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Structural and electronic properties of alkaline-earth fluorohalides under pressure

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The electronic band structure of the mixed alkaline-earth fluorohalides—CaFCl, SrFCl, BaFCl, BaFBr, and BaFI in the PbFCl-type structure—were calculated using the tight-binding linear muffin-tin orbital method within the local-density approximation. The total energies calculated within the atomic sphere approximation were used to determine the ground-state properties of these systems. The calculated equilibrium lattice parameters, c/a ratio, the bulk modulus, and the pressure-volume relation were found to be in good agreement with the experimental results. The energy band-gap value at ambient conditions and the pressure dependence of the band gap for these systems were also obtained. These systems are found to be direct band-gap insulators with the band gap initially increasing with pressure which decreases upon further compression leading to band-overlap metallization at high pressures. [S0163-1829(97)01432-X]

I. INTRODUCTION

The alkaline-earth fluorohalides MFX ($M=\text{Ca}$, Sr, Ba, Eu; $X=\text{Cl}$, Br, I) crystallizing in the PbFCl-type structure[1] form an important class of materials, showing interesting spectroscopic properties with a wide range of technological applications. These compounds when activated with divalent impurity, namely, Eu^{2+} are used as x-ray phosphors for medical imaging via a photostimulated luminescence (PSL) process.[2,3] Also, SrFCl:Sm^{2+} find special applications as a more sensitive material than the ruby sensor which is currently used for pressure measurements in diamond-anvil cells.[4]

Apart from the PSL process, the structural systematics of these compounds at ambient conditions[5,6] and that of BaFCl in the extended pressure range[7] have been studied. Recently extensive high-pressure x-ray-diffraction studies have been carried out by Shen *et al.*[8] on MFCl compounds. In their studies, structural phase transitions have been observed in the BaFCl and BaFBr crystals from the tetragonal to an unidentified phase at 210 and 270 kbar, respectively.

To the best of our knowledge there are no theoretical or experimental results explaining the electronic structure of these compounds. Therefore, for a basic understanding of the properties of these compounds a detailed electronic band-structure calculation of the mixed halide systems CaFCl, SrFCl, BaFCl, BaFBr, and BaFI has been performed at the ambient as well in the high-pressure region. The calculations were done using the tight-binding linear muffin-tin orbital (TB-LMTO) method within the local-density approximation (LDA).[9] These compounds can be grouped into those varying with an alkaline-earth metal atom, namely, Ca, Sr, and Ba (CaFCl, SrFCl, BaFCl) and those changing with a halogen anion, namely, Cl, Br, and I (BaFCl, BaFBr, BaFI). They are ionic insulators with the excess two electrons of the metal atom being transferred to the halide anions, which are in deficit of a single electron. The bottom of the conduction bands are formed from the metal atom s and d states and the top of the valence bands arise from the halogen p states. The band-gap values of these mixed halide systems are not available except for BaFBr, for which it is reported to be 8.3 eV.[3]

II. CRYSTAL STRUCTURE AND METHOD OF CALCULATION

The alkaline-earth fluorohalides studied here crystallize in the primitive tetragonal-PbFCl-type structure with two molecules/unit cell (space group $P4/nmm$). The coordinates of the atom and the values of the internal parameters u and v can be found elsewhere.[10,11]

The experimental values of lattice parameters, cell volume, and the interplanar distances[10,11] for these compounds are given in Table I. From the table it can be seen that the lattice parameters and hence the unit cell volume increase as the size of the metal atom or the halogen anion increases. A distinguishing feature in these compounds is that the c/a ratio decreases in going from CaFCl to BaFCl whereas it increases in going from BaFCl to BaFI. This changing trend is also reflected in the interplanar distances. The M-F inter planar distance increases from CaFCl to BaFCl,

TABLE I. Lattice parameters (a and c), molecular volume (V_0), and interplanar distances along the c axis (Refs. 10 and 11).

	CaFCl	SrFCl	BaFCl	BaFBr	BaFI
a Å	3.894	4.126	4.394	4.508	4.654
c Å	6.818	6.958	7.225	7.441	7.962
c/a	1.751	1.686	1.644	1.651	1.711
V_0 Å^3	103.33	118.5	139.7	151.3	172.5
Plane (M)-Plane (F)	1.338	1.402	1.480	1.422	1.357
Plane (M)-Plane (Y)	1.095	1.083	1.069	1.185	1.412
Plane (Y)-Plane (Y)	1.953	1.989	2.127	2.228	2.424

TABLE II. The equilibrium lattice parameter (a), c/a ratio, and bulk modulus (K_0) of the alkaline-earth fluorohalides.

	CaFCl		SrFCl		BaFCl		BaFBr		BaFI	
Expt.[a]	TB-LMTO	Expt.[b]	TB-LMTO	Expt.[b]	TB-LMTO	Expt.[a]	TB-LMTO	Expt.[a]	TB-LMTO	
a (Å)	3.894	3.886	4.129	4.118	4.391	4.392	4.508	4.509	4.654	4.662
c/a	1.749	1.742	1.687	1.68	1.646	1.65	1.651	1.652	1.711	1.718
K_0 (kbar)	970[c]	718	610[c]	609	620[c]	516	440[c]	477		412

[a] Reference 10.

[b] Reference 11.

[c] Reference 8.

whereas it decreases from BaFCl to BaFI. Similarly, the M-Y interplanar distance decreases from CaFCl to BaFCl and it increases in going from BaFCl to BaFI. Also the difference in the electronegativities ($\phi_Y - \phi_M$) (Ref. 12) as a function of cell volume varies little from CaFCl to BaFCl (values of 2.0, 2.0, 2.1) but then decreases in a more pronounced way from BaFCl to BaFI (2.1, 1.9, and 1.6). These changing trends may lead to differences in the bonding and hence the electronic properties among the two group of compounds.

The electronic band structure of each of the compounds in the primitive tetragonal unit cell were calculated by means of the TB-LMTO method within the atomic sphere approximation. The details of the calculations can be found elsewhere.[13,14] For each of the compounds, the following basis orbitals were used as valence states:

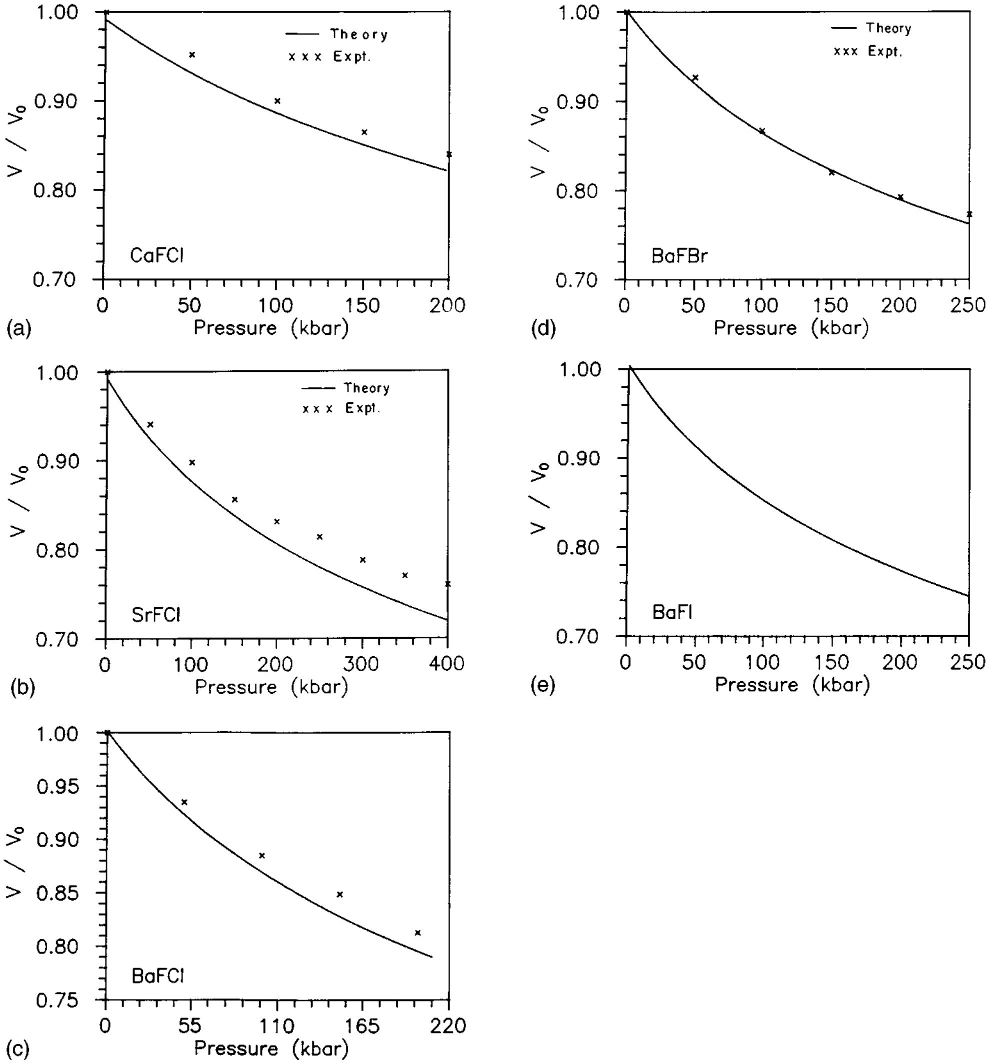

FIG. 1. Pressure-volume curve for (a) CaFCL, (b) SrFCl, (c) BaFCl, (d) BaFBr, and (e) BaFI. (Experimental data points are from Ref. 8).

CaFCl; Ca: $4s^2,3p^6,3d^0$; F: $2s^2,2p^5,3d^0$; Cl: $3s^2,3p^5,3d^0$,
SrFCl; Sr: $5s^2,4p^6,4d^0$; F: $2s^2,2p^5,3d^0$; Cl: $3s^2,3p^5,3d^0$,
BaFCl; Ba: $6s^2,5p^6,5d^0$; F: $2s^2,2p^5,3d^0$; Cl: $3s^2,3p^5,3d^0$,
BaFBr; Ba: $6s^2,5p^6,5d^0$; F: $3s^0,2p^5,3d^0$; Br: $4s^2,4p^5,4d^0$,
BaFI; Ba: $6s^2,5p^6,5d^0$; F: $3s^0,2p^5,3d^0$; I: $5s^2,5p^5,5d^0$.

In the case of BaFBr and BaFI, since the lattice constants are large compared to BaFCl, the lowest-lying valence state, i.e., F-$2s$ state is well below the other states and hence is kept in the core.

III. RESULTS AND DISCUSSIONS

For each of these compounds, the total energies were calculated both as a function of c/a ratio and reduced volume V/V_0: In these calculations the internal parameters u and v were both kept constant. The calculated total energies as a function of reduced volume were fitted to Birch equation of state to obtain the equilibrium properties. The calculated equilibrium properties are summarized in Table II where they are compared with the experimental values. The calculated values of lattice parameters and bulk modulus are found to be in good agreement with the experimental results. The deviation in the case of lattice parameter is only 0.4% and the error in the bulk modulus ranges from 8% to 26%. Also in Figs. 1(a)–1(c) the calculated P-V curve has been compared with the experimental data points which show good agreement. These calculations show that the total-energy calculations based on density-functional theory within the frame work of the LDA is sufficiently accurate in predicting the ground properties for which it is designed.

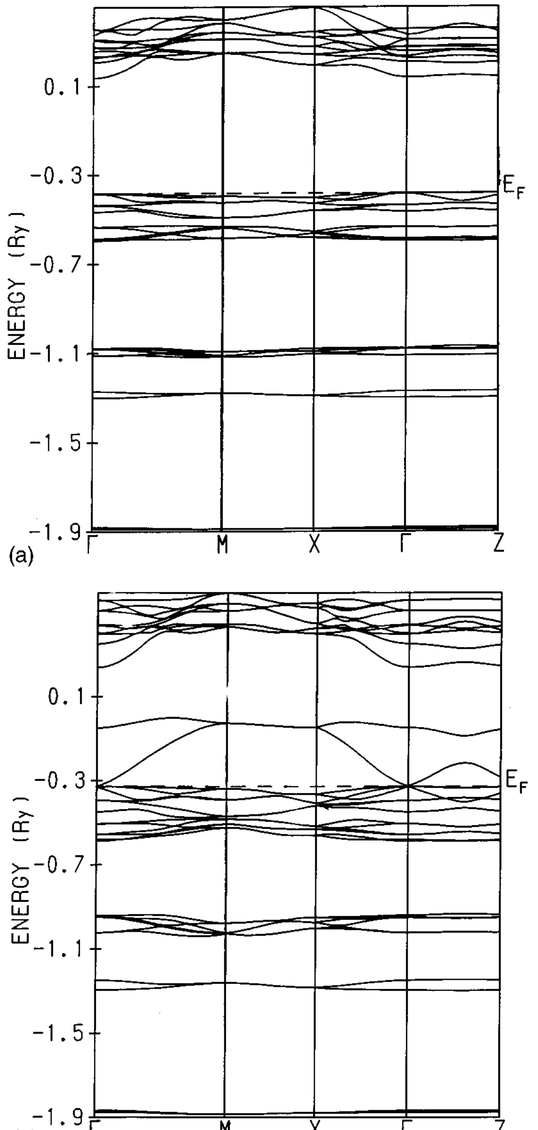

FIG. 2. Band structure of BaFCl (a) at equilibrium volume and (b) at metallization volume.

The self-consistent scalar relativistic band structure for these compounds were obtained at ambient conditions. Also, to study the effect of pressure on the band gap the band structures were calculated in the high-pressure region. Figure 2(a) shows the band-structure plot for BaFCl at equilibrium volume. The lowest-lying band arises from the F-$2s$ states, which is very small indicating negligible overlap with the neighboring states. Above this are the bands arising from the semicore like Ba-$5p$ states. Well above these are the bands arising from the Cl-$3s$ state. The upper valence bands which lie above these bands are due to the Cl-$4p$ and F-$3p$ states and the top of the valence bands occur at the Γ point. The conduction bands arise from the metal atom Ba-$5d$ and $6s$ states with the bottom occurring at Γ point making the compound to be a direct band-gap insulator. Since the x-ray photoemission spectroscopy or the photoemission spectra are not available for these materials, it is not possible to compare the band structure. The overall band profiles for other compounds studied here are similar to that of BaFCl with the band gap occurring between Γ points. However, the bandwidths are different depending upon the size of the atoms and the interplanar distances.

Figure 2(b) shows the band structure for BaFCl at metallization volume. The effect of compression on the band gap

TABLE III. Fundamental band gap (E_g), metallization volume (V_m), and pressure (P_m) of the alkaline-earth fluorohalides.

	CaFCl	SrFCl	BaFCl	BaFBr	BaFI
E_g (eV)	6.47	8.22	7.07	6.11	5.10
V_m/V_0	0.604	0.677	0.790	0.701	0.677
P_m (kbar)	1096	541	209	402	435

is found to be the same for these compounds. Upon compression, initially the direct band gap at Γ increases. This is similar to that observed in the case of MgO (Ref. 13) and other II-IV semiconductors.[15–17] Upon further compression, the band gap decreases, leading to band-overlap metallization at very high pressures.

The calculated values of the band gap at ambient conditions, the metallization volumes, and pressures are given in Table III. Except for BaFBr, the experimental values of band gap are not available for comparison. The calculated values of band gap are found to vary from 5 to 8 eV. These values are typical of other alkaline-earth halides.[18,19] For BaFBr, the reported value of band gap is 8.3 eV.[3] The calculated value is 6.1 eV which is 26% less than the experimental value. This order of error arises due to the use of LDA which underestimates the zero pressure band gap by 30–50 %. This error may also be reflected in the metallization pressure and volume.

From the same table it can also be seen that except for CaFCl, the band-gap value decreases with increasing size of the metal atom or the halogen anion, which is similar to the trend observed in our earlier calculations on alkaline-earth chalcogenides.[13,14] The low value of band gap for CaFCl may be due to the fact that $3d$ excited states of elemental Ca are very low in energy.[20] This has been confirmed by several band-structure calculations.[21,22] These calculations show that the electron states of Ca are highly susceptible to modifications by a crystal potential, which leads to nontrival consequences in the physical properties of Ca compounds. Even though the band-gap value is very low for CaFCl, the decreasing trend in metallization volume and pressure are reproduced in BaFCl, SrFCl, and BaFCl, i.e., as the size of metal atom (Ca, Sr, Ba) increases, the metallization pressure and volume decreases. But a reverse trend is observed, in going from BaFCl to BaFI, i.e., as the size of the halogen anion increases, the metallization volume and pressure increases. As said earlier the different trend observed in the c/a value and interplanar distances in going from BaFCl to BaFI may be a reason for this.

IV. CONCLUSIONS

The structural and electronic properties of the mixed alkaline-earth fluorohalides CaFCl, SrFCl, BaFCl, BaFBr, and BaFI in the teragonal PbFCl-type structure have been calculated using the TB-LMTO method. From the total-energy calculations the ground-state properties were calculated. The calculated equilibrium lattice constant, c/a ratio, and the bulk modulus are found to be in good agreement with the experimental results. The calculated P-V curves also show a very good agreement with the experimental data points.

The band structures for these compounds were obtained at ambient as well in the high-pressure region. The overall band profiles are found to be the same, with the direct band gap (Γ-Γ) occurring between the p-like valence bands of the halogen anions and sd-like conduction bands of the metal atom. The calculated value of band gap for BaFBr is 6.1 eV. This is 26% less than the experimental value of 8.3 eV. As said earlier this order of error arises due to the usage of LDA. For these compounds the calculated values of band-gap range from 5 to 8 eV. This is within the range found for the other alkaline-earth halides. Upon compression, initially, the band gap at Γ increases with pressure which is similar to that observed in the case of MgO and II-IV binary semiconductors. Upon further compression the band gap decreases leading to band-overlap metallization at high pressures. For these compounds, these, to our knowledge, are the first ever band-structure calculations reported. Because of the non-availability of the experimental or theoretical results it is not possible to compare the calculated band-structure results.

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