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Preparation and characterization of haematite nanowire arrays

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Abstract

Arrays of α-Fe_2O_3 nanowires embedded in anodic alumina membranes were obtained after heat-treating β-FeOOH nanowire arrays fabricated by electrochemical deposition. Haematite polycrystalline nanowires with maximum length of about 7 μm and average diameter of about 120 nm were characterized by means of x-ray diffraction and transmission electron microscopy. The Morin temperature below 80 K and Néel temperature of about 350 K for the α-Fe_2O_3 nanowire arrays, far lower than those of bulk material, were measured by Mössbauer spectroscopy and using a Magnetic Property Measurement System.

In the past few years, nanowires have attracted much attention due to their importance for fundamental studies and the wide range of potential applications in nanodevices [1, 2]. The nanowire arrays whose preferred magnetization direction is perpendicular to the film plane, with enhanced coercivity and high remanence, are expected to be suitable for use as high-density perpendicular magnetic recording media. So far, various metallic nanowires have been successfully synthesized and studied [3, 4]. However, there has been no report on research into nanowires of ferrite, which are also important candidates for use as perpendicular media.

Using the electrodeposition mechanism, it is very difficult to directly deposit ferrite into a nanoporous matrix. Ferrite nanowire arrays may be obtained by treating a precursor that can be deposited into anodic alumina membranes (AAM). However, it is also difficult to prepare pure ferrite nanowire arrays indirectly by oxidizing the metallic nanowire arrays in AAM because of the high packing of the alumina. Here we report a method for the preparation of α-Fe_2O_3 nanowire arrays embedded in AAM. Their nanostructure and magnetic properties were characterized simultaneously.

The fabrication process for the haematite consists in three steps. First of all, aluminium plates (99.999% purity) were anodized by using direct current in 0.5 M phosphoric acid

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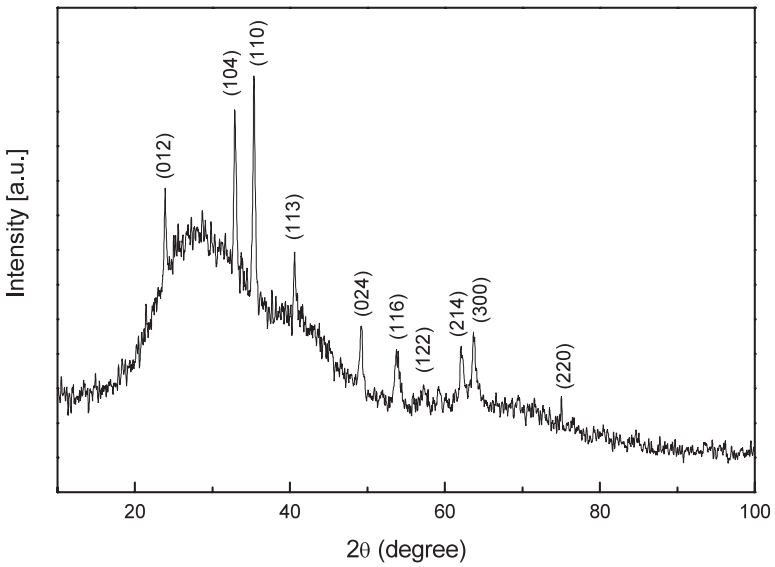

Figure 1. The x-ray pattern of haematite nanowire arrays.

Figure 2. The TEM morphology of haematite nanowires.

(H_3PO_4) electrolyte for 1 h after being degreased and electropolished. The AAM with maximum length of about 7 μm and average diameter of about 120 nm were obtained using a 120 V anodizing voltage. Then, the β-FeOOH nanowire arrays were synthesized by using an alternating current electrodeposition method at room temperature (RT) [5]. The electrolyte for the electrodeposition contained 9 g l^{-1} $FeCl_3{\cdot}6H_2O$ and 14 g l^{-1} $(NH_4)_2C_2O_4{\cdot}H_2O$. The pH value of the electrolyte was adjusted to 5–6. Finally, after removing the remaining aluminium layers from the bottom of the AAM in a saturated $HgCl_2$ solution, the α-Fe_2O_3 nanowire arrays were fabricated by heat-treating the β-FeOOH nanowire arrays in AAM at 600 °C for 1.5 h in air.

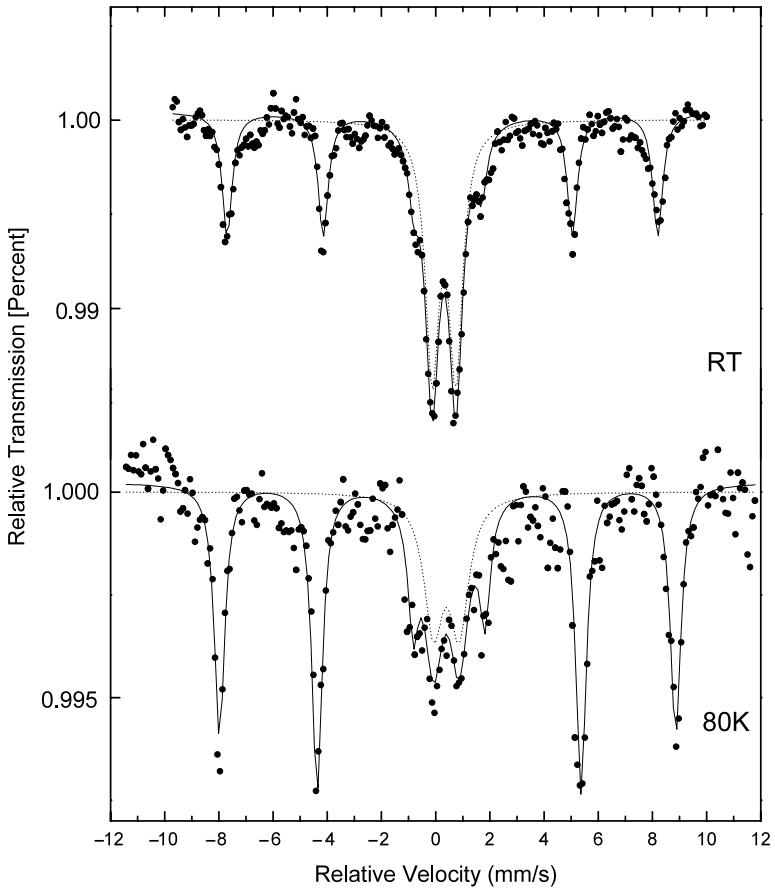

Figure 3. The Mössbauer spectra of haematite nanowire arrays.

The x-ray diffraction (XRD) pattern of the sample with AAM is shown in figure 1, which was obtained with an x-ray diffractometer (Rigaku D/max-2400) with Cu Kα_1 radiation. It shows that the nanowires are composed of polycrystalline α-Fe_2O_3. A [110] texture is observed on comparing with the standard diffraction spectrum of JCPDS (33-0664). XRD linewidth analysis of the five low-angle peaks reveals that the crystallite diameters distribute in the range 10–20 nm, calculated by using the Scherrer formula.

The transmission electron microscope (TEM) image of the α-Fe_2O_3 nanowires, obtained after dissolving the AAM in an aqueous solution of 0.1 M NaOH, shows that the average diameter of the nanowires is about 120 nm and the maximum length is up to 7 μm; see figure 2.

The Mössbauer spectra (MS) of the α-Fe_2O_3 nanowire arrays are shown in figure 3. The direction of the γ-rays was parallel to the direction of the nanowires. The MS obtained at RT and 80 K are composed of a doublet and a sextet. The relative area of the doublet reduces from 54.8 to 30.5% when temperature decreases from RT to 80 K. This suggests that there is a superparamagnetic phase in the nanowire arrays. It reveals that there are many small crystallites in the nanowires. This is in agreement with the results from XRD and TEM [6]. The formation of the crystallites is due to the loss of the crystallization water during the heat-treatment process [7]. The broadening of the doublets and sextets is due to the size distribution

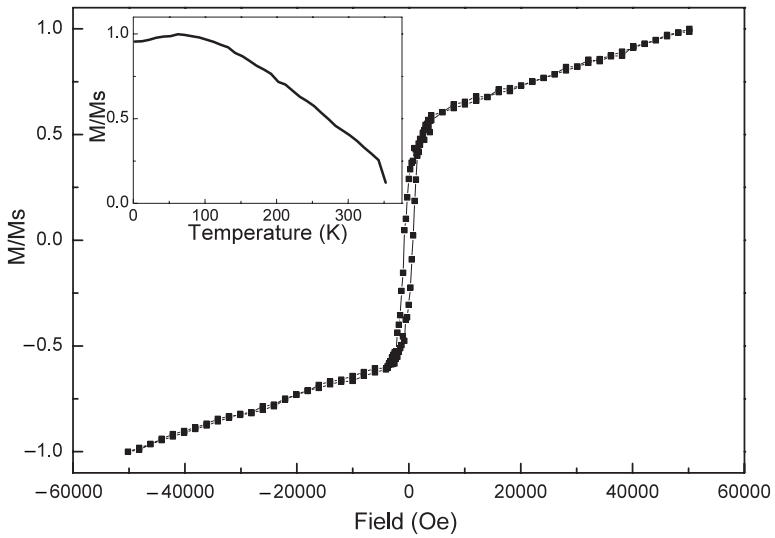

Figure 4. The M–H hysteresis loop of haematite nanowire arrays at 80 K. The inset shows the M–T curve of haematite nanowire arrays with a maximum at about 80 K.

of the crystallites. The hyperfine field at RT is about 50.11 T which is less than that of well-crystallized haematite (≈51.5 T). This is probably due to the existence of collective magnetic excitation caused by the distribution of the crystallites [8]. The intensity ratio of the sextet peaks in the 80 K MS is nearly 3:4:1, suggesting that almost all of the magnetic moments of the antiferromagnetic and weak ferromagnetic crystallites are perpendicular to the nanowires at 80 K.

It is known that α-Fe_2O_3 undergoes a Morin transition at the Morin temperature (T_M). Below T_M, α-Fe_2O_3 shows antiferromagnetic behaviour, while above T_M, α-Fe_2O_3 displays weak ferromagnetism due to non-complete antiparallelism of the spin. Furthermore, the Morin temperature reduces as the particle size decreases [7, 9]. The 80 K MS shows that the space between the first peak and the second peak (Δ_{12}) is a little larger than (nearly equal to) the space between the fifth peak and the sixth peak (Δ_{56}) of the sextet, revealing that the Morin temperature of the nanowire arrays is inferior to (close to) 80 K [10]. Because of the distribution of the crystallite sizes, the Morin temperature distributes around 80 K. So weak ferromagnetic, antiferromagnetic and superparamagnetic phases coexist at 80 K.

The magnetization versus temperature (M–T) curve and magnetization versus field (M–H) hysteresis loop at 80 K for the α-Fe_2O_3 nanowire arrays with AAM are shown in figure 4; these were obtained using a Magnetic Property Measurement System (MPMS). The applied magnetic field was perpendicular to the nanowires. The inset shows the M–T curve of haematite nanowire arrays with a maximum magnetization value around 80 K, due to competition among the temperature dependences of the antiferromagnetic, weak ferromagnetic and superparamagnetic phases. The Néel temperature of the arrays is about 350 K because of the existence of the small crystallites. It can be seen from the hysteresis loop that the magnetization firstly shows a rapid increase at lower field and then an almost linear behaviour at higher field, suggesting the existence of two kinds of contribution [9]. The curvature behaviour may result from the weak ferromagnetic crystallites. The linear behaviour may result from the antiferromagnetic and superparamagnetic crystallites. The coercivity of the weakly ferromagnetic phase is about 800 Oe at 80 K.

In summary, after heat-treating the β-FeOOH nanowire arrays fabricated by electrochemical deposition, α-Fe_2O_3 nanowire arrays in AAM were prepared for the first time. The nanowires consist of small crystallites of 10–20 nm. The nanowires show antiferromagnetic, weak ferromagnetic and superparamagnetic behaviours due to the small crystallites which also cause the decrease of the Morin temperature and Néel temperature of α-Fe_2O_3. Almost all of the magnetic moments of the antiferromagnetic and weak ferromagnetic crystallites are perpendicular to the nanowires at 80 K. The preparation of and research into α-Fe_2O_3 nanowire arrays have significance for the preparation of and research into ferrite nanowire arrays.

Acknowledgments

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