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Structural, mechanical, electronic and thermal properties of $KZnF_3$ and $AgZnF_3$ Perovskites: FP-(L)APW+lo calculations

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ABSTRACT

This study presents a theoretical prediction of the structural, mechanical, electronic and thermal properties of the zinc-based Perovskites ($AgZnF_3$ and $KZnF_3$) within the framework of Density Functional Theory (DFT) using All-electron self consistent Full Potential Augmented Plane Waves plus local orbital FP-(L)APW + lo method. To make our work comparable and reliable, several functional were used for the exchange-correlation potential. Also, this study intends to provide a basis and an improvement for updating either the values already predicted by other previous work (by using obsolete functional) or to predict them for the first time. GGA-PBE and GGA-PBEsol were used to predict the structural properties of $AgZnF_3$ and $KZnF_3$ Perovskites such as lattice parameter, bulk modulus and its pressure derivative and the cohesive energy. For these properties, the found values are in very good agreement; also those found by GGA-PBEsol are closer to other available previous and experimental results. The electronic properties of these materials are investigated and compared to provide a consolidated prediction by using the modified Becke Johnson potential TB-mBJ with other functional; the values found by this potential are closer to the available proven results and show that these materials exhibit an indirect gap from R to Γ point. The charge densities plot for [110] direction and QTAIM (Quantum Theory of Atoms in Molecules) theory indicate that ionic character is predominate for (K, Ag, Zn)–F bonds. Finally, the effect of temperature and pressure on the unit cell volume, the heat capacity C_V and entropy were studied using the quasi-harmonic Debye model.

1. Introduction

Perovskites have found their way into many different applications and devices [1]. This high penetration leads – in some areas – to the necessity of developing new research in requirements modeling that is concerned with providing models and tools (new functional) to support precise specification of physical properties [2,3]. Fluoride Perovskites are relevant for most high-tech innovative areas in their physical and structural properties [4] such as piezo-electricity [5], photoluminescence [6], high-temperature superconductivity [7] and colossal magneto-resistivity [8]. Significant studies have been strategically allocated to this topic defining it as one of the priority areas in physics and technology [9]. This is why they are a current topic of high interest. Among the most prominent compounds in this field, we focus mainly on $KZnF_3$ and $AgZnF_3$ perovskites, which have been proven to be effective, but also are innovative for fields such as mentioned above.

A large part of Fluoride Perovskites materials like $KZnF_3$ have a cubic structure at room temperature [10] of a highest symmetry with space group of Pm-3m. For these studied (K, Ag) ZnF_3 compounds, there are two types of positions to build the unit cell. The idea is to take, as the origin atom in position for the first case, either the cation (K, Ag) or that of Zn for the second case.

For the first case, cations (K, Ag) are in (0,0,0) position in a cuboctahedral site, Zinc is at the center of the cube at (0.5,0.5,0.5) position in an octahedral site and the anions of fluoride in the centers of the faces of the cube in the positions (0.0,0.5,0.5), (0.5,0.0,0.5) and (0.5,0.5,0.0).

In the second case, cations (K, Ag) are in the centers of the cube at position (0.5, 0.5, 0.5), Zinc is at original position (0,0,0) (the tops

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of cubes). Fluorine anions are at edge centers of the cube in positions (0.0, 0.0, 0.5), (0.0, 0.5, 0.0) and (0.5, 0.0, 0.0).

Murtaza et al. [11] contribute to an integral success; for the first time, they give measurable benefits in calculating the structural, mechanical, electronic and thermal properties of $AgZnF_3$ using the full-potential linearized augmented plane wave method within the generalized gradient approximation (GGA-PBE). In the same way, T. Seddik et al. [12] contribute effectively in improving calculations of pressure effect on electronic and elastic properties of $KZnF_3$ compound using the same method.

Ab-initio methods with related FP-LAPW [13,14] are being today's main areas of applications for all physical properties prediction at any temperature or pressure, this is mainly due to the recent development of their functional, especially GGA-PBEsol and TB-mBJ [15].

The glaring lack of information on the physical behavior of AgZnF3 including its elastic and thermodynamic properties and the absence of many experimental results for both Perovskites $AgZnF_3$ and $KZnF_3$, especially their band-gap energy values have motivated us to accomplish a complementary study.

The overall aim of this study is to try to make a further study comparable to those performed by Murtaza et al. [11] and T. Seddik et al. [12]. For the involved compounds, we use the FP-LAPW method to determine their structural, mechanical, electronic and thermal properties through several recent functional and the quantum theory of atoms in molecules (QTAIM) [16,17] to predict the different information on the bonding of their atoms in their crystal structure.

The outline of the paper is as follows:

The complete computational method is described in detail in chapter 2. In chapters 3, the most relevant results are listed and discussed in terms of comparisons and trends of other works. For the last section, a short conclusion summarizes the most important outcomes selected with respect to future competitiveness and/or their respective technological challenges.

2. Computational method

The well-founded full potentiel-linearized augmented plane wave plus local orbital FP-(L)APW + lo [13,14] methodology as implemented in the WIEN2K computer package [18] allows us to predict properly the structural, mechanical, electronic and thermal properties of $KZnF_3$ and $AgZnF_3$ Perovskites. The density functional theory (DFT) [19] which intends to solve the problems inherent from many body quantum mechanics is the basis on which FP-(L) APW + lo method is heavily based.

The successful mastery of the latest versions of functional plays a crucial role for predicting physical properties of materials, such as GGA-PBEsol [20,21] for the prediction of structural and mechanical properties. However, this functional is a revised version of the GGA-PBE functional which is known by its important underestimation of the band-gap values. These hurdles are overcome by the modified Becke Johnson potential TB-mBJ [15] which, according to previous tests on Perovskites, gives values very close to those of the experiment, but it cannot be used to predict properties other than the band-gap value. The success of this potential gave us an opportunity to predict properly, confirm and complement the structural, mechanical, electronic and thermal properties of $KZnF_3$ and $AgZnF_3$ Perovskites.

For the basis function, we have adopted the value of $R_{MT} \cdot K_{MAX} = 8.5$, where R_{MT} stands for the smallest radius of the atomic sphere whose wave functions inside it are spherical harmonic basis set around the nuclei and K_{MAX} for the magnitude of the largest K vector in the plane wave expansion. Similarly, we have used a maximum value of lmax = 10 for the partial waves inside atomic spheres, while the charge density (of Fourier) is raised to Gmax = 22.67 $Å^{-1}$. K-points mesh integration over Brillouin zone is performed till (12, 12, 12) grid which give 84 k-points in the IBZ (Irreducible Brillouin Zone) [22]. Regarding R_{MT} values for $KZnF_3$ and $AgZnF_3$ compounds, they are taken to be equal to 1.0583, 1.0054, 1.1112 and 0.8732 Å for Ag, K, Zn and F respectively. The self-consistent calculations converge when the total energy converges below the taken value of 1.36×10^{-3} eV.

3. Results and discussions

3.1. Structural properties

The study of the structural properties is a prerequisite to predict other physical properties using first principle methods by means of the variation of the unit cell volume of the studied compounds and its adjustment with the well-known Murnaghan equation [23]. This allows us to determine the different structural parameters such as lattice parameter, the bulk modulus and its pressure derivative. Fig. 1 and Fig. 2 show the variation of the unit cell volume as function of energy for studied compounds ($KZnF_3$,$AgZnF_3$) where the continuous line presents the Murnaghan fit of our calculated points.

The cohesive energy means the energy required to separate a material to several free atoms. It represents a measure of the intensity of the bonding force between a set of atoms of a solid material and has a correlation with its ground state structural stability. The cohesive energy of $KZnF_3$ and $AgZnF_3$ cubic Perovskites is given by:

$$E_{coh} = 3E^{F}_{atom} + E^{K,Ag}_{atom} + E^{Zn}_{atom} - E^{(K,Ag)ZnF_3}_{total} \quad (1)$$

Where $E^{(K,Ag)ZnF_3}_{total}$ represents the total energy of the unit cell which contains three atoms of fluorine of E^{F}_{atom} energy and a potassium atom for the $KZnF_3$, or Silver for $AgZnF_3$ of $E^{K,Ag}_{atom}$ energy, and a zinc atom of E^{Zn}_{atom} energy.

The success of PBEsol functional in the prediction of the structural properties of solid materials is well known and has already been tested in many previous works. The obtained results of lattice parameter, bulk modulus and its pressure derivatives and the cohesive energy of $KZnF_3$ and $AgZnF_3$ compared to some experimental and other theoretical works are grouped in Table 1.

According to our results, we can say that the values of the lattice parameter obtained by PBE are similar to available theoretical work but those obtained by PBEsol are the closest to the experiment values compared to other authors results and those obtained by PBE. We can also notice that our results are very close to those found by G. Murtaza et al. [11] in the case of $AgZnF_3$ and those calculated by T. Seddik et al. [12] in the case of $KZnF_3$.

It should be noted also that although silver has a number of electrons relatively important compared to potassium, $AgZnF_3$ lattice parameter is close to that of $KgZnF_3$ and since the lattice parameter depends on the number of Z electrons of atoms and the type of bonding, this means that for these two compounds this parameter depends primarily on the bonding between zinc and fluorine. It can be concluded also that the bonding between silver and fluorine is too strong compared to the existing one between fluorine and potassium.

The same interpretation is approved for the predicted bulk modulus value of $KZnF_3$ by PBEsol. The success of functional PBEsol in predicting the structural and elastic properties that was already tested on this family of materials and confirmed in several previous works [24], allows us to believe that for $AgZnF_3$ value using this functional will be closer to that of experiment once measured. For our calculated values of pressure derivatives of bulk modulus and