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Magnetic Properties of Fe_2O_3 Nanoparticles

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Fe_2O_3 nanoparticles surrounded by amorphous SiO_2 were prepared by mixing aqueous solutions of $FeCl_2 \cdot 4H_2O$ and $Na_2SiO_3 \cdot 9H_2O$. From the analysis of X-ray powder diffraction patterns, the production of Fe_2O_3 nanoparticles were confirmed. The 923 K annealed sample was composed of only γ-Fe_2O_3 particles, and additional α-Fe_2O_3 phase was included in the 1023 K annealed one. The coercive forces H_c were estimated from magnetization curves, and remarkable difference between the 923 K annealed sample and 1023 K annealed one was observed. The H_c of former sample decreased as the temperature increased and disappeared at the blocking temperature T_B, however the latter sample, especially the 10 hours annealed one, showed H_c of about 1 kOe even at 300 K. Larger coercivity at room temperature can be expected by more precise controls of annealing temperature and time which would realize the new high density magnetic recording materials.
Key words: nanoscopic clusters, Magnetization, Fe-oxide,

1 Introduction

Since 1995 the magnetic properties of $Ni(OH)_2$ monolayer nanoparticles surrounded by amorphous SiO_2 have been reported[1]-[5]. Those $Ni(OH)_2$ nanoparticles were obtained from mixtures of $NiCl_2 \cdot 6H_2O$ and $Na_2SiO_3 \cdot mH_2O$ (m=0,9). We expected that such a wet method would also supply the nanoparticle systems of the other transition metal hydroxide. Especially the nanoparticles of Fe-system should be the starting material of high density magnetic storage media by oxidation. Here we will report the preparation of Fe_2O_3 nanoparticles and magnetic properties of this system, taking note of the coercivity and saturation magnetization.

2 Experimental Procedures

The Fe-hydroxide fine particles were produced by mixing aqueous solutions of $FeCl_2 \cdot 4H_2O$ and $Na_2SiO_3 \cdot 9H_2O$. Obtained precipitates were rapidly oxidized in air while they washed several times by distilled water and dried at room temperture. These samples were calcinated in air at annealing temperatures of 723 K, 923 K, 1023 K and 1133 K in the furnace, anneling times were also controled as 4 hours, 7 hours and 10 hours.

The CuKα X-ray powder diffractions were measured for each sample. The diffraction patterns are shown in Figure 1. Figure 1(a) indicates a sample annealed at 723 K, 1(b) at 923 K, 1(c) at 1023 K, and 1(d) at 1133 K, respectivly. Annealing times for all samples were same as 4 hours.

As shown in Figure 1(a) and (b), both of 723 K and 923 K annealed samples had the only broad peaks of (311)-reflection and (440)-reflection of γ-Fe_2O_3 at 2θ=35 and 60 degrees, respectively. The broadned peak belw 2θ=30 degrees is due to the amorphous SiO_2 [4]. The Figure 1(c) for the 923 K annealed one showed the additional broad peaks of (104)- and (214)-reflections of α-Fe_2O_3 at 2θ=33 and 61 degrees, respectively. While, for the 1133 K annealed sample, rather large crystalline particles of α-Fe_2O_3 was confirmed from Figure 1(d), where the broad peaks by γ-Fe_2O_3 clearly disappeared. From the half width of the peak intensity, the diameter of the fine particle can be roughly estimated as about 1.3 nm for 723 K annealed sample, 1.8 nm for 923 K, and 3.5 nm for 1023 K, respectively. While the diameter of α-Fe_2O_3 particle was estimated as 4.5 nm and 23.1 nm for 1023 K and 1133 K annealing, respectively. Thus, the longer annealing time promotes larger diameter particles of γ- and α- Fe_2O_3.

3 Magnetization of Fe_2O_3 nanoparticles

Before the discussion upon nanoparticles, magnetic properties of bulk crystal of γ- and α-Fe_2O_3 will be summarized. The γ-Fe_2O_3 (Maghemite) has the crystal type of cubic inverse spinel of $MgAl_2O_4$ with lattice constant of a= 0.8322 nm. The Fe ions are positioned as

$$(Fe^{3+})O \cdot (Fe^{3+}_{5/3}V_{1/3})O_3 \qquad (1)$$

(where V shows a vacancy.) It is ferrimagnetically ordered below Curie temperature of T_C=1020 K. Average magnetic moment was estimated as 1.10 μ_B per Fe atom[6][7][8]. While, α-Fe_2O_3 has Rhom-

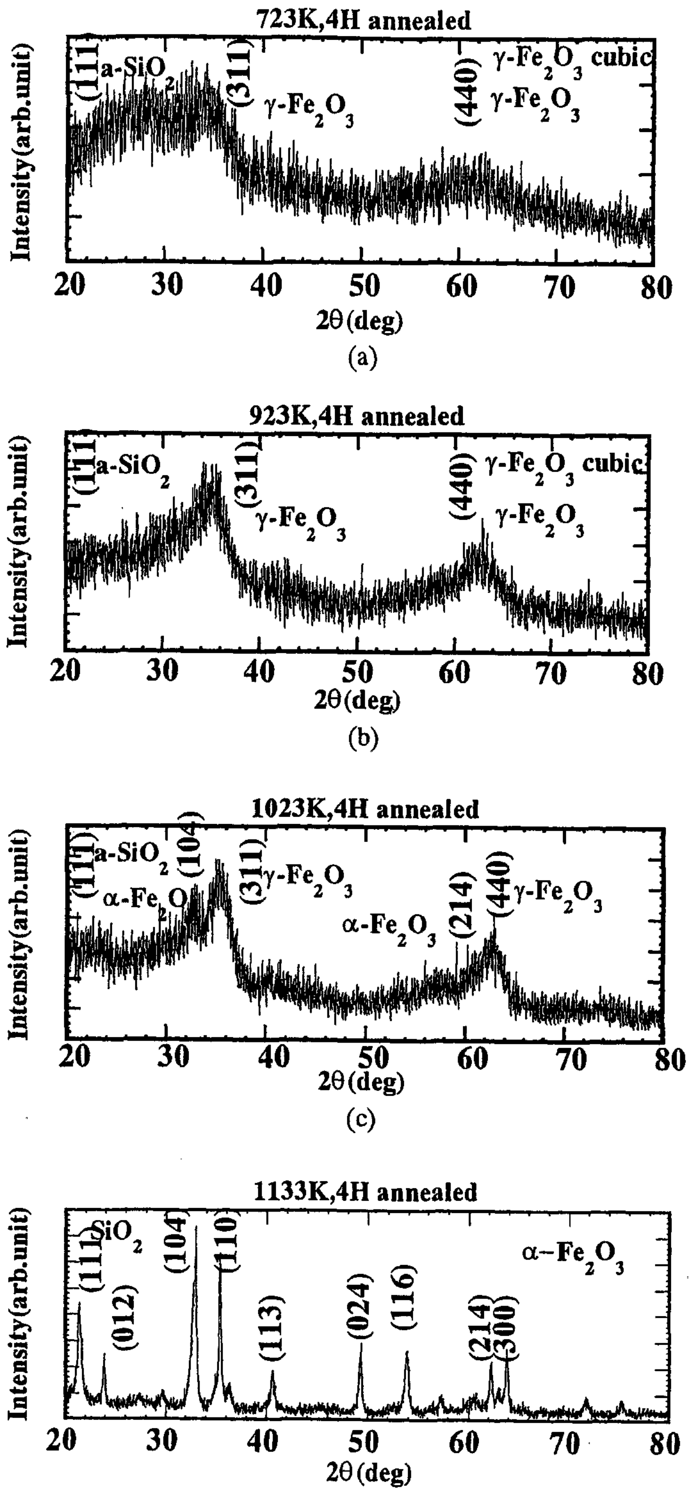

Figure 1: Powder X-ray diffracton patterns of (a)723 K annealed,(b)923 K anneled, (c)1023 K annealed and(d)1133 K anneled samples.

bohedral crystal type(D_{3d}^6-R$\bar{3}$) of corundum structure with lattice constant of a=0.5424 nm[9]. It shows weakferromagnetic phase under Néel temperature of T_N=958 K and reorders at T_M=260 K into antiferromagnetic phase[11][12]. Average magnetic moment is estimated as 4.9 μ_B[13], and paramagnetic Curie temperature was Θ_p=-2940 K[10]. In the present study, magnetizations were measured by SQUID magnetometer under the magnetic field between -50 kOe and 50 kOe, and from 5K to 300 K. Ferromagnetic hysteresis loops were observed at 5K for all samples. Figures 2(a) and (b) show $M - H$ curves of 923 K for 10 hours, and 1023 K for 10 hours annealed sample, respectively, after the field-cooled(FC) process. Remarkable coersivity was observed between 5K and 300 K in 1023 K for 10 hours annealed sample. It maintained large coersive force H_c of 1500 Oe even under 300 K, while H_c of the other samples disappear as the temperture increases up to about 50 K.

According to the particle size dependence of H_c value of γ-Fe_2O_3[14], largest coersive force appeared when the particle diameter was about 45 nm, and no H_c was observed for the smaller particle diameter than 10 nm. So H_c of γ-Fe_2O_3 nanoparticles with a few nanometers diameter should be 0 at room temperature, however large H_c of about 1 kOe was ovserved for 1023 K-10 hours annealed samples as given in Figure 2(b). These results were considered to be due to the coexistance of γ- and α-Fe_2O_3 phase, as shown in Figure 1(c).

The DC χ results were given in Figures 3(a) and 3(b) for 923 K annealed and 1023 K annealed samples. The field-cooled(FC) and zero-filed-cooled(ZFC) process under 5 kOe were measured for each sample with various annealing time. The measured temperature region was between 4 K and 300 K. From Figure 3(a), the superparamagnetic behaviours were observed between 30 K and 300 K, and the FC- and ZFC-χ curves were split below 30 K. These splitting temperatures were defined as the blocking temperature T_B, below which the Fe^{3+} magnetic moments in the γ-Fe_2O_3 nanoparticles would be blocked. The hysteretic magnetizations in Figure 2(a) also correspond to the blocked state of γ-Fe_2O_3 below T_B.

From Figure 3(b), T_B of γ-Fe_2O_3 were estimated as 100-120 K for 1023 K annealed samples. The hysteretic behaviors of magnetizations above T_B would show the importance of the interaction among the magnetic moments in γ- and α-Fe_2O_3 to know the mechanism of large H_c behaviors.

The correlations among annealing time, existence of magnetic hysteresis and blocking temperature for each temperature are shown in Figure 4.

While the temperature dependences of H_c for all annealing temperatures and times are given in Figure 5. In these Figures, the coersivity by γ-Fe_2O_3 exists only below T_B for all of the samples. However, for the 1023 K- 10 hours annealed sample, the coersive force H_c survived above T_B, and it was about 1 kOe at 300 K with the saturation magnetization M_s of about 0.21 μ_B per Fe ion. The isolated α-Fe_2O_3 particle should have large H_c of

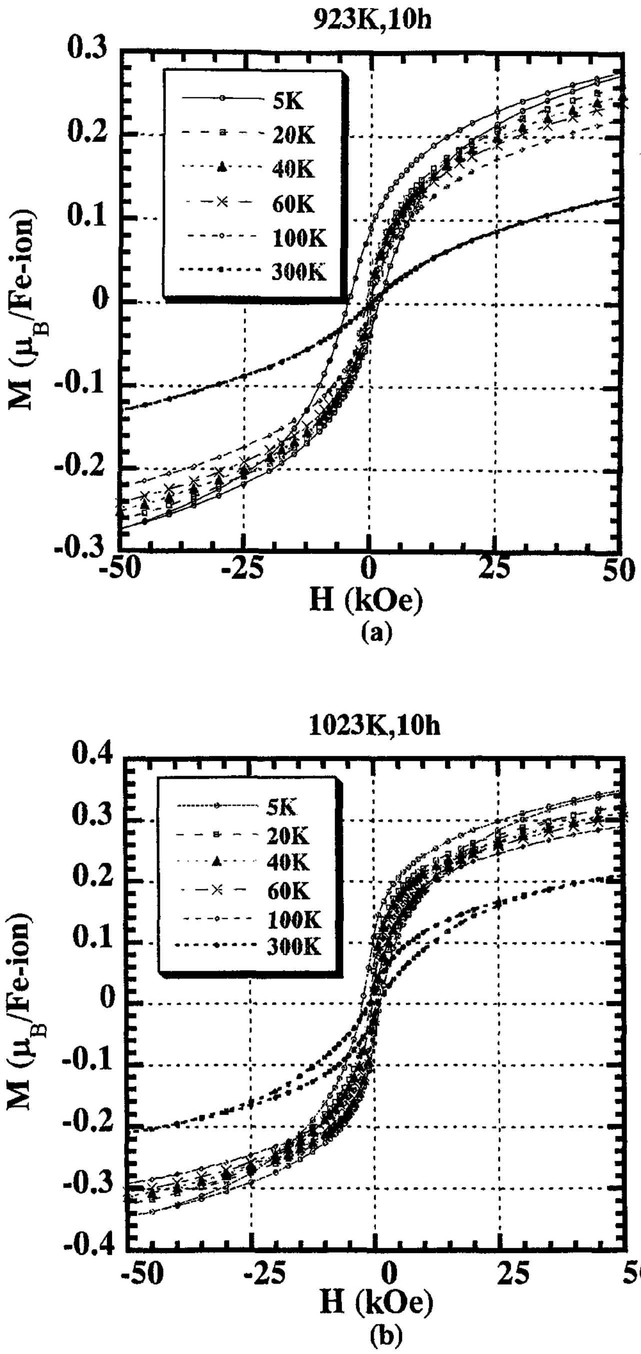

Figure 2: FC M-H curve of 923 K annealed sample(a) and 1023 K annealed sample(b) under the external field between -50 kOe and 50 kOe at 5 K,20 K,40 K,60 K,100 K and 300 K.

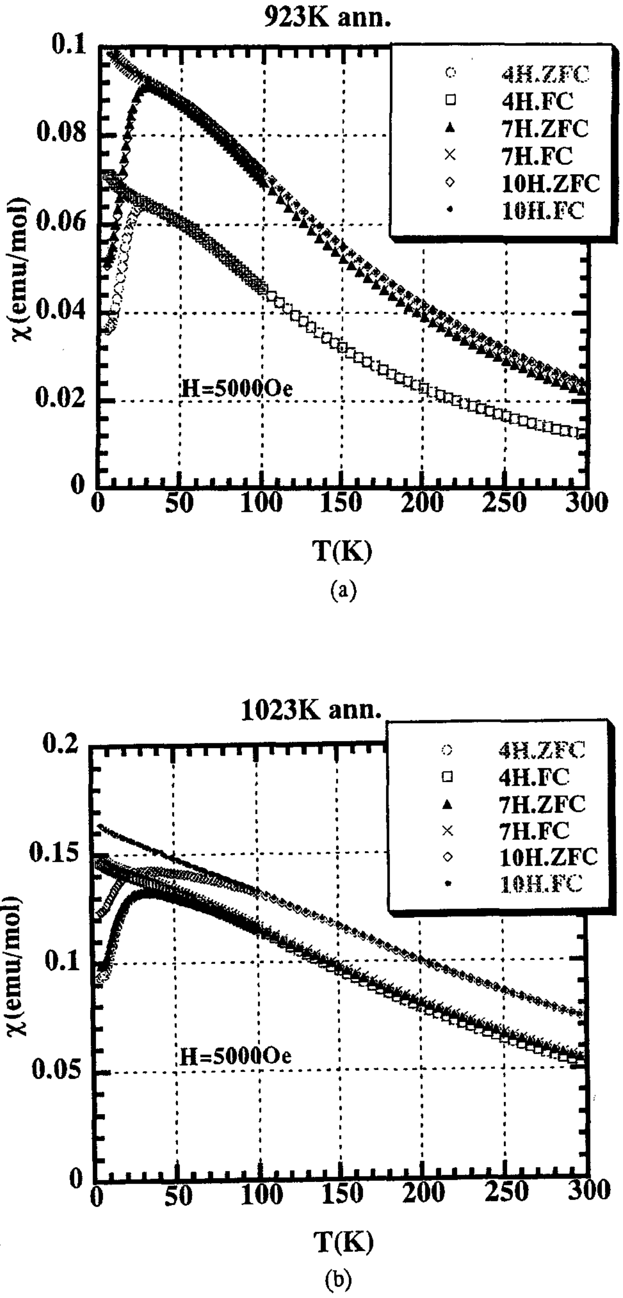

Figure 3: DC magnetic susceptibilities χ of the 923 K annealed sample(a) and 1023 K annealed sample(b) after 5 kOe field-cooled and zero-field-cooled process.

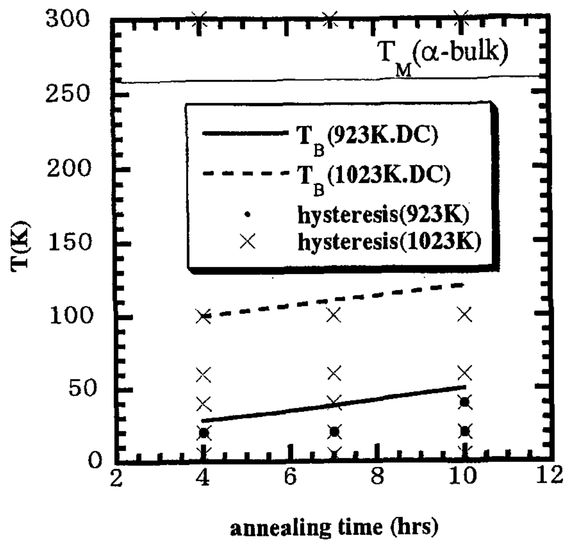

Figure 4: Correlations among annealing time, T_B and existence of magnetic hysteresis for each temperature.

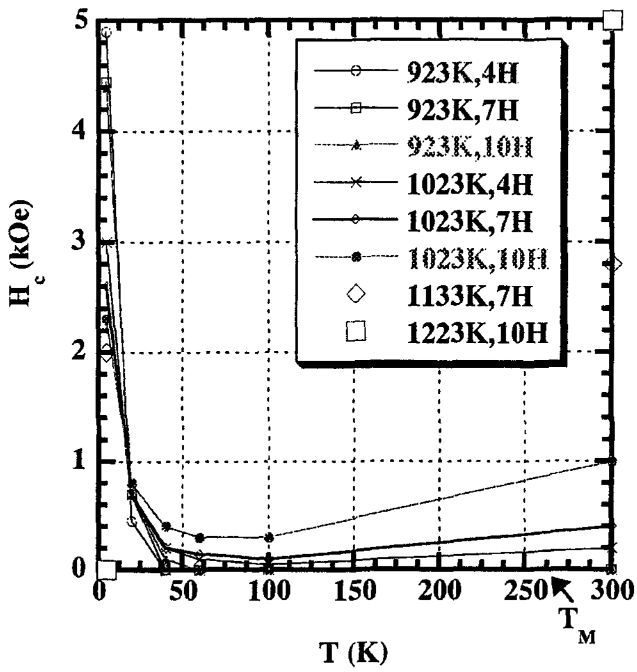

Figure 5: Temperature dependence of H_c for all samples.

about 5 kOe at 300 K, but it has very low M_s of 0.035 μ_B per Fe ion. So the present 1023 K-10 hours annealed sample is expected to be suitable to apply to the magnetic recording materials.

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