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# DFT study of the electronic and optical properties of ternary alkali metal tetrafluoridobromates materials $ABrF_4$ (A=Na, K and Rb)

**Ishak Mebarkia**[1*]

*[1] Applied optics laboratory, Institute of Opticsand Precision Mechanics, Ferhat Abbas University Setif 1, Setif, 19000, Algeria.*

** Corresponding author: Tel.: +213 657308527; E-mail:ishak.mebarkia@univ-setif.dz*

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## Abstract

This work deals with a theoretical investigation of structural, electronic, and optical properties of alkali metal tetrafluoridobromates materials that crystallize in tetragonal structure ($NaBrF_4$, $KBrF_4$, and $RbBrF_4$) using the Density Functional Theory (DFT) within the pseudo-potential plane-wave approach as implemented in Cambridge Serial Total Energy Package (CASTEP) code. The structural parameters are in good agreement compared to the experimental values stated in the literature. The calculated electronic properties indicate that these ternary compounds are wide bandgap semiconductor materials. $NaBrF_4$ is a semiconductor compound with a direct band gap, whereas, $KBrF_4$ and $RbBrF_4$ are semiconductors compounds together with an indirect band gap.The main optical parameters are studied in detail. The large optical absorption range in the ultraviolet (UV) region suggests that these semiconductor materials could be helpful for specific implementations in UV optoelectronic devices; therefore, this theoretical investigation is probable to motivate future experimental works.

**Keywords:** $ABrF_4$, alkali metal tetrafluoridobromates, DFT, electronic properties, optical properties, semiconductor materials.

## 1. Introduction

The alkali metal fluorides family has many characteristics desirable foroptoelectronic properties, such as wide bandgaps, large absorption in the UV region, and lower refractive indices compared to those of oxides[1]. Our studied materials are ternary compounds belonging to the same crystalline structure and sharing one of the alkali elements such that Sodium "Na", Potassium "K", and Rubidium "Rb" as a cation with an anion formed by Bromine bonded with four Fluorine "$BrF_4$" [2,3]. To the best of our knowledge, no theoretical nor experimental studies of the electronic, and optical properties have been carried out on the herein-studied compounds exceptour recent theoretical investigation using a different exchange-correlation function (Perdew-Burke-Ernzerhof for solids (PBE-sol))[4]. The results presented in this work may be useful in evaluating potential technological applications of $NaBrF_4$, $KBrF_4$, and $RbBrF_4$ materials.

## 2. Method of calculations

To carry out our first-principle calculations, we employed the density functional theory (DFT) framework and utilized the Cambridge Serial Total Energy Package (CASTEP) code[5]. Our method relied on the pseudopotential plane-wave (PP-PW) approach. For the electronic exchange potential, we applied the Wu-Cohen (WC) exchange-correlation function, which was specifically designed for solids and followed the generalized gradient approximation (GGA)[6].The energy cut-off for the basis set of plane-waves used was 60 Ry. The Monkhorst-Pack special k-point sampling was used to cover the Brillouin zone (BZ) with a mesh of 4×4×2, which is equivalent to 3 irreducible points within the first BZ [7].

## 3. Results

The structure of $ABrF_4$ (A=Na, K and Rb) ternary compounds istetragonal space group I4/mcm (No. 140) as shown in Figure 1, where the unit cell contains four formula units (Z=4) in which the atoms are positioned in the followingWyckoff sites: A: 4a(0; 0; ¼), Br: 4d(½; 0; 0), and F: 16l($x_F$; $y_F$; $z_F$).To determine the equilibrium structural parameters including the lattice parameters (a and c) and the internal coordinates of Fluorine atom ($x_F$, $y_F$, and $z_F$), we applied different values of hydrostatic pressures and for each value we calculated the volume V and its total energy E.Thereafter, we extract the different equilibrium parameters, according tothe equilibrium volume $V_0$, which is corresponding to the minimum value of the ground state energy $E_0$.

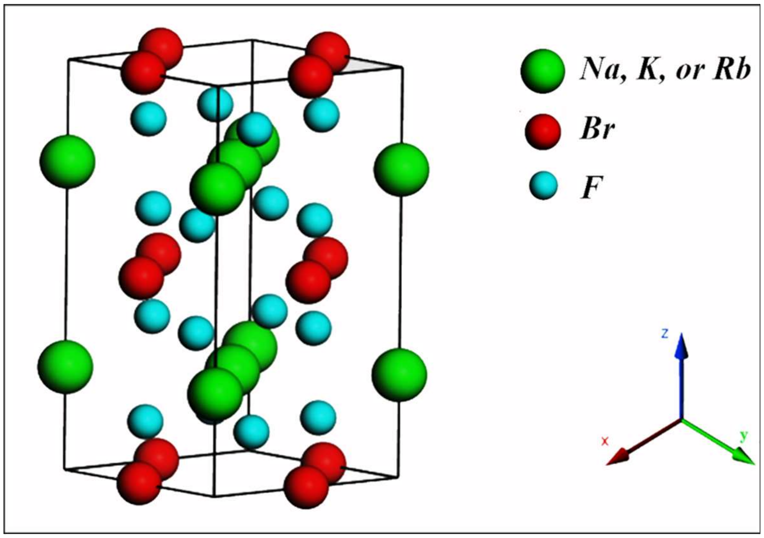

**Figure 1.**Crystal structure ofABrF$_4$ (A=Na, K and Rb) ternary compounds.

Furthermore, The calculated cell volumes V at fixed applied hydrostatic pressures and the associated total energies E were fitted to the following Birch-Murnaghan isothermal equation of states (BMEOS) [8], to obtain the bulk modulus $B_0$ and its pressure derivative$B_0'$, as shown in Figure2.

$$E(V) = E_0 + \frac{9V_0B_0}{16}\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2 \left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\} \quad (1)$$

where $E_0$and $V_0$arethe energy and volume at zero pressure, respectively.Table1displays the computed ground states parameters such as the lattice constants a and c, the internal coordinates of Fluorine atom$x_F$, $y_F$, and $z_F$, the Bulk modulus $B_0$ and its pressure derivative B' along with the experimental data, as well as the other theoretical calculations for comparison.We can notice that there is an excellent agreement between our calculated results and the experimental ones for all studied compounds which affirms the reliability of our computations in this work.

The electronic band structure along the Brillouin zone high symmetry lines is shown in Figure 3 forABrF$_4$ (A= Na, K, and Rb) ternary compound. The Fermi level $E_F$ positioned at 0 eV and indicated by the horizontal dashed line.The calculated values of the energy gap are3.006 eV, 3.180 eV, and 3.222 eV for NaBrF$_4$, KBrF$_4$, and RbBrF$_4$, respectively,which gives these materials the characteristic to become semiconductors with wide band gaps. Furthermore, it is clear from the forms of electronic structure that NaBrF$_4$has a direct band gap, owing to its VBM and its CBM arelocated at Γ point, while the other studied compounds have an indirect band gap, which their VBM aresituated near the point Γ in the Γ-X orientation, and their CBM situated at the Γ point.

**Table 1.** The lattice constants a and c (in Å), the internal coordinates of Fluorine atom $x_F$,$y_F$ and $z_F$, the Bulk modulus $B_0$ and its pressure derivative $B_0$’ of $ABrF_4$ (A = Na, K and Rb) materials.

| materials | Parameters | calc. | other calc. | Expt. |
|---|---|---|---|---|
| $NaBrF_4$ | a | 5.792 | 5.546[d], 5.788[e]m 5.7814[f] | 5.762[a], 5.7848[b], 5.7239[c] |
| | c | 10.432 | 10.09[d], 10.44[e], 10.4294[f] | 10.327[a], 10.400[b], 10.331[c] |
| | $x_F$ | 0.3346 | 0.33452[f] | 0.6633[b], 0.33524[c] |
| | $y_F$ | 0.1653 | 0.16548[f] | –0.1633[b], 0.16476[c] |
| | $z_F$ | 0.1312 | 0.13140[f] | 0.1299[b], 0.13080[c] |
| | $B_0$ | 28.683 | 28.09621[f] | / |
| | $B_0$’ | | 6.89523[f] | / |
| $KBrF_4$ | a | 6.183 | 6.1769[f] | 6.192[a], 6.162[g], 6.174[h], 6.17[i], 6.0999[j] |
| | c | 11.170 | 11.1626[f] | 11.108[a],11.081[g], 11.103[h], 11.1[i], 11.0509[j] |
| | $x_F$ | 0.6542 | 0.65585[f] | 0.161[g], 0.152[h], 0.152[i], 0.65508[j] |
| | $y_F$ | 0.1533 | 0.15585[f] | 0.661[g], 0.652[h], 0.652[i], 0.15508[j] |
| | $z_F$ | 0.3777 | 0.37835[f] | 0.147[g], 0.880[h], 0.121[i], 0.37889[j] |
| | $B_0$ | 19.225 | 20.42155[f] | / |
| | $B_0$’ | 6.5501 | 6.42551[f] | / |
| $RbBrF_4$ | a | 6.446 | 6.20[n], 6.94[o], 6.3895[f] | 6.401[a], 6.351[k], 6.37181[l], 6.2991[m] |
| | c | 11.612 | 11.74[n], 8.93[o], 11.5819[f] | 11.1538[a], 11.489[k], 11.4934[l], 11.4659[m] |
| | $x_F$ | 0.6499 | 0.154[n], 0.1458[o], 0.6508[f] | 0.1490[k], 0.151[l], 0.6501[m] |
| | $y_F$ | 0.1498 | -0.346[n], -0.3542[o], 0.1508[f] | -0.3510[k], -0.349[l], 0.1501[m] |
| | $z_F$ | 0.6087 | 0.1145[n], 0.1411[o], 0.6171[f] | 0.1162[k], 0.1193[l], 0.61660[m] |
| | $B_0$ | 17.634 | 18.27326[f] | / |
| | $B_0$’ | 7.0203 | 6.75771[f] | / |

**Note:** [a]Ref.[9], [b,c,d,e]Ref.[10], [f]Ref.[4], [g]Ref.[11],[h]Ref.[12], [i]Ref.[13], [j]Ref.[14],[k]Ref.[15], [l,n,o]Ref.[16], [m]Ref.[17].

The main optical parameters such as the refractive index n and the absorption coefficient α that describe the optical behaviour of the material when it interacts with an external electromagnetic field can be computed from the dielectric permittivity ε, which is a complex function depends of the angular frequency ω of the applied electric field, given as:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\,\varepsilon_2(\omega) \qquad (2)$$

where$\varepsilon_1$ and $\varepsilon_2$ are respectively the real and imaginary parts of the dielectric function.

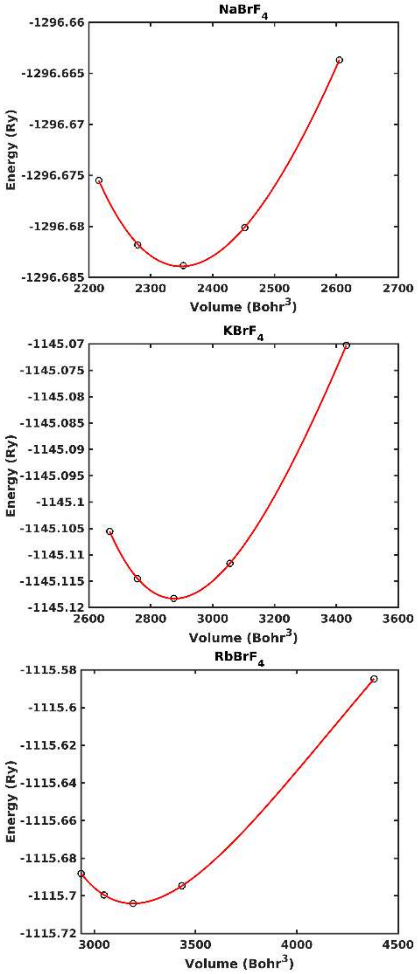

**Figure 2.**The total energy versus cell volume data. The black circles are the calculated results and the red lines represent the BMEOS fits.

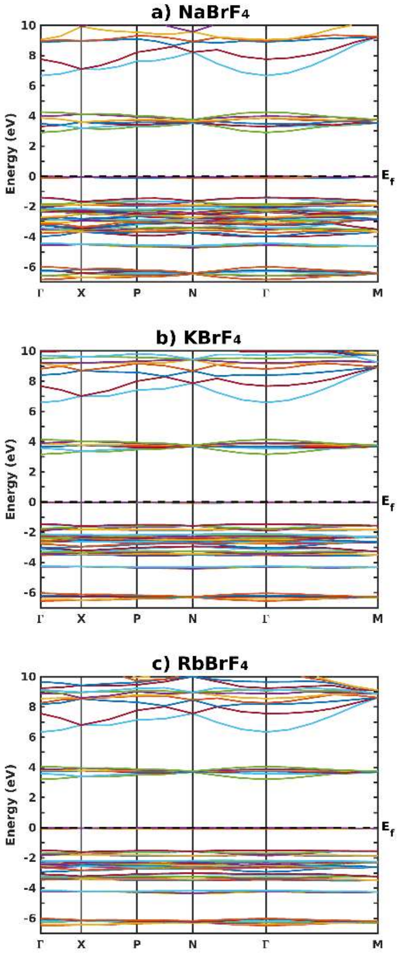

**Figure 3.**The calculated electronic structure of ABrF$_4$(A = Na, K and Rb) ternary alkali metal tetrafluoride-bromates materials.

As ABrF$_4$ (A = Na, K and Rb) ternary compounds crystallize in the tetragonal structure, the optical spectra of the dielectric function $\varepsilon_1$ and $\varepsilon_2$, the refractive index n and the absorption coefficient α are plotted in Figure 4 and Figure 5 for only two components indicating by the superscripts xx and zz, which concerning the polarization of the applied electric field along the x (or y) and z directions, respectively.

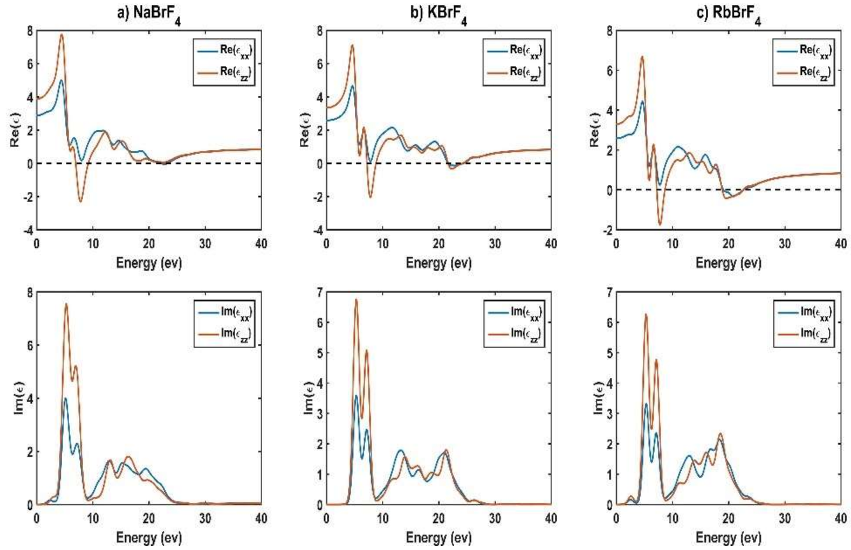

**Figure 4.**The spectra of thereal and imaginary parts of the dielectric function forABrF$_4$ (A=Na, K and Rb) ternary compounds.

It is clear from the different optical spectra that the polarized components are not identical when the energy less than 25 eV, indicating that these materials having an optical anisotropy behavior in this energy region.According to the spectra of the real part $\varepsilon_1$ (called also the dispersive part) we can affirm that the herein studied compound shows a Drude like behavior, which $\varepsilon_1$ crosses the zero frequency and represents the dielectric response to a static electric field. The calculated values of the zero-frequency limit for the different polarized components ($\varepsilon_1^{xx}(0)$ and$\varepsilon_1^{zz}(0)$) are mentioned in Table2. Furthermore, we can notice that $\varepsilon_1^{zz}$ is the dominant component owing to its prominent peak located at around 4.7eV, 4.8 eV, and 4.9 eV for NaBrF$_4$, KBrF$_4$, and RbBrF$_4$, respectively.

**Table 2.** Thecalculated values of the static dielectric constant $\varepsilon_1(0)$, the energy values correspond to the maximum peaks of $\varepsilon_2(\omega)$, and the static refractive index n(0).

| **Compounds** | $\varepsilon_1^{xx}(0)$ | $\varepsilon_1^{zz}(0)$ | $\varepsilon_2^{xx}(\omega)$ | $\varepsilon_2^{zz}(\omega)$ | $n^{xx}(0)$ | $n^{zz}(0)$ |
|---|---|---|---|---|---|---|
| NaBrF$_4$ | 2.77 | 3.70 | 5.50 | 5.11 | 1.68 | 1.95 |
| KBrF$_4$ | 2.43 | 3.24 | 5.81 | 5.14 | 1.61 | 1.83 |
| RbBrF$_4$ | 2.22 | 3.15 | 5.92 | 5.22 | 1.60 | 1.82 |

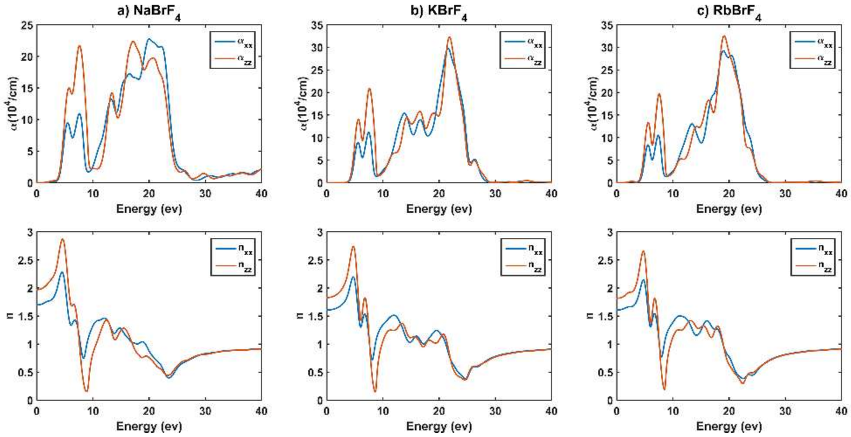

**Figure 5.**The absorption spectrum and the refractive indexprofile of $ABrF_4$ (A=Na, K and Rb) materials.

As shown in Figure 5, the refractive index profile n takes the shape of the dispersive part spectrum $\varepsilon_1$, where $n^{zz}$ is the dominant component of the refractive index that possess a significant peak situated at about 4.8 eV, 4.9 eV, and 5.0 eV for $NaBrF_4$, $KBrF_4$, and $RbBrF_4$, respectively. Moreover, the obtained values of the static refractive index for the different polarized components ($n^{xx}(0)$ and $n^{zz}(0)$) are mentioned in Table2, which are close to the values obtained by the following semi-empirical relation:

$$n(0) = \sqrt{\varepsilon_1(0)} \tag{3}$$

These consequences confirm the reliability of the obtained results for $ABrF_4$ (A = Na, K and Rb) ternary compounds.

The imaginary part of the dielectric function $\varepsilon_2$ (called also the absorptive part) shows an anisotropy between its polarized components, where$\varepsilon_2^{xx}$ and $\varepsilon_2^{zz}$ have prominent peaks at the lower energy region. The energy values correspond to these peaks mentioned in Table2, which principally originate from the optical transition between the highest occupied valence band and the lowest unoccupied conduction band.

As mentioned in Figure 5, the absorption profile α takes the shape of the absorptive part spectrum $\varepsilon_2$, where represents the maximum absorbance in the ultraviolet (UV) optical range, which the first main peak located at about 5.4 eV signifies that this ternary compound can be used for producing specified UV optoelectronic devices. Furthermore, the absorption thresholds situated at3.0 eV, 3.2 eV, and 3.3 eV for $NaBrF_4$, $KBrF_4$, and $RbBrF_4$, respectively. These results confirm the reliability of the obtained energy gap results for these semiconductors.

## 4. Conclusion

In this study, the electronicand optical properties of $ABrF_4$ (A = Na, K and Rb)materials were investigated in details using the pseudopotential planewave method within the generalized gradient approximation as enhanced by Wu and Cohen. Our calculated equilibrium structural parameters agree well with the other available results of the literature.Based on the results of electronic properties, it can be concluded that these ternary compoundsare semiconductor materials, $NaBrF_4$has a direct band gap, whereas, $KBrF_4$ and $RbBrF_4$have an indirect band gap.The outcome of our investigation in the optical properties suggests that these semiconductors could be useful materials for specific applications in UV optoelectronic devices owing to their wide absorption in the UV region.Finally, our results can be considered as a source for future experimental research works.

## References

[1] A.J. Stevenson, H. Serier-Brault, P. Gredin, M. Mortier. J. Fluor. Chem. 132 (2011) 1165–1173.
[2] O. Materials. Optical & Wiley Series in Materials for Electronic and Optoelectronic, 2005.
[3] R. Burkhalter, I. Dohnke, J. Hulliger. 2001.
[4] I. Mebarkia, A. Manallah, R. Belghit. Phys. B Condens. Matter. 624 (2022) 413450.
[5] S.J. Clark, M.D. Segall, C.J. Pickard, P.J. Hasnip, M.I.J. Probert, K. Refson, M.C. Payne. Zeitschrift Fur Krist. 220 (2005) 567–570.
[6] Z. Wu, R.E. Cohen. Phys. Rev. B - Condens. Matter Mater. Phys. 73 (2006).
[7] Hendrik J Monkhorst, J.D. Pack. Phys. Rev. B. 13 (1976) 5188–5192.
[8] F. Birch. Phys. Rev. 71 (1947) 809–824.
[9] A.I. Popov, Y.M. Kiselev, V.F. Sukhoverkhov, N.A. Chumaevskij, O.A. Krasnyanskaya, A.T. Sadikova. Zh. Neorg. Khim.; 32:5 (1987).
[10]S.I. Ivlev, R. V. Ostvald, F. Kraus. Monatshefte Fur Chemie. 147 (2016) 1661–1668.
[11]S. Siegel. Acta Crystallogr. 9 (1956) 493–495.
[12]W.G. Sly, R.E. Marsh. Acta Crystallogr. 10 (1957) 378–379.
[13]A.J. Edwards, G.R. Jones. J. Chem. Soc. A Inorganic, Phys. Theor. Chem. (1969) 1936–1938.
[14]S.I. Ivlev, F. Kraus. IUCrData. 3 (2018).
[15]A.R. Mahjoub, A. Hoser, J. Fuchs, K. Seppelt. Angew. Chemie. 101 (1989) 1528–1529.
[16]S.I. Ivlev, A.J. Karttunen, R. Ostvald, F. Kraus. Zeitschrift Fur Anorg. Und Allg. Chemie. 641 (2015) 2593–2598.
[17]A. V. Malin, S.I. Ivlev, R. V. Ostvald, F. Kraus. IUCrData. 4 (2019).