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MODELING OF ELECTRONIC PROPERTIES OF PBFX

Physics

M. Sharma Department of Physics, Faculty of Science, Mewar University, Chittorgarh (Raj.) 312901, India

G. Ahmad Department of Physics, Faculty of Science, Mewar University, Chittorgarh (Raj.) 312901, India

G. Arora* Department of Physics, Geetanjali Institute of Technical Studies, Udaipur (Raj.) 313022, India *Corresponding Author

ABSTRACT

In the present work we have studied the electronic properties of PbFX (X = Cl, Br and I) compounds by employing the first-principles methods in the density functional theory (DFT) framework. We report the energy bands, density of states and Mulliken's populations of these matlockites using linear combination of atomic orbitals method as embodied CRYSTAL09 package, within various exchange and correlation operators of density functional theory (DFT) and also a posteriori hybridization of Hartree–Fock (HF) and the DFT so-called Becke's three-parameter hybrid functional (B3LYP). The band structure calculations show that these compounds are direct-gap semiconductor with valence band maximum and the conduction band minimum at the point of irreducible Brillouin zone.

KEYWORDS

Band Structural Calculations; Density Functional Theory; Matlockite Compounds

Introduction

The alkaline-earth fluoro-halides MFX, where M = Ca, Sr, Ba, Pb, Eu and X = Cl, Br, I, form an important class of materials crystallizing in the PbFCl-type tetragonal structure (P4/nmm), which is also called the matlockite structure [1, 2]. They are layer structures based on metal-oxygen or metal-fluorine layers in which the anions are in quadratic packing with the metal cations (Pb, Ca, Bi) fitting into the interstices between the anions, half on each side of the layer. These layers are separated by double layers of Cl or (Cl, OH), each in quadratic packing which coordinate the metal anions of the first-described layers.

For a long time, the PbFCl has been a subject of thorough experimental and theoretical investigations with respect to a variety of potential applications such as room temperature hole burning, scintillator material, radiation detection and pressure sensors [3-5].

Computational Method

We have computed the electronic structure using local density approximation (LDA) and generalized gradient approximation (GGA) within DFT and B3LYP using CRYSTAL09 code [6] wherein the Bloch orbitals are generated from linear combination of atomic orbitals (LCAO) with Gaussian-type basis sets.

We have used the exchange and correlation potentials suggested by von Barth-Hedin [7] and VWN [8], respectively for DFT-LDA calculations, whereas, the WCGGA [9] and PWGGA [10] exchange and correlation potentials have been used for DFT-GGA computations. In the B3LYP, the exchange correlation density functional energy involves the Becke's gradient correction [11] to the exchange and correlation functionals using prescription of Lee–Yang–Parr [12]. To compute the electronic properties of PbFCl, PbFBr and PbFI, we have employed the Gaussian basis sets for Pb, F, Cl, Br and I which have been taken from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. For faster convergence of self consistent-field cycles, the BRODYEN scheme [13] was applied for all the calculations.

In matlockite structure, the F ions occupy the Wyckoff positions 2*a* but the M and X atoms are at the positions 2*c* which depend on the internal parameters v and u. For PbFCl (PbFBr) the lattice parameters were a = 4.11Å (4.18Å) and c = 7.246Å (7.59Å) [14] and in the case of PbFI we have used a = 4.23Å and c = 8.77Å [15].

Results and Discussion

3.1 Electronic Band Structure and Density of States

In figures 1, 2 and 3, we have shown the energy bands (E–k relations) and the density of energy states (DOS) of PbFCl, PbFBr and PbFI, respectively by employing DFT-GGA approach of CRYSTAL09 method. The energy is plotted in Hartree. Except for some fine structures and band gaps, the overall shape of our energy bands is in agreement with the earlier reported data [14, 16]. The valence band maximum (VBM) and the conduction band minimum (CBM) occurs at the Γ point, resulting in a direct band gap semiconductor.

The band gaps of these compounds as calculated using various approximations of LCAO (DFT-LDA, DFT-GGA and B3LYP) methods along with the available data [14] are summarized in Table 1. We can observe that our calculations are overestimating the EV-GGA calculations.

3.2 Mulliken's Population

The relative nature of bonding in these compounds is explained in terms of Mulliken's population analysis. The Mulliken's population analysis of PbFX have been undertaken by using DFT-LDA, DFT-GGA and B3LYP theories of LCAO theory is shown in Table 2, which shows that the amount of charge transfer from Pb to F and X (X=Br, Cl, I) atoms increases as we move from Br→Cl→I, so the iconicity increases or covalency decreases from PbFBr→PbFCl→PbFI.

Conclusions

The electronic properties of PbFX (X = Cl, Br and I) have been presented using the LCAO method based on the density functional theory with different approximations for the calculation of exchange-correlation energy functionals based on CRYSTAL09 code. Our calculations show that these compounds exhibit direct band-gap at Γ point of the irreducible Brillouin zone. Our results give overestimated values of band gaps as compared to previous values.

Acknowledgment

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Table 1 Band gap of Matlockite Compounds

	Band Gap (in eV)		
Theory	PbFCl	PbFBr	PbFI
DFT-LDA	4.79	3.79	2.98
DFT-GGA	4.81	3.83	3.01
B3LYP	4.95	3.95	3.09
EV-GGA [16]	4.28	3.31	2.61

Table 2 Mulliken's population analysis (in electrons)

	PbFCl	PbFBr	PbFI
DFT-GGA	2.838	2.685	2.883
DFT-LDA	2.821	2.672	2.877
B3LYP	2.777	2.612	2.863

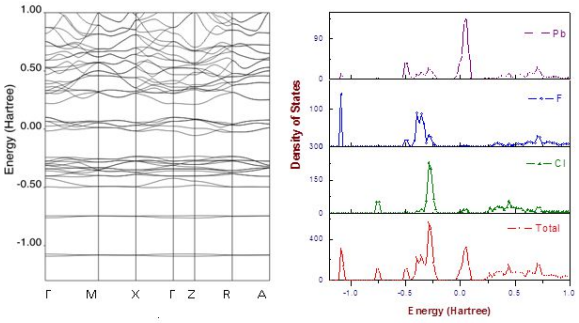

Fig.1 Energy bands and DOS curves for PbFCl computed using DFT-GGA theory of LCAO method.

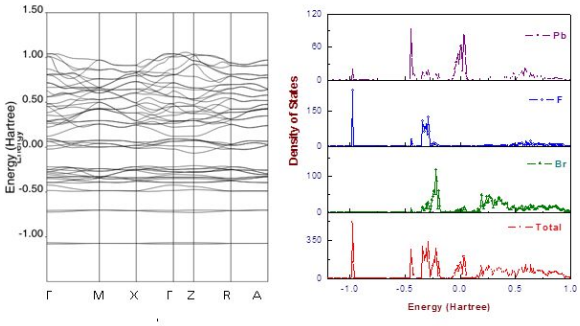

Fig.2 Energy bands and DOS curves for PbFBr computed using DFT-GGA theory of LCAO method.

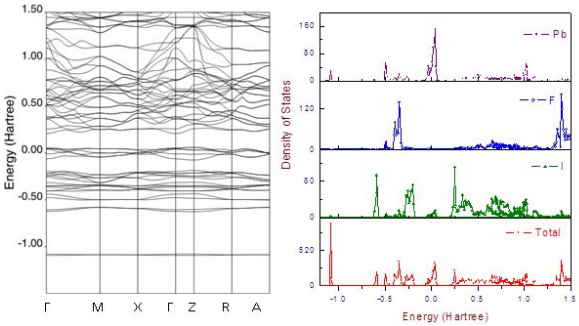

Fig.3 Energy bands and DOS curves for PbFI computed using DFT-GGA theory of LCAO method.

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