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Elastic Behavior of Cubic Perovskites

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Abstract: ***The structural and elastic properties of cubic perovskites $CsCaCl_3$ and $KCdF_3$ are calculated using the full potential linearized augmented plane wave method in the density functional theory. The calculated structural properties lattice constant, bulk modulus and its pressure derivatives have been compared to experimental results and demonstrated to be in good agreement with them. The elastic properties such as elastic constant, anisotropy factor, shear modulus, Young's modulus and Poisson's ratio are calculated. $CsCaCl_3$ and $KCdF_3$ are considered ductile and elastically anisotropic.***

Keywords: DFT, perovskite, young's modulas, elastic properties, bulk modulus.

1. Introduction

Many experimental and theoretical investigations are devoted to the study of perovskite-type.

Perovskite (ABX_3) is one of the most frequently encountered structures in solid-state physics, and it accommodates most of the metallic ions in the periodic table with a significant number of different anions. However, there are very few studies that have focused on the evolution of the bonding mechanism of ferroelectric perovskite materials according to the lattice distortions. Among the perovskite oxidesstudied most intensively are zirconates of alkaline earth metals. Indeed, they are currently gaining considerable importance in the field of electrical ceramics, refractories, geophysics, astrophysics, particle accelerators, fission, fusion reactors, heterogeneous catalysis etc. Additionally, they have received great attention as high temperature proton conductors with the possibility of applications in fuel cells or hydrogen sensors [1,2].

Although majority of the perovskite compounds are oxides or fluorides, other forms like heavier halides, sulphides, hydrides, cyanides, oxyfluorides and oxynitrides are also reported [3-5]. Oxide perovskites are popular in major industrial applications due to their diverse physical properties [5]over a wide temperature range. Above the Curie temperature, most of them have ideal cubic crystal structure. As the temperature is lowered, they transform from the high-symmetry para electric phase to slightly distorted ferroelectric structures with tetragonal, orthorhombic and rhombohedral symmetries. Typically, the phase transitions are characterized by a small macroscopic lattice strain and microscopic displacement of ions [6-10]. A large number of the perovskites undergo a series of the structural phase transitions ranging from nonpolar antiferrodistortive to ferroelectric to antiferroelectric in nature as temperature is reduced. These transitions are an outcome of the delicate balance between long-range dipole–dipole interactions that favor the ferroelectric state and short-range forces that favor the cubic perovskite phase [11]. These structural phase transitions involve very small atomic displacements away from the ideal cubic structure and the energy differences are small. First principles density functional calculations have significant success in providing accurate total-energy surfaces for the perovskites to explain the ferroelectric distortions [8,12].

Note that the majority of previously reported theoretical works dedicated to structural, electronic and optical properties at ambient conditions [13-16] and only a few reports of them discuss the elastic behavior [17-19] for cubic perovskites.In this work, we will contribute to the study of the cubic perovskites of $CsCaCl_3$ and $KCdF_3$by performing a first-principles investigation of their structural and elastic properties using the full potential linearized augmented plane wave (FP-LAPW) method within the local density approximation (LDA), generalized gradient approximation (GGA) in the framework of density functional theory.

2. Computational Methods

When Density Functional Theory is used to calculate physical properties of crystal, full potential linearized augmented plane wave (FP-LAPW) method with reasonable computational efficiency and high accuracy is one of the most powerful tool. Kohn-sham equation of a many-electron system is solved using FP-LAPW method. We used WIEN2k [20] package to calculate physical properties of $CsCaCl_3$ and $KCdF_3$.The FP-LAPW method expands the Kohn-Sham orbitals in atomic like orbitals inside the muffin-tin (MT) atomic spheres and plane waves in the interstitial region. The Kohn-Sham equations were solved using the recently developed Wu-Cohen generalized gradient approximation (WC-GGA) [20-21] for the exchange-correlation (XC) potential. It has been shown that this new functional is more accurate for solids than any existing GGA and meta-GGA forms. For a variety of materials, it improves the equilibrium lattice constants and bulk moduli significantly over local-density approximation [20,23] and parametrized by Perview and Zunger [22] as well as the generalized gradient approximation (GGA) byPerdew-Burke-Ernzerhof (PBE) [23] and therefore is a better choice. For this reason, we adopted the new WC approximation for the XC potential in studying the present systems.

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3. Results and Discussion

ABX_3 (A = Cs, K; B = Ca, Cd; X = F, Cl) crystallize in cubic structure having space group Pm3m (#221). The A, B and X atoms are positioned at (0 0 0), (1/2, 1/2,1/2), (1/2, 1/2, 0) sites of Wyckoff coordinates respectively. Energy versus volume minimization process [24] is used to calculate equilibrium lattice parameters such as lattice constants (a_o), ground state energy (E_o), bulk modulus (B), and its pressure derivative (B') by LDA and GGA exchange correlation schemes as shown in Table (1). In addition to it, we use lattice parameters calculated by generalized gradient approximation (GGA) for investigating elastic properties.

We can also provide a prediction of the bulk modulus by using the semi-empirical equation developed by Verma et al [1]

$$B\,(GPa) = S + V\frac{(Z_a Z_b Z_c)^{0.35}}{a^{3.5}} \quad (1)$$

where Z_a,, Z_b and Z_c are the ionic charges on the A, B and X, respectively and a is lattice parameter in Å. The S and V are constants and the values are 1.79 and 5505.785 respectively. The crystal structure of $CsCaCl_3$ as shown in figure1. The calculated elastic stiffness constants C_{11} , C_{12} and C_{44} , bulk modulusB, shear modulus G, anisotropic factor A and Young's modulus E as well as Poisson ratio νfor cubic $CscaCl_3$ and $KCdF_3$ at zero pressure are listed in Table 2 and good agreement with previously reported data [25-26]. The elastic constants C_{ij} are fundamental and indispensable for describing the mechanical properties of materials. The elastic constants are important parameters that describe the response to an applied macroscopic stress. The elastic constants of solids provide a link between the mechanical and dynamical behavior of crystals, and define how a material undergoes stress deformations and then recovers and return to its original shape after stress ceases [27]. The elastic constants are important parameters of a material and can provide valuable information about the structural stability, the bonding character between adjacent atomic planes, and anisotropic character. For cubic system, there are three independent elastic constants C_{11}, C_{12} and C_{44}. In order to determine them, the cubic unit cell is deformed using an appropriate strain tensor to yield an energy-strain relation. In this work, we have used the method developed by Charpin and implemented in the WIEN2K package [20].

In Table II, we summarize the calculated elastic constants and the bulk modulus. From Table 2, we remark that the calculated elastic constants within the LDA are higher than the GGA calculated values. The obtained bulk modulus using the LDA is higher than that obtained within the GGA. The calculated elastic constants Cij are positive and satisfy the mechanical stability criteria [27] in a cubic crystal: $(C_{11} + C_{12}) > 0$; $(C_{11} + 2C_{12}) > 0$; $C_{11} > 0$; $C_{44} > 0$, and the bulk modulus B also should satisfy a criterion: $C_{12} < B < C_{11}$.

The bulk modulus calculated from the elastic constants $B = (1/3)(C_{11} + 2C_{12})$ within the LDA and GGA approximations is in good agreement with that obtained from the total energy minimization calculations (see Table I). One can notice that the unidirectional elastic constant C_{11}, which is related to the unidirectional compression along the principal crystallographic directions, is about 85.01% for LDA and 82.01% for GGA, indicating that this compound presents a weaker resistance to the unidirectional compression. To the best of our knowledge no experimental or theoretical values for the elastic constants of this material have been published; hence our results can serve as a reference for future investigations.

Similar work to calculate elastic properties has been reported in the literature [28-33]. The anisotropy factor (A), Young's modulus (E), Shear modulus (G) and Poisson's ratio ν which are the most interesting elastic constants (are listed in Table 2), by using the following relations [34]:

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \quad (2)$$

$$E = \frac{9GB}{3B + G} \quad (3)$$

$$\nu = \frac{3B - 2G}{2(2B + G)} \quad (4)$$

$$G = \frac{1}{2}(G_V + G_R) \quad (5)$$

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (6)$$

$$G_R = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})} \quad (7)$$

where G is the shear modulus, G_V is Voigt's shear modulus corresponding to the upper bound of G values and G_R is Reuss's shear modulus corresponding to the lower bound of G values. The anisotropy factor (A) is equal to one for an isotropic material, while any value smaller or larger than one indicates anisotropy. The magnitude of the deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. We have obtained that the value of the anisotropy factor A are 0.350 in the LDA (0.429 in the GGA) for $CsCaCl_3$ and 0.319 in the LDA (0.320 in the GGA) for $KCdF_3$. This indicates that our compound is anisotropic. Young's modulus (E) is a good indicator about the stiffness of the material. When it is higher for a given material, the material is stiffer. Poisson's ratio provides more information for dealing with the characteristic of the bonding forces than does any of the other elastic property. The value of the Poisson ratio (ν) for covalent materials is small ($\nu < 0.1$), whereas for ionic materials a typical value of ν is 0.25 [35]. In our calculations ν are 0.268 in LDA (0.364 in GGA) for $CsCaCl_3$ and 0.295 in the LDA (0.281 in the GGA) for $KCdF_3$. Hence, a higher ionic contribution in an intra-atomic bonding for this compound should be assumed. Mechanical properties such as ductility and brittleness of materials can be explained from the proposed relationship. The shear modulus G represents the resistance to plastic deformation, while the bulk modulus B represents the resistance to fracture. We know that there is a criterion for B/G ratio which separates the ductility and brittleness of materials. According to Pugh's criteria [36], the critical value is 1.75 i.e., if B/G > 1:75 the material is ductile, otherwise it is brittle. For the $CsCaCl_3$, the B/G ratio is 1.77 within LDA and 1.79 within the GGA, and for $KCdF_3$, the B/G ratio is 2.1 within LDA and 2.0 within the GGA, thus according to Pugh's criteria, our materials are ductile.

4. Conclusions

In this work, we have studied the structural and elastic properties of the cubic perovskite $CsCaCl_3$ and $KCdF_3$ using the FP-LAPW method within the local density approximation (LDA), generalized gradient approximation

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(GGA) in the framework of density functional theory. The lattice constants is found to be in good agreement with the experimental result. The elastic and mechanical properties shows that the materials used in this study are ductile in nature.

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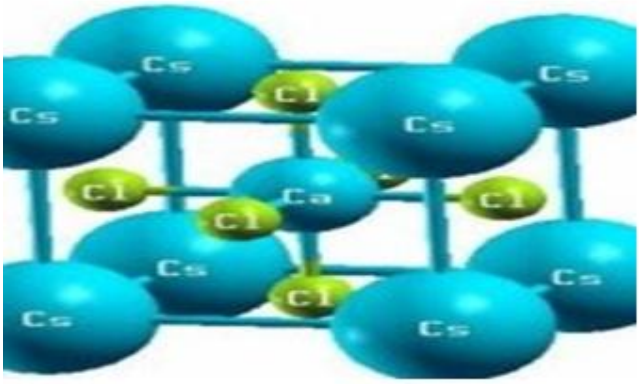

Figure 1: Crystal structure of $CsCaCl_3$

Table 1: Structural parameters, lattice constants a (Å), ground state energies E_o (Ry) bulk modulus B (GPa) and its pressure derivative B′ (GPa) with experimental and other theoretical values of $CsCaCl_3$ and $KCdF_3$ cubic perovskites.

Structural analysis	a (Å)	a (Å) exp. [1]	E_o (Ry)	B′	B (GPa)	B (GPa) [1]
$CsCaCl_3$	5.37 (GGA), 5.25 (LDA)	5.39	-19711.201 (GGA), -19688.001 (LDA)	4.51 (GGA), 4.72 (LDA)	23 (GGA), 32 (LDA)	23, 28
$KCdF_3$	4.39 (GGA), 4.31 (LDA)	4.29	-12987.502 (GGA), -12980.052 (LDA)	4.27 (GGA), 5.27 (LDA)	66 (GGA), 74 (LDA)	63

Table 2: Calculated elastic constants and the bulk modulus (B in GPa), anisotropy factor (A), shear modulus (G in GPa), Young's modulus (E in GPa) and Poisson's ratio (ν) of $CsCaCl_3$ and $KCdF_3$.

		C_{11}	C_{12}	C_{44}	B	A	G	E	ν	B/G
$CsCaCl_3$	LDA	77	11	12	33	0.350	18	45	0.268	1.77
	GGA	57	10	10	25	0.429	14	36	0.364	1.79
$KCdF_3$	LDA	170	30	23	76	0.319	36	93	0.295	2.11
	GGA	146	22	20	64	0.320	32	82	0.281	2.0

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