
Ab-initio studies of exotic properties of ϵ -Fe₂O₃: 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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July 2020

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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Department: **School of Basic Sciences**

Thesis title: ***Ab-initio* studies of exotic properties of ϵ -Fe₂O₃: A rare polymorph of iron oxide**

Thesis supervisor: **Dr. Arti Kashyap**

Month and year of thesis submission: **July 2020**

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 in it. The mechanism of such coupling between the ferroic orders is thoroughly understood for example in BaTiO₃, BiFeO₃, Cr₂O₃ 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 -Fe₂O₃. It is one of the polymorphs of Fe₂O₃ but least explored due to its metastable state in bulk form. Fe₂O₃ is abundant in the earth's crust but the content of ϵ -Fe₂O₃ in the iron-oxide is very small.

This phase of Fe₂O₃ 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 Fe₂O₃. Apart from the magnetic property of the nanoparticles of ϵ -Fe₂O₃, the other important properties are yet not known experimentally.

The nanoparticles of $\epsilon\text{-Fe}_2\text{O}_3$ 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 $\epsilon\text{-Fe}_2\text{O}_3$ are studied and various applications of it are being explored.

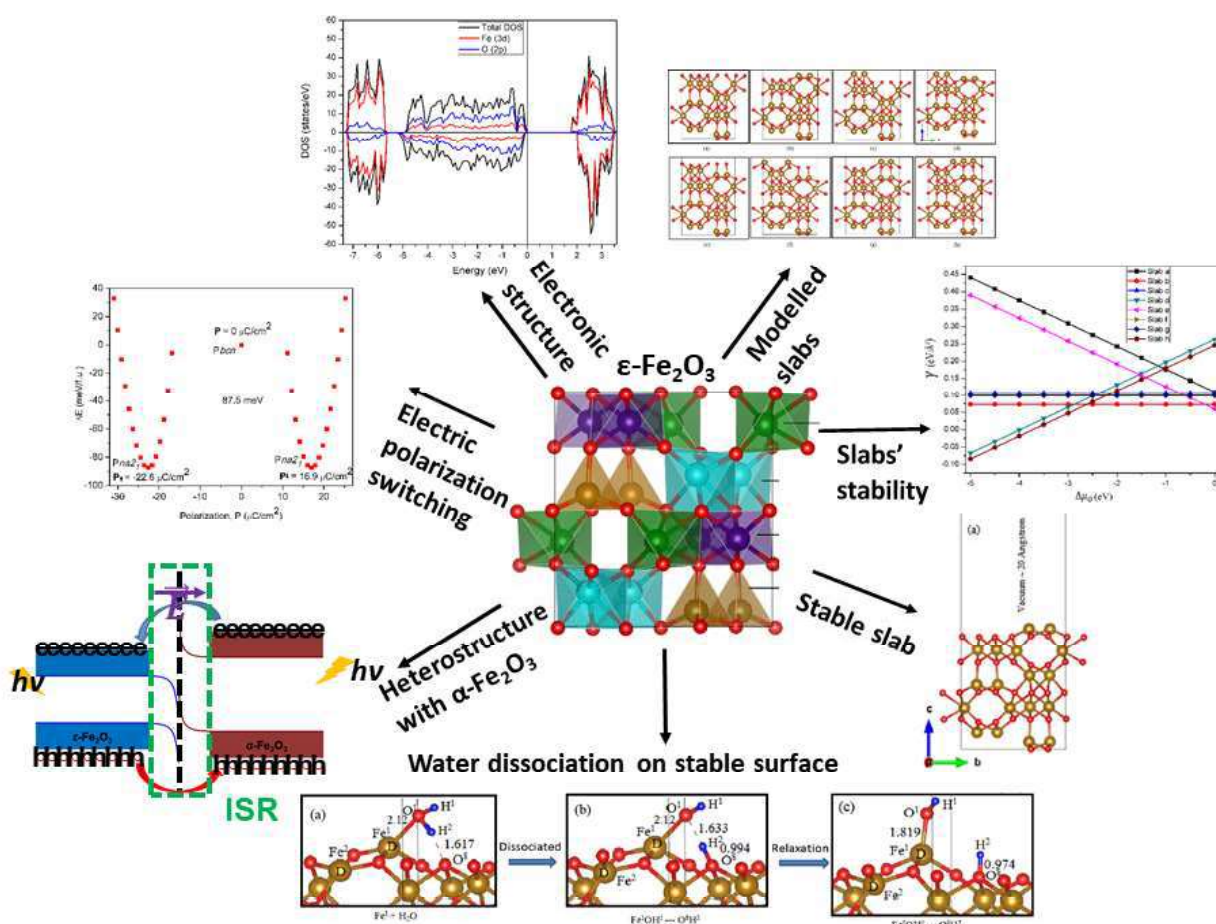
The bulk $\epsilon\text{-Fe}_2\text{O}_3$ is an orthorhombic crystalline phase of Fe_2O_3 with four different sites of Fe-atoms. It is strongly correlated because of the presence of localized d-orbitals of Fe-atoms. In this thesis $\epsilon\text{-Fe}_2\text{O}_3$ is explored for its various properties 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 $\epsilon\text{-Fe}_2\text{O}_3$ 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 $\epsilon\text{-Fe}_2\text{O}_3$ 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 H_2 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 $\alpha\text{-Fe}_2\text{O}_3$ and $\epsilon\text{-Fe}_2\text{O}_3$. The two oxides coexist in nanoparticle form and are also grown as thin-film. The growth of $\alpha\text{-Fe}_2\text{O}_3$ on top of $\epsilon\text{-Fe}_2\text{O}_3$ 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 $\epsilon\text{-Fe}_2\text{O}_3$ and the holes move towards the valence band of $\alpha\text{-Fe}_2\text{O}_3$. 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.



Acknowledgements

I take this opportunity to express my heartfelt gratitude and profound indebtedness towards my thesis supervisor Dr. Arti Kashyap for her excellent guidance, support and encouragement which made this thesis possible. She is always enthusiastic, energetic and full of scientific ideas. She has guided me with her invaluable suggestions, lightened up the way and encouraged me a lot in academic life. I would like to thank her for being supportive and giving me the freedom to work in my own ways which helped me to bring out my best. It was a great pleasure to have a chance of working with her. I am also thankful to her for giving me a chance to work in collaboration with the International Center for Theoretical Physics (ICTP), Italy.

I would like to thank my Doctoral Committee members Dr. Aditi Halder, Dr. Ajay Soni, Dr. Kausatv Mukherjee and Dr. Sudhir Kumar Pandey for their timely support and evaluation of my research work and giving suggestions whenever needed. I gratefully acknowledge Ministry of Human Resource Development (MHRD) and IIT Mandi for the financial support and fellowship during my Ph.D. tenure. I am very thankful to the computational facilities team of IIT Mandi and the University of Nebraska, Lincoln for providing the excellent facilities to run the computational codes. I am also thankful to Science and Engineering Research Board (SERB), India for the financial support provided to attend the 2019 Joint MMM-Intermag conference.

I am thankful to Simons Foundation which awarded the fellowship to my thesis supervisor and through which I got the chance to work at the prestigious institute, ICTP. I am thankful to Dr. Ralph Gebauer, Dr. Nicola Seriani and Dr. Kanchan A. Ulman under their guidance I have worked at ICTP on many occasions. They were really helpful through discussions and ideas. Special thanks to Dr. Kanchan for the detailed discussions we had, which helped me in completing a nice work.

Finally, and most importantly I want to thank my friends, seniors and labmates at IIT Mandi for all their help and encouragement. I am thankful to my parents, brothers and sisters for their affectionate support, good wishes and encouragement they showered on me all through my life.

Above all I am grateful to God who has given me spiritual support and courage to carry out this work.

Imran Ahamed
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List of Publications

In thesis

1. **Imran Ahamed**, Rohit Pathak, Ralph Skomski, and Arti Kashyap, “Magnetocrystalline anisotropy of ϵ -Fe₂O₃,” AIP Advances **8**, 055815 (2018)
2. **Imran Ahamed**, Kanchan Ulman, Nicola Seriani, Ralph Gebauer, and Arti Kashyap, “Magnetoelectric ϵ -Fe₂O₃: 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 -Fe₂O₃,” AIP Advances **9**, 035231 (2019)
4. **Imran Ahamed**, Ralph Skomski, and Arti Kashyap, “Born effective charges and electric polarization in bulk ϵ -Fe₂O₃: An ab-initio approach,” Chemical Physics **535**, 110789 (2020)
5. **Imran Ahamed**, Nicola Seriani, Ralph Gebauer, and Arti Kashyap, “Heterostructures of ϵ -Fe₂O₃ and α -Fe₂O₃: insights from density functional,” (Accepted, In press, RSC Advances)

Others

1. Rohit Pathak, **Imran Ahamed**, W. Zhang, S. Valloppilly, D.J. Sellmyer, R. Skomski, Arti Kashyap, “Half-metallic magnetism in Ti₃Co_{5-x}Fe_xB₂,” 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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