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# First-principles investigation of electronic and structural properties and bowing parameters in $\text{SrFCl}_x\text{Br}_{1-x}$ alloy

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## Abstract

The first *ab initio* calculations have been performed to study the structural and electronic properties of technologically important  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloys (for  $x$  equal to 0.0, 0.25, 0.5, 0.75 and 1.0) using the full-potential linearized augmented-plane-wave method within density-functional theory. The Perdew *et al* generalized-gradient approximation (GGA96), which is based on exchange–correlation energy optimization, is utilized to optimize the internal parameters by relaxing the atomic positions in the force directions and to calculate the total energy. Both the Engel–Vosko’s generalized-gradient approximation (EV-GGA), which optimizes the exchange–correlation potential, and GGA96 are used for band structure calculations. The effect of composition on the equilibrium volume, cohesive energy, band gap and mean values of the bond length, shows nonlinear dependence, but on the bulk modulus it exhibits nearly linear concentration dependence (LCD). The results obtained show that the quaternary alloy of interest could be an appropriate material for using in an optical apparatus.

## 1. Introduction

The alkaline-earth fluoro-halides MFX ( $M = \text{Ba, Sr, Ca}$ ;  $X = \text{Cl, Br, I}$ ) form an important class of materials crystallizing at ambient conditions in the  $\text{PbFCl}$ -type structure (with the space group  $P4/nmm$ ), which is also called the matlockite structure [1]. These compounds find utility in x-ray image storage properties on dilute doping with rare-earth ions, and also as pressure calibrants in diamond anvil cells [2–4]. Some of them, such as  $\text{BaFCl}$  and  $\text{BaFBr}$ , are also used in spectroscopic and nuclear detectors. The electronic and structural properties of these compounds at ambient conditions and high pressure have been studied [5–8]. Thermal expansion and defect properties, high-temperature x-ray diffraction studies and measurements of the elastic constants, and also long-wavelength Raman and infrared active phonons, have already been reported [9–13] for these compounds.

In our previous work [14], first-principles calculations have been used to study the physical properties of some MFX compounds using the full-potential linearized-augmented-plane-wave method within density-functional theory. In the present work, by selecting the SrFCl and SrFBr compounds, the  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy is introduced as a technologically important compound. To the best of our knowledge, no theoretical work has yet been reported on the electronic and structural properties of this alloy.

In this work, the variation of different structural and electronic parameters such as equilibrium volume, bulk modulus, cohesive energy, average values of the bond length and band gap with concentration  $x$  are taken into consideration. Some of these parameters are expressed with a quadratic expression, which has been written below for the energy gap:

$$E_g(\text{SrFCl}_x\text{Br}_{1-x}) = x E_g(\text{SrFCl}) + (1 - x) E_g(\text{SrFBr}) - bx(1 - x)$$

where the so-called bowing parameter  $b$  characterizes the deviation from linear interpolation between the two ternary SrFCl and SrFBr compounds. Higher-order terms which can be defined as a concentration-dependent bowing function  $b(x)$ , are neglected in the expansion. In many cases,  $b(x)$  shows an approximately linear dependence on concentration [15].

Section 2 gives an outline of the computational method and some important parameters. Results and discussion concerning structural and electronic properties and bowing parameters are in section 3, and section 4 contains the conclusions.

## 2. Computational details

Calculations are performed by the scalar relativistic full-potential linearized-augmented-plane-wave (FP-LAPW) method to solve the Kohn–Sham equations as implemented in the WIEN2k code [16] within the framework of density-functional theory [17, 18]. The exchange–correlation energy of electrons is described in the generalized-gradient approximation (GGA96) [19] to calculate the total energy and in Engel–Vosko’s generalized gradient (EV-GGA) [20] formalism, which optimizes the corresponding potential, for band structure calculations. In the FP-LAPW approach the wavefunction, charge density and potential are expanded differently in two regions of the unit cell. Inside the non-overlapping spheres of radius  $R_{\text{MT}}$  around each atom, spherical harmonics expansion is used, and in the remaining space of the unit cell the plane wave basis set is chosen.  $R_{\text{MT}}$  values for Sr, F, Cl and Br atoms are chosen as 2.3, 1.8, 1.9 and 2.1 au respectively. The maximum  $l$ -value for the wavefunction expansion inside the atomic spheres is confined to  $l_{\text{max}} = 10$ . The plane-wave cutoff of  $K_{\text{max}} = 7.0/R_{\text{MT}}$  is chosen for the expansion of the wavefunctions in the interstitial region, while the charge density is Fourier expanded up to  $G_{\text{max}} = 14$ . For  $x = 0, 0.5$  and 1 a mesh of 45 special  $k$ -points and for  $x = 0.25$  and 0.75, 72 special  $k$ -points are taken in the irreducible wedge of the Brillouin zone. Both the plane-wave cutoff and the number of  $k$ -points are varied to ensure total-energy convergence.

## 3. Results and discussion

### 3.1. Total-energy calculations

The alkaline-earth fluoro-halides MFX crystallize at ambient conditions in the tetragonal structure with two molecules per unit cell in the following positions [21]:

$$\begin{aligned} \text{M: } & 0.25 \ 0.25 \ v; \ 0.75 \ 0.75 \ \bar{v} \\ \text{F: } & 0.75 \ 0.25 \ 0; \ 0.25 \ 0.75 \ 0 \\ \text{X: } & 0.25 \ 0.25 \ u; \ 0.75 \ 0.75 \ \bar{u}. \end{aligned}$$

The F ions occupy the Wyckoff positions 2a but the M and X atoms are at the positions 2c, which depend on the internal parameters  $v$  and  $u$ . These two parameters are obtained by relaxing the atomic positions in the force direction and subsequently by lattice parameter optimization. Their dimensionless values were obtained as 0.1871, 0.6456 and 0.2015, 0.6429 for SrFBr and SrFCl, respectively.

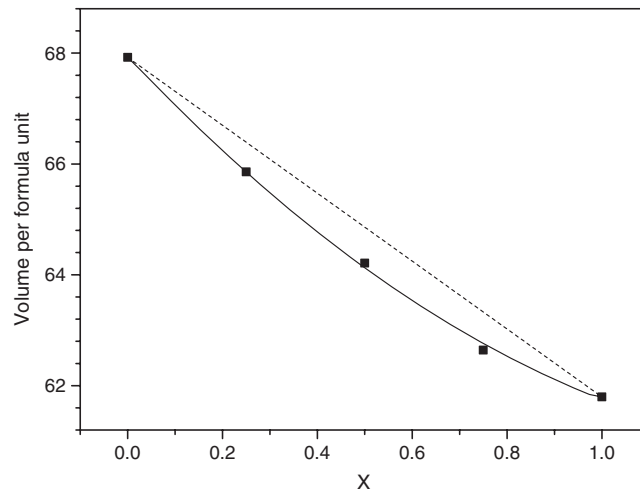
To model the  $\text{SrFCl}_x\text{Br}_{1-x}$  random alloy in general, a supercell approach is needed, and different atomic configurations should be considered, but quantum calculations for such supercells are very time consuming. In this work, by considering the symmetry of the system and using the SrFCl structure, a  $2 \times 2 \times 1$  supercell was constructed. In this supercell, the 8 Cl atoms are arranged inside that in different distances respect to each other. For  $x = 0.75$ , three pairs of these atoms with different distances (3.58, 4.18 and 6.92 Å) are randomly selected and for each one the two corresponding Cl atoms are substituted by Br elements. Using this procedure, three random structures are obtained. For making the structures related to  $x = 0.25$ , all positions of Cl and Br atoms in previous random structures are replaced with each other. For constructing the structure with  $x = 0.5$ , since the symmetry of the two Cl atoms is similar, one of the Cl atoms in the unit cell is replaced by Br. Such substitutions decrease the number of symmetry operations from the original value of 16 to 4 or 8 depending on the concentration. Huge calculations were performed for different structures at the  $x = 0.25$  and 0.75 concentrations. For both of them separately, the differences between the total energies in all three cases are insignificant (less than 0.2 Ryd).

As no calculated or experimental value for the internal parameters of this alloy has been reported in the literature, first their roughly optimized values for each concentration were calculated by relaxing the atomic positions in the force directions using the lattice parameters that were obtained from Vegard's law. Then the optimized internal parameters were used to calculate the total energy for several lattice volumes, and by fitting the results with Murnaghan equation of state [22], the equilibrium lattice parameters at each composition were calculated. Finally, using the new optimized lattice parameters, once again the more accurate values of internal parameters were recalculated.

The calculated equilibrium volume, cohesive energy per formula unit, bulk modulus and its pressure derivative for all compositions are presented in table 1. A downward bowing, figure 1, with bowing parameter equal to  $2.878 \text{ \AA}^3$ , is obtained for the equilibrium volume by fitting the calculated values with a polynomial function. In figure 2, the composition dependence of the bulk modulus is compared with the results predicted by LCD. A very small deviation from LCD is clearly visible. The mean interatomic distances calculated using the optimized internal parameters and equilibrium lattice constants are reported in table 2, and the composition dependence of the mean bond length for Sr-F, Sr-Cl, Sr-Br, F-Cl, and F-Br are shown in figure 3.

The main features to note from the above calculations are as follows:

- (1) In all concentrations, the strontium halide bond length increases with increasing atomic number of the halide atom. This behavior is consistent with Pauling's empirical rule that the cation-anion distance is determined by the sum of the radii.
- (2) The cohesive energy is defined as the energy of a formula unit in the solid minus the energy of isolated atoms. In order to obtain an accurate value for the cohesive energy, the energy calculations for isolated atoms and crystal must be performed at the same level of accuracy. To fulfill such a requirement the energy of an isolated atom was calculated by considering a unit cell containing just one atom. The size of this cell was chosen sufficiently large so that the energy convergence with respect to the size of the cell was less than 0.001 Ryd. (A large cubic cell with dimensions of 17, 18, 21 and 23 au was used for F, Cl, Br and



**Figure 1.** Composition dependence of the calculated volume ( $\text{\AA}^3$ ) per formula unit of  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy (solid squares) compared with LCD (dashed line). A bowing parameter equal to  $2.878 \text{\AA}^3$  is obtained by fitting the calculated values with a polynomial function (solid line).

**Table 1.** Equilibrium volume of formula unit, bulk modulus ( $B$ ), its pressure derivative ( $B'$ ) and cohesive energy per formula unit obtain using GGA96 for  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy.

$x$		Volume of one molecule ( $\text{\AA}^3$ )	$B$ (GPa)	$B'$	Cohesive energy (Ryd/molecule)
0.0	Our previous work <sup>a</sup>	67.922	46.05	4.02	-1.056
	Experiment <sup>b</sup>	65.268	47.8, 51.0	6	
	TB-LMTO <sup>c</sup>	58.212	79.98		
	Calculation <sup>d</sup>	61.960	49.0	4.9	
0.25	Present work	65.857	47.81	4.3	-1.062
0.5	Present work	64.212	49.00	3.9	-1.075
0.75	Present work	62.643	50.10	4.7	-1.091
1.0	Our previous work <sup>a</sup>	61.799	51.79	3.85	-1.116
	Experiment <sup>e</sup>	59.226	61, 53.7	5	
	TB-LMTO <sup>f</sup>	59.380	60.9		
	Calculation <sup>d</sup>	59.158	55	4.3	

<sup>a</sup> Reference [14].

<sup>b</sup> Reference [23].

<sup>c</sup> Reference [24].

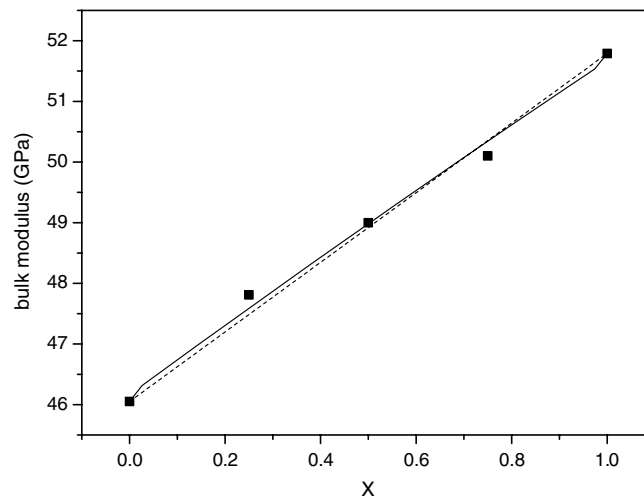
<sup>d</sup> Reference [2].

<sup>e</sup> Reference [21].

<sup>f</sup> Reference [25].

Sr atoms, respectively.) The results of cohesive energy show an upward bowing, with the value of  $-0.0462$  Ryd per formula unit, from linear interpolation between the end points, as is seen in figure 4.

- (3) The formation energy per formula unit of the alloy is defined as  $E_{\text{formation}}(x) = E(\text{SrFCl}_x\text{Br}_{1-x}) - xE(\text{SrFCl}) - (1-x)E(\text{SrFBr})$ , where  $E(\text{SrFCl}_x\text{Br}_{1-x})$ ,  $E(\text{SrFCl})$  and  $E(\text{SrFBr})$  respectively are the energies per formula unit of  $\text{SrFCl}_x\text{Br}_{1-x}$  alloy, and SrFCl and SrFBr compounds. By using the results of cohesive energy and the above definition,



**Figure 2.** Composition dependence of the calculated bulk modulus of  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy (solid squares) compared with the results of polynomial fitting (solid line) which shows nearly linear concentration dependence (dashed line).

**Table 2.** Calculated average bond lengths ( $\text{\AA}$ ) using optimized internal parameters and equilibrium lattice constants within GGA96 for  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy.

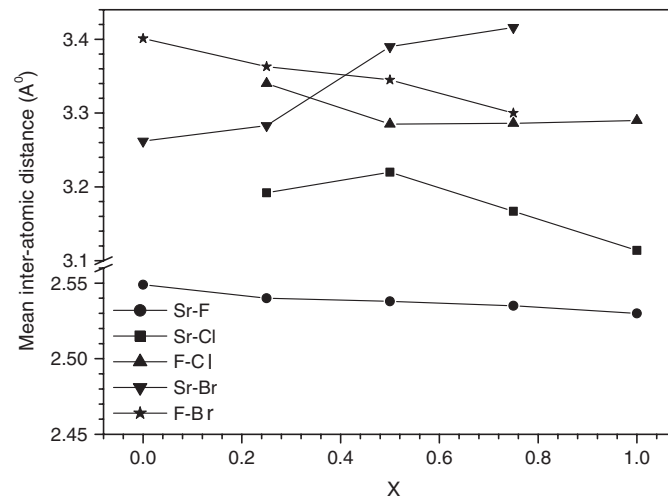
X	Sr-F	Sr-Cl	Sr-Br	F-Cl	F-Br
0.0	2.549	—	3.262	—	3.401
0.25	2.540	3.192	3.283	3.340	3.363
0.5	2.538	3.220	3.390	3.285	3.345
0.75	2.535	3.167	3.416	3.286	3.301
1.0	2.530	3.114	—	3.290	—

it is clearly seen that the formation energy of this alloy is positive for all concentrations. Therefore, it seems that this alloy is thermodynamically unstable. A similar behavior is predicted for disordered alloys, but these alloys can be formed as a solid solution in a metastable phase [26].

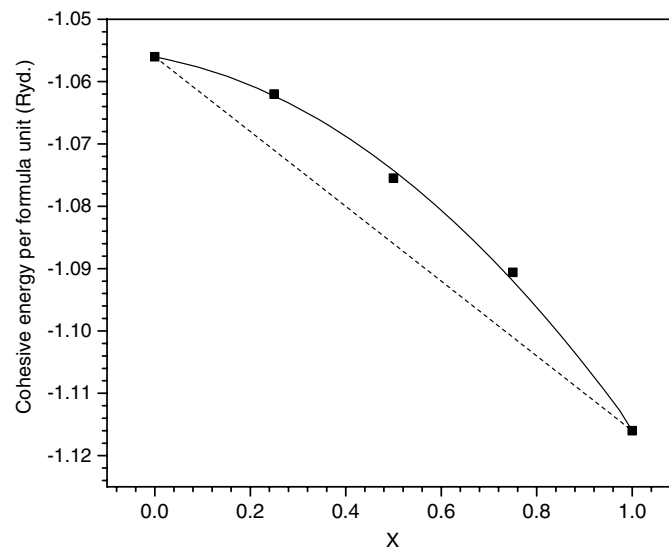
- (4) The 10% and 5.7% mismatch between the end point for the volume and cohesive energy, respectively, can be treated as a possible source for deviation from the LCD prediction. It should be noted that a violation of LCD have been reported in many alloys both experimentally [27] and theoretically [28–30].

### 3.2. Electronic properties

The major shortcoming in density functional theory to calculate energy gap arises in exchange correlation term that cannot be handled accurately in this method. Although in most solids the GGA improves the results compared to the local density approximation, none of these approximations can simultaneously obtain the exchange correlation energy and its charge derivative accurately. This is due to the fact that the GGA has a simple form and is not sufficiently flexible to accurately reproduce both of them. Engel and Vosko [20], by considering this shortcoming, constructed a new functional form of the GGA (EV-GGA) and attempted to

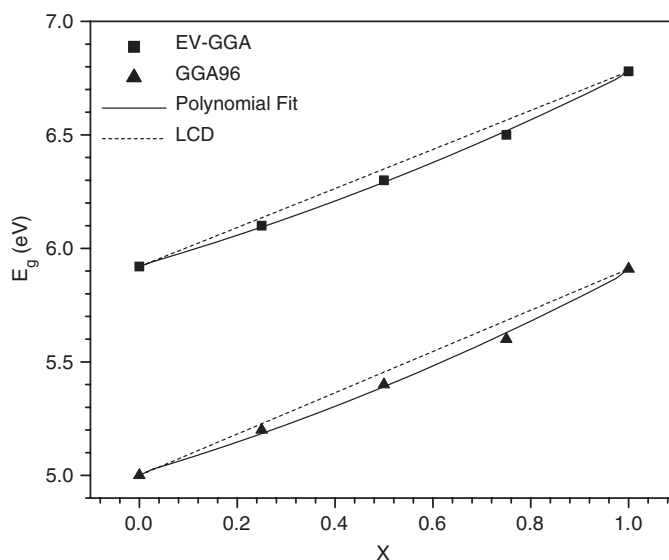


**Figure 3.** Composition dependence of the calculated average bond lengths in  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy for different bonds.



**Figure 4.** Composition dependence of the calculated cohesive energy of  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy (solid squares) compared to the LCD prediction (dashed line). The bowing parameter equal to  $-0.0462$  Ryd per formula unit was obtained by polynomial fitting (solid line).

better reproduce the exchange potential at the expense of less agreement in the exchange energy. Dufek *et al* [31] applied the EV-GGA to a wide range of solids and compared the results with other GGA-based calculations. They concluded that the EV-GGA improves the estimation of the band gap and some other properties, which mainly depend on the accuracy of the exchange correlation potential, while the results that are based on total-energy calculations, such as the equilibrium lattice parameter and bulk modulus, are not satisfactory. In our previous work, similar behavior was obtained for some semiconductor compounds [30, 32, 33].



**Figure 5.** Composition dependence of the calculated band gap of  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy compared to the LCD prediction (dashed line). The bowing parameters, equal to 0.229 and 0.251 eV, are obtained by using the EV-GGA and GGA96 respectively. The solid curves are the results of a polynomial fit.

**Table 3.** The band gap ( $\Gamma - \Gamma$ ) calculated using different approximations for the exchange-correlation energy for different compositions of  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy.

$x$	Present work		
	EV-GGA	GGA96	TB-LMTO <sup>a</sup>
0.0	5.9	5.0	4.5
0.25	6.1	5.2	—
0.5	6.3	5.4	—
0.75	6.5	5.6	—
1.0	6.8	5.9	5.2

<sup>a</sup> Reference [24].

The results of band structure calculations using both GGA96 and the EV-GGA are given and compared with the results of the tight binding linear muffin-tin orbital (TB-LMTO) method in table 3. Figure 5 shows the variation of the energy gap with the concentration  $x$  of the  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy. For both GGA96 and the EV-GGA there is a small bowing, 0.251 and 0.229 respectively, compared to the LCD prediction. The fundamental points to note from these calculations are as follows:

- (1) Although GGA96 and the EV-GGA predict different values for the band gap, the corresponding bowing parameters using these two approximations are rather close to each other. This result confirms the calculated band gap bowing.
- (2) The physical origins of the band gap bowing can be treated as three different contributions [34, 35]: volume deformation, charge exchange and structural relaxation. The first contribution represents the relative response of the band structure of SrFCl and SrFBr to the hydrostatic pressure, which here arises from the change of their individual



equilibrium volume to the alloy volume,  $V(x)$ , (from the LCD prediction). The second reflects a charge-transfer effect, which is due to the different bonding behavior at the volume  $V(x)$ . The final contribution is rooted in passing from the unrelaxed to the relaxed alloy.

#### 4. Conclusion

The electronic and structural properties and bowing parameters of  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy were studied by first-principles FP-LAPW calculations within the framework of density-functional theory. To our knowledge no theoretical and experimental study has been reported so far on the structural and electronic properties of this alloy; hence the present results can serve as a prediction for future study. In this work the effect of concentration on some physical properties have been investigated. Although the equilibrium volume per formula unit, band gap and cohesive energy do not follow the LCD, they can be explained by constant bowing parameters. It is shown that for each Cl:Br ratio the bulk modulus of  $\text{SrFCl}_x\text{Br}_{1-x}$  quaternary alloy closely follows Vegard's law.

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