OPTIMIZING CONFIGURATIONS FOR DETERMINING THE ELECTROMAGNETIC PROPERTIES OF CsFeF₃, NaFeF₃, AND RbFeF₃ FLUORIDES: GGA VS GGA+U and TB-mBj APPROACHES

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Article Info	Abstract
<p>Received: 06.07.2020 Accepted: 11.09.2020</p> <p>Keywords: Ferromagnetic Fluorides, perovskites, magnetic moment, GGA+U, GGA-mBJ</p>	<p>The structural, electronic and magnetic properties of (Cubic Pm-3m, Hexagonal-4H, orthorhombic Pnma, and orthorhombic Pbnm) phases of AFeF₃ Fluorides (A= Cs, Na, and Rb) are reported theoretically using full potential linearized augmented plane waves method within the density functional theory (DFT). Using different exchange–correlation approximations including the generalized gradient approximation (PBE-GGA, WC-GGA, and PBEsol-GGA), also (GGA) with Hubbard potential (GGA + U) and The modified Becke Johnson potential (<i>mBJ</i>), we carried to determine various physical properties. The Calculations revealing that the estimated structural parameters are reliable with the experimentally reported data. Magnetically all these intermetallics are Ferromagnetic (FM). The ground-state energy of different magnetic phases studied showed that the magnetic moments are evaluated per atom, and overestimated by (GGA+U). Transfer charge reveals a strong covalent interaction between Fe-Fe atoms. Their electronic band structure and density of states indicate insulator behavior.</p>

1. Introduction

Different classes of perovskite materials, such as chalcogenide/ Oxides perovskite (AMO₃) and halide perovskite (ABX₃) that is again classified as alkali halide and organometal halide, were regarded as derived from the BO₃ structure, they have been extensively studied [1,7]. Ternary crystals with Fluoro-perovskite (Fluorides) structure ABF₃ have been extensively studied in various scientific works. They are very promising because they

attracted much attention due to their physical properties in different field: optical properties [8], Semiconducting [9], Ferroelectricity [10], (anti)-ferromagnetism, magnetoresistance [11, 12], and many others technological applications [13-17]. Fluoro-perovskites (Fluorides) ABF_3 doped with Mn^{2+} show unique photo and thermo stimulated luminescence [18, 19], Dielectric [18, 20], optical [18, 21], Mechano-lumescence, thermos power [18, 22], piezoelectric, laser source, catalytic and magnetoresistance properties, solid-state fuel cell, oxygen membranes [23, 24]. Crystals with ABF_3 have been a subject of immense interest also due to high temperature proton conductors with the possibility of applications in fuel cells or hydrogen sensors, crystal field [25, 26]. For understanding on the rule of the alkali cations on the fluorides characteristics we investigated in the present work the structural, electronic and magnetic properties of the $CsFeF_3$, $NaFeF_3$, and $RbFeF_3$ fluorides using the Full-potential Linearized Augmented Plane Wave (FP-LAPW) method within different approaches (GGA, GGA+U) in comparison with the Modified Beck Johnson (mBJ-GGA) approach in order to treat the exchange and correlation potential. The Fluoro-pervskite compounds were performed theoretically based on ab-initio calculations [20-38]. B.F. Gachter et al and many others [39-45] confirmed that $RbFeF_3$ crystalized on the cubic (Pm-3m) space group. $CsFeF_3$ is hexagonal [44, 45], and $NaFeF_3$ has orthorhombic distortion [44- 46].

Figure 1. The crystals structures for the $CsFeF_3$ Fluoride within Cubic (Pm-3m space group), 4H-Hexagonal (P63/mmc), Orthorhombic(Pbnm), and Orthorhombic (Pnma) phases

Ito, et al works showed that $RbFeF_3$ is Antiferromagnetic AF below the Néel temperature T_N of 102 K. First order transition at $T_2= 87K$ and $T_1= 40K$ have been also found, and weak Ferromagnetic FM moment has observed in both the phases below 87 K [40-45]. Different scientific works have studied this type of structure and confirmed that most of these Fluorides crystalized in the cubic structure [46-48] with (Pm-3m) space group showing a

Ferromagnetic (FM) character [48-52]. Although most scientific studies have mentioned that these fluorides CsFeF_3 , NaFeF_3 , and RbFeF_3 crystallized sometimes in the ideal cubic phase (Pm-3m), and sometimes in their mother phase. NaFeF_3 is reported that be orthorhombic [53, 54], while RbFeF_3 is cubic [53, 55], and CsFeF_3 is isotype to the hexagonal BaTiO_3 material [55, 61].

Figure 2. Computed total energy versus unit-cell volume for the CsFeF₃, NaFeF₃, and RbFeF₃ Fluoro-perovskites (Fluorides) with GGA and GGA+U respectively in the cubic (Pm-3m) phase

Orthorhombic perovskite is basically built up from the corresponding cubic perovskite. This class of materials has great potential for a variety of device applications due to their crystal structures and unique ferroelectric and dielectric properties [62]. DFT method was successfully applied earlier to simulations of several regular and defective ABO₃ perovskites providing a more adequate description of band gaps and other parameters of the electronic structure [63–67].

Figure 3. Computed total energy versus unit-cell volume for the CsFeF_3 , NaFeF_3 , and RbFeF_3 Fluoro-perovskites (Fluorides) with GGA and GGA+U respectively in the 4H Four-Layered Hexagonal (P6/mmc) phase

Also, a large number [68-75] of ABX_3 hexagonal perovskite calculations are based on density functional theory (DFT) basis have performed in different work. In order to give more details on the series of ABF_3 Fluoro-perovskites (CsFeF_3 , NaFeF_3 , and RbFeF_3) we investigate different structure phases (Pm-3m-cubic, 4H-Hexagonal, Pnma-Orthorhombic and Pbnm-Orthorhombic) in order to compare between them, and to give more details on the ABF_3 fluorides behaviors.

2. Computational methodology

In this paper, our calculations were carried out using the full-potential linearized augmented plane wave (FP-LAPW) within the functional DFT+U description [76-77]

implemented in the Wien2K package [72, 78]. Crystal is divided up into two main regions, inside muffin-tin spheres, and an interstitial region. This is an implementation of a hybrid full potential linear augmented plane wave within local orbitals (L/APW+*lo*) method. The exchange-correlation potential is treated with the generalized gradient approximation GGA [54-77] (PBE-GGA, WC-GGA, and PBEsol-GGA)) in comparison within the corrected GGA+U whereas the *U*-Hubbard Hamiltonian is added to treat the On-Site Coulomb interaction correction. The Modified Becke-Johnson (mBJ) as coupled with GGA approach was also applied to treat the electronic and magnetic properties.

The basis set inside each MT sphere is split into core and valence subsets. The core states are treated within the spherical part of the potential only and are assumed to have a spherically symmetric charge density totally confined inside the MT spheres.

Figure 4. Computed total energy versus unit-cell volume for the CsFeF₃, NaFeF₃, and RbFeF₃ Fluoro-perovskites (Fluorides) with GGA and GGA+U respectively in the Orthorhombic (Pnma) phase.

Table 1. Lattice constants computed using WC-GGA, PBE-GGA, PBEsol-GGA, and GGA+U approaches for Pm-3m-cubic CsFeF₃, NaFeF₃, and RbFeF₃ Fluorides in comparison with others theoretical data.

Cubic Structure						
Material	Approach	Configuration	a ₀ (Å)	B (GPa)	B'	Vol(Å ³)
CsFeF ₃	WC-GGA	NF	4.092	90.09	4.73	68.53
	PBE -GGA		4.186	76.35	4.68	73.36
	PBEsol –GGA		4.093	90.89	4.60	68.59
	GGA+U		4.190	75.427	4.00	79.19
	WC-GGA	FM	4.221	76.80	4.62	79.77
	PBE -GGA		4.306	72.14	3.87	81.34
	PBEsol –GGA		4.222	79.88	4.23	79.79
	GGA+U		4.316	64.45	3.59	81.57
Theoretical Works						
4.28 ^a						
NaFeF ₃	WC-GGA	NF	3.87	101.76	5.07	58.20
	PBE -GGA		3.92	90.38	4.43	60.62
	PBEsol – GGA		3.874	101.98	4.84	58.17
	GGA+U		3.93	94.54	3.98	74.35
	WC-GGA	FM	4.037	79.13	3.78	65.83
	PBE -GGA		4.099	71.12	4.25	68.87
	PBEsol – GGA		4.044	80.04	3.25	66.13
	GGA+U		4.113	70.17	4.61	77.78
RbFeF ₃	WC-GGA	NF	3.995	94.64	4.72	63.76
	PBE -GGA		4.075	82.42	4.67	67.66
	PBEsol –GGA		3.996	94.08	4.82	63.80
	GGA+U		4.076	80.61	4.72	67.71
	WC-GGA	FM	4.138	76.96	4.34	70.85
	PBE -GGA		4.218	68.97	4.14	75.04

PBEsol –GGA	4.143	78.78	3.71	71.11
GGA+U	4.236	67.19	4.29	76.00
Theoretical Works				
	4.10 ^b	-	-	68.92 ^b
	4.08 ^c	-	-	67.91 ^c
	4.17 ^d	-	-	72.51 ^d
	4.172 ^e	-	-	72.61 ^e
	4.174 ^f	-	-	72.72 ^f
	4.152 ^f	-	-	71.57 ^f
	4.174 ⁱ	-	-	72.72 ⁱ

a: Ref [84]. b: Ref [85], c: Ref [86], d: Ref [87], e: Ref [88], f: Ref [89], i: Ref [90].

The modified Becke Johnson potential (mBJ) as proposed by Tran and Blaha [79]:

$$V_{X,\sigma}^{mBJ}(r) = cV_{X,\sigma}^{BR}(r) + (3 - 2c) \frac{1}{\pi} \sqrt{\frac{15}{12} \sqrt{\frac{2t_{\sigma}(r)}{P_{\sigma}(r)}}} \quad (1)$$

Where the electronic density is

$$P_{\sigma}(r) = \sum_{i=1}^{N_{\sigma}} |\varphi(i, \sigma)|^2 \quad (2)$$

The kinetic energy density is $t_{\sigma}(r) = \frac{1}{2} \sum_{i=1}^{N_{\sigma}} |\varphi(i, \sigma) * \nabla \varphi(i, \sigma)|^2$ (3) $V_{X,\sigma}^{BR}(r)$ is the Becke Roussel (BR) potential [80], n Equation (1), c is chosen such that it depends linearly on the square root of the average of $\left| \frac{\sigma \rho}{\rho} \right|$:

$$c = \alpha + \beta \left(\frac{1}{V_{cell}} \int_{ell} \frac{|\nabla \rho(r')|}{(\rho(r'))} d^3 \right)^{\frac{1}{2}}$$

Where α and β are the two free parameters, whose values are:

$\alpha = -0.012$ (dimensionless) and $\beta = 1.023 \text{ Bohr}^{1/2}$ and V_{cell} is the unit cell volume.

The self- consistent calculations are considered to be converged only when the calculated total energy of the crystal converged to less than 1 mRy.

The Brillouin Zone integration is carried out with a modified tetrahedron method [81]. To correct description of the wave functions in the interstitial region like spherical harmonics have been expanded up to the value of $l_{max}=7$.

Table 2. Lattice constants computed using WC-GGA, PBE-GGA, PBEsol-GGA, and GGA+U approaches approach for 4H-Hexagonal CsFeF₃, NaFeF₃, and RbFeF₃ perovskites Fluorides.

4H-Hexagonal Structure						
Material	Approach	Configuration	a ₀ (Å)	c ₀ (Å)	B (GPa)	B'
CsFeF ₃	WC-GGA	NF	5.782	9.175	77.0	3.8
	PBE -GGA		5.909	9.374	73.2	4.3
	PBEsol –GGA		5.782	9.174	78.9	3.9
	GGA+U		5.929	9.375	75.7	4.1
	WC-GGA	FM	5.790	9.472	75.1	4.0
	PBE -GGA		6.067	9.626	79.5	3.2
	PBEsol –GGA		5.970	9.473	76.5	3.9
	GGA+U		6.165	9.634	78.8	3.5
NaFeF ₃	WC-GGA	NF	5.548	8.802	78.8	3.9
	PBE -GGA		5.627	8.928	85.5	3.9
	PBEsol – GGA		5.539	8.788	84.1	3.9
	GGA+U		5.629	8.931	89.5	3.3
	WC-GGA	FM	5.783	9.176	72.2	4.7
	PBE -GGA		5.861	9.300	73.4	4.4
	PBEsol – GGA		5.774	9.162	75.9	4.1
	GGA+U		5.863	9.303	73.9	4.3
RbFeF ₃	WC-GGA	NF	5.670	8.997	96.3	4.0
	PBE -GGA		5.784	9.177	98.7	3.3
	PBEsol –GGA		5.666	8.990	95.9	4.1
	GGA+U		5.785	9.179	75.7	4.1
	WC-GGA	FM	5.885	9.337	62.0	4.8
	PBE -GGA		5.992	9.507	74.3	3.0
	PBEsol –GGA		5.879	9.327	73.4	4.2
	GGA+U		5.994	9.510	70.7	3.2

Table 3. Lattice constants computed using different approach for Pnma-Orthorhombic CsFeF₃ perovskite Fluoride.

Material	Approach	Configuration	a	b	c	B(GPa)	B'
Orthorhombic Pnma							
CsFeF ₃	GGA-WC	NF	5.736	8.201	5.733	86.7	4.6
	GGA-PBE		6.030	8.370	5.996	78.5	3.6
	GGA-PBEsol		5.849	8.305	5.834	99.2	3.3
	GGA+U-PBE		5.986	8.499	5.950	79.4	3.3
	<u>GGA-WC</u>		<u>5.982</u>	<u>8.719</u>	<u>5.945</u>	<u>70.6</u>	<u>4.4</u>

GGA-PBEsol	FM	5.983	8.273	5.945	57.8	4.6
GGA-PBE		5.925	8.569	5.820	68.5	4.4
GGA+U-PBE		6.298	8.441	6.140	72.2	4.3

Table 4. Lattice constants computed using different approach for Pnma-Orthorhombic NaFeF₃ perovskite Fluoride.

Material	Approach	Configuration	a	b	c	B(GPa)	B'
Orthorombic Pnma							
NaFeF ₃	GGA-WC	NF	5.465	7.466	5.308	120.2	3.9
	GGA-PBE		5.309	7.613	5.230	92.3	4.4
	GGA-PBEsol		5.381	7.917	5.224	105.1	4.9
	GGA+U-PBE		5.574	7.882	5.324	94.2	3.8
	GGA-WC	FM	5.679	8.108	5.512	94.9	3.4
	GGA-PBE		5.653	7.8258	5.474	63.3	5.1
	GGA-PBEsol		5.670	7.989	5.412	89.5	4.0
	GGA+U-PBE		5.948	7.973	5.816	68.8	4.8

Table 5. Lattice constants computed using different approach for Pnma-Orthorhombic RbFeF₃ perovskite Fluoride.

Material	Approach	Configuration	a	b	c	B(GPa)	B'
Orthorombic Pnma							
RbFeF ₃	GGA-WC	NF	5.678	7.951	5.623	96.3	4.5
	GGA-PBE		5.573	7.863	5.563	85.1	4.0
	GGA-PBEsol		5.678	8.021	5.632	94.9	4.6
	GGA+U-PBE		5.583	7.894	5.472	123.8	2.6
	GGA-WC	FM	5.927	8.441	5.894	69.8	5.2
	GGA-PBE		5.858	8.254	5.742	62.4	4.6
	GGA-PBEsol		5.890	8.336	5.791	68.8	4.9
	GGA+U-PBE		6.044	9.009	6.023	61.6	4.6

Table 6. Lattice constants computed using GGA+U-PBE approach for Pbnm-Orthorhombic CsFeF₃, NaFeF₃, and RbFeF₃ perovskites Fluorides.

Material	Approach	Configuration	a	b	c	B(GPa)
Orthorombic Pbnm						
CsFeF ₃	GGA+U-PBE	5.745	5.847	8.001	71.7	3.9
NaFeF ₃	GGA+U-PBE	5.349	5.453	7.652	69.8	4.2
RbFeF ₃	GGA+U-PBE	5.500	5.657	7.861	67.2	4.5

The atomic sphere radii (R_{MT}) values were taken as 2.4, 1.7, and 1.5 a.u for A, B, and F atoms respectively for the cubic phase designated with the (Pm-3m) space group. The kinetic

energy value of the cut-off wave function used is 40 Rydberg and the kinetic energy cut-off for the charge density is defined at 320 Rydberg. In the calculation of total energy, Brillouin zone is 11x11x11 in order to get denser electron coverage.

3. Results and Discussions

3. 1. Lattice constant

Before performing the electronic calculations of for the Fluorides (CsFeF_3 , NaFeF_3 , and RbFeF_3), the optimization of some calculation parameters were done firstly. it is known that the optimization of lattice constants is the most crucial part to produce a convergent calculation. To obtain an analytical interpolation of our computed points from which we determine the ground state properties such as the equilibrium lattice constant a_0 and c_0 the bulk modulus $B(\text{GPa})$ and its pressure derivative B' . (Table1), and (Table2) give the computed (PBE-GGA, WC-GGA, and PBEsol-GGA), also (GGA) with Hubbard potential (GGA + U) equilibrium parameters using non-ferromagnetic (NF) and ferromagnetic (FM) configurations. together with other theoretical and experimental values for the (Pm-3m) cubic, (4H) Layered-Hexagonal, whereas (Table3), (Table4), and (Table5) show the lattice parameters for CsFeF_3 , NaFeF_3 , and RbFeF_3 respectively in the (Pnma)-Orthorhombic phase and (Table6) in the (Pbnm)-Orthorhombic phases for three fluorides studied here.

The cubic phase ABF_3 is designated with (Pm-3m) space group. The atomic positions in the elementary cell are: A: 1b (1/2, 1/2, 1/2), B: 1a (0, 0, 0), and F: 3d (0, 0, 1/2), where A is an alkali metal and B is an alkaline earth or transition metal.

The four-layered hexagonal (4H) crystal phase is given here designated by the (P63/mmc) space group, where the atoms are positioned at: A_1 (0, 0, 0), A_2 (1/3, 1/3, 1/4), B (1/3, 2/3, 0.6142), F_1 (0, 0, 1/2) (3d) and F_2 (-0.6129, -1.2258, 1/4). The previous calculation is in excellent agreement with the data results. (Figure. 1) shows the crystals structures for the CsFeF_3 Fluoride within Cubic (Pm-3m space group), 4H- Hexagonal (P63/mmc), Orthorhombic(Pbnm), and Orthorhombic (Pnma) phases respectively.

The calculated total energies versus volume for the considerable Fluorides is given for non-ferromagnetic (NF) and ferromagnetic (FM) configurations in four phases treated in this work as shown in (Figure. 2), (Figure. 3) and (Figure. 4) respectively for Cubic (Pm-3m), 4H (P6/mmc), and Orthorhombic (Pnma). They are fitted with Murnaghan's equation of states [82]. According to the energy-volume curves of all ABF_3 Fluorides given here the most stable state is illustrated with the ferromagnetic (FM) order for using (GGA) and (GGA+U) approaches. We remark that the lattice constant is overestimated by (GGA + U) than others

approaches, they should be increased with increase of the atomic size of the A element in $AFeF_3$ ($A = Cs, Na$ and Rb) fluorides $a(CsFeF_3) > a(RbFeF_3) > a(NaFeF_3)$. This remark is taken for cubic (Pm-3m) as well as for the hexagonal (4H), (Pnma) and (Pbnm) orthorhombic phases. The magnetic moment is given in (Table .7), (Table .8), (Table .9), and (Table .10) for $CsFeF_3$, $NaFeF_3$, and $RbFeF_3$ Fluorides with (Pm-3m) cubic, (4H) Layered-Hexagonal, (Pnma)-Orthorhombic and (Pbnm)-Orthorhombic phases respectively. These tables summarized the calculated spin magnetic moments for A(μ_A), B (μ_B), F (μ_F) atoms, interstitial region ($\mu_{interst}$) and cell (μ_{Cell}) respectively versus the exchange correlation potential.

Table 7. Magnetic moments (μ_A , μ_B , and μ_F , interstitial moment ($\mu_{interstitiel}$) and cell moment ($\mu_{Cellule}$)) calculated using GGA-PBE, WC-GGA, PBEsol-GGA and GGA+U-PBE approaches for considerable (FM) Fluoro-perovskite in the (Pm-3m)Cubic phase for $CsFeF_3$, $NaFeF_3$, and $RbFeF_3$ studied.

Approches	μ_A	μ_B	μ_F	$\mu_{interstitiel}$	μ_{Cell}
CsFeF₃					
WC-GGA	-0.0015	3.341	0.078	0.406	3.98079
PBE -GGA	-0.0003	3.352	0.074	0.425	4.00057
PBEsol –GGA	-0.0048	3.342	0.071	0.331	3.88525
GGA+U	-0.0023	3.547	0.046	0.314	4.00095
NaFeF₃					
WC-GGA	-0.0013	3.344	0.075	0.400	3.97118
PBE -GGA	-0.0004	3.355	0.071	0.431	4.00024
PBEsol –GGA	-0.0010	3.345	0.081	0.400	3.99013
GGA+U	0.0021	3.592	0.048	0.352	4.09443
RbFeF₃					
WC-GGA	-0.0013	3.333	0.101	0.362	4.00000
PBE -GGA	-0.0005	3.353	0.072	0.430	4.00059
PBEsol –GGA	-0.0034	3.344	0.069	0.363	3.91409
GGA+U	-0.0010	3.542	0.043	0.332	4.00479

In this part for calculation, we also find that the (GGA+U) also overestimated the magnetic moment than others. The contribution of the element Fe is the most dominant because we find for (Pm-3m) cubic phase 3.547 μ_{Bohr} ($CsFeF_3$), 3.592 μ_{Bohr} ($NaFeF_3$), and 3.542 μ_{Bohr} ($RbFeF_3$). For 4H-Hexagonal phase 3.437 μ_{Bohr} ($CsFeF_3$), 3.447 μ_{Bohr} ($NaFeF_3$), and 3.438 μ_{Bohr} ($RbFeF_3$). The Fe magnetic moment revelation for the Pnma-Orthorhombic phase show same values 3.47 μ_{Bohr} ($CsFeF_3$) 3.47 μ_{Bohr} for $NaFeF_3$, and 3.45 μ_{Bohr} $RbFeF_3$ Fluorides, as well (Pbnm) Orthorhombic phase are respectively 3.55 μ_{Bohr} ($CsFeF_3$) 3.57 μ_{Bohr} for $NaFeF_3$, and 3.57 μ_{Bohr} $RbFeF_3$ Fluorides. the contribution of the

other elements A (A = Cs, Na and Rb) and B is almost negligible in comparison with the element Fe (Ferrite).

Table 8. Magnetic moments (μ_A , μ_B , and μ_B , interstitial moment ($\mu_{\text{interstitiel}}$) and cell moment (μ_{Cellule}) calculated using GGA-PBE, WC-GGA, PBEsol-GGA and GGA+U-PBE approaches for considerable (FM) Fluoro-perovskite 4H-Hexagonal phase for CsFeF_3 , NaFeF_3 , and RbFeF_3 studied.

4H-Hexagonal Structure							
Approches	μ_{A1}	μ_{A2}	μ_B	μ_{F1}	μ_{F2}	$\mu_{\text{interstitiel}}$	μ_{Cell}
CsFeF₃							
WC-GGA	15.843	0.0001	-0.001	3.427	0.081	0.087	1.125
PBE -GGA	16.002	-0.001	-0.003	3.434	0.078	0.084	1.214
PBEsol -GGA	15.844	0.000	-0.001	3.430	0.081	0.087	1.111
GGA+U	16.112	-0.001	-0.002	3.437	0.083	0.089	1.217
NaFeF₃							
WC-GGA	15.817	0.0003	-0.001	3.411	0.098	0.098	0.993
PBE -GGA	16.000	0.0006	-0.000	3.440	0.082	0.086	1.225
PBEsol -GGA	15.820	0.0004	-0.001	3.412	0.098	0.098	0.990
GGA+U	16.002	0.0005	-0.000	3.447	0.082	0.086	1.231
RbFeF₃							
WC-GGA	16.000	0.000	-0.000	3.429	0.082	0.088	1.256
PBE -GGA	16.195	-0.001	-0.002	3.436	0.077	0.082	0.900
PBEsol -GGA	16.000	0.000	-0.000	3.427	0.088	0.092	1.204
GGA+U	16.207	-0.002	-0.002	3.438	0.089	0.095	0.904

Table 9. Magnetic moments (μ_A , μ_B , and μ_B , interstitial moment ($\mu_{\text{interstitiel}}$) and cell moment (μ_{Cellule}) calculated using GGA-PBE, WC-GGA, PBEsol-GGA and GGA+U-PBE approaches for considerable (FM) Fluoro-perovskite (Pnma) Orthorhombic phase for CsFeF_3 , NaFeF_3 , and RbFeF_3 computed.

Approch	μ_A	μ_B	μ_{F1}	μ_{F2}
CsFeF₃				
WC-GGA	0.000	3.45	0.07	0.08
PBE -GGA	0.001	3.46	0.08	0.07
PBEsol - GGA	0.000	3.44	0.09	0.08
PBE-GGA+U	0.001	3.47	0.09	0.10
NaFeF₃				
WC-GGA	0.000	3.43	0.09	0.07
PBE -GGA	0.000	3.45	0.08	0.08
PBEsol - GGA	0.000	3.41	0.09	0.09
PBE-GGA+U	0.000	3.47	0.10	0.12
RbFeF₃				
WC-GGA	0.000	3.42	0.08	0.07
PBE -GGA	-0.001	3.43	0.09	0.08
PBEsol - GGA	0.000	3.42	0.08	0.09
GGA+U	-0.001	3.45	0.11	0.10

3.2. Electronic properties

a. Band structure

Next, we discuss in details the band structure for the considerable Fluoro-perovskites (CsFeF_3 , NaFeF_3 , and RbFeF_3) on the Ferromagnetic (FM) configuration, (Figure. 5), (Figure. 6), (Figure. 7) and (Figure. 8) illustrate respectively (Pm-3m-cubic) phase, (4H-Hexagonal), (Pnma-Orthorhombic) and (Pbnm-Orthorhombic). These band structures are shown within (*Spin-Up* and *Spin Dn*) states along the high symmetry directions using (GGA+U) and (GGA-mBJ) approaches respectively. We present the calculated electron band structures of AFeF_3 compound to visualize the contribution of each band near the Fermi level.

This figure proves that the insulator behavior is a common factor for them with some differences given between *Spin-Up* and *Spin Dn* states. We remark also that (GGA-mBJ) has expanded the band gap in comparison with (GGA+U) approach. (GGA-mBJ) overestimated the gap values.

Table 10. Magnetic moments (μ_A , μ_B , and μ_B , interstitial moment ($\mu_{\text{interstitiel}}$) and cell moment (μ_{Cellule})) calculated using GGA-PBE, WC-GGA, PBEsol-GGA and GGA+U-PBE approaches for considerable (FM) Fluoro-perovskite (Pbnm) Orthorhombic phase for CsFeF_3 , NaFeF_3 , and RbFeF_3 computed.

Material	Approch	μ_A	μ_B	μ_{F1}	μ_{F2}
CsFeF_3	WC-GGA	0.001	3.51	0.05	0.07
	PBE -GGA	0.001	3.54	0.08	0.08
	PBEsol – GGA	0.000	3.48	0.08	0.05
	PBE-GGA+U	0.001	3.55	0.09	0.09
NaFeF_3	WC-GGA	0.000	3.53	0.07	0.07
	PBE -GGA	0.000	3.55	0.08	0.11
	PBEsol – GGA	0.000	3.51	0.10	0.09
	PBE-GGA+U	0.000	3.57	0.11	0.13
RbFeF_3	WC-GGA	0.001	3.47	0.07	0.08
	PBE -GGA	-0.001	3.51	0.09	0.09
	PBEsol – GGA	0.000	3.52	0.08	0.10
	GGA+U	-0.001	3.57	0.10	0.11

Figure 5. Band Structures for the CsFeF_3 , NaFeF_3 and RbFeF_3 Cubic (Pm-3m) Fluorides with GGA+U and mBJ-GGA approaches respectively.

The materials have proven an insulating behavior with an indirect gap within (GGA+U) and (GGA-mBJ) approaches, most of the structures is oriented from N to Γ . We see a widening of band increases from left to right (GGA+U, and mBJ-GGA). The figures show

also the position of the last valence band that sometimes which are exceed the Fermi level E_F using (GGA+U) approach.

Figure 6. Band Structures for the CsFeF_3 , NaFeF_3 and RbFeF_3 4H-Hexagonal (P6/mmc) Fluorides with GGA+U and mBJ-GGA approaches respectively.

Using (GGA-mBJ), this last valence band falls backwards down to lower levels, thus is giving a very wide gap that can even change the behavior of the Fluoride. The top valence

bands of Fluorides are mainly formed by the p -F states, the bottom conduction bands are created by A and F states.

Figure 7. Band Structures for the CsFeF_3 , NaFeF_3 and RbFeF_3 Orthorhombic (Pnma) Fluorides with GGA+U and mBJ-GGA approaches respectively.

The band conduction is positioned above the Fermi-Level E_F using (GGA+U), but these positions have changed according to (GGA-mBj) plots. The insulator character with indirect gap according to the Up states drawn appears clearly on both Pm-3m-cubic and 4H-

Hexagonal phases, while Dn states sometimes have a tendency to be metallic. gaps given by Up states are enlarged more within (GGA-mBJ), than (GGA+U) approach. The figures show for CsFeF₃ 8eV, NaFeF₃ 6.7 eV and RbFeF₃ 6eV in the cubic phase, while for the 4H-hexagonal structure we give CsFeF₃ 6.2eV, NaFeF₃ 6.1 eV and RbFeF₃ 6.0 eV in the cubic phase. The most remarkable is that this gap decreases clearly for the orthorhombic structures (Pnma and Pbnm) in comparison with the too wide values found for the two previous cases. This revelation shows that the fluorides in the orthorhombic structure have a tendency to change their behavior and become metallic, a transition phase caused by a thermal change or pressure exerted contribute actually to this change. This clearly means the metallic character found for NaFeF₃ in the (Pbnm) phase which is not the case for the (Pnma) phase. In the Pnma-Orthorhombic phase (GGA-mBJ) also expanded the gap, we report 3.1eV, 0.9 eV, and 2.7 eV for the CsFeF₃, NaFeF₃, and RbFeF₃ respectively in the Spin Up states by (GGA+U) and 6 eV, 5.9 eV, and 6.2 eV by (GGA-mBJ).

Figure 8. Band Structures for the CsFeF_3 , NaFeF_3 and RbFeF_3 Orthorhombic (Pbnm) Fluorides with GGA+U and mBJ-GGA approaches respectively.

b. Charge densities

To complete the property analysis of our selected compound, let us investigate their bonding properties. The contour map of the spin charge densities in (110) directions is plotted using GGA, GGA+U and GGA-mBJ approaches for CsFeF_3 , NaFeF_3 and RbFeF_3 Fluorides respectively in the (Pm-3m) Cubic phase (Figure. 9). The electron density of Spin-Up and Spin-Dn plots as illustrated is containing (A) atom (Cs/Na/ Rb), (Fe) and Fluoride (F) atoms. As seen in this figure, the valence charge densities for all cases are quite similar, with some smaller differences in the details. The near spherical charge distribution around the A atom (Cs/Na/ Rb), indicates that the bonding between A and F is predominantly ionic and a covalent-ionic bonding between Fe and F atoms. The transfer plot reveals that the sphere charge between Fe-F is more important than A-F atoms, where the F-F bonding are ionic and a strong covalent interaction between Fe-Fe. This nature of chemical bonding is responsible to have a high bulk modulus, It's due essentially to the hybridization between the $3d$ -A and $2p$ -F states. The majority of magnetic moments reside on the $3d$ -states of Fe-cation which is the main contributor. From this figure, we also notice that the spin magnetic moment decreases going from $\text{NaFeF}_3 > \text{RbFeF}_3 > \text{CsFeF}_3$. We see clearly that the Fe atom contribution is bigger than other atoms, this contribution is more important in the NaFeF_3 Fluoride than others. GGA+U illustrate clearly their behaviors, where the GGA neglected some details. GGA-mBJ unheeded completely the Rb atom contribution on the RbFeF_3 Fluoride and show some bonding but not as GGA+U which confirms that it is the most effective.

Figure 9. Charge Densities for the CsFeF_3 , NaFeF_3 , and RbFeF_3 Fluorides with GGA, GGA+U and TB-mBJ approaches respectively in the Cubic (Pm-3m) phase.

4. Conclusions

To summarize, we have explored different structural phases, electronic states, chemical bonding, and magnetic properties of CsFeF_3 , NaFeF_3 and RbFeF_3 fluorides using the full-potential linearized augmented plane wave (FP-LAPW) method within the U-Hubbard

correction added to the density functional theory (DFT+U) basis. This comparative study is based on evolution of the lattice parameters and magnetic moment given by the Fe atom. The calculated ground-state properties such as lattice constant and bulk modulus agree very well with the theoretical and experimental works. From these electronic structures, there is a varying energy gap value for each of the cations ranging. The current fluorides exhibit a Ferromagnetic (FM) behavior. The magnetic moments are evaluated per atom, and overestimated by (GGA+U). The modified Becke-Johnson mBJ-GGA approach correct the d-states and give wide gaps with insulator behaviors but remains that GGA+U give more details on the magnetic interaction systems, specially the magnetic moment revelation which appears clearly on the charge densities plots. The present study would be helpful for future experimental and theoretical explorations for different spintronic applications.

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