CHAPTER 6

STRUCTURAL, ELECTRONIC AND HIGH PRESSURE BEHAVIOUR OF ALKALINE-EARTH FLUOROHALIDES

6.1 INTRODUCTION

The alkaline-earth fluorohalides MFX \((M = \text{Ca, Sr, Ba, Eu}; X = \text{Cl, Br, I})\) crystallizing in the PbFCl-type structure (Sauvage 1974, Liebich and Nicollin 1977) form an important class of materials, showing interesting spectroscopic properties with wide range of technological applications. Besides the fluorohalides there are two other families of compounds which crystallize in the PbFCl-type structure. These are the hydride halides MHX \((M = \text{Ca, Sr, Ba}; X = \text{Cl, Br, I})\) and oxide halides MOX \((M = \text{La, Th, Pu, Bi}; X = \text{Cl, Br, I or S, Se or Te})\) (Flahaut 1974, Beck 1976). These compounds are found to be interesting host materials for divalent impurities in the case of divalent fluoride halides (Shen and Holzapfel 1993, 1995, 1995a) and trivalent impurities in the case of trivalent oxide halides (LnOX) with high local symmetry at the impurity site (Shen et al 1994).

BaFCl and BaFBr activated with divalent impurity Eu\(^{2+}\) are used as x-ray phosphors for medical imaging via PSL (Takahashi et al 1984, Takahashi and Miyahara 1985, Inabe et al 1988, 1988a, Krochuk et al 1989). The image stored on the plates made from these materials can be stable for several days and is believed to be composed of pair of electrons and holes trapped by lattice imperfections or chemical impurities. The information stored on these plates can be recovered by optical stimulation within microseconds. The results of the luminescence measurement for several of these systems have been reported (Gacon et al 1978, Bauer et al 1983,
Niklas et al 1983, Takahashi et al 1984, von Seggern et al 1988, Crawford et al 1989, Eachus et al 1995). According to them the PSL process can be explained as follows: Exposure of BaFBr:Eu²⁺ to x-rays creates electrons and holes in BaFBr lattice. Some fraction of the electrons will be trapped at anion vacancies yielding F centers and an equal number of holes will be trapped at other unspecified sites. The F centers, which strongly absorb visible light can be released from their traps by exposure to light radiation from a laser source and will recombine with the trapped holes. Some of the energy released by this recombination process appears as Eu²⁺ ⁴f⁵d → ⁸S⁷/²⁶ luminescence completing the PSL cycle. Also, SrFCl: Sm²⁺ find special applications as a more sensitive material than the ruby sensor which is currently used for pressure measurements in diamond anvil cells (Shen et al 1991).

Apart from the PSL process, the structural systematics of these compounds have been reported by few workers. Beck (1976) has studied the structural properties of mixed halide compounds MFX (M = Ca, Sr, Eu, Ba; X = Cl, Br, I) under ambient conditions. Also, the structural properties of BaFCl crystals have been studied in the extended pressure range by Beck et al (1983). Recently an extensive high pressure XRD studies have been carried out by Shen et al (1994) on MFC₁ compounds. In their studies, pressure region was extended upto 500 kbar for BaFCl and BaFBr, upto 420 kbar for SrFCl and upto 270 kbar for CaFCl. Also structural phase transitions have been observed in BaFCl and BaFBr crystals from the tetragonal to an unidentified phase at 210 kbar and 270 kbar respectively.

These compounds 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. As in the case of other alkaline-earth chalcogenides discussed previously, here also the conduction bands are formed from the metal atom s and d states and the valence bands arise from the halogen p
states. The band gap values of these mixed halides are not available except for BaFBr, for which it is reported to be 8.3 eV (Takahashi et al. 1984).

To the best of our knowledge there are no theoretical or experimental results explaining the electronic structure of these compounds. Therefore, a detailed electronic band structure calculation has been performed for a basic understanding of the electronic structure at ambient as well in the high pressure region and also the structural properties of these compounds.

6.2 PRESENT STUDY

In the present work, the electronic band structure calculation of the mixed halide systems CaFCl, SrFCl, BaFCl, BaFBr and BaFI have been performed using TB-LMTO method (Andersen and Jepsen 1984) in a similar manner as discussed earlier. These compounds can be grouped into those varying with alkaline-earth metal atom, namely, Ca, Sr and Ba (CaFCl, SrFCl, BaFCl) and those changing with halogen anion, namely, Cl, Br and I (BaFCl, BaFBr, BaFI).

6.2.1 Crystal structure

The alkaline-earth fluorohalides crystallize in the primitive tetragonal-PbFCl-type structure (space group P4/nmm) (Wyckoff 1963). This structure, often termed as matlockite, is shown in the Figure 6.1. The coordinates of the atoms are given below:

\[
\begin{align*}
M &: (2c) \quad 0 \quad 0.5 \quad u \quad ; \quad 0.5 \quad 0 \quad -u \\
X &: (2a) \quad 0 \quad 0 \quad 0 \quad ; \quad 0.5 \quad 0.5 \quad 0 \\
Y &: (2c) \quad 0 \quad 0.5 \quad v \quad ; \quad 0.5 \quad 0 \quad -v
\end{align*}
\]
Fig. 6.1  Unit cell of PbFCl-type structure
where \( X = F, M = Ca^{2+}, Sr^{2+}, Br^{2+} \) and \( Y = Cl, Br \) and \( I \). From the figure it can be seen that the stacking of the layers is of the type \( X-M-Y-Y-M-X \). The cations (M) are surrounded by nine anions namely, four equivalent X anions, four equivalent Y anions and one extra Y anion from the next plane, which is located on the symmetry axis just above the M cation. This structure is featured by the presence of the successive Y-Y planes inspite of the strong repulsive interaction between them. Hence a cleavage plane exists between them.

The lattice parameters, cell volume and the interplanar distances (Sauvage 1974) for these compounds are given in Table 6.1. 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 type of reverse trend can also be seen in the interlayer distances. The M-F interplanar distance increases from \( CaFCl \) to \( BaFCl \), 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 \( (\phi_Y - \phi_M) \) (Pauling 1960) as a function of cell volume varies very 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 groups of compounds.

6.2.2 Method of calculation

The electronic band structure of each of the compounds in the primitive tetragonal unit cell were calculated by means of the TB-LMTO method. For calculating the exchange correlation part of the potential, von Barth and Hedin scheme (1972) within the LDA is used. The tetrahedron
Table 6.1  Lattice parameters (a and c), molecular volume ($V_0$) and interplanar distances along the c-axis. [Values from Liebich and Nicollin (1977) and Sauvage (1974)]

<table>
<thead>
<tr>
<th></th>
<th>CaFCl</th>
<th>SrFCl</th>
<th>BaFCl</th>
<th>BaFBr</th>
<th>BaFI</th>
</tr>
</thead>
<tbody>
<tr>
<td>a Å</td>
<td>3.894</td>
<td>4.126</td>
<td>4.394</td>
<td>4.508</td>
<td>4.654</td>
</tr>
<tr>
<td>c Å</td>
<td>6.818</td>
<td>6.958</td>
<td>7.225</td>
<td>7.441</td>
<td>7.962</td>
</tr>
<tr>
<td>c/a</td>
<td>1.751</td>
<td>1.686</td>
<td>1.644</td>
<td>1.651</td>
<td>1.711</td>
</tr>
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<td>$V_0$ Å$^3$</td>
<td>103.3</td>
<td>118.5</td>
<td>139.7</td>
<td>151.3</td>
<td>172.5</td>
</tr>
<tr>
<td>Plane (M) - Plane (F)</td>
<td>1.338</td>
<td>1.402</td>
<td>1.480</td>
<td>1.422</td>
<td>1.357</td>
</tr>
<tr>
<td>Plane (M) - Plane (Y)</td>
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<td>1.083</td>
<td>1.069</td>
<td>1.185</td>
<td>1.412</td>
</tr>
<tr>
<td>Plane (Y) - Plane (Y)</td>
<td>1.953</td>
<td>1.989</td>
<td>2.127</td>
<td>2.228</td>
<td>2.424</td>
</tr>
</tbody>
</table>
method (Jepsen and Andersen 1971) is used for the BZ integration in the total energy calculation. The self-consistent potential is constructed by using 91-k-points in the IBZ. The numerical accuracy in the total energy calculation is checked by increasing the number of k-points to 1000, where the total energy is found to change only by 0.2 to 0.4 mRy. The energy eigenvalues were converged to $10^{-6}$ Ry. All angular momentum components upto $l = 2$ have been retained. The cc terms which account for the non-spherical shape of the potential and the truncation of the higher partial waves ($l > 2$) were included. The cc terms were added to improve the accuracy of the LMTO calculations. Since the unit cell has a close packed structure no empty spheres were included.

For each of the compounds the following basis orbitals were used as valence states.

- 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 larger when 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.

### 6.2.3 Total energy calculation

For each of the compounds to determine the equilibrium $c/a$ value the ASA total energies within LDA were calculated for various $c/a$ values by keeping the equilibrium lattice parameter as a constant value. Figures. 6.2 to 6.6 show the plot of variation of total energies as a function of $c/a$ values. The equilibrium $c/a$ value corresponds to the minimum energy in the $c/a$
Fig. 6.2 Calculated Total Energy as a function of c/a ratio of CaFCl
Fig. 6.3 Calculated Total Energy as a function of c/a ratio of SrFCl
Fig. 6.4 Calculated Total Energy as a function of $c/a$ ratio of BaFCl
Fig. 6.5 Calculated Total Energy as a function of $c/a$ ratio of BaFBr
Fig. 6.6 Calculated Total Energy as a function of $c/a$ ratio of BaFI
curve. Then by keeping the $c/a$ value as constant, the total energies were calculated as a function of reduced volume ranging from $1.2 \ V_0$ to $0.6 \ V_0$. Figures 6.7 to 6.11 show the plot of variation of total energies as a function of reduced volume. The calculated total energies were fitted to Birch (1978) EOS as a function of volume to obtain the equilibrium properties, such as equilibrium lattice constants, bulk modulus and the P-V relation. Figures 6.12 to 6.16 show the calculated P-V curves along with the experimental data points (Shen et al 1994). The agreement between the calculated curves and the experimental data points are found to be good. The calculated equilibrium properties were summarized in Table 6.2 and are compared with the experimental values. The calculated values of the $c/a$ ratio, the lattice parameter, P-V relation and the bulk modulus (Kalpana et al 1995) are in very good agreement with the experimental values.

6.2.4 Band structure

The self-consistent scalar relativistic band structure along the high symmetry directions $\Gamma$-M-X-$\Gamma$-Z and the DOS for all the five compounds in the primitive tetragonal lattice were obtained at ambient as well in the high pressure region. The effect of compression on the band gap has also been studied.

Figure 6.17 shows the band structure plot for CaFCl at equilibrium volume and the corresponding DOS plot is shown in Figure 6.18. The lowest lying bands arise from the F-2s states, which show very slight broadening indicating negligible overlap with the neighbouring states. Above these are the bands arising from the semicore-like Ca-3p states. Well above these are the bands arising from the Cl-3s state. The upper valence bands lie above these bands, which are due to the Cl-3p and F-2p states and the top of the valence bands occur at the $\Gamma$-point. Similar to the alkaline-earth chalcogenides, the conduction bands are formed from the metal atom Ca-3d and 4s states. The bottom of the conduction band is found to occur at $\Gamma$-point.
Fig. 6.7 Calculated Total Energy as a function of reduced volume of CaFCl
Fig. 6.8 Calculated Total Energy as a function of reduced volume of SrFCl
Fig. 6.9 Calculated Total Energy as a function of reduced volume of BaFCl
Fig. 6.10 Calculated Total Energy as a function of reduced volume of BaFBr
Fig. 6.11 Calculated Total Energy as a function of reduced volume of BaFI
Fig. 6.12 Pressure-volume curve of CaFCl. Experimental data points are from Shen et al. (1994)
Fig. 6.13  Pressure - volume curve of SrFCl. Experimental data points are from Shen et al (1994)
Fig. 6.14 Pressure - volume curve of BaFCl. Experimental data points are from Shen et al (1994)
Fig. 6.15 Pressure-volume curve of BaFBr. Experimental data points are from Shen et al. (1994)
Fig. 6.16  Pressure - volume curve of BaFI
<table>
<thead>
<tr>
<th></th>
<th>CaFCl</th>
<th>SrFCl</th>
<th>BaFCl</th>
<th>BaFBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (Å)</td>
<td>3.894</td>
<td>3.896</td>
<td>4.394</td>
<td>4.394</td>
</tr>
<tr>
<td>(c/a)</td>
<td>1.751</td>
<td>1.742</td>
<td>1.686</td>
<td>1.751</td>
</tr>
<tr>
<td>(K_0) (kbar)</td>
<td>970</td>
<td>718</td>
<td>610</td>
<td>570</td>
</tr>
</tbody>
</table>

Table 6.2 Equilibrium lattice parameter (\(a\)), c/a ratio and Bulk modulus (\(K_0\)) of the alkaline-earth fluorohalides

1. Liebich and Nicollin (1977)
Fig. 6.17 Band structure of CaFCl at equilibrium volume
Fig. 6.18 Density of states of CaFCl at equilibrium volume
making the compound to be a direct band gap insulator with gap occurring between $\Gamma$-points. Since the XPS or the photoemission spectra are not available for these materials, it is not possible to compare the DOS curves.

Upon compression, the direct gap at $\Gamma$ increases, since the lowest energy in the conduction band, namely, the $\Gamma$-point moves away from the valence bands. This is similar to that observed in the case of MgO (Chang and Cohen 1984, Kalpana et al. 1995) and other II-IV semiconductors (Edwards et al. 1959, Cerderia et al. 1970, Camphausen et al. 1971, Chang et al. 1984, Ves et al. 1990, Mang et al. 1995). Upon further compression, as more and more conduction states get filled, the band gap decreases, leading to band-overlap metallization at very high pressures (Figures 6.19 and 6.20).

Figures. 6.21 and 6.22 show the band structure and DOS plot for SrFCl at equilibrium volume. The band structure and the effect of compression on SrFCl are similar to those observed for CaFCl, except that the valence bands are narrow in SrFCl. This is because the interplanar (M-F and Y-Y) distances increase (Table 6.1) in going from CaFCl to BaFCl, leading to reduced overlap between the neighbouring states.

Figures. 6.23 and 6.24 show the band structure and DOS plot for BaFCl at equilibrium volume. The band structure is similar to CaFCl and SrFCl. The Ba-5p bands have moved to the higher energy side compared to Ca-3p and Sr-4p bands in CaFCl and SrFCl respectively. This is because of the larger size of the Ba ion and also the orbital angular momentum involved is higher. The valence bands are further narrowed down in BaFCl compared to CaFCl and SrFCl which is due to the increasing interplanar distances.

The effect of compression on the band gap in SrFCl and BaFCl are the same as that observed in CaFCl. Initially the band gap increases and
Fig. 6.19  Band structure of CaFCl at metallization volume
Fig. 6.20 Density of states of CaFCl at metallization volume
Fig. 6.21 Band structure of SrFCl at equilibrium volume
Fig. 6.22 Density of states of SrFCl at equilibrium volume
Fig. 6.23 Band structure of BaFCl at equilibrium volume
Fig. 6.24 Density of states of BaFCl at equilibrium volume
upon further compression, the band gap decreases leading to band-overlap mettallization at high pressures (Figures. 6.25 to 6.28).

Figures. 6.29 to 6.36 show the band structures and DOS plots for BaFBr and BaFI at equilibrium as well at the metallization volume. For BaFCl, the lowest lying valence bands, namely, F-2s bands are flat indicating that they are deep inside and have no overlap with neighbouring states. For BaFBr and BaFI, since the lattice constants are larger than BaFCl, the F-2s states are further deep inside and these semicore-like orbitals are treated as core states in the calculations for BaFBr and BaFI.

In the valence band structure of BaFBr, the low lying bands arise from the Br-4s states and slightly above these, are the bands arising from the Ba-5p states. The upper valence bands are due to the F-2p and Br-4p states. The valence band structure of BaFI is similar to that of BaFBr except that instead of Br-4s and 4p states, there are I-5s and 5p states. The conduction bands in BaFBr and BaFI are the same as in BaFCl arising from the Ba-6s and 5d hybrids. The widths of the valence and conduction bands are larger in BaFBr and BaFI compared to BaFCl. This is because the size of the halogen anion increases and the interplanar (M-F) distance (Table 6.1) decreases in going from BaFCl to BaFI, leading to a larger overlap with neighbouring states resulting in broadening of bands.

The band gap is found to be direct occurring at Γ-point. The effect of compression is similar to those observed in CaFCl, SrFCl and BaFCl. Upon compression initially the band gap increases and at high pressures the band gap starts decreasing leading to band-overlap metallization.

The calculated values of band gap at ambient conditions, the metallization volumes and pressures (Kalpana et al 1996) are given in Table 6.3 and the variation of the gap values as a function of reduced volume are given in Table 6.4. Except BaFBr, the experimental values of band gap are
Fig. 6.25  Band structure of SrFCl at metallization volume
Fig. 6.26 Density of states of SrFCl at metallization volume
Fig. 6.27  Band structure of BaFCl at metallization volume
Fig. 6.28 Density of states of BaFCl at metallization volume
Fig. 6.29 Band structure of BaFBr at equilibrium volume
Fig. 6.30 Density of states of BaFBr at equilibrium volume
Fig. 6.31  Band structure of BaFI at equilibrium volume
Fig. 6.32  Density of states of BaFI at equilibrium volume
**Fig. 6.33** Band structure of BaFBr at metallization volume
Fig. 6.34 Density of states of BaFBr at metallization volume
Fig.6.35  Band structure of BaFI at metallization volume
Fig. 6.36 Density of states of BaFI at metallization volume
Table 6.3  Fundamental band gap ($E_g$), metallization volume ($V_m$) and pressure ($P_m$) of the alkaline-earth fluorohalides

<table>
<thead>
<tr>
<th></th>
<th>CaFCl</th>
<th>SrFCl</th>
<th>BaFCl</th>
<th>BaFBr</th>
<th>BaFI</th>
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<tr>
<td>$E_g$ (eV)</td>
<td>6.47</td>
<td>8.22</td>
<td>7.07</td>
<td>6.11</td>
<td>5.10</td>
</tr>
<tr>
<td>$V_m/V_0$</td>
<td>0.604</td>
<td>0.677</td>
<td>0.790</td>
<td>0.701</td>
<td>0.677</td>
</tr>
<tr>
<td>$P_m$ (kbar)</td>
<td>1096</td>
<td>541</td>
<td>209</td>
<td>402</td>
<td>435</td>
</tr>
</tbody>
</table>
### Table 6.4 Variation of band gap $E_g$ (eV) as a function of reduced volume in the alkaline-earth fluorohalides

<table>
<thead>
<tr>
<th>$\frac{V}{V_0}$</th>
<th>CaFCl</th>
<th>SrFCl</th>
<th>BaFCl</th>
<th>BaFBr</th>
<th>BaFI</th>
</tr>
</thead>
<tbody>
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<td>1.0</td>
<td>6.47</td>
<td>8.22</td>
<td>7.07</td>
<td>6.11</td>
<td>5.02</td>
</tr>
<tr>
<td>0.95</td>
<td>6.70</td>
<td>8.46</td>
<td>7.20</td>
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<tr>
<td>0.9</td>
<td>6.94</td>
<td>8.71</td>
<td>5.52</td>
<td>6.31</td>
<td>5.26</td>
</tr>
<tr>
<td>0.85</td>
<td>7.20</td>
<td>8.98</td>
<td>3.06</td>
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<tr>
<td>0.8</td>
<td>7.48</td>
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<tr>
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not available for comparison. The calculated values of band gap are found to vary from 5 to 8 eV. This value is typical of other alkaline-earth halides (Nicklaus 1979, Ching et al 1995). For BaFBr, the experimental value of band gap is 8.3 eV (Takahashi et al 1984). The calculated value is 6.1 eV which is 26% less than the experimental value. As said earlier, this order of error is due to the use of LDA.

From Table 6.3, it can be seen that except CaFCl, the band gap value decreases with increasing size of the metal atom or the halogen anion, which is similar to the trends observed for the barium chalcogenides and alkaline-earth oxides. 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 (Moore, 1949). This has been confirmed by several band structure calculations (Vasvari and Heine 1967, Vasvari et al 1967, Vasvari 1968, McCaffrey et al 1970). These calculations show that the electron states of Ca are highly susceptible to modification by a crystal potential, which leads to non-trivial consequences in the physical properties of Ca compounds. Even though the band gap value is very low for CaFCl, the decreasing trends in metallization volume and pressure are reproduced in CaFCl, SrFCl and BaFCl i.e., as the size of metal atom (Ca, Sr, Ba) increases, the metallization pressure and volume decrease. But a reverse trend is observed, in going from BaFCl to BaFI i.e., as the size of the halogen anion increases (Cl, Br, I), the metallization volume and pressure also increase. As said earlier, the different trends observed in the c/a value and interplanar distances in going from BaFCl to BaFI may be a reason for this.

6.3 SUMMARY

To summarize, the structural and electronic properties of mixed alkaline-earth fluorohalides CaFCl, SrFCl, BaFCl, BaFBr and BaFI have been calculated using the TB-LMTO method. These compounds at ambient conditions crystallize in the tetragonal PbFCl-type structure with two
formula units/unit cell. The calculations were performed for 91 k-points in the IBZ. The total energies were calculated as a function of $c/a$ value and also as a function of reduced volume. The calculated total energies were fitted to the Birch EOS to obtain the equilibrium lattice constant, bulk modulus and the pressure-volume relation. The calculated equilibrium lattice constant, $c/a$ ratio are found to be in good agreement with the experimental results. The calculated P-V curve also shows a very good agreement with the experimental data points.

The band structures and the DOS for all the five compounds were obtained at ambient as well in the high pressure region. The overall band profiles for all the five compounds are found to be the same, with direct band gap ($\Gamma$-$\Gamma$) 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 which is 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.

The effect of pressure on the band gap has been studied. Initially, the band gap at $\Gamma$ increases with pressure which is similar to those observed in the case of MgO and II-IV binary semiconductors. This is because the lowest energy in the conduction band, namely, the $\Gamma$-point moves away from the valence band. Upon further compression, as more and more conduction states get occupied, the conduction bands move down and the band gap decreases leading to band-overlap metallization at high pressures. For these compounds, these 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 present results.