Ab-initio studies of exotic properties of ϵ-Fe_2O_3: A rare polymorph of iron oxide

A thesis submitted in fulfillment of the requirements

for the degree of Doctor of Philosophy

by

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Declaration by the Research Scholar

I hereby declare that the entire work embodied in this Thesis is the result of investigations carried out by me in the School of Basic Sciences, Indian Institute of Technology Mandi, under the supervision of Dr. Arti Kashyap, and that it has not been submitted elsewhere for any Degree or Diploma. In keeping with the general practice, due acknowledgments have been made wherever the work described is based on finding of other investigators.

Mandi
July 2020

Imran Ahamed

Declaration by the Research Advisor

It is certify that the entire work in this Thesis has been carried out by Imran Ahamed, under my supervision in the School of Basic Sciences, Indian Institute of Technology Mandi, and that no part of it has been submitted elsewhere for any Degree or Diploma.

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Abstract

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The functional materials are being explored for their various tunable properties which are employed in applications. The presence of more than one property simultaneously makes the functional material interesting such as multiferroics. The presence of the electric and magnetic ferroic order in the magnetoelectric materials are being utilized for the sensors and devices. The presence of two or more ferroic order in a multiferroic material is usually because of two or more different types of elements present it. The mechanism of such coupling between the ferroic orders is thoroughly understood for example in $BaTiO_3$, $BiFeO_3$, Cr_2O_3 to name a few. There are few materials which are having exciting properties but attract less interest because of the complexity and lack of synthesis techniques. One of such a material is ϵ-Fe_2O_3. It is one of the polymorphs of Fe_2O_3 but least explored due to its metastable state in bulk form. Fe_2O_3 is abundant in the earth's crust but the content of ϵ-Fe_2O_3 in the iron-oxide is very small.

This phase of Fe_2O_3 was very well known to ancient people as it is present in the pigments on the centuries-old potteries in different parts of China, Japan and Europe. Nowadays it is only being synthesized in laboratories in nanoparticle form and thin-films with the presence of other phases of Fe_2O_3. Apart from the magnetic property of the nanoparticles of ϵ-Fe_2O_3, the other important properties are yet not known experimentally.

The nanoparticles of ϵ-Fe_2O_3 is reported to be magnetoelectric and also has a very high coercivity of 2 T, which is very huge as compared to the other polymorphs of Fe_2O_3. A possible way to study or predict the properties of this phase of Fe_2O_3 is to study from density functional theory (DFT) method. The DFT gives a very accurate prediction of the various electronic and magnetic properties. With the use of DFT, the lack of the availability of the bulk sample is no longer a hindrance and the properties of ϵ-Fe_2O_3 are studied and various applications of it are being explored.

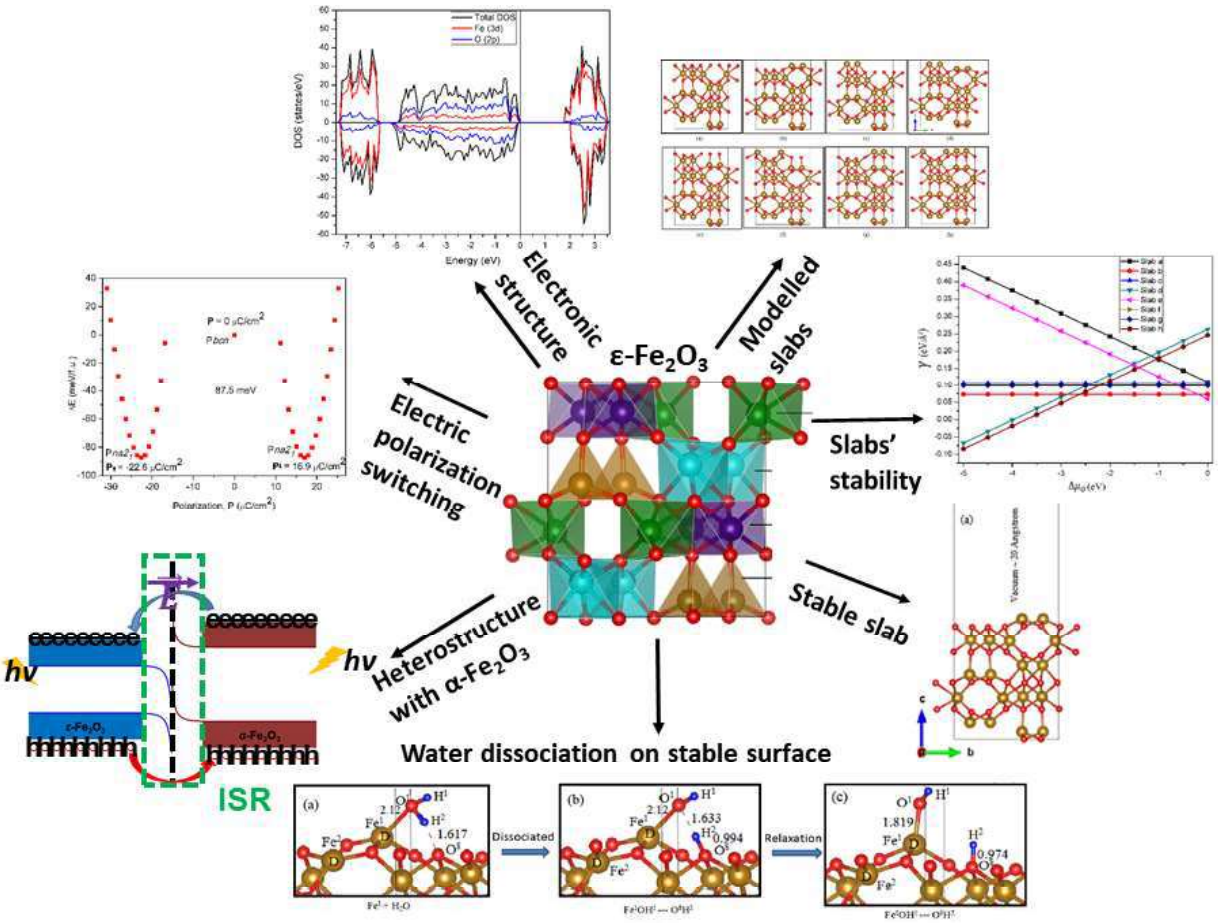
The bulk ϵ-Fe_2O_3 is an orthorhombic crystalline phase of Fe_2O_3 with four different sites of Fe-atoms. It is strongly correlated because of the presence of localized d-orbitals of Fe-atoms. In this thesis ϵ-Fe_2O_3 is explored for its various properties by the method of DFT with proper care of the strong correlation. By the means of DFT and Hubbard U parameter, we have explored the electronic structure in the bulk and thin-film forms. The modelling of various thin-film surfaces and studying their stability gives us a stable thin-film surface for various other studies. The magnetic properties such as the spin arrangement, magnetocrystalline anisotropy and the anisotropy field have been studied. The ferroelectric property of the bulk ϵ-Fe_2O_3 is explored by studying the polarization lattice, the magnitude of electric polarization and the switching of the polarization from one direction to the other.

The stable thin-film surface has been explored for the application of ϵ-Fe_2O_3 in the photoelectrochemical cell (PEC). The stable surface has been hydrolyzed to see the effect of adsorption. The stable surface shows the good adsorption of a water molecule and further leading to the dissociation and creating H^+ and OH^- ions. The water dissociation reaction is studied for the use of this material in PEC for the production of H2 gas from sunlight to be used as fuel.

The surfaces of the thin-film give rise to the surface states which acts as trapping sites for the electron-hole pairs leading to the loss of charges and a decrease in the efficiency of the devices. To overcome the problem of electron-hole pair trapping and also their recombination, we have explored the possibility of modelling the heterostructure of two

polymorphs of Fe_2O_3, namely α-Fe_2O_3 and ϵ-Fe_2O_3. The two oxides coexist in nanoparticle form and are also grown as thin-film. The growth of α-Fe_2O_3 on top of ϵ-Fe_2O_3 gives rise to the charge localization at the interface of the two Fe_2O_3. The alignment of the band edges at the interface of both the materials are such that it gives rise to a rare type-III broken band-gap heterostructure. This kind of band alignment in the heterostructure gives rise to the migration of the different types of charges towards different materials. The electron easily migrates to the conduction band of ϵ-Fe_2O_3 and the holes move towards the valence band of α-Fe_2O_3. This heterostructure helps in the charge separation and can result in good PEC device performance.

The graphical abstract as shown in the figure below describes the various work done in this thesis.



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List of Publications

In thesis

1. **Imran Ahamed**, Rohit Pathak, Ralph Skomski, and Arti Kashyap, "Magnetocrystalline anisotropy of ϵ-Fe_2O_3," AIP Advances **8**, 055815 (2018)

2. **Imran Ahamed**, Kanchan Ulman, Nicola Seriani, Ralph Gebauer, and Arti Kashyap, "Magnetoelectric ϵ-Fe_2O_3: DFT study of a potential candidate for electrode material in photoelectrochemical cells ," J. Chem. Phys. **148**, 214707 (2018)

3. **Imran Ahamed**, Ralph Skomski, and Arti Kashyap, "Controlling the magnetocrystalline anisotropy of ϵ-Fe_2O_3," AIP Advances **9**, 035231 (2019)

4. **Imran Ahamed**, Ralph Skomski, and Arti Kashyap, "Born effective charges and electric polarization in bulk ϵ-Fe_2O_3: An ab-initio approach," Chemical Physics **535**, 110789 (2020)

5. **Imran Ahamed**, Nicola Seriani, Ralph Gebauer, and Arti Kashyap, "Heterostructures of ϵ-Fe_2O_3 and α-Fe_2O_3: insights from density functional," (Accepted, In press, RSC Advances)

Others

1. Rohit Pathak, **Imran Ahamed**, W. Zhang, S. Vallopilly, D.J. Sellmyer, R. Skomski, Arti Kashyap, "Half-metallic magnetism in $Ti_3Co_{5-x}Fe_xB_2$," AIP Advances, **7** 055713 (2017)

2. Ankan Mukhopadhyay, Sarathlal Koyiloth Vayalil1, Dominik Graulich, **Imran Ahamed**, Sonia Francoual, Arti Kashyap, Timo Kuschel, and P S Anil Kumar, "Asymmetric modification of the magnetic proximity effect in Pt/Co/Pt trilayers by the insertion of a Ta buffer layer," arXiv:1911.12187 (2019)

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