Structural and optoelectronic properties of cubic perovskite RbPbF₃

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Abstract. The structural and optoelectronic properties of cubic perovskite RbPbF₃ are calculated using all electrons full potential linearized augmented plane wave (FP-LAPW) method. The calculated lattice constant is in good agreement with the experimental result. The calculated band structure shows a direct band gap of 3.07 eV. The contribution of different bands is analysed from the total and partial density of state curves. We identified hybridization of Pb *s*, Pb *p* states with F *p* states in the valence bonding region. Calculations of the optical spectra, viz., the dielectric function, optical reflectivity, absorption coefficient, real part of optical conductivity, refractive index, extinction coefficient and electron energy loss are performed for the energy range of 0–30 eV. Based on the direct bandgap, as well as other optical properties of the compound, it is predicted that this material is useful for vacuum-ultraviolet-transparent (VUV-transparent) applications.

Keywords. Band structure; DOS; optical properties; FP-LAPW; DFT.

1. Introduction

Technological demands on optical lithography in semiconductors require increasingly minute details, and this in turn requires shorter wavelength lithographic light. In the semiconductor industry, perovskite-like fluorides that have wide band gaps are potential candidates for vacuum-ultraviolet-transparent lens materials in optical lithography steppers. In materials science, perovskites have great potential for a variety of device applications in optical, ferroelectric, anti-ferromagnetic and piezoelectric properties (Shimamura *et al* 2001; Takeshi Nishimatsu *et al* 2002; Lim *et al* 2004; Riadh El Ouenzerfi *et al* 2004; Setter *et al* 2006; Fen Zhang *et al* 2008). RbPbF₃ shows the phase transition from *Im-3m* to *Pnma* takes place at 340–400 K and at 490 K, it changes from *Pnma* to *Pm-3m* (Hull and Berastegui 1999; Yohei Yamane *et al* 2008). RbPbF₃ is a cubic perovskite structure with space group *pm-3m* [#221], which had potential applications in lithography technology (Takeshi Nishimatsu *et al* 2002). Though, it is a potential compound for optical devices, no experimental or theoretical data is available about its optoelectronic properties. In this work, we contribute to the study of the perovskite fluoride RbPbF₃ by performing a first-principles investigation of its structural, electronic and optical properties using the full potential linearized augmented plane wave (FP-LAPW) method in the density functional theory (DFT) framework within GGA and LDA using the WIEN2K code (Blaha *et al* 2001). The use of first-principles calculations offers one of the most powerful tools for carrying out theoretical studies of an important number of physical

and chemical properties of the condensed matter with great accuracy (Goudochnikov and Bell 2007; Li *et al* 2008). This paper is organized as follows: after a brief introduction in § 1, the theoretical framework within which all the calculations have been performed is outlined in § 2. In § 3, we present and discuss the results of our study. A conclusion of the present investigation is given in § 4.

2. Computational method

On the base of first-principles approach, several computational methods are developed to study the electronic structure of materials. The first-principles calculations are performed using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in WIEN2K code (Blaha *et al* 2001). The exchange–correlation potential is calculated within the local density approximation (LDA) developed by Ceperley and Alder (1980) and parameterized by Perdew and Zunger (1981), as well as the generalized gradient approximation (GGA) by Perdew *et al* (1996) (PBE). The experimental lattice constant is $a_0 = 4.790$ Å as reported by Jiang *et al* (2006). In this FP-LAPW method, there are no shape approximations to the charge density or potential. Space is divided into two regions: (i) a spherical muffin-tin (MT) around the nuclei in which the radial solutions of the Schrodinger equation and their energy derivatives are used as basis functions and (ii) the interstitial region between the muffin-tins, in which the basis set consists of plane waves. The cut-off energy which defines the separation between the core and valence states is set at -9.0 Ry. The sphere radii used are 2.2 a.u. for Rb, 2.0 a.u. for Pb and 1.8 a.u. for F, respectively. Augmented plane wave (APW) plus local

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valence orbitals are used with the wave functions, the potentials and charge densities expanded in terms of spherical harmonics inside the muffin-tin spheres. The Brillouin zone integration is carried out by using the modified tetrahedron method (Blochl *et al* 1994) up to 35 k -points in the irreducible wedge of the simple cubic Brillouin zone. Well-converged solutions are obtained with $R_{\text{MT}} K_{\text{max}} = 7.0$ (where R_{MT} is the smallest of all muffin-tin radii and K_{max} is the magnitude of the largest k vector in the plane wave expansion) and k -point sampling is checked. Self-consistent calculations are considered to be converged when the total energy of the system is stable within 0.0001 Ry. The optoelectronic properties of the compound are calculated using a denser mesh of 3500 k -points in the irreducible Brillouin Zone (IBZ).

The dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is known to describe the optical response of the medium at all photon energies. The imaginary part, $\varepsilon_2(\omega)$ is directly related to the electronic band structure of a material and describes the absorptive behaviour. The imaginary part of the dielectric function, $\varepsilon_2(\omega)$ is given (Smith 1971; Ambrosch-Draxl and Sofo 2006) by

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2} \right) \sum_{i,j} \int_k \langle i|M|j \rangle^2 f_i (1 - f_j) \delta(E_{j,k} - E_{i,k} - \omega) d^3k, \quad (1)$$

where M is the dipole matrix, i and j the initial and final states respectively, f_i the Fermi distribution function for the i -th state and E_i the energy of electron in the i -th state with crystal wave vector k . The real part, $\varepsilon_1(\omega)$ of the dielectric function can be extracted from the imaginary part using the Kramers–Kronig relation in the form (Wooten 1972; Fox 2001):

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{\omega'^2 - \omega^2}, \quad (2)$$

where P implies the principal value of the integral. The knowledge of both the real and imaginary parts of the dielectric tensor allows the calculation of important optical functions such as the refractive index, $n(\omega)$, extinction coefficient, $k(\omega)$ and reflectivity, $R(\omega)$ using the following expressions:

$$n(\omega) = \left\{ \frac{\varepsilon_1(\omega)}{2} + \frac{\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}}{2} \right\}^{\frac{1}{2}}, \quad (3)$$

$$k(\omega) = \left\{ \frac{\varepsilon_1(\omega)}{2} - \frac{\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2}}{2} \right\}^{\frac{1}{2}}, \quad (4)$$

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2. \quad (5)$$

Other optical parameters like energy loss function, $L(\omega)$, absorption coefficient, $\alpha(\omega)$, and frequency dependent

optical conductivity, $\sigma(\omega)$ are calculated by the following expressions:

$$L(\omega) = \text{Im} \left(-\frac{1}{\varepsilon(\omega)} \right), \quad (6)$$

$$\alpha(\omega) = \frac{4\pi k(\omega)}{\lambda}, \quad (7)$$

$$\sigma(\omega) = \frac{2W_{\text{cv}} \hbar \omega}{E_0^2}, \quad (8)$$

where W_{cv} is the transition probability per unit time.

3. Results and discussion

3.1 Structural properties

The total energy per unit cell of RbPbF₃ in the cubic perovskite structure is shown in figure 1. The volume vs energy is fitted by the Birch–Murnaghan equation of state (Murnaghan 1944). From this fit, we can get the equilibrium lattice constant (a_0), bulk modulus (B_0) and pressure derivate of the bulk modulus (B'). These values are shown in table 1.

Our calculated equilibrium lattice parameter (a_0) is in reasonable agreement with the experimental value. The bulk modulus (B_0) is a measure of the crystal rigidity, thus, a large B_0 is for high crystal rigidity. No previous experimental or theoretical result for this parameter is available for the RbPbF₃ compound to be compared with the present calculation. We performed our calculations by using LDA and GGA approximations. The results show that the calculated equilibrium lattice constant within the LDA is 1.81% lower than the experimental value, while the GGA calculated value is 1.67% larger. The LDA underestimates the lattice constant while the GGA, overestimates it.

Figure 1. Dependence of total energy of cubic perovskite RbPbF₃ crystal on unit cell volume.

Table 1. Calculated lattice constant, a (Å), bulk modulus, B_0 (GPa), and pressure derivative (B') and ground state energy (E_0) of RbPbF_3 .

Method	Lattice constant a_0 (Å)	B_0 (GPa)	B'	E_0 (Ry)
GGA	4.870	39.31	4.67	-48419.2511
LDA	4.703	52.66	4.83	-48386.3959
Experiment	4.790

Figure 2. Band structure of RbPbF_3 along the high symmetry point.

3.2 Band structure, density of states (DOS) and charge density

Now, we discuss our results of the electronic properties of RbPbF_3 via the energy band and the total and partial density of states. The calculated energy bands along the high symmetry lines in the Brillouin zone and total, partial density of states of RbPbF_3 are shown in figures 2 and 3, respectively. The zero of energy is chosen to coincide with the valence band maximum (VBM), which occurs at R point and conduction band minimum (CBM) occurring at the R point with direct band gap of 3.07 eV. Thus, RbPbF_3 is a direct band gap insulator. On the basis of different bands; the total density of states (TDOS) could be grouped into four regions and the contribution of different states in these bands can be seen from the partial density of states (PDOS). The first region, around -10.0 eV comprising a narrow band due to the Rb $4p$ state is clearly seen in figure 3(b). In the second region,

Figure 3. (a) Total and partial density of states (DOS), (b) Rb, (c) Pb and (d) F in RbPbF_3 .

around -9 to -6 eV contributed single band by Pb $6s$ state is seen in figure 3(c). In the third region, -5 eV to Fermi energy level, majority contribution is due to F $2p$ states and minority contribution is due to Pb $6s$ and Pb $6p$ states as observed from

figures 3(c and d). There is a hybridization of Pb *s*, Pb *p* and Pb *d* with the F *p* states observed in this region. The first, second and third regions within the range of $-10.0-0$ eV comprise the valence band. The upper part of the valence band is composed of the F *2p* and Pb *6s* states. The fourth region after the Fermi level is the conduction band. The lower part of this band near the Fermi level is mainly due to the Pb *6p* and F *2p* states. In the conduction band from 3.07 to 10 eV, majority contribution is from Pb *6p* states (these states given small contribution up to 20 eV) and minor contribution of F *2p* states. From 11 to 20 eV, a small contribution of Pb *5f* states is observed. The calculated band gap of RbPbF₃ is shown in table 2.

The charge density distributions are shown in figure 4. Charge density maps serve as a complementary tool to achieve a proper understanding of the electronic structure of the system being studied. The ionic character of any material can be related to the charge transfer between the cation and anion, while covalent character is related to the sharing of the

charge between the cation and anion. The covalent behaviour is due to hybridization of Pb *s* and Pb *p* with the F *p* states in the valence band near the Fermi energy level. From the figures, it is clear that the highest charge density resides in the immediate vicinity of the nuclei. The near spherical charge distribution around the Rb indicates that the bond between Rb and F is strong ionic, with no charge sharing among the contours of the respective atoms. It can be seen that most of the charge is populated in the Pb–F bond direction, while the maximum charge resides on the Pb and F sites. The corresponding contour maps of the charge density distributions are shown in figure 4(a), along (1 0 0) plane in 2D representation, in figure 4(b) along (1 0 0) plane in 3D representation and in figure 4(c) along (1 1 0) plane in 2D representation. Hence, we conclude that there exist a strong ionic bonding in Rb–F and strong covalent bonding in Pb–F.

3.3 Dielectric and optical properties

The FP-LAPW is a good theoretical tool for the calculation of the optical properties of a compound. The optical properties give useful information about the internal structure of the RbPbF₃ compound. The calculated optical properties of RbPbF₃ are shown in figure 5. The imaginary part, $\varepsilon_2(\omega)$ and real part, $\varepsilon_1(\omega)$ of the dielectric function, refractive index, $n(\omega)$, extinction coefficient, $k(\omega)$, reflectivity, $R(\omega)$, energy

Table 2. Energy gap at high symmetry points for RbPbF₃.

Method	Band gap type	Symmetry points	Energy gap (eV)
WIEN2K	Direct gap	$R \rightarrow R$	3.07
	Indirect gap	$R \rightarrow \Gamma$	3.95

Figure 4. Charge density distribution of RbPbF₃ (a) along (1 0 0) plane in 2-D representation, (b) along (1 0 0) plane in 3-D representation and (c) along (1 1 0) direction.

Figure 5. Optical spectra as a function of photon energy for cubic perovskite RbPbF_3 . (a) Imaginary $\varepsilon_2(\omega)$, (b) real $\varepsilon_1(\omega)$ parts of dielectric function, (c) refractive index, $n(\omega)$ (d) extinction coefficient, $k(\omega)$, (e) reflectivity, $R(\omega)$, (f) energy loss function, $L(\omega)$, (g) optical conductivity, $\sigma(\omega)$ and (h) absorption coefficient, $\alpha(\omega)$ of RbPbF_3 .

loss function, $L(\omega)$, optical conductivity, $\sigma(\omega)$ and absorption coefficient, $\alpha(\omega)$ of RbPbF_3 are shown in figure 5, as functions of the photon energy in the range of 0–30 eV. The imaginary part, $\varepsilon_2(\omega)$ gives the information of absorption behaviour of RbPbF_3 . In the imaginary part, $\varepsilon_2(\omega)$, the threshold energy of the dielectric function occurs at $E_0 = 3.08$ eV, which corresponds to the fundamental gap at the equilibrium. It is well known that the materials with band gaps larger than 3.1 eV work well in the ultraviolet region of the spectrum (Maqbool *et al* 2009). From figure 5(a), for the imaginary part, $\varepsilon_2(\omega)$, it is clear that there are strong absorption peaks in the energy range of 3.07–30.0 eV. The maximum absorption peak is at 4.99 eV. The peak around 3.6–15 eV appear due to the electronic transition from Rb 4p state of the valence band (VB) to the unoccupied Pb 6p state in the conduction band (CB). The peaks in the range of 16–20 eV appear due to the Rb 4p state of the VB to the unoccupied Pb 5f state of the CB.

The real part of the dielectric function $\varepsilon_1(\omega)$ is also displayed in figure 5(b). This function $\varepsilon_1(\omega)$ gives us information about the electronic polarizability of a material. The static dielectric constant at zero is obtained as $\varepsilon_1(0) = 2.84$. From its zero frequency limit, it starts increasing and reaches the maximum value of 4.24 at 4.33 eV, and goes below 0 in negative scale for the range of 19.14–20.45 eV. In this range, the incident photon beam is completely attenuated. As materials behave metallic for negative values of $\varepsilon_1(\omega)$ and are dielectric otherwise (Okoye 2006; Murtaza *et al* 2011a, b), RbPbF_3 is metallic in this range of energy. The refractive index and extinction coefficient are displayed in figures 5(c and d). The static refractive index, $n(0)$ is found to have the value 1.68. The value of static refractive index is obtained from the real part of dielectric function to be $n(0) = (\varepsilon_1(0))^{1/2} = (2.84)^{1/2} = 1.68$, which is same as that obtained from figure 5(c). The refractive index reaches a maximum value of 2.12 at 4.50 eV. The refractive index is

Table 3. Calculated zero frequency limits of refractive index $n(0)$, reflectivity $R(0)$, energy range for $n(\omega) < 1$, maximum values of refractive index $n(\omega)$, reflectivity $R(\omega)$ and optical conductivity $\sigma(\omega)$ of RbPbF₃.

RbPbF ₃	$n(0)$	Maximum $n(\omega)$	Energy range (in eV) for $n(\omega) < 1$	$R(0)$ %	Maximum $R(\omega)$	Maximum $\sigma(\omega)$ (in $\Omega^{-1} \text{ cm}^{-1}$)
This work	1.68	2.12	19.25–30.00	6.53	29.34	6821.80

greater than one as photons enter a material, they are slowed down by the interaction with electrons. The refractive index of the compound starts decreasing beyond maximum value and goes below one for the range given in table 3. Refractive index lesser than unity shows that the group velocity ($V_g = c/n$) of the incident radiation is greater than c . When we look at the behaviour of imaginary part of dielectric function, $\epsilon_2(\omega)$ and extinction coefficient, $k(\omega)$, a similar trend is observed from figures 5(a and d). The extinction coefficient, $k(\omega)$ reaches the maximum absorption in the medium at 19.25 eV. Frequency dependent refractive index, $n(\omega)$, reflectivity, $R(\omega)$ and optical conductivity, $\sigma(\omega)$ are also calculated and the salient features of the spectra are presented in table 3.

The optical reflectivity, $R(\omega)$ is displayed in figure 5(e), the zero-frequency reflectivity is 6.53%, which remains almost the same up to 3.07 eV. The small value of reflectivity in infrared and visible energy range shows that the material is transparent in this range. Thus, it can be used as an anti-reflecting coating in this part of the energy range. The maximum reflectivity value is about 29.34% which occurs at 19.42 eV. Interestingly, the maximum reflectivity occurs where the real part of dielectric function, $\epsilon_1(\omega)$ goes below zero, as seen from figures 5(b and e). The energy loss function is displayed in figure 5(f). The energy loss function, $L(\omega)$ is an important factor describing the energy loss of a fast electron traversing in a material. The peaks in $L(\omega)$ spectra represent the characteristic associated with the plasma resonance. The resonant energy loss is seen at 22.43 eV. The optical conductivity, $\sigma(\omega)$ is shown in figure 5(g). It starts from 3.06 eV and the maximum value of optical conductivity of the compound is obtained at 18.31 eV with a magnitude of $6821.80 \Omega^{-1} \text{ cm}^{-1}$. Similar features are also observed in absorption coefficient, $\alpha(\omega)$, in the absorption range up to 30 eV and it is shown in figure 5(h). The maximum absorption occurs at 19.30 eV. RbPbF₃ is a direct band gap compound with high absorption power in ultraviolet energy range and hence, it can be used in the optoelectronic devices such as UV detector and vacuum-ultraviolet-transparent (VUV-transparent) applications.

4. Conclusions

In this paper, we have studied the electronic, structural and optical properties of the cubic perovskite RbPbF₃ using the

FP-LAPW method within the generalized gradient approximation (GGA) in the framework of density functional theory. The lattice constant is found to be in good agreement with the experimental result. It is found that the compound has a direct band gap of 3.07 eV. The compound exhibits strong ionic bonding in Rb–F and strong covalent bonding in Pb–F. The optical properties such as dielectric function, reflectivity, absorption coefficient, real part of optical conductivity, refractive index, extinction coefficient and electron energy loss are studied in the energy range of 0–30 eV. The above properties of RbPbF₃ suggest that it is useful in VUV-lithography applications.

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