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Elastic and optoelectronic properties of $RbMF_3$ (M=Zn, Cd, Hg): A mBJ density functional calculation

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ABSTRACT

Bonding nature as well as the structural, elastic, electronic and optical properties of cubic fluoroperovskites $RbMF_3$ (M=Zn, Cd and Hg) compounds have been calculated using a full-potential augmented plane (FPLAPW) method within the density functional theory. The exchange-correlation potential was treated with the generalized gradient approximation of Wu and Cohen (WC-GGA) to calculate the total energy. Moreover, the modified Becke–Johnson potential (TB-mBJ) was also applied for the electronic and optical properties. It is found that lattice constant increases while bulk modulus decreases with the change of cation (M) in going from Zn to Hg in $RbMF_3$ in accordance with the experimental results. The calculations of the electronic band structure, density of states and charge density show that these compounds have an indirect energy band gap (M–Γ) with a mixed ionic and covalent bonding. The optical properties (namely: the absorption coefficient and the reflectivity) were calculated for radiation up to 45.0 eV.

1. Introduction

Actually ab initio methods, which use only the atomic constants as input parameters to solving the Schrödinger equation, have become the most powerful probes for investigating important number of physical and chemical properties for atoms, molecules and solids. Needless to mention that they are also a tool of choice for the prediction of new materials.

Perovskite structure with the general chemical formula AMX_3 is one of the most commonly occurring ones and important in solid state physics. Compounds with this structure have revived great interests in material sciences because they have relatively simple crystal structure and display varied physical properties, such as superconductivity, colossal magnetoresistance, ionic conductivity, and a multitude of dielectric properties, which are of great importance in microelectronics and telecommunication [1]. The ternary fluorides ABF_3 with the perovskite crystal structure where A are alkali metals and B stands for alkaline earth metals have been extensively studied over several decades, as they have many potential applications due to their optical properties [2,3], high-temperature super-ionic behavior [4], and other physical properties, such as ferroelectricity [5], antiferromagnetism [6], and semiconductivity [7]. Moreover, the fluoroperovskite compounds can be used in the medical field to measure the dose during radiation therapy, and they may also be used in the manufacture of radiation imaging plates for X-rays, gamma-rays and thermal neutrons for medical and non-destructive testing applications. Fluoroperovskite compounds are generally characterized by their large energy band gap and low hygroscopicity as well as mechanical and thermal durability [1].

$RbMF_3$ (M=Zn, Cd, Hg) compounds belong to the fluoride perovskite family. They are favorable hosts for many transition elements [8–11]. Also they are widely studied because of their interesting structural properties [12]. It has been experimentally confirmed that they crystallize in the cubic structure and do not exhibit structural phase transition under pressure and temperature [1,13]. From the above it is clear that there is a good amount of experimental work focusing on the structural properties of $RbMF_3$ (K, Rb, Cs) compounds has been carried out. No theoretical and experimental reports on the electronic and optical properties on these compounds have appeared in the literature. Moreover, the elastic constants of the investigated compounds have not been calculated and measured yet. The reasons mentioned above motivate us to perform these calculations using the full-relativistic version of the full-potential augmented plane-wave plus local orbitals method (FP-APW+lo), based on the density functional theory (DFT), in order to provide reference data for the experimentalists and to complete existing theoretical and

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experimental works on these compounds. The organization of the paper is as follows. The computational method we have adopted for the calculations is described in Section 2. The most relevant results obtained for the structural, elastic, electronic and optical properties of $RbMF_3$ (M=Zn, Cd, Hg) compounds are presented and discussed in Section 3. Finally, in Section 4 we summarize the main conclusions.

2. Computational details

The present calculations were done with the full-potential linearized augmented plane wave method (FP-LAPW) [14] to solve the Kohn Sham equations as implemented in the WIEN2K code [15]. This method is based on density functional theory (DFT) [16] and has been proven to be one of the most accurate methods for computation of the electronic structure and optical properties of various solids. The exchange-correlation contribution is described within the generalized gradient approximation as proposed by Wu and Cohen (WC-GGA) [17] to calculate the total energy, while for electronic properties the recent modified Becke–Johnson potential (TB-mBJ) [18] was applied. In our calculations the core electrons are treated fully relativistically and the valence electrons are treated semi-relativistically. The muffin-tin radii (RMT) were taken to be 2.5, 1.88, 2.08, 2.0, and 1.78 a.u. for Rb, Zn, Cd, Hg, and F respectively. The integrals over the Brillouin zone (IBZ) are performed with 35 k-points, using the modified tetrahedron method [19]. The self-consistent calculations are considered to be converged when the total energy is stable within 0.1 mRy. For the calculations of the optical properties, a dense mesh of uniformly distributed k-points is required. Hence, the Brillouin zone integration was performed with 75 k-points in the irreducible part of the Brillouin zone.

3. Results and discussions

3.1. Structural properties

The ternary fluorides $RbMF_3$ (M=Zn, Cd and Hg) crystallize in the cubic perovskite-type structure with space group P_m3_m (# 221) and its unit cell contains one molecule. The Rb, M and F atoms are positioned at 1a (0 0 0), 1b (1/2 1/2 1/2) and 3c (0 1/2 1/2) sites of Wyckoff coordinates, respectively. Our aim in this subsection is to calculate the total energy as a function of unit-cell volume around the equilibrium cell volume V_0. The calculated total energies versus volume were fitted with the Murnaghan's equation of state (EOS) [20] to determine the ground state properties such as the equilibrium lattice constant a_0, the bulk modulus B_0 and ground state unit cell energy E. The calculated ground-state parameters (a_0, B_0 and E) for the studied compounds are quoted in Table 1. Results from earlier experimental and theoretical studies are also quoted for comparison. The computed lattice constants are slightly overestimated compared to the measured data. This could be attributed to our use of the generalized gradient approximation (GGA) which is known to slightly overestimate the lattice constant values compared to the measured ones. It is observed that the lattice constant increases from $RbZnF_3$ to $RbHgF_3$. This could be explained by the increase of the size of cation (M) atom in going from Zn to Hg. In inverse sequence to lattice constant, the bulk modulus value decreases from $RbZnF_3$ to $RbHgF_3$, suggesting that the rigidity increases from $RbHgF_3$ to $RbZnF_3$. The inverse relation between the lattice constant and bulk modulus has been seen also for other fluoroperovskites compounds [22,23]. To date, no experimental data for the bulk moduli of these compounds are available to be compared with our theoretical results.

Table 1
Calculated lattice parameter α (in Å), bulk modulus B (in GPa), ground state energy E (in Ry), elastic constants C_{ij} (in GPa), shear modulus G (in GPa), Young's modulus E (in GPa), Poisson's ratio v, anisotropy factor A and B/G ratio at equilibrium volume for cubic $RbMF_3$ (M=Zn, Cd, Hg) compounds.

	Present calc.	Experimental data	Other calc.
$RbZnF_3$			
α (Å)	4.188	4.122[a]	3.900[b]
B (GPa)	69.34		86.92[b]
E (Ry)	−10,154.98		
C_{11}	113.81		
C_{12}	47.16		
C_{44}	35.76		
E	89.36		
G	34.76		
v	0.285		
A	1.07		
B/G	1.99		
$RbCdF_3$			
α (Å)	4.459	4.398[a]	
B (GPa)	62.37		
E (Ry)	−17,754.76		
C_{11}	122.46		
C_{12}	32.32		
C_{44}	19.90		
E	72.60		
G	27.79		
v	0.305		
A	0.441		
B/G	2.24		
$RbHgF_3$			
α (Å)	4.633	4.470[a]	
B (GPa)	49.32		
E (Ry)	−45,886.2		
C_{11}	78.24		
C_{12}	34.85		
C_{44}	11.75		
E	41.80		
G	15.08		
v	0.388		
A	0.541		
B/G	4.14		

[a] Ref. [13].
[b] Ref. [21].

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 returns to its original shape after stress ceases [24]. These constantly play an important role in providing valuable information on the stability and stiffness of materials. To calculate the elastic moduli C_{ij} we have used the numerical first-principle calculation by computing the components of the stress tensor δ for small stains, using the method developed by Charpin and integrated in WIEN2K code [15] which has been applied with successful results in some previous works [25–27]. Since the studied compounds have cubic symmetry, we need to calculate only 3 independent elastic parameters C_{11}, C_{12}, and C_{44} to completely characterize the mechanical properties. Hence, a set of 3 equations is needed to determine all the constants.

The first equation involves calculating the bulk modulus (B), which is given by [28]

$$B=\frac{1}{3}(C_{11}+2C_{12}) \quad (1)$$