Dielectric response of Fe$_2$O$_3$ crystals and thin films

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1. Introduction

Iron sesquioxide or haematite (α-Fe$_2$O$_3$) is becoming one of the most studied visible light photocatalysts, in particular for photo-electrochemical water splitting [1–7]. Recently, nanostructured Fe$_2$O$_3$ has demonstrated some of the largest solar-to-hydrogen conversion efficiencies achieved to date (in excess of 2%) [6]. Further optimisation of the materials performance towards commercially viable hydrogen generation requires a deeper understanding of the factors that limit the photoelectrochemical processes. Indeed, even the dielectric constants of haematite, which are required to interpret data from optical, transport, capacitance and impedance measurements, are found lacking.

Reported values of the dielectric constants for Fe$_2$O$_3$ range from 5 to 120 [8]. In the analysis of electrochemical measurements of Fe$_2$O$_3$, values of 12 [9], 80 [10], 100 [5] and 120 [11] are commonly used. While it has been possible to compute the dielectric response of materials for some time using first-principles electronic structure techniques, it has traditionally been a convoluted process involving the application of a homogeneous electric field across a large supercell [12], where convergence in the dielectric constants was difficult to achieve. Recent developments in perturbation theory, and increased computational power, allow for the prediction of both the low and high frequency dielectric response on an equal footing.

In this communication, we apply density functional perturbation theory (DFPT) to calculate the dielectric response of α-Fe$_2$O$_3$. The electron exchange and correlation effects are treated using a gradient corrected functional with an on-site Coulomb potential. The resulting values are critically examined with respect to literature data, employing an effective medium approximation to understand the behaviour of Fe$_2$O$_3$ thin-films in aqueous solutions.

2. Dielectric response

We report the static ($\varepsilon_0$) and high frequency ($\varepsilon_\infty$) dielectric constants of haematite (α-Fe$_2$O$_3$) as calculated using density functional perturbation theory. The values for bulk iron oxide are $\varepsilon_0^1 = 26.41$; $\varepsilon_0^2 = 17.84$; $\varepsilon_0^3 = 7.87$ and $\varepsilon_0^4 = 7.57$. The effective static dielectric screening of porous thin-films is predicted in aqueous solutions, using effective medium theory, to range between 33 and 44 depending on the crystal packing density. The large spread in literature values (12–120) can only be explained through surface and micro-structuring effects. These results will be important for interpreting and modelling the materials behaviour, particularly in electrochemical and photoelectrochemical cells.

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Clausius–Mosotti relation [15]. We employ the effective medium theory developed by Bruggeman [16], which can be formulated as:

\[
p_1 \left( \frac{\varepsilon_1 \varepsilon_r}{\varepsilon_1 + (d - 1)\varepsilon_r} \right) + p_2 \left( \frac{\varepsilon_2 \varepsilon_r}{\varepsilon_2 + (d - 1)\varepsilon_r} \right) = 0
\]

The parameter \(d\) represents the dimensionality of the system, i.e., 3 for three dimensional. The equation is quadratic in \(\varepsilon_r\). Applied to the case of a nano-particulate film in contact with a solution, the dielectric constants of the two components are fixed and the packing density determines the respective volume fractions. A python script, which can be used to calculate arbitrary mixtures, is available online [17].

3. Computational approach

The total energy and electronic structure of \(\alpha\)-Fe₂O₃ were calculated using density functional theory within the code \textit{VASP} [18,19]. The plane wave basis set (500 eV kinetic energy cut-off) and \(k\)-point sampling \((6 \times 6 \times 2)\) \(\Gamma\)-centered mesh; hexagonal crystal setting) were both checked for convergence, and nuclear forces were optimised to within 1 meV/Å using a Quasi–Newton algorithm. The quantum mechanical effects of electron exchange and correlation were treated at the level of the local density algorithm. The quantum mechanical effects of electron exchange–correlation potentials.

Following local optimisation of the lattice vectors and internal positions, within the space group symmetry, the dielectric response was calculated from a tightly converged wave function (tolerance of \(10^{-5}\) eV) using density functional perturbation theory [21]. Within DFPT the interatomic force constants are calculated from the linear response of the electron density with respect to atomic displacements. The response to a homogeneous electric field is also computed in the linear regime, which avoids difficulties in re-defining periodic boundary conditions [21]. It should be emphasised that the macroscopic bulk response function is computed with no account for surface or boundary effects. However, in addition to the macroscopic effects, the contributions of microscopic ‘local fields’ are explicitly included in both the Hartree and exchange–correlation potentials.

4. Crystal and magnetic structure

The primitive unit cell of haematite is trigonal (space group \(R\overline{3}c\)) with two formula units (10 atoms) per cell. The equilibrium lattice vectors at the specified level of theory are in good agreement with typical diffraction data for bulk samples \((a = 5.36 \text{ Å}; \alpha = 55.22^\circ)\). However, the stable magnetic configuration cannot be modelled within this basis. The \(d^5\) electronic configuration of Fe(III), spin polarisation was performed at a similar level of theory in Ref. [24], firstly the re-splitting) and the high-frequency response from 6.7 to 7.0 [22]. However, the static values are significantly below the majority of dielectric constants reported (e.g., 80 [10], 100 [5] and 120 [11]) and significantly above the value of 12 reported in the CRC Handbook of Chemistry and Physics [9]. These discrepancies are well above the typical uncertainties in capacitance measurements, e.g., from estimates of sample area and thickness [23].

It should be noted that when comparing to recent calculations performed at a similar level of theory in Ref. [24], firstly the reported ‘static macroscopic dielectric constants’ refer to the high-frequency optical response, and secondly the primitive trigonal unit cell was used for modelling, which cannot be used to describe the AFM ground-state of Fe₂O₃. However, the study does highlight the dependence of the high-frequency response on the treatment of exchange and correlation within density functional theory. Values obtained using the semi-local PBE functional are more than double those calculated using an on-site Coulomb potential (PBE + U) or a non-local hybrid functional. A local or semi-local treatment produces \(d\)-orbitals too diffuse and a band gap too small, resulting in an exaggerated high-frequency dielectric constant.

One source of discrepancy between the predicted values for bulk haematite and experimental measurements is that the majority of recent work has focused on nano-particulate and porous thin-films of Fe₂O₃ in contact with aqueous solution. To first-order, the response of the system can be treated as a homogeneous dielectric mixture of Fe₂O₃ and water, with the water content being determined by the packing density of the inorganic film. We have applied an effective medium approximation (Eq. (1)), taking the dielectric constant of neutral water at room temperature (80.1) and an isotropic average for Fe₂O₃ (23.55). The density range from 0.52 to 0.74, which determines \(p_1\) and \(p_2\), corresponds to the stacking of mono-dispersed spherical particles from loosely to tightly packed. The resulting behaviour is plotted in Figure 2, where the effective static dielectric constant ranges from 33 (densely packed film) to 44 (highly porous film).

While the dependence of the effective dielectric constant on packing density could be used to explain some of the observed variation in experiments, and may be important for interpreting the behaviour of real systems, it does not explain the colossal dielectric response of 100 or more. An effective dielectric constant above 50...
would require significant contributions from interfacial polarisability, e.g., the aggregation of dipoles at grain boundaries, dislocations and clusters of point defects, which will depend on the stoichiometry and doping density of the sample. Future modelling work could address the behaviour of such extended defects, taking into account the revised bulk dielectric response reported here.

6. Conclusion

We have reported the bulk dielectric constants of Fe$_2$O$_3$ at the low and high frequency regimes, calculated within density functional perturbation theory. The results set an upper limit on the characteristic dielectric response of the material at ca. 44. Reports of dielectrics constants in excess of 50 must be related to the preparation and morphology of the samples. Caution should be applied when choosing a value to interpret the (photo)electrochemical behaviour of systems containing haematite.

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References

[8] Collected from ISI Web of Knowledge (July 2013).