Abstract

First-principle calculations within the framework of density functional theory (DFT) are considered as one of the most advanced computational methods in quantum mechanics to address the microscopic properties of many body systems in finer detail. The entire research work in this dissertation is primarily focused on understanding the structural, electronic and optical properties of technologically relevant materials using first-principle calculations. In the early phase of research, technologically relevant material Mercurous Chloride (Hg_2Cl_2) is considered as a reference compound and its structural, electronic and optoelectronic properties have been studied in detail from first-principle calculations. The electronic band gap of the Hg_2Cl_2 compound has been estimated from the DFT calculations upon inclusion of different hybrid and non-hybrid exchange-correlation functionals and on-site Coulomb repulsion term. Detailed investigations show that the Hg_2Cl_2 system is a wide band gap charge transfer insulator. The Mulliken bond population, electronic charge density distribution and Bader charges analyses have been performed to unveil the covalent and ionic interactions between Hg and Cl atoms of Hg_2Cl_2. The Natural Bond Orbital analyses have been studied to gain deeper insights into the charge transfer interactions between Hg and Cl atoms of the Hg_2Cl_2 compound. The pressure-driven structural phase transitions from the body–centred tetragonal to base–centred orthorhombic and from the base–centred orthorhombic to primitive orthorhombic phases of the same compound have been explored from first-principle DFT and Born – Oppenheimer molecular dynamics (BOMD) calculations. The key phonon modes behind these phase transitions and the nature of structural phase transitions have been unveiled. The electronic and optoelectronic properties of the Hg_2Cl_2 system in its various phases have also been explored. Modulations of electronic band gaps and optoelectronic parameters such as complex dielectric functions, absorption coefficients, optical conductivities, refractive indices of the system have been critically unveiled under external pressure. Temperature-induced structural phase transition and negative thermal expansion behaviour of the Hg_2Cl_2 compound have been further studied from DFT and BOMD calculations. The key phonon modes responsible for the body–centred tetragonal to base–centred orthorhombic phase transition and negative thermal expansion of the compound have been investigated. Recently, the band gaps of nitride perovskites with general formula ABN_3 ("A" and "B" are cationic elements) have been predicted from machine learning models and DFT calculations. Four machine learning models such as multi-layer perceptron, gradient boosted decision tree, support vector regression and random forest regression have been considered to predict the band gaps of the nitride perovskite compounds. The band gaps of two nitride perovskites $CeMoN_3$ and $CeWN_3$ have been further predicted from DFT calculations as well as machine learning methods. The entire study is expected to provide a wealth of information in understanding the structural, electronic and optical properties of technologically relevant materials from first-principle calculations.

The aforementioned research work has been framed in the form of a thesis entitled **"Understanding the Structural, Electronic and Optical Properties of Technologically Relevant Materials from First-Principle Calculations"** under Registration No: SOPHY1112119 (Dated: 06/11/2019) and **Index No: 121/19/Phys./26** for the award of Ph.D (Science) degree at Jadavpur University, Kolkata, India. The work was done under the guidance of Prof. (Dr.) Joydeep Chowdhury, at the Department of Physics, Jadavpur University. This thesis is a presentation of the original research work. All the results incorporated in the thesis have been published in different peer-reviewed journals of international repute. The list of publications with the reprints of the published papers that are included in the thesis and the list of papers presented in the international and/ or national conferences/ seminars have been incorporated into the thesis. Moreover, wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

J Chowdhury 19/06/2024

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(Signature of the Supervisor(s) date with official seal)

Swarup Ghosh 19.06.2024

Swarup Ghosh

Prof. Joydeep Chowdhury
Professor
Department of Physics
Jadavpur University
Kolkata - 700 032