ISSN 2350-1030

International Journal of Recent Research in Physics and Chemical Sciences (IJRRPCS)
Vol. 10, Issue 1, pp: (10-19), Month: April 2023 – September 2023, Available at: www.paperpublications.org

# Zone Center Phonon Frequencies of Ternary Mixed Fluorides

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**DOI:** https://doi.org/10.5281/zenodo.8000895

**Published Date: 03-June-2023**

***Abstract:*** **Crystals respond to perturbations like displacement, electric field and stress. The responses are described by properties like dielectric constant, polarization, phonon frequency and so on. Phonons defined as periodic excitation in solids are seen as acoustic waves. Most important phonon applications use frequencies that are higher than those human can hear. High frequency phonons are used for imaging of many things. The study of phonon frequencies of different solids is therefore essential. Although phonon frequency of many materials have been investigated, phonon frequencies of divalent metal mixed fluorides seem to be missing in the literatures. This paper deals with the calculation of phonon frequencies of mixed divalent metal fluorides by using Density Functional Pertubation Theory (DFPT) within the Generalized Gradient Approximations. Phonon frequencies of some constituent binary fluorides are calculated and compared with experimental values, reasonable agreement is found. Infrared and Raman active phonons of nine ternary alloys ($Ca_xCd_{1-x}F_2$, $Ca_xMg_{1-x}F_2$ and $Ca_xSr_{1-x}F_2$) with composition range $0<x<1$are investigated. Each alloy has 36 distinct phonon modes at the center (Γ) of the Brillouin zone. There are 36 phonon modes which are divided into Raman active, Infrared active, Acoustic and Silent phonon modes.Frequencies of the acoustic and optical phonons of the alloys investigated at Γ point are of the order of $10^{12}$Hz, indicating their usefulness in building phonon lasers that emit sound in much the same way that optical lasers emit light. The limitation of this research is that there seems to be no experimental data to compare the phonon frequencies of the mixed ternary fluoride alloys with. However, this research can be used as a reference data.**

***Keywords:*** **Phonons, Ternary Fluorides, Density Functional Pertubation Theory, Phonon frequency.**

## I. INTRODUCTION

Phonons are vibrational modes propagating in a crystal lattice [1], such as the atomic lattice of a solid. They are characterized by a vibrational frequency and by the displacements of the atoms. The study of phonons is important because phonons play an important role in heat conductivity and electrical conductivity. The properties of long-wavelength phonons give rise to sound in solids- hence the name phonon. Phonon frequencies form dispersion bands similar to electronic states [2, 3]. For system with N atoms in the unit cell, there are 3N phonons for a given wave vector. Phonon frequencies are the square roots of its eigen-values while the atomic displacements are related to its eigen-vectors [4]. In terms of the dispersion relations for phonons, acoustic phonons exhibit linear dispersion, i.e., a linear relationship between frequency and phonon wave vector, in the long-wavelength limit. The frequencies of acoustic phonons tend to zero with longer wavelength, and correspond to sound waves in the lattice. Longitudinal and transverse acoustic phonons are abbreviated as LA and TA phonons, respectively [5]. Phonon frequencies are important in explaining physical properties such as superconductivity, phase transitions, heat conduction and ferroelectricity which conribute to the efficiency of useful materials that are being discovered in our world. Optical, dielectric and vibrational properties of alkaline earth fluorides were calculated by using experimental methods [6,7]. The electronic and dynamical properties of $CaF_2$ and $CdF_2$ have been studied from first principles [8-10]. The lattice dynamics of $CaF_2$ using the PBE functional and $CeO_2$ using the HSE hybrid functional were calculated [11]. Phonon related properties of some ternary alloys using both theoretical and experimental methods have been reported [12-21]. Mpourazanis and his colleagues studied the vibrational and elastic properties of Sr-Mg fluorophosphate glasses by using vibrational and ultrasonic spectroscopies in 2019 [22]. Mateusz et al. predicted the crystal

structures of ternary silver fluorides $AgMF_4$ (M = Cu, Ni, Co) up to 20 GPa by using evolutionary algorithm with DFT calculations [23]. Zhu and his coworkers analysed the thermodynamic properties of Cu-Pb-F ternary system using first principles and found to be in agreement with phonon calculation [24]. In some previous papers, we have presented the electronic, structural and lattice dynamics of some mixed fluorites systems [25-29]. Group II metal fluorides and their ternary alloys are useful as optical materials. For more exploitation of the ternary fluoride alloys, this paper will present a study on the phonon frequencies, analysis and potential application of the mixed fluorides which include $Ca_xCd_{1-x}F_2$, $Ca_xMg_{1-x}F_2$ and $Ca_xSr_{1-x}F_2$ with varying composition $0<x<1$ by using DFPT.

## II. METHOD

Many physical properties depend on a crystal response to some perturbations. Examples include polarization, phonon frequencies, Raman intensities and infra-red absorption cross-sections and so on. Density functional perturbation theory (DFPT) is a technique used for the calculation of physical properties within the density functional theory (DFT) [30], System responses to perturbations can be calculated using DFT with the inclusion of perturbing potential. However, the methods involve calculation of the system response at different energies, which makes the method tedious and unattractive.

DFPT is based on the works of Baroni and Gonze [31-33]. The two methods are equivalent, although there are differences in their implementation. The Baroni formalism involves a series of equations solved self-consistently using Green's function methods; the Gonze formalism involves a perturbative expansion of the Kohn-Sham energy functional, resulting in a variational problem for even orders of expansion related to the zeroth order problem.

The Born effective charges, the dielectric tensors and the dynamical matrices are computed using the DFPT. In DFPT the energy is analytically expanded as a Taylor series, around small perturbation (λ). The series are well defined and converged. The dynamical matrices are 2nd-order derivatives of the total energy with respect to atomic displacements. Hence, they can be accurately and efficiently computed using DFPT.

The perturbations can be atomic displacements, electric fields, lattice strain and so on or combinations. Each term of the series is related to a physical property and is obtained by calculating the relevant derivative of the total energy with respect to these perturbations.

$$E(\lambda) = E(0) + \sum_i \frac{\delta E}{\delta \lambda_i}\lambda_i + \sum_{ij} \frac{\delta^2 E}{\delta \lambda_i \delta \lambda_j}\lambda_i\lambda_j + \sum_{ijk} \frac{\delta^3 E}{\delta \lambda_i \delta \lambda_j \delta \lambda_k}\lambda_i\lambda_j\lambda_k + \cdots \qquad (1)$$

The first term of the above series stands for the ground-state energy. If the perturbation (λ) represents the atomic displacements then the derivative in the second term corresponds to the forces on the atoms. This term is zero at equilibrium. The third term is the second derivative of the total energy with respect to atomic displacements which is equal to a matrix of size 3xN by 3xN where N is the number of atoms per unit cell and whose entries are the inter-atomic force constants. By diagonalization, the matrix produces the phonon frequencies and the phonon eigenvectors, their corresponding displacements. The diagonalization gives the frequencies of phonon visible in Raman (g-modes), infrared (u-modes) and of the silent modes. The remaining higher terms correspond to other physical properties like anharmonic elastic constants, phonon-phonon interaction, Gruneisen parameters etc.

## III. RESULTS

**Table 1. Vibrational Frequencies for the Γ-point Phonons in the Divalent Metal Fluorides**

| Systems | LO Present | LO Expt | TO Present | TO Expt |
|---|---|---|---|---|
| $CaF_2$ | 454 | 463[a] | 242 | 257[a] |
| $SrF_2$ | 273 | | 209 | |
| $CdF_2$ | 362 | 374[b] | 196 | 217[b] |

LO - Longitudinal Optical Phonon Frequency

TO - Transverse Optical Phonon Frequency

[a]Kaiser et al., 1962 and Russell, 1965[34, 35]

[b] Ferraro et al., 1971[36]

**Table.2. Frequencies of Raman Active Optical Phonons of $Ca_xCd_{1-x}F_2$ at Γ**

| System | Phonon mode | Number | Frequency, ν $(cm)^{-1}$ |
|---|---|---|---|
| $Ca_{0.25}Cd_{0.75}F_2$ | $T_{2g}$ | 3<br>3 | 153.4<br>298.2 |
| | $A_{1g}$ | 1 | 382.4 |
| | $E_g$ | 2 | 388.2 |
| | | | |
| $Ca_{0.50}Cd_{0.50}F_2$ | $E_g$ | 2<br>2<br>2 | 146.2<br>151.6<br>304.8 |
| | $B_{2g}$ | 2<br>1 | 180.5<br>307.7 |
| | $A_{1g}$ | 1<br>1 | 383.0<br>389.5 |
| | $B_{1g}$ | 1 | 391.0 |
| | | | |
| $Ca_{0.75}Cd_{0.25}F_2$ | $B_{2g}$ | 1<br>1 | 141.8<br>309.7 |
| | $E_g$ | 2<br>2<br>2 | 143.9<br>184.6<br>335.9 |
| | $B_{1g}$ | 1 | 382.7 |
| | $A_{1g}$ | 1<br>1 | 385.2<br>392.2 |

**Table 3. Frequencies of Infrared Active Optical and Acoustic Phonons of $Ca_xCd_{1-x}F_2$ at Γ**

| System | Phonon mode | Number | Frequency, ν $(cm)^{-1}$ |
|---|---|---|---|
| $Ca_{0.25}Cd_{0.75}F_2$ | $T_{1u}$ | 3 | 20.0 |
| | | 3 | 126.3 |
| | | 3 | 202.2 |
| | | 3 | 248.0 |
| | | 3 | 334.4 |
| | | | |
| $Ca_{0.50}Cd_{0.50}F_2$ | $A_{2u}$ | 2 | 12.9 |
| | | 2 | 180.5 |
| | | 1 | 204.6 |
| | | 1 | 274.0 |
| | | 1 | 328.4 |
| | $E_u$ | 2 | 22.3 |
| | | 2 | 125.1 |
| | | 2 | 136.8 |
| | | 2 | 238.9 |
| | | 2 | 271.7 |
| | | 2 | 331.8 |
| | | 2 | 335.8 |
| | | | |
| $Ca_{0.75}Cd_{0.25}F_2$ | $A_{2u}$ | 1 | 21.8 |
| | | 1 | 133.3 |

| | | | |
|---|---|---|---|
| | | 1 | 238.2 |
| | | 1 | 293.0 |
| | | 1 | 329.0 |
| | $E_u$ | 2 | 32.0 |
| | | 2 | 132.8 |
| | | 2 | 183.6 |
| | | 2 | 238.2 |
| | | 2 | 295.1 |
| | | 1 | 327.6 |
| | | 1 | 329.9 |

**Table 4. Frequencies of Infrared Active Optical and Acoustic Phonons of $Ca_xSr_{1-x}F_2$ at Γ**

| System | Phonon mode | Number | Frequency, ν $(cm)^{-1}$ |
|---|---|---|---|
| $Ca_{0.25}Sr_{0.75}F_2$ | $T_{2g}$ | 3<br>3 | 131.4<br>291.2 |
| | $A_{1g}$ | 1 | 330.2 |
| | $E_g$ | 2 | 367.0 |
| | | | |
| $Ca_{0.50}Sr_{0.50}F_2$ | $B_{2g}$ | 1<br>1 | 75.9<br>294.1 |
| | $E_{2g}$ | 2<br>2<br>2 | 149.7<br>174.2<br>307.6 |
| | $A_{1g}$ | 1<br>1 | 333.7<br>364.6 |
| | $B_{1g}$ | 1 | 390.0 |
| | | | |
| $Ca_{0.75}Sr_{0.25}F_2$ | $T_{2g}$ | 3<br>3 | 193.9<br>311.8 |
| | $E_g$ | 2 | 355.2 |
| | $A_{1g}$ | 1 | 403.8 |

**Table 5. Frequencies of Infrared Active Optical and Acoustic Phonons of $Ca_xSr_{1-x}F_2$ at Γ**

| System | Phonon mode | Number | Frequency, ν $(cm)^{-1}$ |
|---|---|---|---|
| $Ca_{0.25}Sr_{0.75}F_2$ | $T_{1u}$ | 3 | -8.5 |
| | | 3 | 134.2 |
| | | 3 | 184.7 |
| | | 3 | 229.1 |
| | | 3 | 287.9 |
| | | | |
| $Ca_{0.50}Sr_{0.50}F_2$ | $A_{2u}$ | 1 | 23.3 |
| | | 1 | 147.7 |
| | | 1 | 212.6 |
| | | 1 | 252.9 |
| | | 1 | 264.6 |
| | $E_u$ | 2 | 23.6 |

| | | | |
|---|---|---|---|
| | | 2 | 144.6 |
| | | 2 | 144.9 |
| | | 2 | 187.9 |
| | | 2 | 242.1 |
| | | 2 | 307.7 |
| | | 2 | 314.3 |
| | | | |
| $Ca_{0.75}Sr_{0.25}F_2$ | $T_{1u}$ | 3 | 9.5 |
| | | 3 | 156.6 |
| | | 3 | 209.9 |
| | | 3 | 277.5 |
| | | 3 | 337.0 |

**Table 6. Frequencies of Raman Active Optical Phonons of $Ca_xMg_{1-x}F_2$ at Γ**

| System | Phonon mode | Number | Frequency, ν $(cm)^{-1}$ |
|---|---|---|---|
| $Ca_{0.25}Mg_{0.75}F_2$ | $T_{2g}$ | 3<br>3 | 166.5<br>376.3 |
| | $E_g$ | 2 | 406.1 |
| | $A_{1g}$ | 1 | 484.6 |
| | | | |
| $Ca_{0.50}Mg_{0.50}F_2$ | $E_g$ | 2<br>2<br>2 | 57.1<br>139.1<br>360.5 |
| | $B_{2g}$ | 1<br>1 | 254.5<br>338.7 |
| | $B_{1g}$ | 1 | 364.2 |
| | $A_{1g}$ | 1<br>1 | 413.6<br>453.2 |
| | | | |
| $Ca_{0.75}Mg_{0.25}F_2$ | $T_{2g}$ | 3<br>3 | -30.7<br>334.6 |
| | $A_{1g}$ | 1 | 357.8 |
| | $E_g$ | 2 | 413.7 |

**Table 7. Frequencies of Infrared Active Optical and Acoustic Phonons of $Ca_xMg_{1-x}F_2$ at Γ**

| System | Phonon mode | Number | Frequency, ν $(cm)^{-1}$ |
|---|---|---|---|
| $Ca_{0.25}Mg_{0.75}F_2$ | $T_{1u}$ | 3 | 30.5 |
| | | 3 | 161.0 |
| | | 3 | 243.4 |
| | | 3 | 340.7 |
| | | 3 | 460.9 |
| | | | |
| $Ca_{0.50}Mg_{0.50}F_2$ | $A_{2u}$ | 1 | -13.9 |
| | | 1 | 202.4 |
| | | 1 | 206.6 |
| | | 1 | 263.4 |
| | | 1 | 412.2 |

ISSN 2350-1030

International Journal of Recent Research in Physics and Chemical Sciences (IJRRPCS)
Vol. 10, Issue 1, pp: (10-19), Month: April 2023 – September 2023, Available at: www.paperpublications.org

| | | | |
|---|---|---|---|
| | $E_u$ | 2 | -10.2 |
| | | 2 | 49.4 |
| | | 2 | 178.9 |
| | | 2 | 241.7 |
| | | 2 | 289.0 |
| | | 2 | 392.1 |
| | | 2 | 410.9 |
| | | | |
| $Ca_{0.75}Mg_{0.25}F_2$ | $T_{1u}$ | 3 | 28.5 |
| | | 3 | 67.7 |
| | | 3 | 232.2 |
| | | 3 | 315.5 |
| | | 3 | 363.6 |

## IV. DISCUSSION

Table 1 shows the vibrational frequencies for the Γ-point phonons in $CaF_2$, $SrF_2$ and$CdF_2$. There are three acoustic phonon modes and six optical phonon modes of the cubic fluorites. At Γ point, the three acoustic modes are degenerate with$T_{1u}$ symmetry. The six optical modes form two triple modes: three degenerate Raman (R) active modes with $T_{2g}$ symmetry, two degenerate infrared-activeTO $T_{1u}$ symmetry, and one infrared-active non-degenerate LO $T_{1u}$ symmetry. Infrared (IR) active modes splits into TO and LO at long wavelengths. LO and TO mean longitudinal and transverse optical phonons respectively. It is clear that our calculated frequencies for the $T_{1u}$ LO-TO modes are in overall fair agreement with experiments [31-33]. The computed phonon frequencies of the alloys are reported in Tables 2-7. All theu modes are infrared active and the g modes are Raman active [37]. The phonon frequencies of the alloys are obtained from the inter-atomic force constants matrix. Since there are 12 atoms in the ternary alloys structure, there would be a total of 36 modes of vibrations. The number and types of the different modes can be assigned by symmetry considerations.

$Ca_{0.25}Cd_{0.75}F_2$, $Ca_{0.25}Cd_{0.75}F_2$and $Ca_{0.25}Cd_{0.75}F_2$ have the same Raman active ($T_{2g}$, $A_{1g}$ and $E_g$) and Infrared active ($T_{1u}$) phonon modes. $Cd_{0.75}F_2$, $Ca_{0.25}Cd_{0.75}F_2$ and $Ca_{0.25}Cd_{0.75}F_2$ have the same infrared active ($A_{2u}$ and $E_u$) phonon modes while $Ca_{0.50}Cd_{0.50}F_2$ and $Ca_{0.50}Mg_{0.50}F_2$ have the same Raman active ($E_g$, $B_{2g}$, $A_{1g}$ and $B_{1g}$) phonon modes. $Ca_{0.75}Sr_{0.25}F_2$ and $Ca_{0.75}Mg_{0.25}F_2$ have the same Raman active ($T_{2g}$, $A_{1g}$ and $E_g$) and Infrared active ($T_{1u}$) phonon modes.

The representation of the 36 phonon modes at the center of the zone for each concentration of x in the ternary alloys are given below.

$Ca_{0.25}Cd_{0.75}F_2$:

$6T_{2g} + 1A_{1g} + 2E_g$ (9 Raman active Optical Phonons)

$3T_{1u}$ (3 Acoustic Phonons)

$12T_{1u}$ (12 Infrared active Optical Phonons)

$2E_u + 6T_{2u} + 3T_{1g} + 1A_{2u}$ (12 silent Phonons)

$Ca_{0.50}Cd_{0.50}F_2$:

$6E_g + 3B_{2g} + 2A_{1g} + 1B_{1g}$(12 Raman active Optical Phonons)

$1A_{2u} + 2E_u$ (3 Acoustic Phonons)

$5A_{2u} + 10E_u$ (15 Infrared active Optical Phonons)

$1A_{1u} + 2B_{1u} + 2B_{2u} + 1A_{2g}$ (6 silent Phonons)

$Ca_{0.75}Cd_{0.25}F_2$:

$2B_{2g} + 6E_g + 1B_{1g} + 2A_{1g}$ (11 Raman active Optical Phonons)

$1A_u + 2E_u$ (3 Acoustic Phonons)

$4A_{2u} + 12E_u$ (16 Infrared active Optical Phonons)

$2B_{1u} + 6A_{1u} + 1A_{2g} + 2B_{2u}$ (6 silent Phonons)

$Ca_{0.25}Sr_{0.75}F_2$:

$6T_{2g} + 1A_{1g} + 2E_g$ (9 Raman active Optical Phonons)

$3T_{1u}$ (3 Acoustic Phonons)

$12T_{1u}$ (12 Infrared active Optical Phonons)

$1A_{2u} + 6T_{2u} + 2E_u + 3T_{1g}$ (12 silent Phonons)

$Ca_{0.50}Sr_{0.50}F_2$:

$2B_{2g} + 6E_{2g} + 2A_{1g} + 1B_{1g}$(11 Raman active Optical Phonons)

$1A_{2u} + 2E_u$ (3 Acoustic Phonons)

$4A_{2u} + 12E_u$ (16 Infrared active Optical Phonons)

$2B_{1u} + 2B_{2u} + 1A_{1u} + 1A_{2g}$ (6 silent Phonons)

$Ca_{0.75}Sr_{0.25}F_2$:

$6T_{2g} + 2E_g + 1A_{1g}$ (9 Raman active Optical Phonons)

$3T_{1u}$ (3 Acoustic Phonons)

$12T_{1u}$ (12 Infrared active Optical Phonons)

$2E_u + 3T_{1g} + 6T_{2u} + 1A_{2u}$ (12 silent Phonons)

$Ca_{0.25}Mg_{0.75}F_2$:

$6T_{2g} + 2E_g + 1A_{1g}$ (9 Raman active Optical Phonons)

$3T_{1u}$ (3 Acoustic Phonons)

$12T_{1u}$ (12 Infrared active Optical Phonons)

$2E_u + 3T_{1g} + 6T_{2u} + 1A_{2u}$ (12 silent Phonons)

$Ca_{0.50}Mg_{0.50}F_2$:

$6E_g + 2B_{2g} + 1B_{1g} + 2A_{1g}$(11 Raman active Optical Phonons)

$1A_{2u} + 2E_u$ (3 Acoustic Phonons)

$4A_{2u} + 12E_u$ (16 Infrared active Optical Phonons)

$1A_{1u} + 1A_{2g} + 2B_{1u} + 2B_{2u}$ (6 silent Phonons)

$Ca_{0.75}Mg_{0.25}F_2$:

$6T_{2g} + 1A_{1g} + 2E_g$ (9 Raman active Optical Phonons)

$3T_{1u}$ (3 Acoustic Phonons)

$12T_{1u}$ (12 Infrared active Optical Phonons)

$1A_{2u} + 2E_u + 6T_{2u} + 3T_{1g}$ (12 silent Phonons)

A comparison between calculated phonon frequencies with experiment is not possible presently since as far as we know there are no corresponding experimental data. However, our results can be used in mode allocation of the ternary alloys. The results show that the alloys have phonons with high frequencies which makes them potential sound emitting diodes.

## V. CONCLUSION

We have used density functional perturbation theory (DFPT) to investigate the vibrational properties of $Ca_xCd_{1-x}F_2$, $Ca_xSr_{1-x}F_2$ and $Ca_xMg_{1-x}F_2$. Firstly, the vibrational modes at the center of the Brillouin zone for $CaF_2$, $CdF_2$ and $SrF_2$ have been evaluated and compared with experiment. The calculated zone-center phonon mode frequencies for the divalent metal fluorides are in good agreement with the anvil cell experiment. This allows a general confidence in the DFPT predictions of the vibrational mode calculations for $Ca_xCd_{1-x}F_2$, $Ca_xSr_{1-x}F_2$ and$Ca_xMg_{1-x}F_2$.The frequencies of the acoustic and optical phonons of the alloys are investigated atdifferent symmetry points. The Infrared active phonon modes at Γ-point of $Ca_xSr_{1-x}F_2$ and$Ca_xMg_{1-x}F_2$ for x= 0.25 and 0.50 are the same. The frequencies of all the alloys are high of the order of $10^{12}$Hz. The alloys are obviously useful for building phonon lasers, which emit sound in much the same way that optical lasers emit light. The obtained results for phonon frequencies can be used as a reference data in studies of other group II-fluorides alloys.

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