Electronic and elastic properties of ternary fluoro-perovskite RbCaF$_3$

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Abstract. We present the electronic and elastic properties of cubic perovskite type RbCaF$_3$, computed using linear combination of atomic orbitals method within the framework of density functional theory (DFT). We have performed ab-initio calculations using the hybrid approach of Hartree-Fock and DFT namely, B3LYP (Becke’s 3 parameter functional combined with the non-local correlation functional of Lee-Yang-Parr) to determine the electronic response of Rb based cubic perovskite. In addition, we have computed elastic constants, bulk modulus, shear modulus, Young’s modulus and elastic anisotropies of RbCaF$_3$. The results are found to be consistent with previously reported studies. The studied perovskite compound is mechanically stable, brittle in nature and show large elastic anisotropy. The band structure calculations reveal that RbCaF$_3$ possesses indirect band gap with valence band maximum at R point and the conduction band minimum at the $\Gamma$ point of the irreducible Brillouin zone.

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1. Introduction

The perovskite-type alkaline earth fluorides (ABF$_3$ type) have been extensively studied because of their potential applications in electro-optic, mechanical, semiconducting, ferroelectric and antiferromagnetic systems [1-4]. They show interesting structural properties [5], high temperature super ionic behavior [6-7], photo-luminescence properties (on doping with lanthanide ions) [8]. Due to their wide band gaps these materials are promising candidates for vacuum-ultraviolet-transparent lenses used in optical lithography steppers and transparent optical coatings [9] and are also useful in fast scintillators [10].

Recently, Ehsan et al [11] have reported the structural, elastic, vibrational and electronic properties of RbCaF$_3$ in the cubic and low temperature tetragonal phases using density functional theory (DFT). Li et al [12] have performed a comparative study of electronic, optical, elastic and thermodynamic properties of XCaF$_3$ (X= K, Rb, Cs) compounds. The structural, elastic, electronic and optical properties of KCaF$_3$ and RbCaF$_3$ have been studied by Ghebouli et al [13] using plane wave pseudopotential approach. Using full-potential linearized augmented plane wave (FP-LAPW) theory, Babu et al [14] have analysed various properties of KCaF$_3$ and RbCaF$_3$ perovskites. Mubark [15] has explored the elastic, electronic and optical properties of RbCaF$_3$ and RbCaCl$_3$ using FP-LAPW method. Studies on bonding characteristics and other
related properties using FP-LAPW approach have been reported by Murtaza et al [16]. Mousa et al [17] have performed first-principles study of structural, electronic and optical properties of RbCaF₃. Few experimental studies on RbCaF₃ have also been reported [18-21].

Although, reasonable work has been carried out on the electronic and elastic properties of RbCaF₃ using LDA and GGA schemes, but still no data is available on these properties using hybrid density functionals. Therefore, in the present work, we have analysed the effect of hybrid B3LYP function within linear combination of atomic orbitals (LCAO) method. The elastic constants, bulk modulus, shear modulus, Young’s modulus and elastic anisotropies of RbCaF₃ are discussed in the forthcoming sections. In addition, to elastic properties we have explored the energy bands, DOS and energy band gap of the compound.

2. Computational Method

The B3LYP approach as embodied in CRYSTAL14 package [22] consists of hybridization of HF+DFT and uses the Becke’s 3 parameter functional [23] in combination with the non-local correlation Lee-Yang-Parr [24]. Here the relative weight of the local and non-local parts in the exchange and the correlation potentials can be modified by choosing the values of \(a, b\) and \(c\) as follows:

\[
E_{xc} = (1 - a) \times (E_x^{LDA} + b \times E_x^{BECKE}) + a \times E_x^{HF} + (1 - c) \times E_c^{LDA} + c \times E_c^{GGA}
\]

(1)

The values of \(a, b\) and \(c\) in the present computations were taken to be 0.2, 0.9 and 0.81, respectively. To compute the structural, elastic and electronic properties of RbCaF₃, we have used the Gaussian basis sets for Rb, Ca, and F from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. The fluoro-perovskite crystallizes in the cubic perovskite type structure with space group Pm3m and contains one molecule in its unit cell. The Rb atoms are positioned at the (0, 0, 0) positions, the Ca atoms at (0.5, 0.5, 0.5) and the three F atoms at (0, 0.5, 0.5), (0.5, 0, 0.5) and (0.5, 0.5, 0). We have used the experimental lattice parameter \(a = 4.455\) Å [18]. For a faster convergence of self-consistent-field cycles, the BROYDEN scheme [25] was applied.

3. Results and Discussion

3.1. Electronic properties

The band structure for RbCaF₃ is plotted in figure 1 (a) for the first Brillouin zone (BZ) along high symmetric directions (where the symmetry points are \(\Gamma (0, 0, 0), X (1, 0, 0), M (1, 1, 0)\) and \(R (1, 1, 1)\) at equilibrium volume computed by the LCAO-B3LYP method.

![Figure 1. (a) Energy bands and (b) Density of states (DOS) of RbCaF₃ computed using LCAO-B3LYP method.](image-url)
The valence band maximum (VBM) is shifted to 0 eV. Except some fine structures and band gaps, the overall shape of our energy bands is in agreement with the earlier reported data [11-17]. Our computations show indirect band gap with VBM at R point and the conduction band minimum (CBM) at the Γ point of the irreducible BZ. We infer that the electronic states are almost flat which show a low mobility of holes at the VBM. The electronic states in the CBM region are more dispersed at the centre of the BZ.

The total and partial DOS as plotted in figure 1 (b) help in explaining the origin of the electronic band structure. From this figure it can be observed that the valence energy bands ranging between −2 eV and $E_F$ (0 eV) are mainly due to the 2p states of F. The lower VB around −16.7 eV are occupied by Ca-3p electronic states. The peak around −7.1 eV is originated due to Rb-4p orbitals. The conduction bands are dominated by the unoccupied 4s, 3d states of Ca, together with the 5s states of Rb and F. The band gap calculated by using LCAO-B3LYP method along with the available data [11-20] are summarized in Table 1. We can observe that our computed band gap value is in reasonable agreement with the available experimental data [18-20], whereas it overestimates the reported LDA and GGA calculations [11-17]. It can be noted that hybrid functional produces accurate structural parameters of RbCaF$_3$ as well as significantly reduces the band gap error as seen in local and semilocal DFT functionals.

**Table 1.** Structural and band gap parameters of RbCaF$_3$ using different exchange correlation potentials within LCAO prescription.

| Theory          | Lattice parameter a (Å) | Band gap $E_g$ (eV) |
|-----------------|-------------------------|---------------------|
| B3LYP (Present work) | 4.5223                   | 11.62               |
| LDA [11]        | 4.355                   | 6.62                |
| PBE [11]        | 4.522                   | 6.40                |
| PBEsol [11]     | 4.444                   | 6.50                |
| WC [11]         | 4.449                   | 6.58                |
| mBJ [11]        | -                       | 10.46               |
| LDA [12]        | 4.3486                  | 6.629               |
| GGA [12]        | 4.5141                  | 6.403               |
| PBE-GGA [13]    | 4.3525                  | 6.29                |
| LDA [14]        | 4.34                    | 6.79                |
| GGA [14]        | 4.44                    | 6.65                |
| mBJ [14]        | -                       | 10.88               |
| PBE-GGA [15]    | 4.51                    | 6.39                |
| WC-GGA [16]     | 4.452                   | 8.75                |
| EV-GGA [16]     | -                       | 10.40               |
| LDA [17]        | 4.37                    | 6.57                |
| WC-GGA [17]     | 4.53                    | 6.38                |
| PBE-GGA [17]    | 4.45                    | 6.57                |
| Experiment      | 4.455 [18, 19]          | 10.92 [18, 19], 11.0 [20] |

### 3.2 Elastic Properties

In cubic systems, three independent elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ define the mechanical hardness and are necessary for describing the instability. The longitudinal elastic behavior is explained by $C_{11}$, whereas $C_{12}$ and $C_{44}$ describe the off diagonal and elastic shear characteristics, respectively. Presently computed constants based on B3LYP theory are expressed in table 2. In order to determine $C_{ij}$, the cubic unit cell is deformed using an appropriate strain tensor to yield an energy-strain relation [26]. The calculated elastic constants of the present cubic compound satisfy the mechanical stability criteria [27, 28] as defined below:

$$C_{11} > 0;\ C_{12} > 0;\ C_{44} > 0;\ (C_{11} - C_{12}) > 0;\ (C_{11} + 2C_{12}) > 0;\ (C_{12} < B < C_{11})$$ (2)
Table 2. Computed elastic constants (C$_{ij}$), shear and bulk moduli (G and B), Young’s modulus (Y) (in GPa), Poisson’s ratio ($\nu$) and elastic anisotropy factor of RbCaF$_3$ using LCAO-B3LYP method along with available data.

| Theory        | Elastic constants | Shear modulus G | Bulk modulus B | Young’s modulus Y | B/G | Poisson’s ratio $\nu$ | Anisotropy factor A |
|---------------|-------------------|-----------------|----------------|-------------------|-----|----------------------|---------------------|
|               | $C_{11}$ $C_{12}$ $C_{44}$ |                 |                 |                   |     |                      |                     |
| B3LYP (Present work) | 110.02 23.37 24.20 | 30.62 | 52.25 | 76.85 | 1.71 | 0.25 | 0.56 |
| LDA [11]      | 143.6 24.1 19.7   | -               | 64.1           | -                 | -   | -                   |                     |
| PBEsol [11]   | 114.9 21.1 19.5   | -               | 52.5           | -                 | -   | -                   |                     |
| WC [11]       | 111.7 20.1 19.2   | -               | 50.8           | -                 | -   | -                   |                     |
| PBE [11]      | 100.3 21.1 19.9   | -               | 46.7           | -                 | -   | -                   |                     |
| LDA [12]      | 141.76 23.55 19.69 | -       | 62.96 | 135.05 | -   | 0.143 -             |                     |
| GGA [12]      | 99.46 20.36 19.66 | -               | 46.72 | 92.54 | -   | 0.170 |                     |
| PBE-GGA [13]  | 139.3 23.2 19.2   | 30.4           | 61.9           | 78.5              | 2.031 | 0.288 |                     |
| LDA [14]      | 141.40 24.49 20.94 | 32.055 | 63.456 | 82.307 | 1.979 | 0.283 | 0.358 |
| GGA [14]      | 110.67 22.45 16.86 | 25.076 | 51.856 | 64.787 | 2.067 | 0.291 | 0.382 |
| PBE-GGA [15]  | 82.23 12.56 16.20 | 22.13          | 35.78 | 55.05 | 1.62 | 0.243 | 0.465 |
| Expt. [21]    |                   |                 |                 |                   |     |                      | 50.40 |

From table 2, we observe that the present calculations give elastic constants in tune with other reported values and the trend $C_{11}>C_{44}>C_{12}$ obtained by us is in agreement with Mubark [15], but it is in contrast with other reported data [11-14]. Further, the bulk modulus (B) computed in present work is in very good agreement with the experimental value reported by Wooten [21].

The bonding strength of materials which is a measure of resistance to external deformation is represented by bulk modulus, whereas the Young’s modulus (Y) is the ratio of stress to strain, which govern the stiffness of the material. The higher value of Y implies that the material is stiffer. The bulk modulus, Young’s modulus, Poisson’s ratio ($\nu$) and Zener anisotropy factor (A) have been computed from the elastic constants using the following formulae [29]:

$$B = \frac{1}{3} (C_{11} + 2C_{12})$$  \hspace{1cm} (3)

$$Y = \frac{9GB}{G + 3B}$$ \hspace{1cm} (4)

$$\nu = \frac{(3B - 2G)}{2(3B + G)}$$ \hspace{1cm} (5)

$$A = \frac{2C_{44}}{(C_{11} - C_{12})}$$ \hspace{1cm} (6)

The shear modulus using the approximations of Voigt [30], Reuss [31], and Hill [32] (denoted by V, R, and H subscripts), respectively have been computed as:

$$G_H = \frac{1}{2} (G_V + G_R)$$ \hspace{1cm} (7)

where $G_V$ and $G_R$ can be calculated using elastic constants [33].

$$G_V = \frac{1}{5} (C_{11} - C_{12} + 3C_{44})$$ and

$$G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})}$$ \hspace{1cm} (8)

According to Pugh [34], the value of B/G defines the plastic properties of materials. If its value is greater than 1.75, the material shows ductile nature otherwise it is brittle. From table 2 it can be observed that RbCaF$_3$ possesses brittle nature as B/G < 1.75. The Poisson’s ratio is consistent with B/G because a smaller value of $\nu$ (< 0.26) represents brittle materials, otherwise it remains ductile. Also, it helps to determine the kind of bonds. It is the ratio of the transverse strain to the longitudinal strain in the elastic loading direction,
which leads to the bonding character of solids. The value of $\nu$ for covalent materials is small, about 0.1, but for ionic materials it has a typical value of 0.25. In present case, its value is 0.25, which shows a strong ionic intra-atomic bonding in RbCaF$_3$.

Another interesting property is elastic anisotropy, which shows different bonding character in different crystallographic directions, and correlates with the possibility to induce microcracks in materials. For isotropic materials $A=1$, while deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. In case of RbCaF$_3$, we obtain that the value of the anisotropy factor as 0.56 which indicates its anisotropic character.

4. Conclusions

The electronic and elastic response of RbCaF$_3$ have been presented using the LCAO method with hybrid functional theory namely B3LYP. Our calculations show that RbCaF$_3$ exhibits an indirect wide band-gap ($\Gamma$, R points) with strong intra-atomic bonding. We have also computed the elastic constants using the present hybrid approach and determined the bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio and Zener anisotropy factor. Presently computed elastic properties show that RbCaF$_3$ is elastically stable, brittle and exhibits large elastic anisotropy.

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