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Theoretical study of structural and electronic properties of CaFI

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Abstract

The full potential linearized augmented plane wave (FP-LAPW) method within density functional theory is applied to study, for the first time, the structural and electronic properties of CaFI and to compare them with CaFCl and CaFBr, all compounds belonging to the tetragonal PbFCl structure group with space group $P4/nmm$. We used the generalized gradient approximation (GGA) based on exchange–correlation energy optimization to calculate the total energy and also the Engel–Vosko GGA formalism, which optimizes the corresponding potential for band structure calculations. Ground state properties such as the lattice parameters, c/a ratio, bulk modulus, pressure derivative of the bulk modulus and cohesive energy are calculated as well as the optimized internal parameters, by relaxing the atomic position in the force directions. The variations of the calculated interatomic distances and angles between different atomic bonds are discussed. CaFCl was found to have a direct band gap at Γ whereas CaFBr and BaFI have indirect band gaps. From these computed bands, all three materials are found to be insulators having band gaps of 6.28, 5.46 and 4.50 eV, respectively. We also calculated the valence charge density and the total density of states at equilibrium volume for each compound. The results are in reasonable agreement with the available experimental data.

1. Introduction

The calcium fluorohalides CaFX ($X = \text{Cl}, \text{Br}, \text{I}$) belong to a class of layered matlockite [1] compounds crystallizing in the tetragonal PbFCl-type structure at ambient conditions with space group $P4/nmm$ [2]. By virtue of their interesting imaging applications, the matlockite

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alkaline earth fluorohalides MFX ($M = \text{Ca, Sr, Ba, Pb}$; $X = \text{Cl, Br, I}$) find utility, for instance, due to their x-ray image storage properties [3] and also as pressure calibrants [4] in diamond anvil cells. Some crystals of such mixed dihalides, such as BaFCl and BaFBr, are also used in spectroscopic and nuclear detectors [5]. Therefore, knowledge of their physical properties is demanded in order to make the best choice of the material for technological application. Furthermore, these compounds due to their layered structure are of considerable scientific interest [6–9]. The fluorohalides are also interesting from the viewpoint of lattice dynamics because of their layer structure, which is derived from the well-known fluorite structure, giving them a more or less two-dimensional character [10].

Several experimental and theoretical studies of MFX compounds have been published during the last few years. Structural studies under high pressure up to 50 GPa have been carried out experimentally to investigate their monoclinic high pressure phase [10–14]. Compared to the cases for other MFX compounds, very few results have been reported for CaFX. The structural properties of CaFCl and CaFBr have been studied experimentally [15, 16]. The structural and electronic properties of these two compounds have also been theoretically investigated using the tight-binding linear muffin tin orbital (TB-LMTO) method [17, 18]. To the best of our knowledge there are no experimental or theoretical reports in the literature of investigations of the structural and electronic properties of CaFI. Hence the purpose of this paper is to study this compound using the full potential linearized augmented plane wave (FP-LAPW) method and to compare its behaviour with the relevant properties of CaFCl and CaFBr compounds. In calcium fluorohalides there are alternating layers of cations and anions along the c axis although the iodine (chlorine, bromine) anions occur in double layers. The calculated total energy of the solids allowed us to investigate several properties and in particular the equilibrium lattice parameters c and a , c/a ratio, internal parameters, cohesive energy, bulk modulus, derivative of the bulk modulus, interatomic distances, interlayer distances along the c axis and angles between different atomic bonds. This will be followed by a detailed presentation of the band structure and the density of states as well as the electron density.

This paper is organized as follows. In section 2, we briefly outline the calculation method. We present our results, compare them with available data and analyse them in section 3. Section 4 contains the conclusions.

2. Method of calculation

The calculations were performed using the FP-LAPW approach [19] within the framework of the density functional theory (DFT) [20, 21] as implemented in the WIEN2K code [22]. The exchange–correlation potential was calculated using the generalized gradient approximation (GGA) based on the Perdew *et al* [23] and also Engel and Vosko (EV-GGA) [24] schemes. Kohn–Sham wavefunctions were expanded in terms of spherical harmonics inside non-overlapping muffin tin spheres surrounding the atomic sites (MT spheres) and in Fourier series in the interstitial region. Inside the muffin tin spheres, the l -expansion of the non-spherical potential and charge density were carried out up to $l_{\text{max}} = 10$. The muffin tin radii were assumed to be 2.2 au for Ca and Cl, while for F, Br and I they were chosen as 2, 2.4, 2.6 au respectively. In order to achieve energy eigenvalue convergence, the wavefunctions in the interstitial region were expanded in plane waves with a cut-off of $K_{\text{max}} = 7/R_{\text{MT}}$ where R_{MT} is the radius of the smallest muffin tin sphere. A mesh of 42 special k -points for CaFCl and 45 special k -points for CaFCl and CaFBr were taken in the irreducible wedge of the Brillouin zone. Both the muffin tin radius and the number of k -points were varied to ensure total energy convergence. In order to consider the relativistic effects in our calculation, the electronic states were classified into two categories, the core and valence states. The core states that are completely confined inside

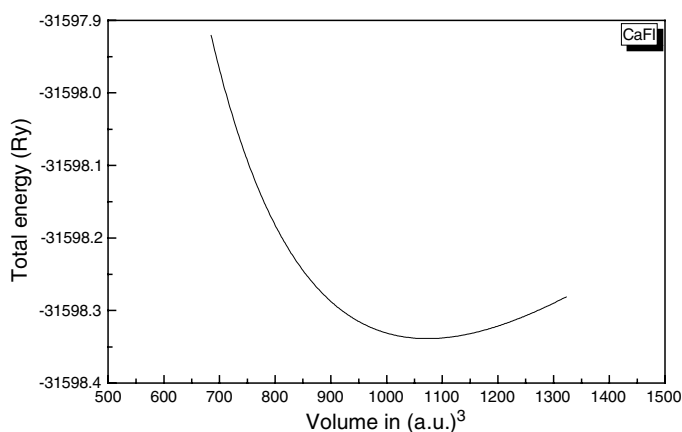


Figure 1. The variation of the total energy with the volume for the tetragonal structure of CaFI.

the corresponding muffin tin spheres were treated fully relativistically, while for the valence states that are rather non-localized we used the scalar relativistic approach that includes the mass velocity and Darwin *s*-shift but omits spin–orbit coupling.

3. Results and discussion

3.1. Structural properties

The alkaline earth fluorohalides CaFX, studied here, crystallize in a tetragonal, PbFCl-type, form with the Ca^{2++} , F^- and X^- ions located at $(0.25, 0.25, v)$, $(0.75, 0.25, 0)$ and $(0.25, 0.25, u)$, respectively [15]. It is clearly seen that two of the atomic positions depend on the internal parameters v and u . These parameters can be optimized by calculating forces on the nuclei and using the damped Newton scheme [25] to find equilibrium atomic positions. The force on each atom after relaxation decreased to less than 1.0 mRyd au^{-1} for all crystals considered here (CaFCl, CaFBr, CaFI). The total energies were then calculated as a function of volume and, as prototypes, the results calculated for CaFI are given in figure 1. The curve was obtained by fitting the calculated values to the Murnaghan equation of state [26]. The c/a ratio has also been optimized at a constant volume. The corresponding equilibrium lattice parameters, c/a ratio and internal parameters calculated within GGA are given in table 1. Our calculated values for CaFCl and CaFBr are in good agreement with the experimental result, although as a general trend, GGA overestimates the lattice parameters [27, 28], while LDA underestimates them [18].

A remarkable feature of CaFX compounds is that the c/a ratio increases on going from CaFCl to CaFI. Such a trend is reflected in the interplanar distances. Our calculated internal parameters, which are the first reported theoretical values, are very close to the available experimental data. One of the two internal parameters, u , increases on going from CaFCl to CaFI while the other one, v , decreases. Hence our predicted values for u and v in CaFI compound are respectively the biggest and the smallest values compared to the similar parameters for other CaFX compounds.

The cohesive energy is defined as the difference between the total energy of isolated atoms and crystal energy per unit cell. The details of the calculations can be found elsewhere [29]. The cohesive energy, bulk modulus and its pressure derivative for each compound are given in table 2. It is clearly seen that the cohesive energy (absolute value) and the bulk modulus

Table 1. Calculated lattice parameters (a and c in Å), c/a ratios and internal parameters (u and v) in the tetragonal structure at equilibrium volume for CaFX compounds, compared to the available experimental and other theoretical results.

		Present work	Experimental	TB-LMTO
CaFCl	a (Å)	3.939	3.894 [15]	3.894 [17]
	c (Å)	6.898	6.818 [15]	6.811 [17]
	c/a	1.751	1.751 [15]	1.749 [17]
	u	0.642 250	0.6432 [15]	
	v	0.194 902	0.1962 [15]	
CaFBr	a (Å)	3.926	3.883 [16]	3.829 [18]
	c (Å)	8.139	8.050 [16]	7.926 [18]
	c/a	2.073	2.073 [16]	2.070 [18]
	u	0.665 408	0.67 [16]	
	v	0.165 145	0.17 [16]	
CaFI	a (Å)	4.029		
	c (Å)	9.669		
	c/a	2.399		
	u	0.691 725		
	v	0.132 683		

Table 2. The bulk modulus in GPa (B), its pressure derivative (B') and the cohesive energy (E_{coh}) per unit cell in Ryd.

		Present work	Experimental	TB-LMTO
CaFCl	B (GPa)	55.66	97 [14]	71.8 [17]
	B'	4.2	2 [14]	
	E_{coh} (Ryd/cell)	-2.215		
CaFBr	B (GPa)	47.41		66.17 [18]
	B'	4.14		
	E_{coh} (Ryd/cell)	-2.124		
CaFI	B (GPa)	38.55		
	B'	4.00		
	E_{coh} (Ryd/cell)	-2.019		

decrease on increasing the halides atomic number. Hence we conclude that CaFI is more compressible compared to the other two compounds.

The interatomic and the interplanar distances along the c axis are reported in tables 3 and 4 respectively. In the CaFX structure the anions (X) form a planar square layer framed by the cations (Ca) which themselves span a planar layer of tetrahedra around each F atom. Each cation (Ca) thus acquires a neighbourhood $\text{Ca}-4\text{F} + 4\text{X} + 1\text{X}$. The four F atoms form a square pyramid and the 4X define a different square pyramid located in the opposite direction. The fifth X atom is located in the neighbouring layer. It is the Ca-X distance which determines the layer character of these compounds. A remarkable feature in these compounds is that the interplanar distance (plane X^i -plane X^{i+1}) as a function of the cell volume increases from CaFCl to CaFI, thus showing a similar trend of variation with the size of the cations. In addition, the angles between different bond directions are given in table 5.

3.2. Electronic properties

The self-consistent scalar relativistic band structures were obtained at equilibrium volume within the LDA, GGA and EV-GGA schemes. The Engel and Vosko scheme, which is based

Table 3. The number of atoms with identical distances and the value of the interatomic distance (Å).

		No of atoms with identical distances	Present work	Experimental [15]
CaFCl	F^i-Ca^i	4	2.384 6	2.362
	F^i-F^{ii}	4	2.785 3	2.753
	F^i-X^i	4	3.157 3	3.116
	Ca^i-X^i	4	3.003 3	2.963
	Ca^i-X^{ii}	1	3.085 1	3.048
	X^i-X^{ii}	4	3.407 2	3.376
CaFBr	F^i-Ca^i	4	2.406 9	
	F^i-F^{ii}	4	2.808 6	
	F^i-X^i	4	3.396 2	
	Ca^i-X^i	4	3.136 1	
	Ca^i-X^{ii}	1	4.114 8	
	X^i-X^{ii}	4	3.912 6	
CaFI	F^i-Ca^i	4	2.388 3	
	F^i-F^{ii}	4	2.848 9	
	F^i-X^i	4	3.597 6	
	Ca^i-X^i	4	3.316 5	
	Ca^i-X^{ii}	1	4.263 62	
	X^i-X^{ii}	4	4.029 0	

Table 4. Interplanar distances along the *c* axis at equilibrium volume compared with the available experimental values.

		Present work	Experimental [15]
CaFCl	Plane (Ca^i)-plane (F)	1.3444	1.338
	Plane (Ca^i)-plane (X^{ii})	1.1233	1.095
	Plane (X^i)-plane (X^{ii})	1.9625	1.953
CaFBr	Plane (Ca^i)-plane (F)	1.3598	
	Plane (Ca^i)-plane (X^{ii})	1.3952	
	Plane (X^i)-plane (X^{ii})	2.7239	
CaFI	Plane (Ca^i)-plane (F)	1.2829	
	Plane (Ca^i)-plane (X^{ii})	1.6978	
	Plane (X^i)-plane (X^{ii})	3.7076	

on potential optimization, is capable of giving a more reliable band structure, while in LDA and even GGA, as the exchange–correlation energy is optimized, in general the structural properties can be reproduced more accurately [29, 30]. Figure 2 shows the band structures of CaFCl, CaFBr and CaFI obtained using EV-GGA along high symmetry directions as well as the total density of states (DOS). A point worth mentioning is that the band structures calculated using the LDA, GGA and EV-GGA for all of the CaFX compounds are similar except as regards the value of the band gap which is higher within EV-GGA (table 6). The conduction bands for all of the CaFX compounds follow the same trend; these bands arise from ‘s’- and ‘d’-like states of the metal atom Ca with their bottom located at the Γ point. The lowest lying band shown in figure 2 arises from the X s states. The upper valence bands that lie above these bands are mainly due to X p and F p states. CaFCl was found to have a direct gap at the Γ point while CaFBr and CaFI have indirect band gaps. The CaFBr valence band has two maxima located

Table 5. Selected bond angles (degree) between different atoms of CaFX compounds.

		Present work	Experimental [15]
CaFCl	$F^i-Ca^i-F^{iii}$	111.36	111.0
	$F^i-Ca^i-F^{ii}$	71.47	71.3
	$F^i-Ca^i-X^i$	124.3	124.5
	$X^i-Ca^i-X^{ii}$	68.03	68.3
	$X^{ii}-X^i-Ca^i$	54.80	54.7
CaFBr	$F^i-Ca^i-F^{iii}$	111.20	
	$F^i-Ca^i-F^{ii}$	71.39	
	$F^i-Ca^i-X^i$	124.40	
	$X^i-Ca^i-X^{ii}$	63.58	
	$X^{ii}-X^i-Ca^i$	45.88	
CaFI	$F^i-Ca^i-F^{iii}$	115.02	
	$F^i-Ca^i-F^{ii}$	73.23	
	$F^i-Ca^i-X^i$	122.49	
	$X^i-Ca^i-X^{ii}$	59.21	
	$X^{ii}-X^i-Ca^i$	37.54	

Table 6. The band gap calculated within different approximations and compared with TB-LMTO results (eV).

	Present work			Others calculated
	EV-GGA	GGA	LDA	TB-LMTO
CaFCl	6.28 ($\Gamma-\Gamma$)	5.62 ($\Gamma-\Gamma$)	5.34 ($\Gamma-\Gamma$)	6.47 [17]
CaFBr	5.46 ($\Delta_{\max}-\Gamma$) ($\Sigma_{\max}-\Gamma$)	4.76 ($\Delta_{\max}-\Gamma$) ($\Sigma_{\max}-\Gamma$)	4.40 ($\Delta_{\max}-\Gamma$) ($\Sigma_{\max}-\Gamma$)	4.16 [18]
CaFI	4.50 ($\Delta_{\max}-\Gamma$) ($U_{\max}-\Gamma$)	4.13 ($\Delta_{\max}-\Gamma$) ($U_{\max}-\Gamma$)	3.80 ($\Delta_{\max}-\Gamma$) ($U_{\max}-\Gamma$)	

along Δ and Σ directions near the Γ point. Our indirect band gap predicted for CaFBr is in contradiction with the direct gap obtained by the TB-LMTO approach [18]. The CaFI valence band also has two maxima, located along the Δ and U directions near the X and R points respectively. It is noticeable that all other matlockite MFX compounds have a direct gap at the Γ point [31].

The bonding nature of the solids can be described accurately by using electronic density plots [32, 33] that have been calculated in the context of the first-principles approach. The charge density in our work is derived from a highly converged wavefunction; hence the results are very reliable. We calculated the valence charge density distribution and the difference density plot for crystalline and superposed atomic densities for tetragonal matlockite CaFI in the (4 0 0) plane at equilibrium as shown in figure 3. From these contours we can conclude that the bonding nature of these compounds is mainly ionic leading to the insulating behaviour of these materials.

4. Conclusions

Using the FP-LAPW method, we studied, for the first time, the structural and electronic properties of CaFI and compared them with those of CaFCl and CaFBr compounds. We optimized the lattice parameters (a and c), c/a ratios and internal parameters (u and v) to

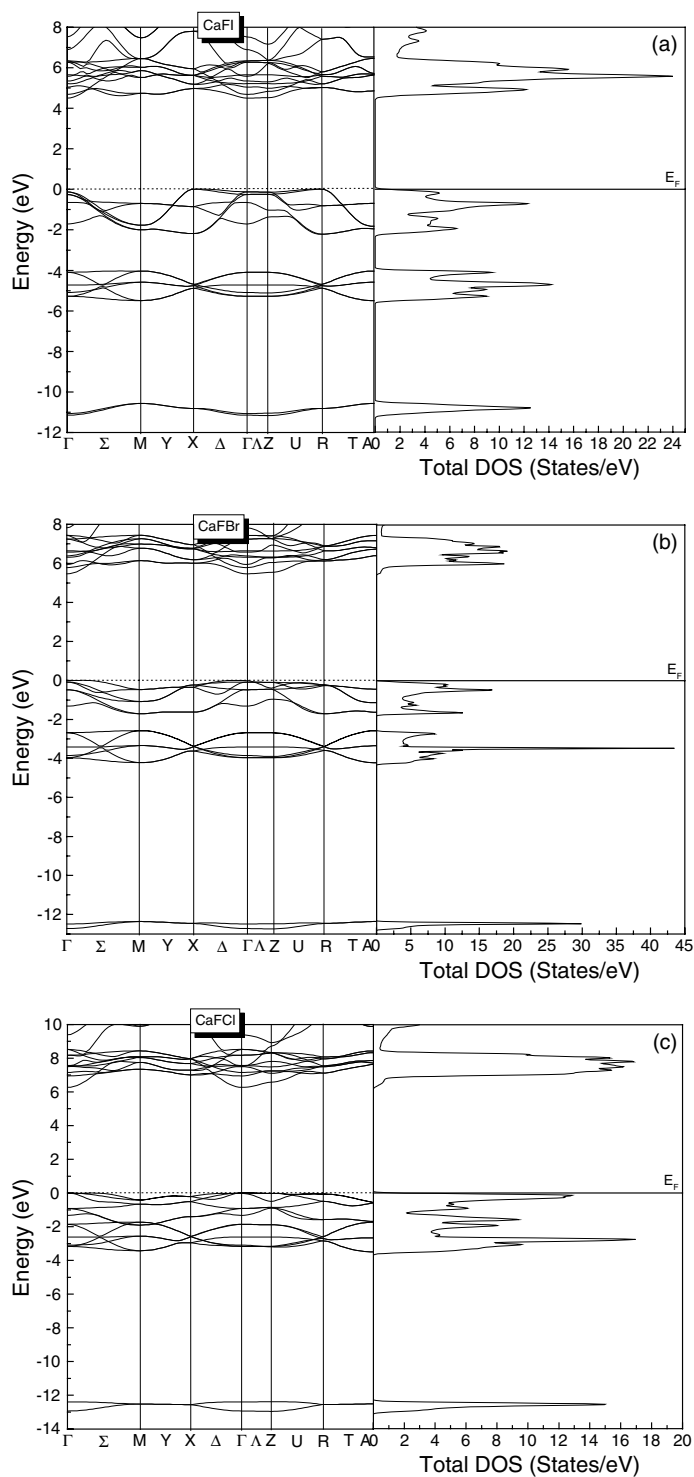


Figure 2. Band structures along the principal high symmetry directions and the total DOSs of (a) CaFI, (b) CaFBr and (c) CaFCl. The energy is referenced to the valence band maximum (eV) and the DOS scale is in states eV^{-1} .

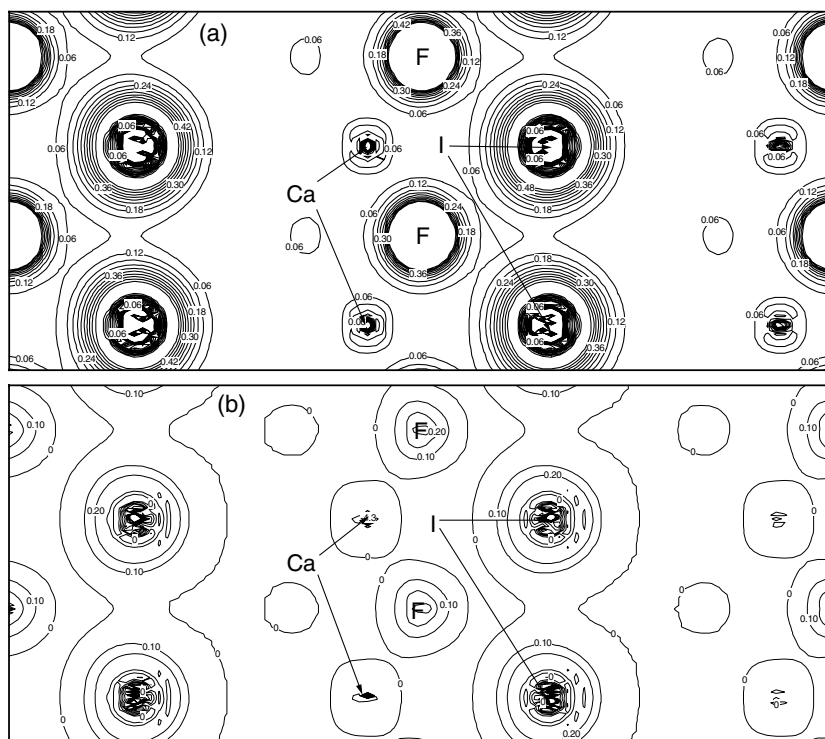


Figure 3. The charge density contours for CaFI in the (400) plane. (a) The valence charge density distribution and (b) the difference density plot for crystalline and superposed atomic densities.

find the ground state properties. The calculated cohesive energy and bulk modulus suggest that CaFI is more compressible than the other two compounds. The interatomic distances and the angles between different atomic bonds were also calculated and compared with available experimental results. The band gap was calculated by LDA, GGA and EV-GGA schemes and the results suggested a direct band gap for CaFCl and indirect band gaps for CaFBr and CaFI compounds. Our results are not in agreement with the direct band gap predicted for CaFBr within the TB-LMTO formalism [18]. The lack of experimental results prevents us from making an ultimate judgment on this issue. The electronic density calculated for these compounds indicates that the bonding nature is mainly ionic.

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