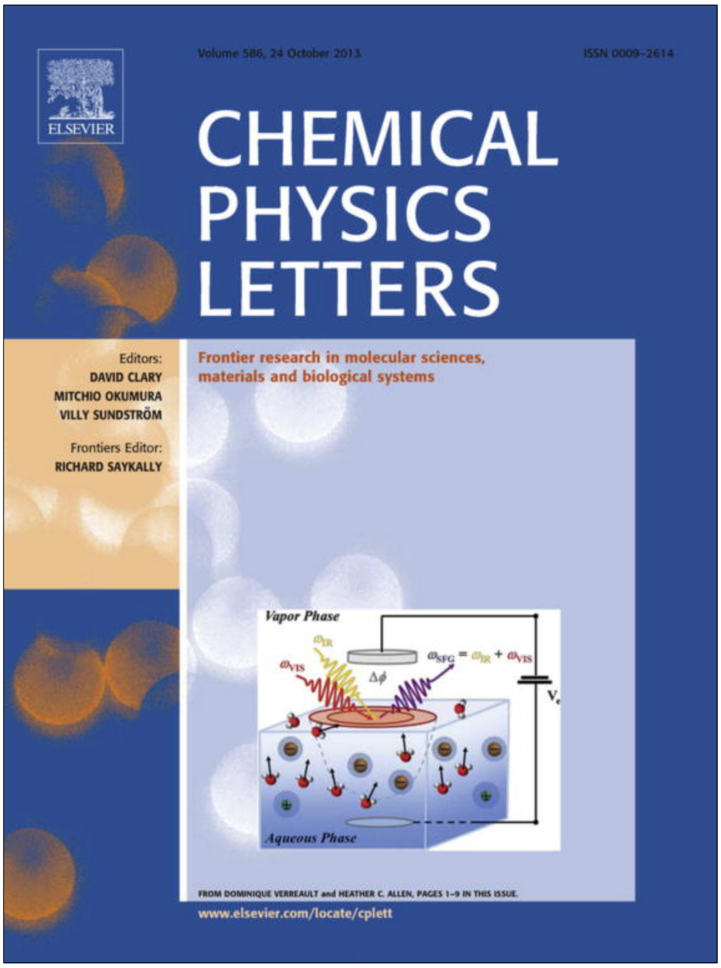

Volume 586, 24 October 2013
ISSN 0009-2614

CHEMICAL PHYSICS LETTERS

Frontier research in molecular sciences, materials and biological systems

FROM DOMINIQUE VERREAULT and HEATHER C. ALLEN, PAGES 1–9 IN THIS ISSUE.

www.elsevier.com/locate/cplett

Chemical Physics Letters 586 (2013) 67–69

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Dielectric response of Fe_2O_3 crystals and thin films

Ruth A. Lunt, Adam J. Jackson, Aron Walsh [*]

Centre for Sustainable Chemical Technologies, Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

ARTICLE INFO

Article history:
Received 7 August 2013
In final form 5 September 2013
Available online 14 September 2013

ABSTRACT

We report the static (ε_0) and high frequency (ε_∞) dielectric constants of haematite (α-Fe_2O_3) as calculated using density functional perturbation theory. The values for bulk iron oxide are $\varepsilon_0^{11} = 26.41$; $\varepsilon_0^{33} = 17.84$; $\varepsilon_\infty^{11} = 7.87$ and $\varepsilon_\infty^{33} = 7.57$. 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.

1. Introduction

Iron sesquioxide or haematite (α-Fe_2O_3) is becoming one of the most studied visible light photocatalysts, in particular for photoelectrochemical water splitting [1–7]. Recently, nanostructured Fe_2O_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_2O_3 range from 5 to 120 [8]. In the analysis of electrochemical measurements of Fe_2O_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_2O_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_2O_3 thin-films in aqueous solutions.

2. Dielectric response

We define the static dielectric constant (ε_0) as the value of the dielectric constant for a material measured in a static electric field, whilst the high-frequency dielectric constant (ε_∞) is the value deduced from the refraction of electromagnetic waves with frequencies high compared to lattice vibrations (phonons) [13], i.e., $\varepsilon_\infty = n^2$, where n is the refractive index. Typical values for an ionic oxide material, taking the example of another sesquioxide In_2O_3, are 9 (ε_0) and 4 (ε_∞) [14]. The static response can be separated into two principal components:

$$\varepsilon_0 = \varepsilon_{\text{ionic}} + \varepsilon_\infty$$

where $\varepsilon_{\text{ionic}}$ is the nuclear response to the electric field (related to the phonon density of states) and ε_∞ is the electronic contribution, described previously. The dielectric response is an anisotropic crystal property, which can be described using a second-rank tensor. For haematite, there are two independent components, which are perpendicular and parallel to the hexagonal c axis of the unit cell: ε_0^{11} and ε_0^{33}, respectively.

The dielectric properties of a mixed system formed from different dielectric materials is a subject that is well developed theoretically [15]. The models are generally based around the concept of a homogeneous mixture, which results in a macroscopic *effective* dielectric constant (ε_e) that is determined by the permittivity of the individual components (ε_i) and their volume fraction (p_i) in the mixture. For binary systems, such theories include those of Wagner and Maxwell (for a spherical core/shell structure), Rayleigh (for a uniform array of spheres in a dielectric medium) and Debye (for a homogeneous mixture, following the

---

[*] Corresponding author.
E-mail address: a.walsh@bath.ac.uk (A. Walsh).

0009-2614/$ - see front matter
http://dx.doi.org/10.1016/j.cplett.2013.09.023

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

$$p_1\left(\frac{\varepsilon_1-\varepsilon_e}{\varepsilon_1+(d-1)\varepsilon_e}\right)+p_2\left(\frac{\varepsilon_2-\varepsilon_e}{\varepsilon_2+(d-1)\varepsilon_e}\right)=0$$

The parameter d represents the dimensionality of the system, i.e., 3 for three dimensional. The equation is quadratic in ε_e. 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 Fe_2O_3 were calculated using density functional theory within the code *VASP* [18,19]. The plane wave basis set (500 eV kinetic energy cut-off) and k-point sampling ($6 \times 6 \times 2$) Γ-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 approximation (LDA) + U, using a on-site potential of 5.5 eV applied to the Fe d channel as previously reported [20]. Due to the d^5 electronic configuration of Fe(III), spin polarisation was treated explicitly.

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^{-9} 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 $R\bar{3}c$) 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 Å; α = 55.22°). However, the stable magnetic configuration cannot be modelled within this basis. The d^5 electronic configuration of Fe(II) results in robust antiferromagnetic ordering along (0001) planes as illustrated in Figure 1. The Néel temperature of Fe_2O_3 is in excess of 900 K. This layer-by-layer antiferromagnetism (AFM) can be described by transforming to the hexagonal space group setting, which is three times larger (30 atoms per unit cell).

5. Dielectric constants

The calculated static dielectric constants of α-Fe_2O_3 are $\varepsilon_0^{11} = 26.41$ and $\varepsilon_0^{33} = 17.84$, while the high frequency dielectric constants are computed as $\varepsilon_\infty^{11} = 7.87$ and $\varepsilon_\infty^{33} = 7.57$, respectively. These values compare well to the dielectric dispersion obtained for single crystals, from infrared reflection spectra, where the static response varies from 20.6 to 24.1 (obtained from the separation of the longitudinal and transverse optic phonon modes: LO–TO 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].

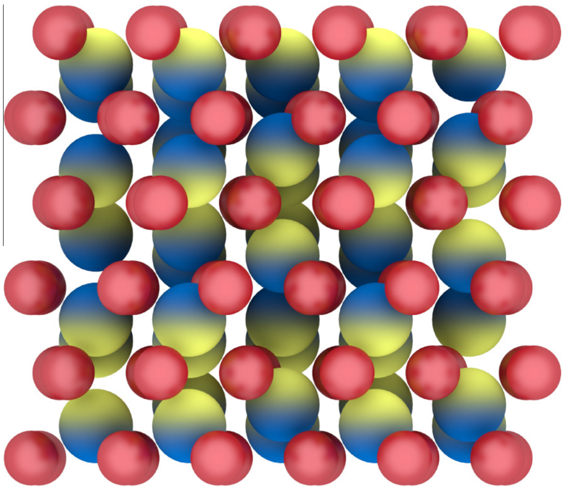

Figure 1. Illustration of the crystal structure of α-Fe_2O_3 (hexagonal setting). The oxygen atoms are coloured red (smaller spheres), while the Fe atoms are shaded from yellow to blue (larger spheres), with the direction of gradient corresponding to the local collinear magnetic moment. The layer-by-layer antiferromagnetic ordering (T_N = 948 K) of Fe is along (0001) planes separated by the oxide anions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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 Fe_2O_3. 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 Fe_2O_3 in contact with aqueous solution. To first-order, the response of the system can be treated as a homogeneous dielectric mixture of Fe_2O_3 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 Fe_2O_3 (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

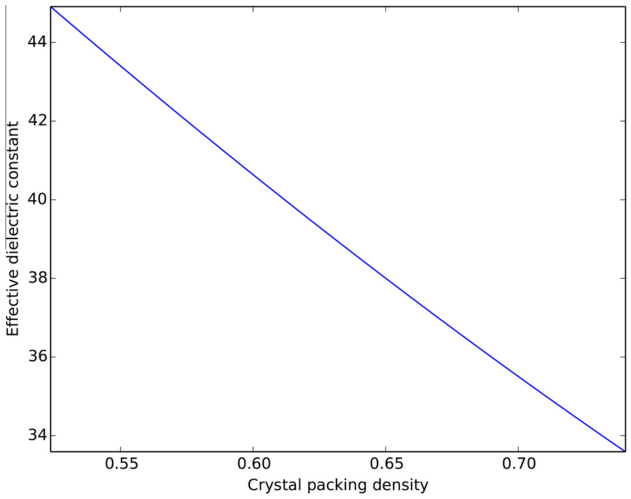

Figure 2. Effective dielectric constant of an Fe_2O_3 film in aqueous solution as a function of the crystal packing density (based on the range typical for mono-dispersed spherical particles).

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_2O_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.

Acknowledgements

We acknowledge L.M. Peter for suggesting the problem, useful discussions with F. Marken and K.T. Butler. R.L. was funded by a Royal Society Summer Studentship, while A.J.J. is funded by EPSRC (Grant No. EP/G03768X/1). Access to the HECToR supercomputer was facilitated through membership of the HPC Materials Chemistry Consortium, which is funded by EPSRC (Grant No. EP/F067496).

References

[1] A. Kleiman-Shwarsctein et al., Chem. Mater. 22 (2009) 510.
[2] A. Kleiman-Shwarsctein, Y.-S. Hu, A.J. Forman, G.D. Stucky, E.W. McFarland, J. Phys. Chem. C 112 (2008) 15900.
[3] C.Y. Cummings, F. Marken, L.M. Peter, A.A. Tahir, K.U. Wijayantha, Chem. Commun. 48 (2012) 2027.
[4] K.U. Wijayantha, S. Saremi-Yarahmadi, L.M. Peter, Phys. Chem. Chem. Phys. 13 (2011) 5264.
[5] K. Sivula, F. Le Formal, M. Grätzel, ChemSusChem 4 (2011) 432.
[6] I. Cesar, A. Kay, J.A. Gonzalez Martinez, M. Grätzel, J. Am. Chem. Soc. 128 (2006) 4582.
[7] Doyle, R.L.; Lyons, M.E.G., ECS Trans. 45 (2013) 3.
[8] Collected from ISI Web of Knowledge (July 2013).
[9] Lide, D.R., CRC Handbook of Chemistry and Physics. (2007) CRC Press: Boca Raton, FL. Note the data for Fe_2O_3 originates from Samokhvalov, A.A., Sov. Phys.-Solid State 3 (1962) 2613.
[10] J.H. Kennedy, K.W. Frese, J. Electrochem. Soc. 125 (1978) 723.
[11] R.K. Quinn, R. Nasby, R. Baughman, Mater. Res. Bull. 11 (1976) 1011.
[12] P. Umari, A. Pasquarello, Phys. Rev. Lett. 89 (2002) 157602.
[13] M. Born, K. Huang, Dynamical Theory of Crystal Lattices, Oxford University Press, Oxford, 1956.
[14] A. Walsh, C.R.A. Catlow, A.A. Sokol, S.M. Woodley, Chem. Mater. 21 (2009) 4962.
[15] D.J. Bergman, Phys. Rep. 43 (1978) 377.
[16] V.D. Bruggeman, Ann. Phys. 416 (1935) 636.
[17] https://github.com/WMD-Bath/dielectric (Accessed 5th August 13).
[18] G. Kresse, J. Furthmüller, Phys. Rev. B 54 (1996) 11169.
[19] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 6 (1996) 15.
[20] M.N. Huda, A. Walsh, Y. Yan, S.-H. Wei, M.M. Al-Jassim, J. Appl. Phys. 107 (2010) 123712.
[21] S. Baroni, S. de Gironcoli, A. Dal Corso, P. Giannozzi, Rev. Mod. Phys. 73 (2001) 515.
[22] S. Onari, T. Arai, K. Kudo, Phys. Rev. B 16 (1977) 1717.
[23] K. Young, H. Frederikse, Compilation of the Static Dielectric Constant of Inorganic Solids, American Chemical Society and the American Institute of Physics, 1973.
[24] P. Liao, E.A. Carter, Phys. Chem. Chem. Phys. 13 (2011) 15189.