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Low-temperature relaxation process and memory effect in a nonstoichiometric magnetite of $Fe_{3-\delta}O_4$ with $\delta=0.03$

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ABSTRACT

The low-temperature relaxation process has been investigated in a nonstoichiometric magnetite $Fe_{3-\delta}O_4$ with $\delta=0.03$. Far below the Verwey transition at $T_V=90$ K, the measurements of AC susceptibility χ_{ac} display a frequency-dependent anomaly of the shoulder in χ' accompanied with the peak in χ'' and their weak thermal hysteresis. These low-temperature anomalies are related to a thermal relaxation process owing to the domain-wall mobility and extra electron exchange inside the walls. Moreover, the low-temperature relaxation process is revealed to exhibit strong memory effect via field-cooling magnetization measurements. Interesting discrete sudden jumps are observed during the logarithmic decay of magnetization in zero field with aging time, indicating the spontaneous magnetization reversals via adjustment of domain configuration.

1. Introduction

Magnetite (Fe_3O_4) is perhaps the oldest known magnetic material, but to date it has been attracting great attention owing to the revealed abundant temperature-dependent characteristics [1,2] since the discovery of the Verwey transition [3]. At low temperature far below the Verwey transition, anomalous frequency-dependent response has been reported in AC magnetic measurements of stoichiometric magnetite crystals and polycrystals [4–6]. The low-temperature anomaly is related to a thermal relaxation process, which is commonly interpreted on the basis of electron hopping and domain wall mobility [4,6]. However, the underlying mechanism is not fully understood. Since the domain-wall motions are determined by the wall pinning and depinning structural defects and/or by ionic and electronic relaxation inside the wall, the nonstoichiometry or doping in magnetite is expected to play an important role in domain wall mobility.

In the present work, via the measurements of AC susceptibility and field-cooling magnetization as a function of temperature, the low-temperature anomalous relaxation process has been investigated in a nonstoichiometric magnetite of $Fe_{3-\delta}O_4$ with $\delta=0.03$.

2. Experimental details

A bulk sample of α-Fe_2O_3 was first sintered at 1350 °C in air for 2 h from commercial powders of α-Fe_2O_3 (purity of 99.99%, −325 mesh, Alfa Aesar, USA). Immediately after the annealing of the sintered α-Fe_2O_3 at 1550 °C in air for 90 min, quenching in liquid nitrogen was performed to prepare the nonstoichiometric magnetite of $Fe_{3-\delta}O_4$. As a contrast, a sample of α-Fe_2O_3 was sintered in air at 1350 °C for 2 h from commercial powders of α-Fe_2O_3 and then cooled down to room temperature at a rate of ~1 °C min^{-1}. The fabricated samples of $Fe_{3-\delta}O_4$ and α-Fe_2O_3 were characterized using powder X-ray diffraction with Cu Kα radiation (SmartLab, Rigaku, Japan) and Mössbauer spectrum. The thermogravimetry (TG) curve was collected in a simultaneous thermogravimetry and differential scanning calorimetry (STA 449C Jupiter, Netzsch, Germany) for determination of the nonstoichiometry δ in $Fe_{3-\delta}O_4$. The AC susceptibility χ_{ac} was collected using PPMS (Quantum Design, USA), and the magnetization and hysteresis loops were measured using a vibrating sample magnetometer (VSM) attached to PPMS.

3. Results and discussion

The XRD measurements (Fig. 1a) show that the sintered α-Fe_2O_3 is transformed to the magnetite of $Fe_{3-\delta}O_4$ after treatments of annealing and quenching. The XRD pattern shows that the fabricated $Fe_{3-\delta}O_4$ has a cubic spinel structure with the lattice constant estimated to be ~8.3957(5) Å. The Mössbauer spectrum of the fabricated $Fe_{3-\delta}O_4$ (Fig. 1b) exhibits two sixtets corresponding to the Fe^{3+} ions at A sites (component A) and the mixed Fe^{3+} and Fe^{2+} ions at B sites (component B). The determined hyperfine fields of 49.5 (A site) and 46.0 T (B site) are consistent with the previously reported ones [7]. From the intensity ratio of

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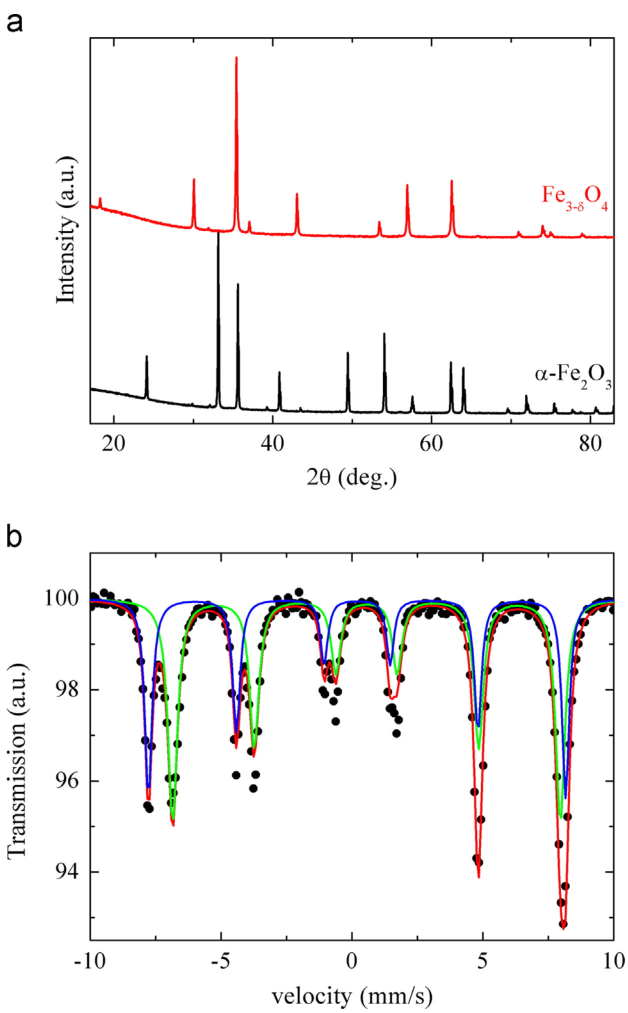

Fig. 1. (a) XRD spectra at room temperature (RT) for the samples of α-Fe_2O_3 and $Fe_{3-\delta}O_4$ and (b) Mössbauer spectrum at RT for the sample of $Fe_{3-\delta}O_4$, exhibiting two sixtets. The fitting of two sixtets to the spectrum generates the hyperfine fields of 49.5 and 46.0 T, corresponding to Fe^{3+} ions at the A sites and the mixed Fe^{3+} and Fe^{2+} ions at the B sites, respectively.

component A to component B, the non-stoichiometry δ is roughly estimated to be 0.04. The more accurate value of $\delta=0.03$ was determined from the measured thermogravimetry (TG) curve during the heating of $Fe_{3-\delta}O_4$ in air, as shown in Fig. 2. Below 250 °C, the mass remains almost a constant. Above 250 °C, the TG curve shows a fast increase in mass with temperature rise, forming a step in the temperature range between 250 and 350 °C. When the temperature is higher than 350 °C, the mass again starts to increase quickly. When the temperature is raised up to 830 °C and above, no change in mass is observed. Structural changes were observed upon the heating of $Fe_{3-\delta}O_4$. When the heating was stopped after the temperature rose to 350 °C, the XRD spectrum for the obtained sample displayed a mixture of α-Fe_2O_3 and $Fe_{3-\delta}O_4$, as shown in the inset on the upper left corner of Fig. 2. After the completion of TG measurement, only the phase of α-Fe_2O_3 was detected by XRD measurement (inset on the lower right corner of Fig. 2).

Shown in Fig. 3 are the magnetization hysteresis loops of $Fe_{3-\delta}O_4$ obtained at 5 and 300 K. At 5 K, saturation tends to be reached in a field of ~15 kOe, while at 300 K, the saturation field is ~5 kOe. From the hysteresis loops, the saturation magnetizations are observed to be 91.2 and 86.5 emu g^{-1} at 5 and 300 K, respectively, comparable to the reported experimental values [7]. The AC susceptibility χ_{ac} of $Fe_{3-\delta}O_4$ with $\delta=0.03$ was measured at

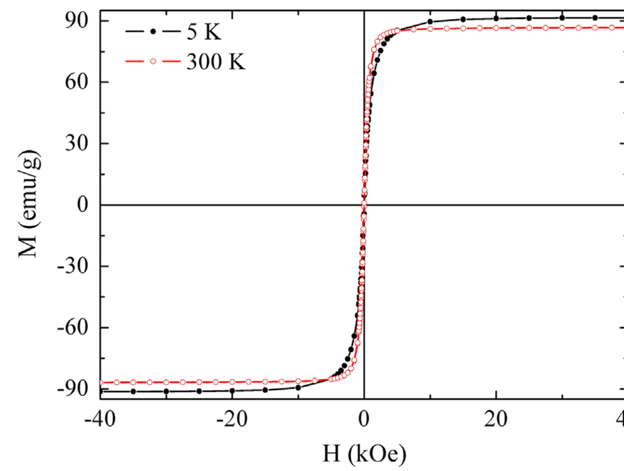

Fig. 2. TG curve obtained during the heating in air at a rate of 10 °C min^{-1} of the nonstoichiometric magnetite $Fe_{3-\delta}O_4$ powders (in average size of ~500 μm). Inset on the upper left corner is the XRD spectrum for the obtained sample when the heating was stopped after the temperature rose to 350 °C, displaying a mixture of α-Fe_2O_3 and $Fe_{3-\delta}O_4$. Inset on the lower right corner is the XRD pattern for the sample obtained after the completion of TG measurement, showing only the presence of α-Fe_2O_3. From the TG curve, the value of δ in $Fe_{3-\delta}O_4$ is determined to be 0.03.

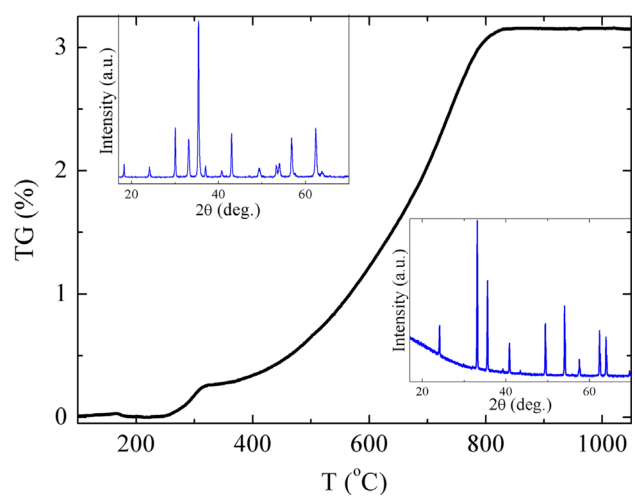

Fig. 3. Magnetization hysteresis loops of $Fe_{3-\delta}O_4$ obtained at 5 and 300 K. The saturation magnetizations are observed to be 91.2 and 86.5 emu g^{-1} at 5 and 300 K, respectively.

an AC driving magnetic field of 5 Oe and different frequencies during processes of cooling and heating. The cooling χ_{ac} was first collected during the decrease of temperature from 300 to 5 K, and the heating χ_{ac} was then obtained during immediate reheating. As a typical example, Fig. 4a displays real (χ') and imaginary (χ'') components of χ_{ac} obtained at a frequency of 80 Hz. At the spin-reorientation (SR) transition of $T_{SR}=120$ K, a maximum peak occurs on χ', while χ'' accordingly goes to a minimum, similar to the previous observations in stoichiometric magnetite [4,6] except for the lowered T_{SR} due to the nonstoichiometry [8]. Above $T_{SR}=120$ K, both χ' and χ'' display obvious thermal hysteresis, similar to that observed in initial permeability of a nonstoichiometric magnetite crystal of $Fe_{3-\delta}O_4$ with $\delta=0.036$ [8]. Below $T_{SR}=120$ K an abrupt drop in χ' begins to occur at 95 K, and accordingly a sharp peak appears at 90 K in χ'' corresponding to the Verwey transition. The reduced Verwey transition temperature is attributed to the influence of nonstoichiometry [8,9]. In the temperature range between T_V and T_{SR}, χ' and χ'' display the opposite temperature-dependent variations with no observable