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Research articles

γ-Fe_2WO_6 – A magnetodielectric with disordered magnetic and electronic ground states

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ABSTRACT

The magnetic, thermodynamic and dielectric properties of the γ-Fe_2WO_6 system is reported. Crystallizing in the centrosymmetric *Pbcn* space group, this particular polymorph exhibits a number of different magnetic transitions, all of which are seen to exhibit a finite magneto-dielectric coupling. At the lowest measured temperatures, the magnetic ground state appears to be glass-like, as evidenced by the waiting time dependence of the magnetic relaxation. Also reflected in the frequency dependent dielectric measurements, these signatures possibly arise as a consequence of the oxygen non-stoichiometry, which promotes a disordered magnetic and electronic ground state.

1. Introduction

The area of magneto-dielectrics – which pertains to the coupling between the magnetic and dielectric properties – has seen a renaissance in the recent past. This is partly due to emergence of the area of magnetoelectric multiferroics, where magnetic and polar orders co-exist. In these systems, the onset of ferroelectric order typically results in a pronounced dielectric anomaly, which can then be tuned by the application of an external magnetic field [1–3]. However, the phenomena of magnetodielectricity is more generic, since it is not constrained by the stringent symmetry considerations which are a prerequisite for the observation of either magnetoelectricity or multiferroicity. A number of potential applications varying from spin-charge transducers to magnetic sensors can be envisaged using magnetodielectric materials [4,5] and this area of research is continuously driven by the investigation of different material and structural classes which could exhibit these properties, especially near room temperatures. Strongly correlated magnetic oxides offer a natural playground for the investigation of such phenomena, since many of them exhibit an insulating (or at-least a semiconducting) antiferromagnetic ground state. Moreover, the large coupling between the spin, charge and lattice degrees of freedom observed in many of these systems is an added advantage, and typically contributes towards a larger magneto-dielectric effect [6–12]. With the dielectric constant being susceptible to changes in the magnetic structure, it is not surprising that a number of magnetic oxides exhibit magneto-dielectricity in the vicinity of their magnetic transitions. Here we report on the magnetic, thermodynamic and dielectric investigation of a relatively unexplored Iron-Tungsten-Oxygen system (Fe_2WO_6). In addition to a complex set of magnetic transitions, including a low temperature glass like magnetic state, we also observe the existence of a finite magneto-dielectric coupling, persisting right up to room temperatures.

The chemical phase diagram of the Fe-W-O system is characterized by the presence of a number of polymorphic modifications, which makes the selective synthesis of Fe_2WO_6 non-trivial [13].Prior structural investigations have revealed that Fe_2WO_6 can exist in three distinct structures, depending on their synthesis conditions [14–16]. Labeled as α, β and γ-Fe_2WO_6, these polymorphs are typically stabilized as a function of increasing reaction temperatures, with ill-defined phase boundaries. For instance, α-Fe_2WO_6 crystallizing in the orthorhombic columbite (*Pbcn*) symmetry is stabilized at reaction temperatures lower than 800 °C. At reaction temperatures between 750 and 900 °C, the monoclinically distorted β-Fe_2WO_6 is favored, whereas at reaction temperatures in excess of 900 °C, the γ phase is reported to be stabilized. This high temperature γ phase is known to crystallize in the tri-α-PbO_2 structure, where the orthorhombic *Pbcn* symmetry of the α-Fe_2WO_6 phase is preserved, but with a tripling of the unit cell along one of the crystallographic directions ($a' = a$, $b' = 3b$, $c' = c$).

2. Experimental

Polycrystalline specimens of γ-Fe_2WO_6 were synthesized using the

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standard solid state ceramic method. An equimolar mixture of previously preheated Fe_2O_3 (Sigma Aldrich, ⩾99%) and WO_3 (Alfa Aesar, ⩾99.8%) precursors, were thoroughly ground for several hours using a dry ball mill. The fine and homogenous mixture was pressed into pellets and loaded into a preheated alumina boat. The charge was slowly heated to 800 °C, kept there for 24 h and then gradually cooled down to room temperature. These pellets were repeatedly reground, pelletized and sintered for several times at 950 °C in air. After about 100 h at this temperature we obtained a well crystallized single phase of γ-Fe_2WO_6. Phase purity was confirmed using X-ray powder diffraction measured using a Bruker D8 Advance diffractometer with Cu K_α source, and Rietveld refinement was carried out using the Fullprof refinement program [17]. These γ-Fe_2WO_6 specimens were observed to slightly degrade with time, though no appreciable changes were observed in their XRD patterns taken after a few months. Specific heat and resistivity measurements (using the standard four probe configuration) were performed using a Quantum Design PPMS, and magnetization measurements were performed using a MPMS-XL SQUID magnetometer. Temperature dependent dielectric measurements were performed in the standard parallel plate geometry, using a NOVOCONTROL (Alpha-A) High Performance Frequency Analyzer. Measurements were typically done using an excitation ac signal of 1 V at frequencies varying from 100 Hz to 100 kHz. Magneto-dielectric measurements were performed by using the Manual Insertion Utility Probe of the MPMS-XL magnetometer.

3. Result & discussions

The Rietveld refinement of room temperature X-ray diffraction pattern of our specimen is as shown in Fig. 1. A good fit, corresponding to goodness of fit value (R_wp/R_e) of 1.85 could be obtained, confirming a single phase γ-Fe_2WO_6 crystallizing in the *Pbcn* space group, with lattice parameters $a = 4.575(1)$Å, $b = 16.747(4)$Å, $c = 4.965(1)$Å, and $\alpha = \beta = \gamma = 90°$. A schematic of this tri-α-PbO_2 columbite structure is depicted in the inset of Fig. 1, and comprises of layered corner-shared FeO_6 octahedra, with Fe occupying two distinct crystallographic sites.The chemical composition of cation as obtained from the Rietveld analysis is Fe2.0(±0.03) W0.9(± 0.08). Elemental analysis using Energy Dispersive X-ray analysis revealed a stoichiometry of Fe1.98(± 0.06) W1.02(± 0.06), further reconfirming the composition of our γ-Fe_2WO_6 specimen.

Preliminary magnetic characterization of the Fe_2WO_6 polymorphs

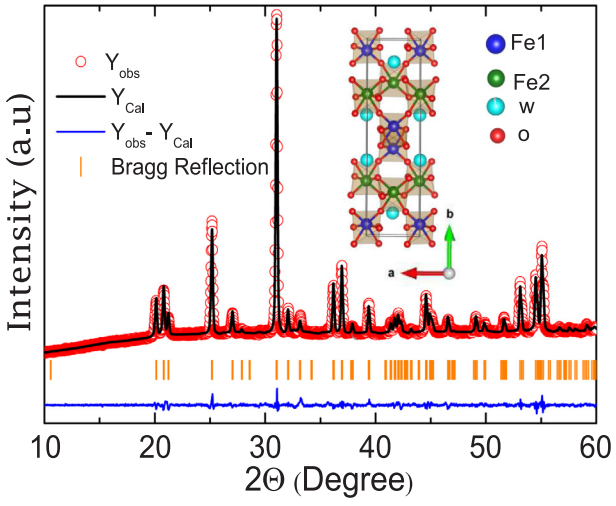

Fig. 1. A Rietveld fit to the room temperature X-ray diffraction data of γ-Fe_2WO_6. This corresponds to a fit with R parameters of R_{wp} = 11.3, R_e = 6.10. The crystal structure of this system as viewed along the crystallographic c axis is shown in the inset.

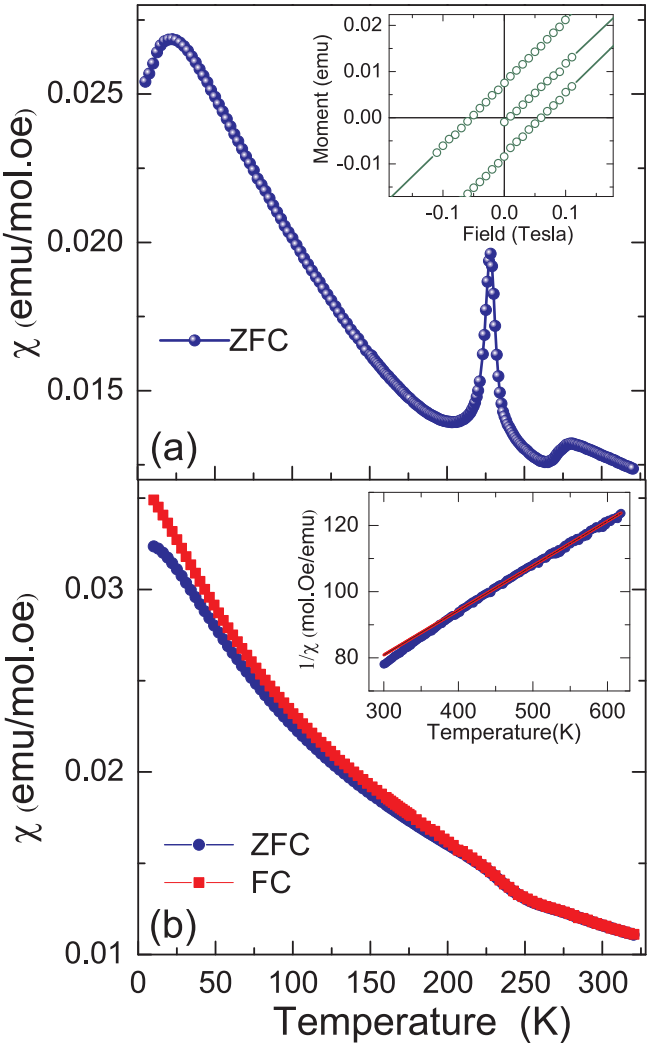

Fig. 2. (a) depicts the temperature dependence of dc magnetization as measured in γ-Fe_2WO_6 in the Zero Field Cooled (ZFC) protocol at an applied field of 10 Oe. The inset depicts an expanded view of the M-H isotherm measured at 2 K. (b) depicts the ZFC and FC measured at an applied field of 1 Tesla. The inset shows the Curie–Weiss fit to the high temperature magnetization data

have been reported earlier, and appears to depend acutely on the synthesis conditions [18,19]. For instance, both the α and γ-Fe_2WO_6 are reported to exhibit two magnetic transitions, with a high temperature transition at $T_1 \approx 240$–260 K, and a lower temperature transition $T_2 \approx 200$–220 K. In addition, the presence of an additional low temperature feature at ≈20 K has also been reported in both these polymorphs. However, the β-Fe_2WO_6 is reported to exhibit a solitary magnetic transition at 260 K. The dc magnetic susceptibility of our γ-Fe_2WO_6 specimen, as measured in the Zero Field Cooled (ZFC) and Field Cooled (FC) measuring protocols is shown inset of Fig. 2(a).

As is evident from the main panel of 2(a), two distinct transitions at 282 K, and 228 K can be discerned from the magnetization measurement performed at low magnetic fields of the order of 10 Oe. An increase in the applied magnetic fields appears to broaden the high temperature transitions 2(b), without a pronounced change in the transition temperatures. An early neutron diffraction investigation of γ-Fe_2WO_6 has suggested that the magnetic structure comprises of ferromagnetic (100) planes coupled antiferromagnetically, with the spins lying along the (001) direction [19]. It was also speculated that the magnetic space group (*Pbc′n′*) could allow for a finite ferromagnetic component along one of the crystallographic axes. Magnetic field isotherms measured in our specimen at different temperatures indicate