

Original Article

Lattice Dynamics of Mixed Divalent Metal Fluorides

Alice Bukola Olanipekun

Department of Physics, College of Pure and Applied Sciences, Caleb University, Lagos, Nigeria.

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Abstract - Density functional perturbation theory is used to study the lattice dynamics of $Ca_xCd_{1-x}F_2$, $Ca_xSr_{1-x}F_2$ and $Ca_xMg_{1-x}F_2$ where $x=0, 0.25, 0.50, 0.75$ and 1 . The result obtained for the dielectric constants of the alloys ranges from 2.157 to 2.609. The calculated Born effective charges of the cations (Ca, Cd, Mg and Sr) and anions (F) of the alloys when the atoms of the alloys are displaced in the presence of an electric field deviate from the nominal ionic values (+2 and -1 respectively). The anions' values range from -0.810 to -0.986 except for $Ca_{0.25}Cd_{0.75}F_2$ in which $Z = -1$, while the cations' values range from +2.354 to +2.566. The deviation is because the ionic bond in the alloy has a certain amount of covalent character, indicating a mixed ionic-covalent nature of the bond. They are weak ionic compounds. The dielectric constants calculations showed that the alloys are dielectric materials that can be used in designing capacitors and optical fibres.

Keywords - Born effective charge, Density Functional Perturbation Theory, Dielectric Constant, Ionic bond, Polarisation.

I. INTRODUCTION

The first derivative of the total energy E concerning electric field ϵ is the polarizability P , while the high-frequency dielectric permittivity tensor ϵ^∞ to the second derivative of the total energy concerning ϵ .

Polarizability is a measure of an atom's displacement by an electric field. Polarizability P is calculated from the electric field derivative of the energy [1,2].

$$P_\alpha = \frac{\delta E}{\delta \epsilon_\alpha}$$

where P_α is the polarizability induced along the α direction and ϵ_α is the electric field along the α direction. It is also given by the expression below

$$D_\alpha = \epsilon_\alpha + 4\pi P_\alpha$$

where D_α is an electrical displacement along the α direction.

The dielectric constant describes the polarizability per unit of electric field strength ϵ in that medium. The high-frequency dielectric constant $\epsilon_{\alpha\beta}^\infty$ is the second derivative of the energy concerning the electric field [3,4].

$$\epsilon_{\alpha\beta}^\infty = \frac{\delta^2 E}{\delta \epsilon_\alpha \delta \epsilon_\beta} = \delta_{\alpha\beta} + 4\pi \frac{\delta P_\alpha}{\delta \epsilon_\beta}$$

where $\delta_{\alpha\beta}$ is 1 if $\alpha=\beta$ and 0 if $\alpha \neq \beta$.

The dielectric constant of the alloys when the polarizability is along the x-direction, and the electric field is also applied in the x-direction is given as

$$\epsilon_{xx} = \delta_{xx} + 4\pi \frac{\delta P_x}{\delta \epsilon_x}$$

The dielectric constant of the alloys when the polarizability is along the y-direction, and the electric field is also applied in the y-direction is given as

$$\epsilon_{yy} = \delta_{yy} + 4\pi \frac{\delta P_y}{\delta \epsilon_y}$$

The dielectric constant of the alloys when the polarizability is along the z-direction, and the electric field is also applied in the z-direction is given as

$$\epsilon_{zz} = \delta_{zz} + 4\pi \frac{\delta P_z}{\delta \epsilon_z}$$

Born or dynamic effective charges are the induced charges when atoms of a system are displaced in an electric field, which causes changes in polarizability. They are the coupling constants important to the absorption of IR radiation by a material through the excitation of phonons [5]. Born effective charge can also be defined as the change in force induced on a given atom when an electric field is applied:

$$Z_{k\beta\alpha}^* = \Omega_0 \frac{\delta P_\beta}{\delta u_{k\alpha}(q=0)} = \frac{\delta F_{k\alpha}}{\delta \epsilon_\beta}$$

$F_{k\alpha}$ is the force induced on atom k along the β direction. $u_{k\alpha}$ is a unit displacement of the atom in the direction α in the presence of electric field ϵ_β along β direction.



Born effective charge [2,6] $Z_{k\alpha\beta}^*$ of atom k in the α,β direction is also given as

$$Z_{k\beta\alpha}^* = \frac{\delta^2 E}{\delta u_{k\alpha} \delta \epsilon_{l\beta}} = \Omega_0 \frac{\delta P_\beta}{\delta u_{k\alpha}}$$

Ω_0 is the volume of the unit cell, and P_β is the polarizability along the β direction.

Born effective charge when induced polarizability is along the x-direction and the atomic displacement is in the same direction is given as

$$Z_{xx} = \Omega_0 \frac{\delta P_x}{\delta u_x}$$

Born effective charge when induced polarizability is along y-direction and the atomic displacement is in the direction y is given as

$$Z_{yy} = \Omega_0 \frac{\delta P_y}{\delta u_y}$$

Born effective charge when induced polarizability is along z-direction and the atomic displacement is in the direction z is given as

$$Z_{zz} = \Omega_0 \frac{\delta P_z}{\delta u_z}$$

The electronic and structural properties of fluorite structures CaF_2 , SrF_2 and their ternary alloy $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ for concentrations $x = 0.25, 0.50, 0.75$ have been studied using first-principles calculation [7]. Olanipekun and Obaze calculated the electronic and structural properties of $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$ and $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$ [8]. Dielectric constants, Polarization, and Born effective charges of crystalline materials, including fluorides, have been studied by different authors [9-25]. Meena investigated the spectral and thermal properties of fluoride glasses [26]. The structure and optical properties of $\text{Ba}_{0.50}\text{Ca}_{0.50}\text{F}_2$ have been investigated [27]. However, not many of these properties have been calculated for the mixed divalent metal fluorides. In this work, we considered the lattice dynamics of these ternary alloys.

II. COMPUTATIONAL METHOD

Density Functional Perturbation Theory (DFPT) is used to obtain the vibrational frequencies from the force constants [28,29]. Different derivatives of the Density Functional Theory (DFT) total energy are obtained in this method by a self-consistent perturbation theory or linear response theory [30]. Specifically, by using only first-order perturbed wave functions, one may obtain up to third-order derivatives of the total energy. This is sufficient to obtain the short-range force constants, which are second derivatives of the total energy concerning displacements of the atoms, and the Born effective charges, which are derivatives concerning displacements of the atoms and the electric field. The second derivatives concerning electric field give the electronic dielectric constant or susceptibility in the zero-frequency limit.

The Born effective charges are required to describe the long-range forces in a polar material and provide the LO-TO splittings and the oscillator strengths of the active infrared modes. Using DFPT [28,29,31–33], we determined the polarizabilities, dielectric constants and Born effective charges. DFPT offers a way to obtain physical properties from the total energy derivatives concerning a certain perturbation.

All calculations are performed using QUANTUM ESPRESSO (QE), which implements the DFPT on plane waves combined with pseudopotentials to represent the interaction of the valence electrons with the ions. We used Ultra-soft Vanderbilt type pseudopotentials [34] as supplied by G. Kresse and J. Hafner [35].

The plane wave cut-off energy used is 60Ry, and a $6 \times 6 \times 6$ Monkhorst-Pack k-point mesh is used for Brillouin zone integrations. We used the generalized gradient approximation of Perdew and Wang (GGA-PW) parametrization for the exchange-correlation potential [36].

III. RESULTS

Table 1. High-frequency dielectric constants of the Divalent Metal Fluorides

Systems	ϵ_{xx}	ϵ_{yy}	ϵ_{zz}	ϵ
SrF_2	2.201	2.201	2.201	2.201
CaF_2	2.241	2.241	2.241	2.241
CaF_2	2.778	2.778	2.778	2.778

Table 2. Polarizability (\AA^3) of the Divalent Metal Fluorides

Systems	P_{xx}	P_{yy}	P_{zz}	P
CaF_2	4.055	4.055	4.055	4.055
SrF_2	4.701	4.701	4.701	4.701
CaF_2	5.726	5.726	5.726	5.726

Table 3. Effective Charges in the Divalent Metal Fluorides

Effective Charges	Cations	Anion	Anion
	Ca	F	F
Z_{xx}	2.414	-1.071	-1.071
Z_{yy}	2.414	-1.071	-1.071
Z_{zz}	2.414	-1.071	-1.071
Z	2.414	-1.071	-1.071
Sr F F			
Z_{xx}	2.201	-1.091	-1.091
Z_{yy}	2.201	-1.091	-1.091
Z_{zz}	2.201	-1.091	-1.091
Z	2.201	-1.091	-1.091
Cd F F			
Z_{xx}	2.565	-1.111	-1.111
Z_{yy}	2.565	-1.111	-1.111
Z_{zz}	2.565	-1.111	-1.111
Z	2.565	-1.111	-1.111

Table 4. Comparison of High-frequency dielectric constants and Effective charge of cation calculated for CaF₂ with those of other works and experiments

Methods	ε	Z
Present work (GGA-PW)	2.241	2.414
^a nd	2.270	2.370
^b TM-GGA	2.02	2.18
^c Expt	2.045	–

- a. Generalized Gradient Approximation (GGA) of Perdew, Burke and Ernzerhof [37]
- b. GGA using Troullier-Martins pseudopotentials [9]
- c. Raman and infrared data [38, 39]

Table 5. Effective Charges on Cations of Ca_xCd_{1-x}F₂ Alloys

Systems	Cations	Z _{xx}	Z _{yy}	Z _{zz}	Z
Ca _{0.25} Cd _{0.75} F ₂	Ca	2.580	2.580	2.580	2.580
	Cd	2.786	2.596	2.596	2.659
	Cd	2.596	2.786	2.596	2.659
	Cd	2.596	2.596	2.786	2.659
Ca _{0.50} Cd _{0.50} F ₂	Ca	2.541	2.680	2.680	2.634
	Ca	2.541	2.685	2.685	2.637
	Cd	2.268	2.987	2.990	2.748
	Cd	2.268	2.990	2.987	2.748
Ca _{0.75} Cd _{0.25} F ₂	Ca	2.453	2.453	2.717	2.541
	Ca	2.452	2.251	2.885	2.529
	Ca	2.251	2.452	2.885	2.529
	Cd	2.369	2.369	2.078	2.605

Table 6. Effective Charges on Cations of Ca_xSr_{1-x}F₂ Alloys

Systems	Cations	Z _{xx}	Z _{yy}	Z _{zz}	Z
Ca _{0.25} Sr _{0.75} F ₂	Ca	2.497	2.497	2.497	2.497
	Sr	2.606	2.585	2.585	2.592
	Sr	2.585	2.606	2.585	2.592
	Sr	2.585	2.585	2.606	2.592
Ca _{0.50} Sr _{0.50} F ₂	Ca	2.381	2.685	2.685	2.584
	Ca	2.381	2.693	2.693	2.589
	Sr	2.394	2.767	2.767	2.644
	Sr	2.394	2.772	2.772	2.644
Ca _{0.75} Sr _{0.25} F ₂	Ca	2.511	2.511	2.481	2.501
	Ca	2.511	2.481	2.511	2.501
	Ca	2.481	2.511	2.511	2.501
	Sr	2.599	2.599	2.599	2.599

Table 7. Effective Charges on Cations of Ca_xMg_{1-x}F₂ Alloys

Systems	Cations	Z _{xx}	Z _{yy}	Z _{zz}	Z
Ca _{0.25} Mg _{0.75} F ₂	Ca	2.479	2.479	2.479	2.479
	Mg	2.278	2.392	2.392	2.354
	Mg	2.392	2.278	2.392	2.354
	Mg	2.392	2.392	2.278	2.354
Ca _{0.50} Mg _{0.50} F ₂	Ca	2.281	2.708	2.708	2.566
	Ca	2.281	2.704	2.704	2.563
	Mg	2.268	2.608	2.608	2.495
	Mg	2.268	2.608	2.608	2.495
Ca _{0.75} Mg _{0.25} F ₂	Ca	2.472	2.472	2.551	2.498
	Ca	2.472	2.551	2.472	2.498
	Ca	2.551	2.472	2.472	2.498
	Mg	2.422	2.422	2.422	2.422

Table 8. Effective Charges on Anions of Ca_xCd_{1-x}F₂ Alloys

Systems	Z _{xx}	Z _{yy}	Z _{zz}	Z
Ca _{0.25} Cd _{0.75} F ₂	-1.000	-1.000	-1.000	-1.000
Ca _{0.50} Cd _{0.50} F ₂	-1.209	-0.708	-0.708	-0.875
Ca _{0.75} Cd _{0.25} F ₂	-1.201	-1.201	-0.524	-0.975

Table 9. Effective Charges on Anions of Ca_xSr_{1-x}F₂ Alloys

Systems	Z _{xx}	Z _{yy}	Z _{zz}	Z
Ca _{0.25} Sr _{0.75} F ₂	-0.986	-0.986	-0.986	-0.986
Ca _{0.50} Sr _{0.50} F ₂	-1.201	-0.702	-0.702	-0.868
Ca _{0.75} Sr _{0.25} F ₂	-1.975	-1.975	-0.975	-0.975

Table 10. Effective Charges on Anions of Ca_xMg_{1-x}F₂ Alloys

Systems	Z _{xx}	Z _{yy}	Z _{zz}	Z
Ca _{0.25} Mg _{0.75} F ₂	-0.893	-0.893	-0.893	-0.893
Ca _{0.50} Mg _{0.50} F ₂	-1.145	-0.643	-0.643	-0.810
Ca _{0.75} Mg _{0.25} F ₂	-0.950	-0.950	-0.950	-0.950

Table 11: Dielectric Constants of the Mixed Divalent Metal Fluorides

Systems	ε _{xx}	ε _{yy}	ε _{zz}	ε
Ca _{0.25} Cd _{0.75} F ₂	2.609	2.609	2.609	2.609
Ca _{0.50} Cd _{0.50} F ₂	2.490	2.439	2.439	2.456
Ca _{0.75} Cd _{0.25} F ₂	2.371	2.371	2.310	2.351
Ca _{0.25} Sr _{0.75} F ₂	2.205	2.205	2.205	2.205
Ca _{0.50} Sr _{0.50} F ₂	2.232	2.185	2.185	2.201
Ca _{0.75} Sr _{0.25} F ₂	2.225	2.225	2.225	2.225
Ca _{0.25} Mg _{0.75} F ₂	2.157	2.157	2.157	2.157
Ca _{0.50} Mg _{0.50} F ₂	2.211	2.166	2.166	2.181
Ca _{0.75} Mg _{0.25} F ₂	2.222	2.222	2.222	2.222

Table 12. Polarizability (\AA^3) of the Mixed Divalent Metal Fluorides

Systems	P_{xx}	P_{yy}	P_{zz}	P
$\text{Ca}_{0.25}\text{Cd}_{0.75}\text{F}_2$	20.736	20.736	20.736	20.736
$\text{Ca}_{0.50}\text{Cd}_{0.50}\text{F}_2$	19.197	28.536	18.536	18.756
$\text{Ca}_{0.75}\text{Cd}_{0.25}\text{F}_2$	17.766	17.766	16.973	17.502
$\text{Ca}_{0.25}\text{Sr}_{0.75}\text{F}_2$	18.155	18.155	18.155	18.155
$\text{Ca}_{0.50}\text{Sr}_{0.50}\text{F}_2$	17.799	17.119	17.119	17.346
$\text{Ca}_{0.75}\text{Sr}_{0.25}\text{F}_2$	16.910	16.910	16.910	16.910
$\text{Ca}_{0.25}\text{Mg}_{0.75}\text{F}_2$	12.492	12.492	12.492	12.492
$\text{Ca}_{0.50}\text{Mg}_{0.50}\text{F}_2$	14.107	13.588	13.588	13.761
$\text{Ca}_{0.75}\text{Mg}_{0.25}\text{F}_2$	15.157	15.157	15.157	15.157

IV. DISCUSSION

Table 1 summarises the high-frequency dielectric constant of the divalent metals. Table 2 presents the results for the polarizability of the binary compounds. Born effective charges for the three binary compounds are given in Table 3. Table 4 compares dielectric constants and effective charges of cation calculated for CaF_2 with those of other works and experiments. There exists good agreement [37,9,38,39]. Tables 5-7 show the effective charges for cations in $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$, $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$ and $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ ternary alloys. The Born effective charge tensors for anions in the $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$, $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$ and $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ alloys are shown in Tables 8, 9, 10, respectively. Table 11 shows the dielectric constants for the cubic fluorite alloys. Table 12 presents the polarizability of the mixed divalent metal fluorides.

The dielectric constant of the fluorides increases from SrF_2 to CdF_2 . From lower to higher bulk modulus. The dielectric constant is directly proportional to bulk modulus and inversely proportional to compressibility. The polarizability of the fluorides increases from CaF_2 to CdF_2 . Polarizability increases down on columns of the periodic table [40]. Likewise, larger molecules are generally more polarizable than smaller ones.

The Born effective charges of the cubic fluorite structures are isotropic, i.e. $Z_{xx} = Z_{yy} = Z_{zz}$. The Born effective charges show values different from those of nominal charges of +2 and -1 for cations and anions, respectively. The Born effective charges have zero component for the non-diagonal elements. The Born effective charge on cation of the mixed divalent metal fluorides is anisotropic (i.e. $Z_{xx} = Z_{yy} \neq Z_{zz}$ or $Z_{yy} = Z_{zz} \neq Z_{xx}$ or $Z_{xx} = Z_{zz} \neq Z_{yy}$) except for Ca ion which is isotropic in $\text{Ca}_{0.25}\text{Cd}_{0.75}\text{F}_2$, $\text{Ca}_{0.25}\text{Mg}_{0.75}\text{F}_2$ and $\text{Ca}_{0.25}\text{Sr}_{0.75}\text{F}_2$, (i.e. $Z_{xx} = Z_{yy} = Z_{zz}$). The Born effective charges on cations of the alloys are larger than the nominal ionic value of +2. This is a result of the interactions of the cations with neighbouring cation-anion bonds. This leads to the transfer of electrons from the cation to other neighbouring anions. The Born effective charge tensors for anions in the $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$,

$\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$ and $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ alloys were also investigated. The resultant effective charges are generally smaller than the nominal charge of -1 on Fluorine ion (F^-). Due to their positive charges, the cations attract the outer electrons of the F and cause deformation of the outer electron orbital towards themselves. The cations are said to polarize the F^- . Since some of the F- electrons are removed to a greater distance from their nucleus, the negative charge on the anion is decreased. As a result of the sharing (covalency), the F atoms acquire a partial negative charge. Thus, the ionic bond in the alloys has a certain amount of covalent character, indicating a mixed ionic-covalent nature of the bond. The deviation of the Born effective charge of the cation and anion from the nominal ionic values indicates that all the alloys are weak ionic compounds with a delocalized structure of the electronic charge distribution. Such an abnormality is observed in other weakly ionic compounds [41].

The measured dielectric constant of the alloys ranges from 2.310 to 2.609 for $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$, 2.185 to 2.232 for $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ and 2.157 to 2.222 for $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$. The average dielectric constant for $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$ decreases as the concentration of Ca increases, whereas it increases as the concentration of Ca increases in $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$. The measured polarizability of the alloys ranges from 16.973 to 20.736 for $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$, 16.910 to 18.155 for $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ and 12.492 to 15.157 for $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$. The average polarizability for $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$ and $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ decreases as the concentration of Ca increases, whereas it increases as the concentration of Ca increases in $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$.

V. CONCLUSION

The Born effective charge tensors, the dielectric permittivity tensors and polarizability have been calculated using DFPT. The polarizability of the fluorides increases from CaF_2 to CdF_2 . From lower to higher atomic numbers. The Born effective charges deviate from values of nominal charges of +2 and -1 for cations and anions, respectively. The deviation is also noticed in the ternary alloys indicating that they are weak ionic compounds with delocalized electronic structures, as revealed by their high polarizabilities. The low dielectric constants in $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$, $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ and $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$ are mainly due to high-frequency phonons. The dielectric constant and polarizability follow the following order: $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2 > \text{Ca}_x\text{Sr}_{1-x}\text{F}_2 > \text{Ca}_x\text{Mg}_{1-x}\text{F}_2$ for the corresponding concentration (i.e. $x = 0.25, 0.50$ and 0.75). The dielectric constant and polarizability of the fluorites increase from $\text{Ca}_x\text{Mg}_{1-x}\text{F}_2$ to $\text{Ca}_x\text{Cd}_{1-x}\text{F}_2$. From lower to higher atomic numbers. Hence, both constants are sensitive to the atomic size of the alloys. The dielectric constants calculation showed that the alloys are dielectric materials that can be used for designing capacitors, and using them as optical fibres is an obvious application.

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