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The Structure and the Optical Properties of $Ba_{0.50}Ca_{0.50}F_2$

Alice Bukola Olanipekun*, Catherine Obaze, Brian Diagbonya

Department of Pure and Applied Physics, Caleb University, Imota, Lagos, Nigeria

Abstract A theoretical investigation of structural, electronic and optical properties of CaF_2, BaF_2 and $Ba_{0.50}Ca_{0.50}F_2$ is presented, using the pseudopotential plane-wave (PP-PW) method as implemented in the QUANTUM ESPRESSO code. In this research, the exchange-correlation (XC) potential was approximated using the generalized gradient approximation (GGA). The calculated lattice constants and bulk moduli are in good agreement with experimental results for both the binary compounds and their alloy. Band structure of $Ba_{0.50}Ca_{0.50}F_2$ is presented and band gap calculated. In addition to DFT-PBE calculation of the band gap, a semi empirical model is used for the calculation of band gap and a good agreement with experiment is obtained. The pressure coefficients of energy gaps and refractive indices are also calculated.

Keywords Generalized Gradient Approximation, Semi empirical model, Optical properties

1. Introduction

Due to the high band gaps of the alkaline earth fluorides, they are transparent in a very high frequency region. This made them useful as window materials which are transparent in infrared and ultraviolet wavelengths. Many of them crystallise in the fluorite structure. Examples are; CaF_2, BaF_2, CdF_2, SrF_2, PbF_2 and they are highly ionic [1-5].

Some authors studied the optical properties of these compounds by experiment [6-15]. Metal and fluorine occupy the positions (0 0 0) and (0.25 0.25 0.25) respectively.

The mixed divalent metal fluoride, $Ca_{0.50}Ba_{0.50}F_2$, are formed when BaF_2 and CaF_2 are doped, with Ca and Ba in the ratio 1:1. They are formed by high energy planetary ball mill [16-21] and Molecular beam epitaxy [22]. $Ba_{1-x}Ca_xF_2$ ($0 < x < 1$) can be prepared by mechano-chemical reaction at low temperatures from the binary fluorides BaF_2 and CaF_2 [18,19]. $Ba_{0.50}Ca_{0.50}F_2$ adopt the cubic fluorite structure [23-25].

Sata et al. observed fluoride ion conductivities in layered BaF_2-CaF_2 composites, prepared by molecular beam epitaxy (MBE), greatly larger than the binary fluorides [22]. Similar result was obtained for high-energy ball-milled BaF_2-CaF_2 alloys [19]. The ion conductivity exhibit a maximum at x= 0.5 and also a minimum in the activation energy at $x = 0.5$ [21]. These properties of $Ba_{0.50}Ca_{0.50}F_2$ alloy are essential in fuel cells, batteries, capacitors and solid electrolytes. The ion conductivities of $Ba_{1-x}Ca_xF_2$ has also been calculated using theory [24,26]. Using X-ray diffraction, the lattice constant of $Ba_{0.50}Ca_{0.50}F_2$ was measured to be 5.87Å [25].

The study of the electronic properties of the mixed $Ba_{0.50}Ca_{0.50}F_2$ crystal is important as they intermediate between the two compounds (BaF_2 and CaF_2) with equal concentration ratio of the cations. Literatures show that the electronic, structural, lattice dynamics, dielectric and photoelastic properties of the binary compounds have been investigated theoretically and experimentally. However, very little electronic and structural theoretical investigations have been done on the mixed fluorides crystal.

2. Method of Calculation

Structural and electronic calculations were carried out using density functional theory (DFT) [27,28] as employed in the QUANTUM ESPRESSO code [29]. We used a kinetic energy cutoff of 60 Ry for the plane wave basis set, while the total energy convergence was set to 0.1mRy. The electron-ion interactions were modeled using ultrasoft pseudopotentials [30]. The pseudopotential was produced using scalar relativistic calculation.

The reciprocal space integration was done by sampling the Brillouin zone of the atoms with a 6 × 6 × 6 Pack-Monkhorst net [31]. The present calculations for $Ba_{0.50}Ca_{0.50}F_2$ are performed on 12-atom supercells, which is sufficient to guarantee converged results.

In our investigations, we used generalized gradient approximation method of Perdew, Burke and Ernzerhof (PBE) [32]. We performed band structure calculations with 96 *k*-points in the Brillouin zone (BZ).

In this work, we present the results of structural and pressure-dependent study of the band gap of $Ba_{0.50}Ca_{0.50}F_2$. The lattice constant and bulk modulus are fitted to the Murnaghan's equation of state [33].

* Corresponding author:
bukkymatt4real@yahoo.com (Alice Bukola Olanipekun)
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The density functional theory is not accurate for wide band gap materials [34]. The GGA-DFT describes the eigenvalues of the electronic states inaccurately, which results to underestimations of band gaps when compared with experiment. This underestimation is corrected by using the empirical model presented by Morales-García, et al. in 2017 for semiconductors and insulators [35]. The relation between experiment and G_0W_0 electronic band gap is given by

$$E_g(exp) = 0.998E_g(G_oW_o) + 0.014 \quad (1)$$

G_0W_0 is an approximation made to the self energy of a many body system of electrons. The self energy is expanded in terms of the single particle Green's function G and the screened Coulomb interaction W.

The relation between DFT(PBE) and G_oW_o band gap energy is

$$E_g(G_oW_o) = 1.358E_g(PBE) + 0.904 \quad (2)$$

From equation 1 and 2, the correlation between modelled experimental and DFT(PBE) band gap energy is derived to be

$$E_g(model) = 1.355284E_g(PBE) + 0.916192 \quad (3)$$

A linear relation between energy gap at p=0 and at any pressure p is given as,

$$E_g(p) = E_g(0) + kp \quad (4)$$

where k = pressure coefficient of the band gap defined by $k = dE_g/dp$ with units of eV/GPa.

For solid materials, the refractive index is related to the dielectric constant by the relation, $\varepsilon = n^2$. To calculate the dielectric constant of the alloy and its constituent binary compounds, we use Herve-Vandamme relation [36] given as

$$n^2 = 1 + \left(\frac{A}{E_g + B}\right)^2 \quad (5)$$

where A=13.6eV, is the hydrogen ionization energy and B= 3.47eV is a constant assumed to be the difference between the UV resonance energy and band gap energy.

In this work, we present the results of DFT(PBE) calculation for both structural and electronic properties of the solids. Band gaps obtained using empirical model are compared with the experimental band gap. The dielectric constants of the compounds are also calculated. Variation of the fundamental band gap of the alloy under pressure is investigated.

3. Results and Discussion

Table 1. Calculated Lattice Parameters, a(Å) of CaF_2, BaF_2 and $Ba_{0.50}Ca_{0.50}F_2$

System	a(Å)	a_{exp}(Å)
CaF_2	5.49	5.46
BaF_2	6.22	6.20
$Ba_{0.50}Ca_{0.50}F_2$	5.91	5.87

Table 2. Calculated Bulk Moduli, B(GPa) of CaF_2, BaF_2 and $Ba_{0.50}Ca_{0.50}F_2$

System	B(GPa)	B_{exp}(GPa)
CaF_2	82.1	82.71
BaF_2	57.8	59
$Ba_{0.50}Ca_{0.50}F_2$	64.1	—

Table 3. DFT(PBE), empirical model and experimental band gap energy of CaF_2, BaF_2 and $Ba_{0.50}Ca_{0.50}F_2$

System	Eg(eV)	Eg_{model}(eV)	Eg_{exp}(eV)
CaF_2	7.43	10.98	11.80
BaF_2	6.78	10.10	10.00
$Ba_{0.50}Ca_{0.50}F_2$	7.10	10.54	—

Table 4. Calculated dielectric constants, **ε,** of CaF_2, BaF_2 and $Ba_{0.50}Ca_{0.50}F_2$

System	ε	ε_{exp}
CaF_2	1.86	2.04
BaF_2	2.00	2.15
$Ba_{0.50}Ca_{0.50}F_2$	1.91	—

Table 1 shows the calculated lattice parameter of the binary compounds and their composites. The lattice parameters are calculated to be 6.22Å , 5.49Å and 5.91Å for BaF_2, CaF_2 and $Ba_{0.50}Ca_{0.50}F_2$ respectively. They compare well with experiment. The experimental lattice constants of CaF_2, BaF_2 and $Ba_{0.50}Ca_{0.50}F_2$ are taken from [37], [38] and [39] respectively. The value of lattice parameter for $Ba_{0.50}Ca_{0.50}F_2$ falls between that of CaF_2 and BaF_2. The bulk modulus of the alloy is given in table 2. For comparison purpose, the bulk moduli of the binary compounds are calculated. The experimental bulk modulus of CaF_2 is 82.71GPa [37] while that of BaF_2 is 59GPa [40]. The calculated bulk moduli are in good agreement with experimental values. The calculated bulk moduli are 57.8GPa, 82.1GPa and 64.1GPa for BaF_2, CaF_2 and $Ba_{0.50}Ca_{0.50}F_2$ respectively. As far as we know, there is no experimental value for the bulk modulus of the $Ba_{0.50}Ca_{0.50}F_2$.

Table 3 shows the band gap of the compounds obtained using PBE, empirical model and experiment. The band gap of CaF_2, BaF_2 and $Ba_{0.50}Ca_{0.50}F_2$ using the empirical model are 10.98eV, 10.10eV and 10.54eV respectively. The experimental band gap of CaF_2 and that of BaF_2 are taken from [41]. The band gap of the alloy intermediate between that of CaF_2 and BaF_2. The band gap obtained using empirical model compare well with experiment. The value of the band gap energy of $Ba_{0.50}Ca_{0.50}F_2$ indicates that this compound might be a good candidate for a frequency conversion material working in the ultraviolet region. $Ba_{0.50}Ca_{0.50}F_2$ can serve as an alternative to quartz (SiO_2) to use as a transparent medium for lasers. Silicon used in solar cells is a very shiny material, which can send photons bouncing away before they have done their job, so an antireflective coating is applied to reduce those losses. $Ba_{0.50}Ca_{0.50}F_2$ can be used in such antireflective coating.

Table 4 shows the dielectric constant of the compounds.

The dielectric constant of the binary compounds are comparable with experiment. The experimental dielectric constants are taken from [38]. $Ba_{0.50}Ca_{0.50}F_2$ is a dielectric and it can be used as optical fiber to transfer information from one point to another using light pulses. The information transmitted is essentially digital information generated by telephone systems, cable television companies, and computer systems.

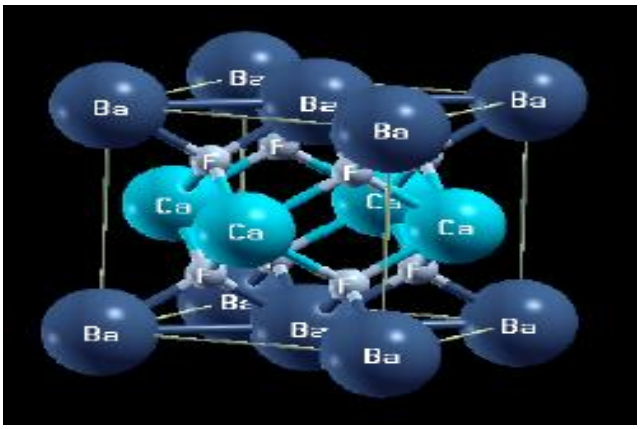

Figure 1. Crystal Structure of $Ba_{0.50}Ca_{0.50}F_2$

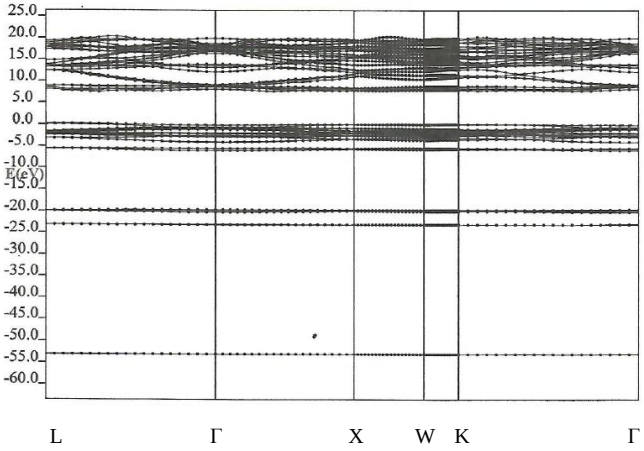

Figure 2. Band Structure of $Ba_{0.50}Ca_{0.50}F_2$

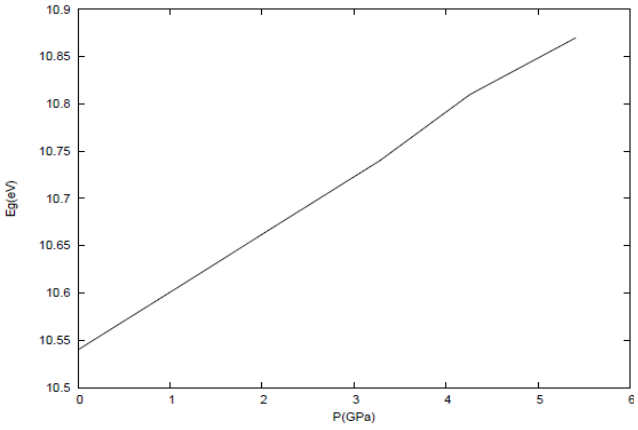

Figure 3. Variation of Band Gap Energy of $Ba_{0.50}Ca_{0.502}F_2$ with Pressure

Figure 1 shows the structure of the cations and anions in the $Ba_{0.50}Ca_{0.50}F_2$ crystal. The milling of fluorite BaF_2 and CaF_2 with x=0.50 results in the formation of $Ba_{0.50}Ca_{0.50}F_2$ crystallising in the cubic fluorite structure.

The band structure of $Ba_{0.50}Ca_{0.50}F_2$ is presented in Figure 2. The band gap which is indirect exists along L-Γ path. It is generally accepted that GGA electronic band structures are in good agreement with experiments in regard to the arrangement of energy levels and structure of bands [42].

There is linear variation of the band gap with pressure as seen in Figure 3. The band gap remains indirect for a pressure up to 5.41GPa. The pressure coefficient of the band gap is calculated to be 0.062eV/GPa.

4. Conclusions

In this work, we have reported the investigated electronic and structural properties of $Ba_{0.50}Ca_{0.50}F_2$ using the PP-PW method within GGA. At equilibrium, the band gap energy of the alloy was calculated to be 10.54eV, indicating its possible application in the UV region of light. It was also shown that for $Ba_{0.50}Ca_{0.50}F_2$, the band gap increases directly with pressure. From the graph, the pressure coefficient of the band gap was obtained. The dielectric constants of the binary compounds and alloy were determined. We have compared our results of structural parameters, band gaps and dielectric constants with experiment. Good agreement is found with the experimental values. There seem to be no previous works on the bulk modulus, band gap energy, dielectric constant and band structure of $Ba_{0.50}Ca_{0.50}F_2$, so our results can serve as reference data for this compound. We can consider the present findings as a prediction study, and hence will motivate more works on this material.

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