band gap occurring at Γ -point. The calculated values of the band gap for all the five compounds are given in table 1 and is compared with the available experimental value for BaFBr . When compared to the experimental value, the calculated value of the band gap is underestimated by about 26%. This is due to the errors introduced by the local density approximation to the exchange–correlation potential. It is usually found that the valence bands of the semiconductors are very well described in this scheme, but the position of the conduction bands relative to the valence bands is not calculated correctly within the LDA, which underestimates the fundamental band gaps in semiconductors and insulators. Even though the band gap value is underestimated the decreasing trend in the band gap value with increasing size of the metal atom or the anion is reproduced. The variation of band gap values as a function of reduced volume for all the five compounds are given in table 2. At low pressures the direct band gap at Γ increases. This trend is similar to that observed in the case of alkaline-earth oxides (Kalpana *et al* 1995). This is because the lowest energy in the conduction band namely, Γ point, moves away from the valence band. At high pressures the band gap starts decreasing and the direct band gap at Γ point closes and the systems go to the metallic state (figure 3).

Table 2. Variation of band gap (eV) as a function of reduced volume.

V/V_0	CaFCl	SrFCl	BaFCl	BaFBr	BaFI
1.0	6.47	8.22	7.07	6.11	5.02
0.95	6.70	8.46	7.20	6.21	5.14
0.9	6.94	8.71	5.52	6.31	5.26
0.85	7.20	8.98	3.06	6.07	5.37
0.8	7.48	7.76	0.38	4.55	4.81
0.79	—	—	0.00	—	—
0.75	7.78	4.80	—	2.39	3.24
0.7	7.18	1.28	—	0.00	1.23
0.68	—	0.00	—	—	—
0.67	—	—	—	—	0.00
0.65	3.25	—	—	—	—
0.6	0.00	—	—	—	—

Figure 3. Band structure of BaFCl at metallization volume.

4. Conclusions

Our theoretical studies offer a better understanding of the ground state properties as well as the high pressure phases of these systems. The calculated lattice constant, bulk modulus, band gap, metallization volume and pressure show good overall agreement with the available experimental results.

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