FIRST PRINCIPLES STUDY OF ELECTRONIC AND OPTICAL PROPERTIES OF BAF_2

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Abstract - Barium fluoride (BaF_2) is an important member of alkaline-earth fluorides for its intrinsic optical properties. The structural, optical properties, phonon frequencies, and dielectric constants have been investigated with ab initio density functional theory (DFT) method and Density functional perturbation theory (DFPT). The calculations had been done using a first principle code Quantum espresso, implemented ultra-soft pseudo-potentials (US-PPs) and projector augmented wave (PAW) data sets with the local density approximation (LDA) and the Generalized Gradient Approximation (GGA) for the exchange-correlation. The optimized lattice parameters, phonon frequencies at main symmetry points of the Brillouin zone and dielectric constants resulting of pseudo-potentials used were in a good agreement with other theoretical and experimental data.

Keywords - Barium Fluoride, Dielectric Constants, Pseudo-Potentials, Quantum Espresso.

I. INTRODUCTION

FLUORIDES constitute a large family of compounds with interesting physical properties, crystallizing in a variety of structures. Many members of this family of compounds are already employed in technological aspects and application such as lenses, optical coatings, and radiation detecting sensors [1-7]. Among these, Barium fluoride (BaF_2) is a vital member of alkaline-earth fluorides [8–10]. Specifically, it is the fastest luminescent material that has been found to date [11], thereby making it an ideal high-density luminescent material for applications in gamma-ray and elementary particle detectors [12]. Recently, BaF_2 has also been found to exhibit super-ionic conductivity by inserting appropriate impurities into the lattice system or by introducing an interface that causes the redistribution of ions in the space-charge region, therefore considered as a candidate material for high-temperature batteries, fuel cells, chemical filters and sensors [13]. Rubloff reported the results of a detailed study of far-ultraviolet reflectance spectra of ionic crystals including BaF_2, using synchrotron radiation as a light source, several strong peaks ranging from 10 to 20 eV composed the spectrum were assigned to electronic excitations in the material [14]. Ionic conduction in solids has aroused much interest in the last few decades because the underlying processes have widespread technical implications, such as the construction of new and more efficient batteries and in the domain of solid-state chemical reactivity, particularly at high temperatures. For these reasons, a extensive research activity is going on in this field. Additionally, these investigations contribute to the theoretical and experimental understanding of the fundamental underlying mechanisms. However, the fast core–valence transition acts together with a much more effective slow luminescence connected with anionic self-trapped excitations. In the present study, the results of a comprehensive theoretical investigation of BaF_2 in the cubic structure have been reported. Details information on electronic and optical properties was provided. Our study is focusing on the phonon dispersion where the main application of the DFT is used to determine the ground state property of the studied systems. Density Functional Perturbation Theory (DFPT) is used to calculate the responses of solids to perturbations at finite wave vector (q) including calculations of phonon frequencies, dielectric response, electron-phonon couplings, and magnetic susceptibility. If q is commensurate, in principle this can be done directly by using a supercell and applying the perturbation. However, because the cost of calculations rapidly increases with the size of the unit cell, this approach is often impractical, and, in any case, incommensurate wave vectors are excluded [15].

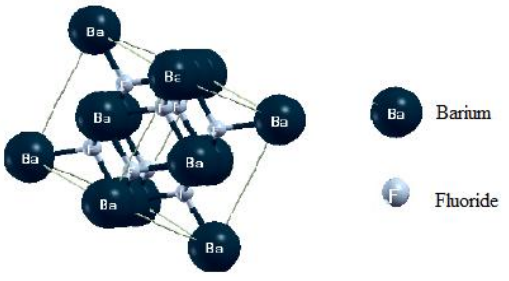


Fig .1 Cubic structure of BaF_2 crystal

II. METHODOLOGY

In fig.1 we have used XcrysDen software [16] to visualize the BaF_2 crystal which crystallized in a cubic fluorite structure with space group $(Fm\bar{3}m)$

consisting of close-packed cubic alkali (Ba) lattice with fluorine (F) occupying tetrahedral sides. A self-consistent calculation has been performed using plane wave (pw.x) in Quantum Espresso code [17]. The total energy as a function of the energy cutoff has been calculated for 10 different energy cutoffs ranging from 10 to 100Ry. The equilibrium lattice constant of BaF_2 has been obtained by minimizing the calculated total energies as a function of lattice constant. Different values around the experimental value have been used in this optimization as shown in table I. The calculations have been performed using Quantum Espresso package, specificity the Ph.x code. We have chosen pseudopotentials generated using Perdew-Zunger (pz) exchange-correlation functional under Local Density Approximation (LDA) and Perdew, Burke and Ernzerh (pbe) of Generalized Gradient Approximation (GGA) for the exchange and correlation energies. Phonon dispersion curves are an essential key ingredient for the calculation of specific heat, thermal expansion, vibrational entropy. and optical properties (see fig.2). Therefore, a systematic characterization of the phonon dispersion relations and phonon density of states (PDOS) of alkaline-earth fluorides is highly desirable. It is expected that the phonon calculation in BaF_2 could be of immense help to understand the origin of ionic conduction in this material. The lattice dynamics calculations have been performed using both empirical potentials as well as ab-initio methods. In the framework of Density Functional Perturbation Theory (DFPT), the phonon frequencies and dielectric constants have been calculated.

III. RESULTS AND DISCUSSION

Several Ultra Soft Pseudo Potentials (US-PPs) and Projector Augmented-wave (PAW) data sets have been used to determine the electronic structure and phonon properties of BaF_2. The US-PPs and the PAW data sets are constructed with the same recipe using the local density approximation (LDA) and the Perdew, Burke, and Ernzerh (PBE) of Generalized Gradient Approximation (GGA) for the exchange and correlation energies. The optimized values for lattice constant (a), theoretical and experimental results are summarized in Table I. Fig. 2 shows the total energy with the optimized lattice constant for all four pseudopotentials which indicate that our results more closed to experimental than theoretical data. This insured that our optimized values in good agreement with the experimental results.

Fig. 3 shows the phonon dispersion curves and phonon densities of states for all pseudopotentials. The lattice dynamics calculations have been performed using both empirical potentials as well as ab-initio methods. A critical assessment of phonon DOS reveals that there are two regions in which phonon modes are distributed to the top region; this is due to the optical phonons because anions are much lighter than the cations. The dispersive longitudinal phonon mode is quite above and well separated from the other modes. The second region is mixed with both optical and acoustical phonon branches arising from the vibrations. The sharp peaks in the phonon DOS correspond to the flat modes of the phonon dispersion curves belonging to both optical and acoustical branches. In the framework of Density Functional Perturbation Theory (DFPT), it is used to calculate phonon frequencies modes and dielectric constants as shown in table (II&III) respectively.

Methods	Pz-paw pz-us	pbe-paw	pbe-us	Theoretical	experimental
lattice constant (a)	6.081 6.083	6.214	6.288	6.14[a]	6.20[b]

[a] [18], [b] [19]

Table I: the optimized values for lattice constant together with other theoretical and experimental Results for the BaF_2 crystal

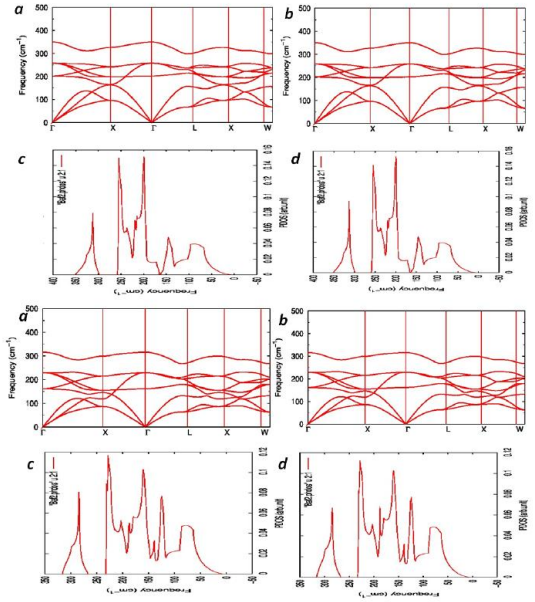


Fig.3 The two upper figures (a, b) Phonon dispersion curves and (c, d) Phonon density of states for BaF_2 Pbe-rrkjus, pbe-pawkj pseudo-potentials and the lower one (a, b) Phonon dispersion curves and (c, d) Phonon density of states for BaF_2 Pz-rrkjus,pz-pawkj pseudo-potentials

Pseudo potential	Parameter	Present calculation	Other calculation	Experimental
Pbe-PAW	LO(cm−1)	316.13	301[a]	326[cf]
	TO(cm−1)	215.32	213[qj]	216[a]
Pbe- US	LO(cm−1)	315.85	301.42[c]	326[cf]
	TO(cm−1)	214.99	213[qj]	216.18[a]
Pz- PAW	LO(cm−1)	350.41	351.46[n]	344[k]
	TO(cm−1)	199.15	199.34[n]	189[a]
Pz- US	LO(cm−1)	326.51	349[o]	226[cf]
	TO(cm−1)	198.63	199.34[no]	189[a]

[a]Ref[18],[c]Ref[20],[f]Ref[21],[q] Ref[22],[j]Ref[23],[n]Ref[24],[k]Ref[25],[o]Ref[26]

Table II: Calculated Frequency of the Phonon Modes at main symmetry points of the Brillouin zone for the BaF2

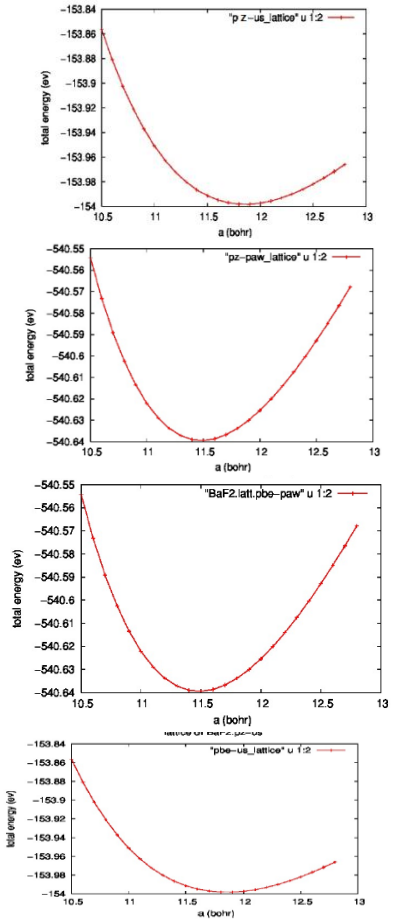


Fig.2. The total energy (eV) versus a (bohr) for BaF_2, using different psuedopotentials.

Pseudo potential	Present calculation	Other calculation	Experimental
Pbe-PAW	2.313	2.12[a]	2.18[b]
Pbe- US	2.312	2.12[c]	2.16[d]
Pz- PAW	2.443	2.12[b]	2.15[b]
Pz- US	2.442	2.12[c]	2.012[B]

[a] Ref [14],[d] Ref [20],[B] Ref [11]

Table III: Dielectric constant ε_∞ of BaF_2

IV. CONCLUSION

The selection of the pseudopotentials constructed by [26] is used for the first time with BaF_2 through Quantum Espresso code, that gave results agreed reasonably well with the earlier theoretical and available experimental results. Structural and phonon properties of BaF_2 have been obtained an overall consistent description of the phonon properties in this compound. These pseudopotentials divided into generalized gradient approximation (GGA) and local density approximation (LDA) of the density functional theory. The longitudinal and transverse optical (LO/TO) splitting for the BaF_2, suggest that BaF_2 has attractive optical properties. This dense work has been done in Sudan Grid Computer.

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