

Magnetic and Optical Properties of LiNbO₃ Type InCoO₃ and InFeO₃ perovskite materials.

Noor E Mustafa Ferdous

20/3/2022

Abstract

Metal oxide perovskites are increasingly popular for magnetic and optoelectronic applications in industrial purposes. In this study, structural magnetic and optical properties of InCoO₃, and InFeO₃ were unearthed using the first principles of density functional theory. These materials exhibit semiconducting behavior with indirect bandgap energy. The high absorption coefficient, low reflectivity, and high optical conductivity make them suitable for photovoltaic and other optoelectronic and memory device applications. Among them, InFeO₃ is more favorable for magnetic and optical applications[4].

Introduction

The use of solar energy to catalyze photo-driven operations has attracted enormous engagement from the scientific society because of its great potential to handle energy and environmental issues. In this regard, several attempts have been made by researchers to design and develop different materials with enhanced photocatalytic efficiencies.[9]

In a quest for nanoparticles, solar cells, and enhanced optical and magnetic properties, perovskite materials suit flawlessly in that range [10]. Perovskite materials contain properties like tunable bandgap, long charge diffusion length, good charge carrier mobility, low carrier recombination rate, high dielectric constant. They have high efficiency in photoconductor-based X-ray detectors, spectroscopy, acoustic wave signal processing, and image storage device. These materials are the class of material that bears the chemical structure of ABO_3 [3, 14, 8].



Figure 1: Cubic Structure of InCoO₃ and InFeO₃

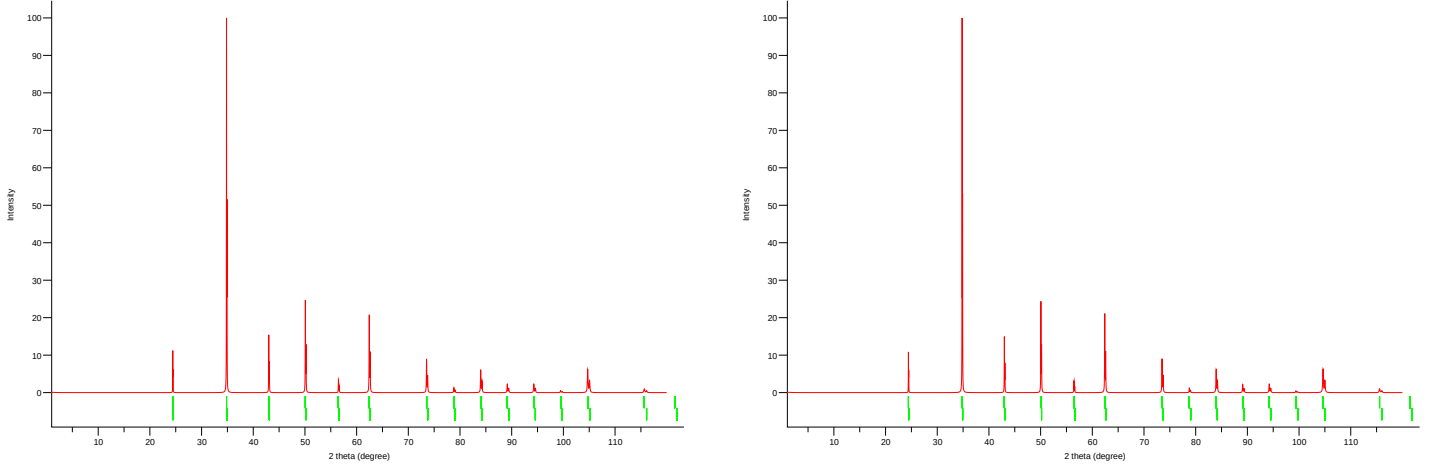


Figure 2: X-Ray diffraction pattern of InCoO3 and InFeO3

In this type of material, O is oxygen with (-2) ionic valence anion, and A and B metal cations give (+6) valence ion combined. Perovskite material family has numerous types of oxide form like transition metal oxides with the general formula of ABO_3 [3]. One perovskite material is LiNbO₃. For that, we took LiNbO₃-like material InCoO₃, InFeO₃ and sampled magnetic and optical properties with DFT calculations[5].

Computaion Method

During the past decade, computer simulations based on a quantum-mechanical description of the interactions between electrons and between electrons and atomic nuclei have developed an increasingly important impact on solid-state physics and chemistry and on materials science—promoting not only a deeper understanding, but also the possibility to contribute sig-

nificantly to materials design for future technologies. This development is based on two important columns:

- (i) The improved description of electronic many-body effects within density-functional theory (DFT) and the upcoming post-DFT methods.
- (ii) The implementation of the new functionals and many-body techniques within highly efficient, stable, and versatile computer codes, which allow to exploit the potential of modern computer architectures.

An understanding of mathematical functions and functionals is required to understand the basic language of DFT. Functions take a number as input and yield a number as output. For example, eq 1, could take $x = 2$ as input and yield $f(x) = 4$ as output. Functionals are functions of functions. Functionals take a function as input and yield a number as output. The input for a function is enclosed in parentheses (for example $f(x)$), whereas the input for a functional is enclosed in square brackets (for example $F[y]$). A very simple functional is the definite integral functional, $F[y]$ that yields the area under any provided function, y . For example, let us say that we are interested in the area under any general curve, $y = f(x)$, from $x = 0$ to $x = 3$. The functional, $F[y]$, is then given by

$$y = f(x) = 2x \tag{1}$$

$$F[y] = \int_0^3 f(x)dx \quad (2)$$

The functional $F[y]$ in eq 2 could take the function given in eq 1 as input and yield the output $F[2x] = 9$. Functionals can be defined as either local or nonlocal. A functional is local if the functional's value can be computed for small segments of the input curve and then summed to find the total value. Other- wise the functional is called nonlocal. A density functional takes the electron density (a function of the position coordinate, r) as an input and outputs a number (an energy). Density func- tionals can be local or nonlocal.

As usual in many-body electronic structure calculations, the nuclei of the treated molecules or clusters are seen as fixed (the Born–Oppenheimer approximation), generating a static external potential V , in which the electrons are moving. A stationary electronic state is then described by a wavefunction $\psi(r_1, \dots, r_N)$ satisfying the many-electron time-independent Schrödinger equation.

$$\begin{aligned} \mathcal{H}\Psi &= [\hat{T} + \hat{V} + \hat{U}] \\ &= \left[\sum_{i=1}^N \left(-\frac{\hbar}{2m_i} \Delta_i^2 \right) + \sum_{i=1}^N V(r_i) + \sum_{i<j}^N U(r_i, r_j) \right] \Psi = E\Psi \end{aligned} \quad (3)$$

In this review, I discuss the implementation of various DFT functionals [local-

density approximation (LDA), generalized gradient approximation (GGA), meta-GGA, hybrid functional mixing DFT, and exact (Hartree-Fock) exchange] and post-DFT approaches [DFT + U for strong electronic correlations in narrow bands, many-body perturbation theory (GW) for quasiparticle spectra, dynamical correlation effects via the adiabatic-connection fluctuation-dissipation theorem (AC-FDT)] in the Vienna ab initio simulation package VASP.

For computing the magnetic and optical properties of InFeO₃ and InCoO₃, we execute Density Functional Theory (DFT)[7, 12, 2, 11] simulations by Vienna ab initio Simulation Package (VASP)[6, 1, 13]. The unit cells of InCoO₃ and InFeO₃ in the cubic form are shown in Fig. 1, which we explored further. First, we perform structural relaxation. Then we execute static calculation for density of states, band, and optical properties of chosen materials.

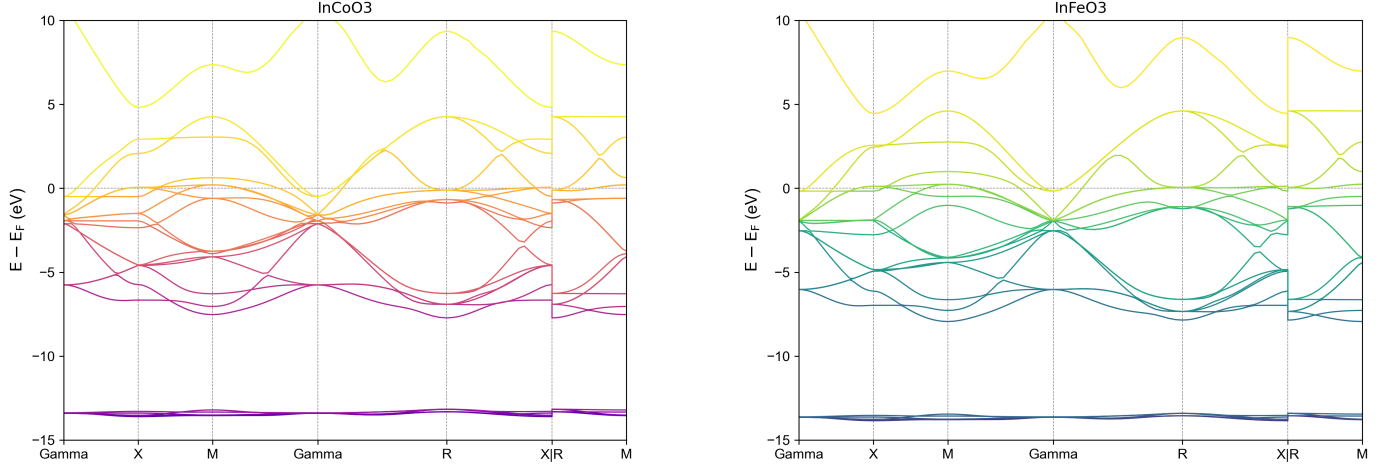


Figure 3: Band Structure Of InCoO3 and InFeO3

Results

InFeO3 and InCoO3 are cubic structures under the space group of Pm3m (no. 221). We visualize the structures in VESTA (3D Visualization for Electronic and Structural Analysis). The unit cell of InCoO3 and InFeO3 constitutes five atoms (shown in Fig. 1). Fe or Co atoms hold the corner positions of the cubes (Wyckoff site (0,0,0)), In situated in the crystal's body-centered positions (Wyckoff site(0.5,0.5,0.5)). O occupies face-centered positions (Wyckoff site (0.5,0.5,0)). The electronic band structures and density of states(DOS) of relaxed InCoO3 and InFeO3 structures through PBE functional considering the GGA approximation. Band structures of InCoO3 and InFeO3 are shown in Fig. 2.

Zero-point energy is Fermi energy. Two structures show indirect bandgap

and the range of the bandgap energy resembles that both the structures are metallic in nature. The outcome of the bandgaps and band structures of the examined materials confirm their wonder for photothermal, photovoltaic, and optoelectronic applications. InCoO3 and InFeO3 show the same bandgap. The density of states of atoms is shown in Fig. 3.

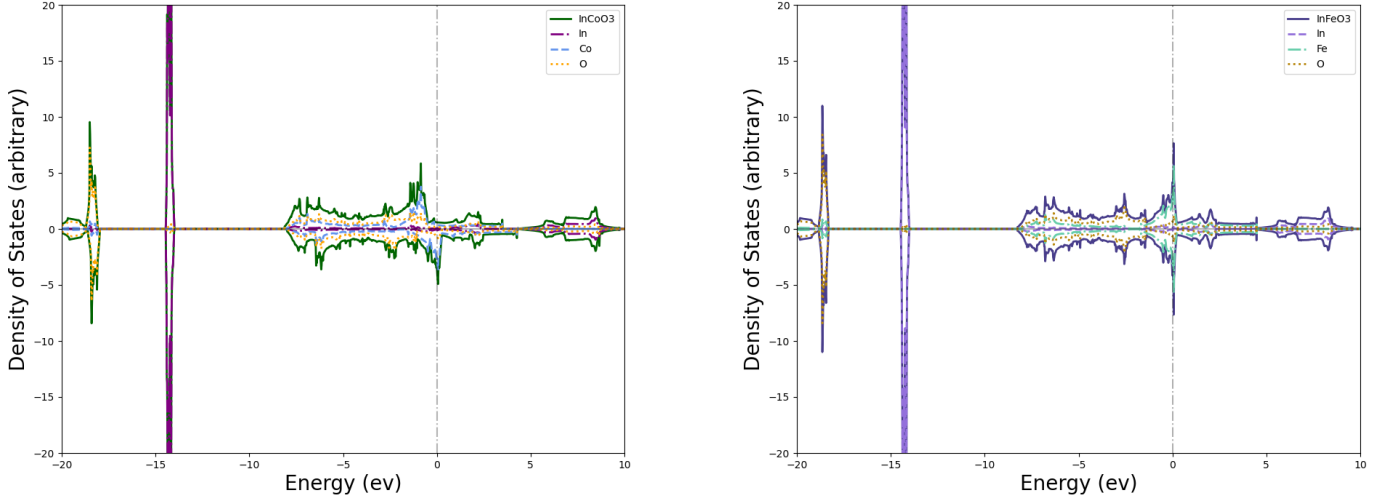


Figure 4: Density of States Of InCoO3 and InFeO3

The orbital projected density of states indicates at the Fermi level, the p-orbital of Co and Fe atom is the main benefactor. The optical properties of a material rely on many parts. Such as absorption spectra, concerning light energy and wavelength, reflectivity, refractivity index, dielectric constants, and optical conductivity. We examined these properties with InCoO3 and InFeO3. The optical absorption coefficient indicates how much light penetrates the substance before being absorbed by the material. This is a piece of important knowledge for solar-energy conversion efficiency for practical

application. In Fig. 4 energy and wavelength-dependent absorption profiles are demonstrated.

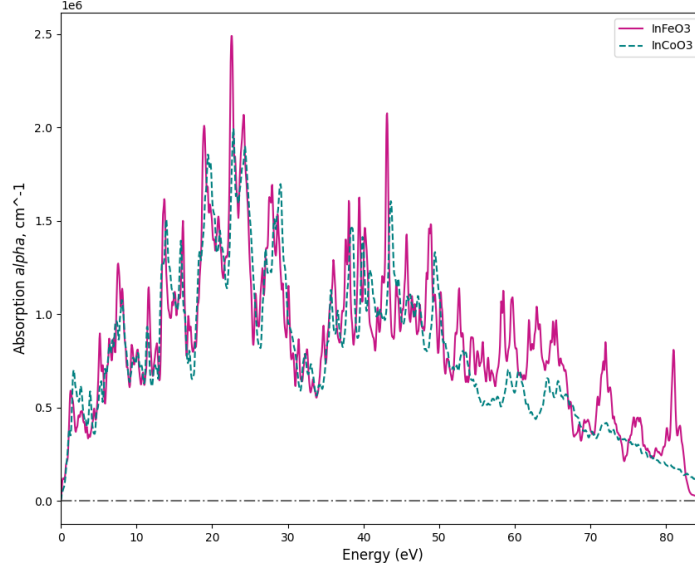


Figure 5: Absorption Of InCoO3 and InFeO3

Reflectivity is an optical property to understand the surface nature of the material. It defines how much energy reflects from incident energy on the surface. Fig 5 represents the optical reflectivity of InCoO3 and InFeO3.

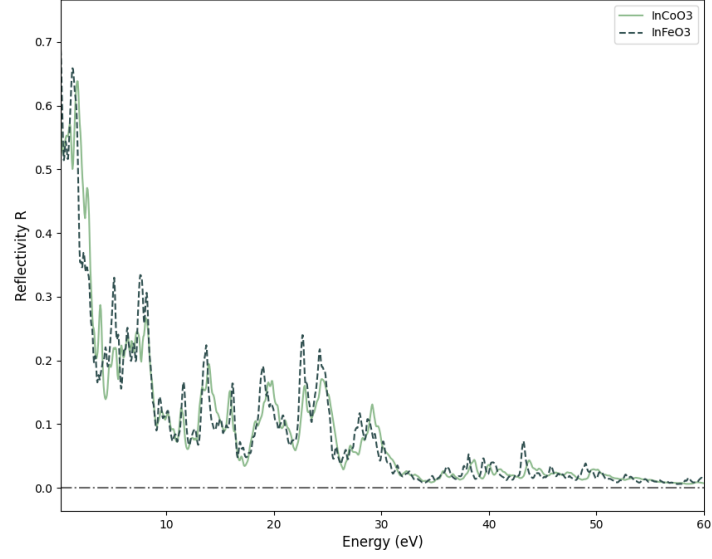


Figure 6: Reflectivity Of InCoO3 and InFeO3

The dielectric constant values are used for determining how well optoelectronic devices work, defined as the response of a material to incident light energy. Higher dielectric values at a lower charge carrier recombination rate are deep in improving the optoelectronic device performance.

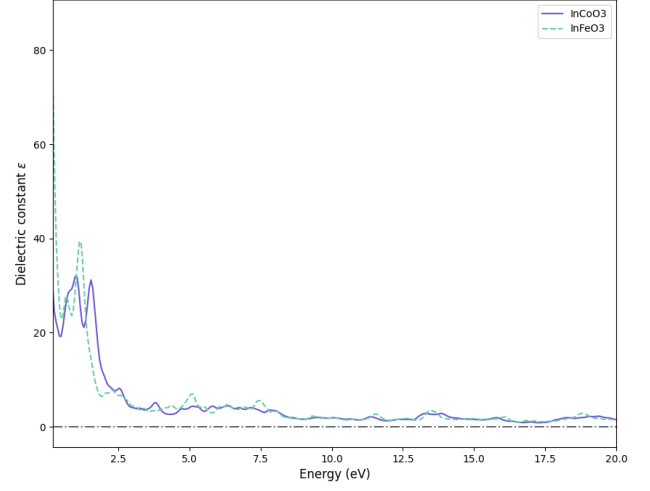
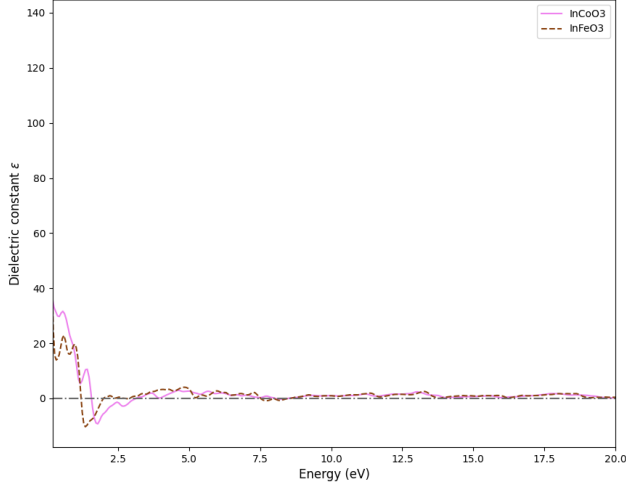


Figure 7: Dielectric constants of InCoO3 and InFeO3

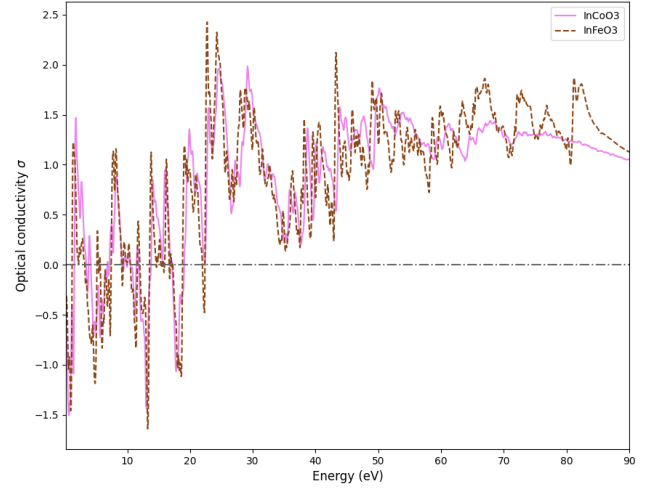
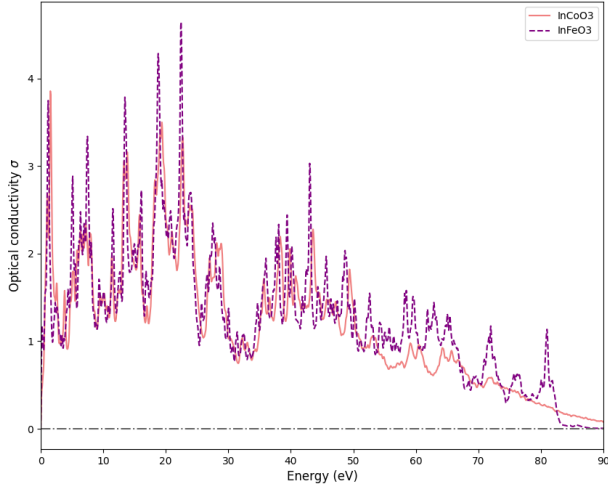


Figure 8: Optical Conductivity of InCoO3 and InFeO3

The optical conductivity of a material specifies the electric conductivity of a photon from electromagnetic absorption. Fig 6 shows the dielectric

constants of InCoO₃ and InFeO₃. Fig 7 shows us optical conductivity between InCoO₃ and InFeO₃. Fig. 9 and 10 shows Extinction and Energuloss spectrum of InCoO₃ and InFeO₃ graph respectively.

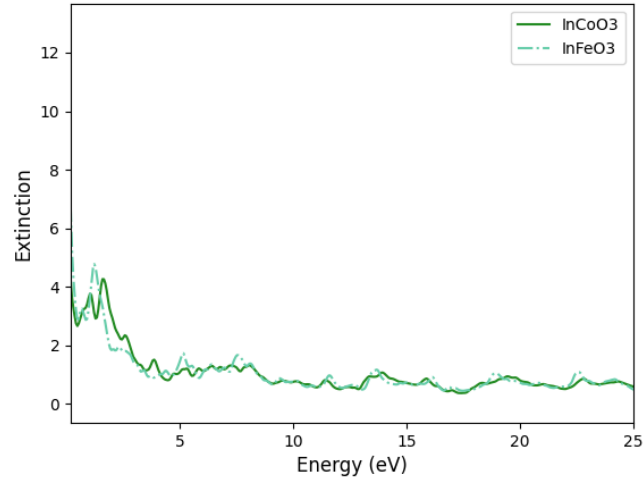


Figure 9: Extinction graph of INCoO₃ and InFeO₃

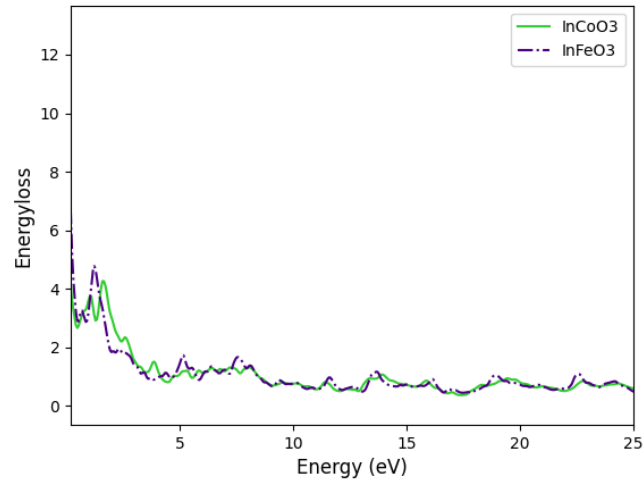


Figure 10: Energyloss spectrum of InCoO₃ and InFeO₃

Conclusion

We performed a study on InCoO₃ and InFeO₃[3] perovskite cubic materials using DFT simulations for their structural, optical, and dielectric properties. InCoO₃ and InFeO₃ structures show identical indirect bandgap while InFeO₃ shows more magnetic than InCoO₃. Fe is a better contender than Co for optical absorption and optical conductivity. Both the material can be an excellent choice for various photovoltaic applications, memory devices, and more. InCoO₃ give band-gap Of 0.0017eV and InFeO₃ give band-gap of 0.0034eV. So, they are magnetic materials.

References

- [1] James E Bear, Tatyana M Svitkina, Matthias Krause, Dorothy A Schafer, Joseph J Loureiro, Geraldine A Strasser, Ivan V Maly, Oleg Y Chaga, John A Cooper, Gary G Borisy, et al. Antagonism between ena/vasp proteins and actin filament capping regulates fibroblast motility. *Cell*, 109(4):509–521, 2002.
- [2] Michel Bockstedte, Alexander Kley, Jörg Neugebauer, and Matthias Scheffler. Density-functional theory calculations for poly-atomic systems: electronic structure, static and elastic properties and ab initio molecular dynamics. *Computer physics communications*, 107(1-3):187–222, 1997.

- [3] Anton R Chakhmouradian and Patrick M Woodward. Celebrating 175 years of perovskite research: a tribute to roger h. mitchell. *Physics and Chemistry of Minerals*, 41(6):387–391, 2014.
- [4] Xiaoyun Chen, Jun Xu, Yueshan Xu, Feng Luo, and Yaping Du. Rare earth double perovskites: a fertile soil in the field of perovskite oxides. *Inorganic Chemistry Frontiers*, 6(9):2226–2238, 2019.
- [5] Koji Fujita, Takahiro Kawamoto, Ikuya Yamada, Olivier Hernandez, Naoaki Hayashi, Hirofumi Akamatsu, William Lafargue-Dit-Hauret, Xavier Rocquefelte, Masafumi Fukuzumi, Pascal Manuel, et al. Linbo3-type infeo3: room-temperature polar magnet without second-order jahn–teller active ions. *Chemistry of Materials*, 28(18):6644–6655, 2016.
- [6] Jürgen Hafner. Ab-initio simulations of materials using vasp: Density-functional theory and beyond. *Journal of computational chemistry*, 29(13):2044–2078, 2008.
- [7] Anubhav Jain, Geoffroy Hautier, Charles J Moore, Shyue Ping Ong, Christopher C Fischer, Tim Mueller, Kristin A Persson, and Gerbrand Ceder. A high-throughput infrastructure for density functional theory calculations. *Computational Materials Science*, 50(8):2295–2310, 2011.
- [8] K-I Kobayashi, T Kimura, H Sawada, K Terakura, and Y Tokura. Room-temperature magnetoresistance in an oxide material with an ordered double-perovskite structure. *Nature*, 395(6703):677–680, 1998.

- [9] Ashish Kumar, Ajay Kumar, and Venkata Krishnan. Perovskite oxide based materials for energy and environment-oriented photocatalysis. *Acs Catalysis*, 10(17):10253–10315, 2020.
- [10] Ashish Kumar, Ajay Kumar, and Venkata Krishnan. Perovskite oxide based materials for energy and environment-oriented photocatalysis. *Acs Catalysis*, 10(17):10253–10315, 2020.
- [11] Kurt Lejaeghere, Gustav Bihlmayer, Torbjörn Björkman, Peter Blaha, Stefan Blügel, Volker Blum, Damien Caliste, Ivano E Castelli, Stewart J Clark, Andrea Dal Corso, et al. Reproducibility in density functional theory calculations of solids. *Science*, 351(6280):aad3000, 2016.
- [12] Ann E Mattsson, Peter A Schultz, Michael P Desjarlais, Thomas R Mattsson, and Kevin Leung. Designing meaningful density functional theory calculations in materials science—a primer. *Modelling and Simulation in Materials Science and Engineering*, 13(1):R1, 2004.
- [13] M Reinhard, K Giehl, K Abel, C Haffner, T Jarchau, V Hoppe, BM Jockusch, and U Walter. The proline-rich focal adhesion and microfilament protein vasp is a ligand for profilins. *The EMBO journal*, 14(8):1583–1589, 1995.
- [14] Stephen J Skinner. Recent advances in perovskite-type materials for solid oxide fuel cell cathodes. *International Journal of Inorganic Materials*, 3(2):113–121, 2001.