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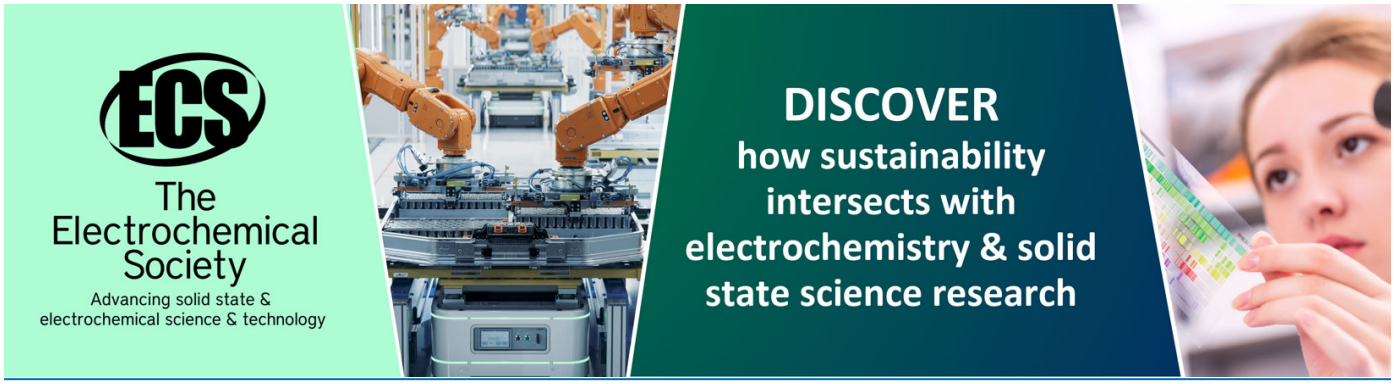

Visualisation of high temperature magnetisation states in magnetite grains using off-axis electron holography

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Abstract. The production of a synthetic basalt comprising Fe_3O_4 grains (~ 50 nm to ~ 500 nm), via a glass ceramic method, has been confirmed using transmission electron microscopy and X-ray diffractometry. Off-axis electron holography combined with *in situ* heating allowed for the visualisation of non-uniform vortex states present in saturation remanent structures, and their variation approaching the Curie temperature; determined separately by bulk thermomagnetic measurements.

1. Introduction

The ability of a rock to reliably record the geomagnetic field depends on the geometry and size of the constituent magnetic particles. In the field of paleomagnetism, the stability of the remanent signal is a critical factor for the recovery of reliable intensity and directional information. Small, magnetically uniform grains, termed single domain (SD), are considered the strongest remanence carriers with good stability over geological time periods [1]. However, the magnetic signature in igneous rocks is usually dominated by larger magnetic grains (~ 0.1 – 10 μm) that display non-uniform magnetic structures, commonly termed pseudo-single domain (PSD), as their bulk magnetic characteristics are similar to SD particles. The most common magnetic minerals on Earth fall within the iron-titanium-oxide ($Fe_{3-x}Ti_xO_4$) system [2], and are commonly found in igneous rocks, including mid-ocean ridge basalts that make up much of ocean plates. In particular, magnetite (Fe_3O_4) is a very important magnetic mineral due to its high abundance and dominating magnetization. In igneous rocks, the leading source of magnetic memory by the constituent magnetic minerals is termed thermal remanent magnetization (TRM) and is acquired in the direction of the ambient geomagnetic field as the grains cool below their Curie temperature (T_C (~ 580 ˚C for magnetite)). However, current understanding of the thermomagnetic behaviour of PSD grains during TRM acquisition is limited and not sufficient to elucidate the intricate details of the stability of PSD states with temperature.

The transmission electron microscopy (TEM) technique of off-axis electron holography permits the nanometre-scale imaging of magnetic induction within and around materials as a function of applied field and temperature [3]. In this context, the synthesis of synthetic basalts containing Fe_3O_4 grains is presented, along with their bulk magnetic properties, and off-axis electron holography is combined with the heating of PSD magnetite (Fe_3O_4) grains *in situ* within the TEM.

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2. Experimental

Samples were prepared by a glass-ceramic method [4] using laboratory grade powders of Fe_2O_3, SiO_2, $CaCO_3$, K_2CO_3, and Na_2CO_3, which were mixed with aqueous polyethylene oxide solution and pressed into pellets (~ 5 mm in diameter) on the end of Pt wires. The pellets were suspended in a vertical temperature controlled tube furnace under an oxygen partial pressure and melted at 1400 ˚C for 15 h to equilibrate Fe^{2+}/Fe^{3+} ratios with the oxygen fugacity, before subsequently quenched in the bottom of the tube furnace. After quenching, the pellets were reheated at 750 ˚C for 3 h and quenched again. For the purpose of structural characterization, quenched pellets of the synthetic basalt were crushed into a fine powder using a pestle and mortar, and were deposited onto single crystal silicon substrates for crystallographic identification using X-ray diffractometry (PANalytical X'Pert PRO Diffractometer). Conventional bright-field (BF) imaging was performed using a FEI Tecnai TEM operated at 200 kV (ER-C). For the purpose of magnetic measurements, the sample was examined at the Natural Magnetism Group laboratory at Imperial College London. The first-order reversal curve (FORC) and high temperature thermomagnetic curve were measured using a Princeton Measurements Vibrating Sample Magnetometer fitted with a furnace; heating was performed in flowing He.

For the purpose of *in situ* heating TEM investigations, desirable regions were deposited and welded with platinum to contacts on a double-tilt EMheaterchip™ before being ion-milled into thin sections. Off-axis electron holograms were acquired at 400˚C, 500 ˚C and 550˚C using an FEI Titan 80–300 TEM in Lorentz mode (ER-C), with a charge-coupled device camera and electron bi-prism operated typically at 90 V. The direction of magnetisation in the particle was reversed at each temperature interval *in situ* in the TEM by tilting the sample ± 75˚ and turning on the conventional microscope objective lens to apply a magnetic field of ~1.5 T to the sample, parallel to the direction of the electron beam. The objective lens was then turned off and the sample tilted back to 0˚ for hologram acquisition in field-free conditions with the particles at remanence of saturation magnetisation.

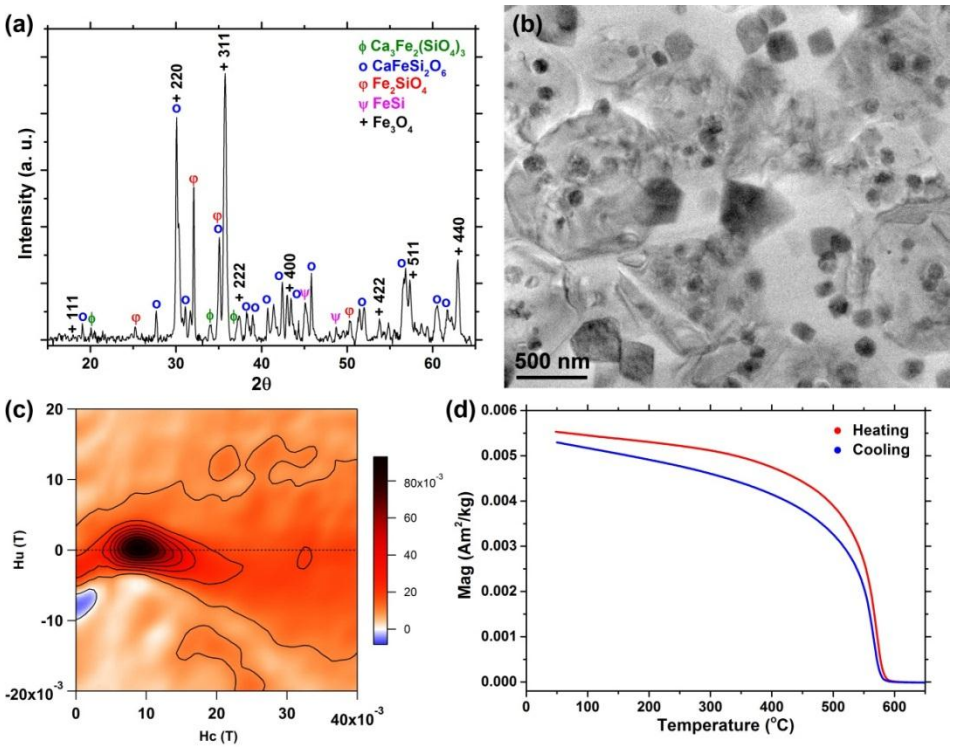

Figure 1 (a) XRD pattern of the synthetic basalt, confirming the Fe_3O_4 phase (indexed, JCPDS 75-449), as well as the additional phases of $CaFeSi_2O_6$, $Ca_3Fe_2(SiO_4)_6$ and FeSi. (b) BF TEM diffraction contrast image of the Fe_3O_4 grains within the silicate matrix ranging from ~ 50 to ~ 500 in diameter. (c) FORC diagram acquired at room temperature (smoothing factor = 7). The measurement time was 250 ms. (d) Thermomagnetic curves of the synthetic basalt. Heating was performed in flowing helium, in a field of 300 mT.

3. Results

The furnace annealing of the precursor powder mixture led to the production of synthetic basalts comprising Fe_3O_4 grains of varied size, the evidence for which is now presented in detail.

Fig. 1 provides information on the size, structure and magnetic properties of the synthesised sample. The peaks in the XRD pattern of Fig. 1a are in good agreement with the presence of Fe_3O_4 (Joint Committee on Powder Diffraction Standards (JCPDS) reference 75-449), as well as pyroxene hedenbergite ($CaFeSi_2O_6$, JCPDS 70-1876), andradite ($Ca_3Fe_2(SiO4)_3$, JCPDS 84-1938), FeSi (JCPDS 86-0795) and Fayalite (Fe_2SiO_4, JCPDS 71-1673). The BF TEM image of Fig. 1b displays Fe_3O_4 grains ranging in size, from ~ 50 nm to ~ 500 nm, along with the surrounding glass ceramic matrix. It is evident that the smaller Fe_3O_4 grains are generally confined within glassy regions, separate from the larger Fe_3O_4 grains. The FORC diagram shows the sample to exhibit behaviour characteristic of a mixture of SD and PSD grains. The negative region close to the vertical H_u-axis indicates that the controlling anisotropy in SD grains is uniaxial, whilst the curvature along the H_c-axis reveals the presence of PSD grains. High-temperature thermomagnetic analysis (Fig. 1d) indicated that the Fe_3O_4 NPs were thermally stable. The T_C was determined from the heating curve using the second-derivative method [5] and calculated as 585 ± 5°C, which is in good agreement with stoichiometric Fe_3O_4.

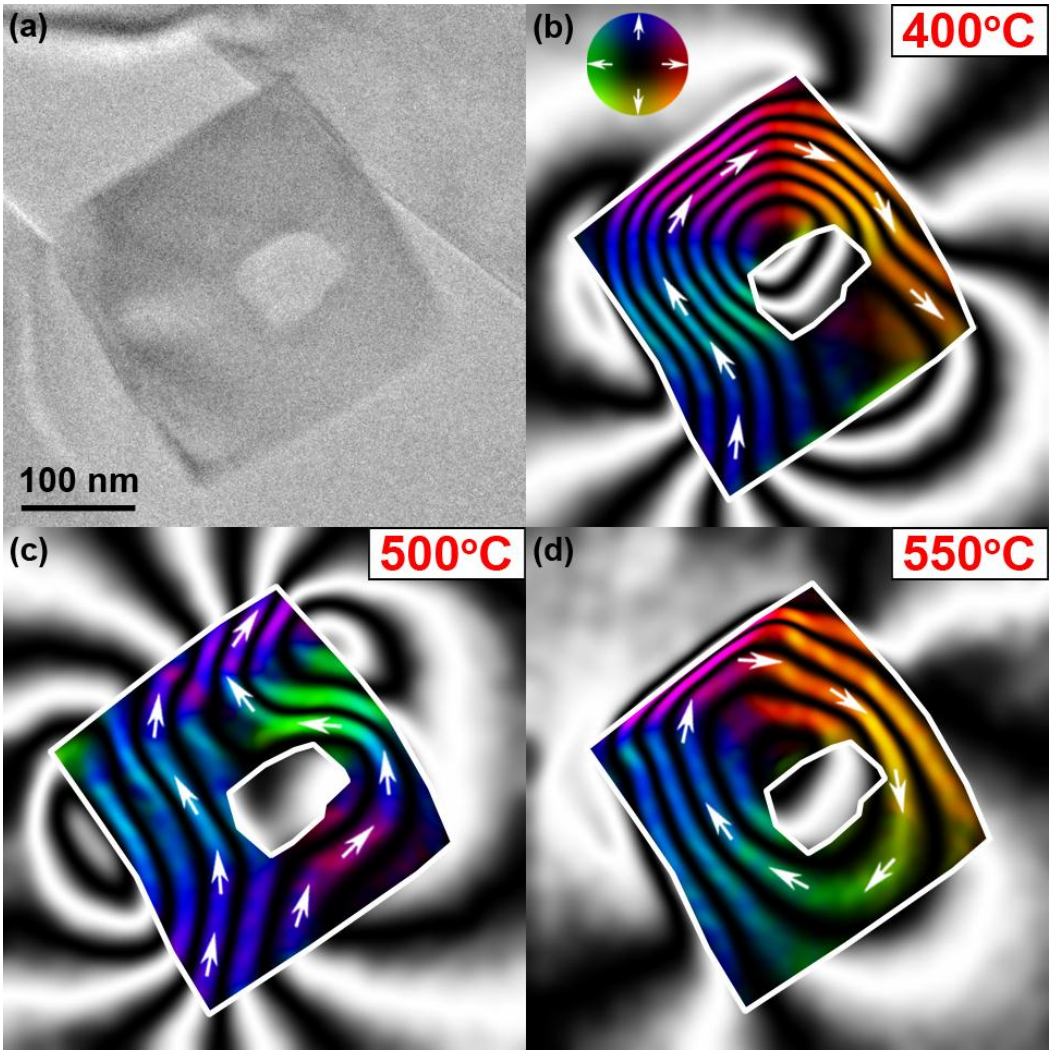

Figure 2 (a) Bright-field TEM image of a square Fe_3O_4 grain within the silicate matrix (~ 300 nm along each side), exhibiting a pore at its centre. (b-d) Magnetic induction maps reconstructed from holograms taken during *in situ* heating to (b) 400˚C; (c) 500˚C; and (d) 550˚C. The contour spacing is 0.39 radians for all magnetic induction maps and magnetisation direction is shown using arrows, as depicted in the colour wheel.

Fig. 2 presents the thermomagnetic behaviour of a Fe_3O_4 grain embedded in a silicate matrix as it is heated to temperatures of 400 ºC, 500 ºC and 550 ºC. The bright-field TEM image of Fig. 2a displays the square Fe_3O_4 grain with sides ~ 300 nm in length and a pore located in its centre. Fig. 2b displays a magnetic induction map of the Fe_3O_4 grain at 400 ºC, and reveals its magnetization to resemble a horseshoe-like shape, with the magnetic contours flowing in a clockwise direction, along with a component of stray magnetic field, indicative of a PSD state. An increase in temperature to 500 ºC (Fig. 2c) results in a marked change in the magnetisation, with the contours flowing vertically through the Fe_3O_4 grain from its bottom to top, as well as exhibiting a prominent stray magnetic field. In particular, the magnetic contours are observed to curve around the right of the centre pore, before re-joining the contours in the left of the grain. At 550 ºC, the magnetization is observed to close into a vortex structure around the centre pore (Fig. 2d), along with a reduced stray magnetic field.

4. Discussion

This combined TEM, XRD and magnetic investigation of the production of synthetic basalts has provided evidence for the growth of Fe_3O_4 grains, ranging from ~ 50 to ~ 500 in diameters, within the silicate matrix. The smaller 50 nm grains are observed to be confined within glassy regions, which have been previously identified as Ca-rich, and these SD domain grains are considered to form during the rapid quenching stage of synthesis [4]. The larger grains, < 500 nm in diameter, are dispersed in-between the Ca-rich regions and suggested to contribute the PSD signal in the FORC diagram. The thermomagnetic curve displays a T_C characteristic of stoichiometric Fe_3O_4, and shows a significant drop in magnetisation above 400 ºC, identifying an ideal temperature range for investigating the high temperature behaviour of PSD Fe_3O_4 grains using electron holography.

The magnetic induction maps of Fig. 2b – 2d provide a visual representation of the variation in remanent magnetisation states within the Fe_3O_4 grain as a function of temperature, all induced under a saturating field of ~ 1.5 T applied in the same direction. It is clear that the temperature at which the electron holograms are acquired plays a critical role into which magnetic configuration is energetically favoured. Considering all three magnetisation states are markedly different, the thermal energy imparted on the Fe_3O_4 grain during magnetic signal recording is considered to actively influence the direction of the remanent signal. In the field of palaeomagnetism, this study provides much insight into the role of the effect of temperature on signal acquisition of the ambient geomagnetic field as the grains cool below their T_C, i.e., it indicates that domain states are likely to be highly temperature dependent. In the case of metamorphic rocks, which experience multiple heatings, a grain may be re-magnetised into different states on each heating cycle. Hence, the overall palaeodirectional information from all the grains in a rock will probably be maintained, but due to some grains re-aligning their magnetisation, the signal will decrease in net palaeointensity.

In summary, complementary TEM and XRD have confirmed the synthesis of Fe_3O_4 grains (~ 50 to ~ 500 nm in diameters) within a synthetic basalt. Off-axis electron holography combined with *in situ* heating showed the variation of induced magnetic domain states at elevated temperatures.

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