

EFFECT OF HEAT TREATMENT ON MAGNETIC MgFe_2O_4 NANOPARTICLES

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MgFe_2O_4 (Mg-ferrite) nanoparticles encapsulated in amorphous SiO_2 were prepared by the wet chemical method. The particle sizes were estimated, based on the X-ray diffraction peaks, to be between 3 and 8 nm, depending on the annealing temperature. The particle size increased as the annealing temperature increased. From the magnetization measurements, the blocking temperature, T_b , was found to be between 30 and 60 K. The magnetization values varied with the annealing or quenching conditions. To clarify the process of crystal growth, thermogravimetric and differential thermal analysis (TG-DTA) measurements were performed and the results were compared with the X-ray diffraction patterns.

Keywords: heat treatment, magnetic nanoparticles, magnetization, TG-DTA measurement

Introduction

Magnetic nanoparticles are drawing much attention because of their attractive potential for use as magnetic recording media, magnetic fluids, catalysis agents and components of biomedical applications.

One of the authors has succeeded in producing magnetic nanoparticles encapsulated in amorphous SiO_2 several years ago, and has reported their magnetic [1–3] and thermal [4, 5] properties. We also succeeded in producing functional magnetic nanoparticles for biomedical applications [6, 7].

In this study, MgFe_2O_4 (Mg-ferrite) nanoparticles were produced, and their magnetic properties and heat-treatment effects were investigated. Mg-ferrite is a very useful soft magnetic material, and is expected to be useful for sensor and catalysis applications [8, 9]. It is very interesting that Mg-ferrite shows magnetization depending on the ion distribution, despite the fact that Mg^{2+} ions have nonmagnetic properties. It is known that Mg-ferrite bulk crystal has an inverse spinel structure, where Mg^{2+} ions prefer to exist at the octahedral B sites. When subjected to heat treatment (annealing or quenching), Mg ions tend to position themselves at the tetrahedral A sites in some cases [10, 11]. In this experiment, the annealing and quenching times were varied in the preparation of the samples, and the magnetization values before and after the heat treatment were compared.

Experimental

Mg-ferrite (MgFe_2O_4) nanoparticles were produced by mixing aqueous solutions of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$. The mole ratio of the prepared reagent was Mg:Fe:Si=1:2:3. The obtained precipitates were washed several times with distilled water and dried at about 350 K in a thermostat. The as-prepared samples were subjected to heat treatment in a furnace in air at annealing temperatures of 873 to 1123 K. Some samples were quenched after annealing. Three quenching methods were adopted: (method 1) the samples were placed on a copper plate cooled by liquid nitrogen, or (method 2) they were quenched to room temperature over a period of 20 h, (method 3) or, for normally annealed samples, they were quenched for 4 h. The particle sizes did not change after quenching. Each sample was examined by CuK_α X-ray powder diffraction ($\lambda=0.154$ nm). We defined the temperature just before quenching as the quenching temperature, T_Q .

Results and discussion

X-ray diffraction

The CuK_α X-ray diffraction patterns are shown in Fig. 1. Figures 1a–c correspond to the samples quenched at 873 K by method 1, i.e. on a copper plate cooled by liquid nitrogen, at 1023 K by method 1, at 1123 K by method 1, and Figs 1d–f correspond to the samples at 873 K by method 2, i.e. quenching to

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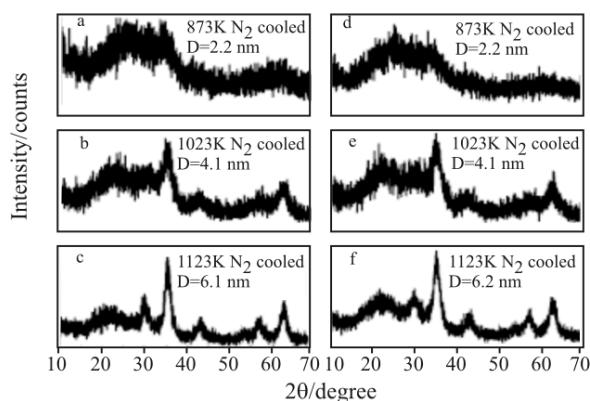


Fig. 1 Powder X-ray diffraction patterns for the samples quenched a – 873 K, b – 1023 K, c – 1123 K, d – 873 K, e – 1023 K, f – 1123 K by method 2

room temperature over a period of 20 h, at 1023 K by method 2 and at 1123 K by method 2, respectively. In all cases, a spinel phase with a lattice constant of about 0.84 nm was produced, even though the patterns of the samples annealed at lower temperatures were fairly broad due to the amorphous state. The peaks sharpened as the annealing temperature increased. This phenomenon corresponds to the transformation typical of crystal growth. Depending on the calcination temperature, the average particle sizes were estimated to be between 2.2 and 8.2 nm using the Scherer formula and the half-width of the diffraction peaks.

Magnetization measurements

Magnetization measurements were performed using an MPMS SQUID magnetometer under an external field of 50 to -50 kOe at a temperature of 5 to 300 K.

Figure 2 shows the temperature dependence of both the field-cooled (FC) (closed marks) and the zero-field-cooled (ZFC) (open marks) magnetization in the samples annealed at 1073, 1023, 973 and 873 K under an external field of 100 Oe. The particle size increased as the annealing temperature increased. The annealing temperatures and particle sizes are summarized in Table 1.

If we define the FC–ZFC bifurcation temperature as the blocking temperature, T_b , the magnetic spins in the particle are supposed to fluctuate with thermal energy and behave superparamagnetically. T_b was observed to be between 32 and 58 K. Below the blocking temperature, ferromagnetic behavior was observed, and above the blocking temperature, the magnetization curves followed the Curie–Weiss law, and the paramagnetic Curie temperature, θ_p , was found to be between -37 and 159 K.

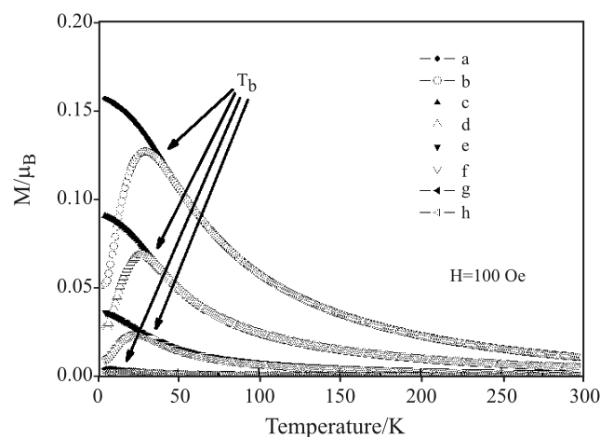


Fig. 2 Temperature dependence of closed marks – FC and open marks – ZFC magnetization in samples annealed at a, b – 1073, c, d – 1023, e, f – 973 and g, h – 873 K

Table 1 Particle sizes of MgFe_2O_4 samples at various annealing temperatures estimated by X-ray diffraction

Annealing temperature/K	D/nm
873	2.2
973	3.1
1023	4.1
1073	4.9
1123	6.1

Quenching effect

The M – H curves for each particle size measured at a temperature of 5 K under a ± 50 kOe field are given in Fig. 3. The closed marks (letters a, c, e, g, i and k) correspond to quenching method 1, i.e. placing the sample on a copper plate cooled by liquid nitrogen, and the open marks (letters b, d, f, h, j and l) correspond to quenching method 2, i.e. quenching the samples to room temperature over a period of 20 h. The magnetization value increased as the quenching time decreased for all the samples, and the maximum saturation magnetization value, M_s , was found to be $1.8 \mu_B$ per one molecule at 5 K. These results indicate that some of the Mg ions were distributed more at the A sites as a result of the quenching.

TG-DTA measurements

In order to clarify the formation process and heat-treatment effect, differential thermal analysis and thermogravimetric (TG-DTA) measurements were carried out using a Rigaku TAS-100 under air. In the TG curve, mass loss by dehydration was observed at temperatures above 370 K, after which the

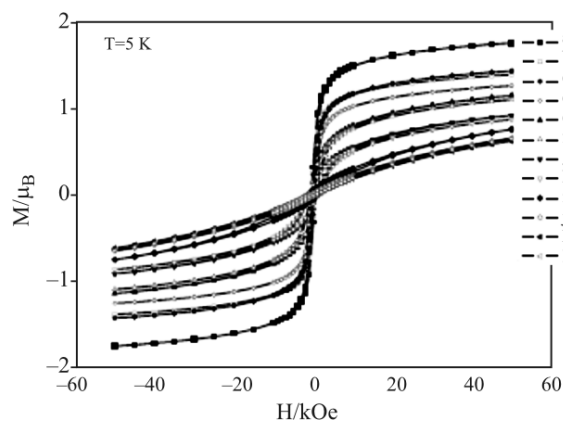


Fig. 3 Magnetization curves for particles of a, b – 6.1; c, d – 4.9; e, f – 4.1; g, h – 3.1; i, j – 2.5 nm and k, l – 2.2 nm quenched by different methods. Closed marks – method 1: placing the sample on a copper plate cooled by liquid nitrogen. Open marks – method 2: quenching to room temperature over a period of 20 h

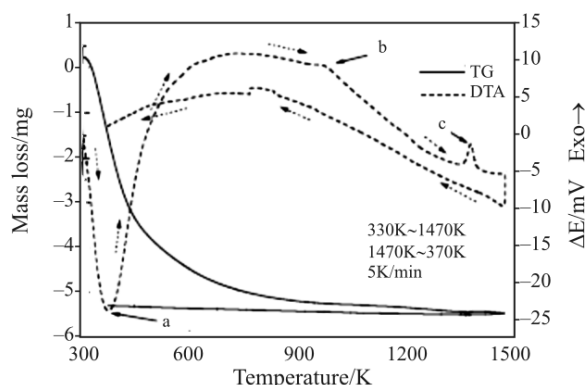


Fig. 4 TG-DTA curve of as-prepared MgFe₂O₄ nanoparticles under air in the temperature range between room temperature and 1500 K

sample mass gradually decreased as the temperature increased up to 1500 K, as shown in Fig. 4.

Figure 4 also shows the DTA curve for the as-prepared samples of Mg-ferrite from room temperature to 1500 K. As can be seen in this figure, there is a deep endothermic peak at around 370 K, corresponding to the above dehydration (Fig. 4a). Two exothermic peaks were observed at around 980 and 1280 K. The former small peak could be considered to have been caused by the crystallization, at that temperature, of the amorphous as-prepared sample (Fig. 4b), and this explanation is consistent with the powder X-ray diffraction patterns. The latter slight shoulder could be due to the sudden aggregation of nanoparticles in this system. The existence of an exothermic peak at 1500 K is unknown at present; however, it is considered that Mg-ferrite was decomposed into other compounds such as α -Fe₂O₃

and MgSiO₃ (Fig. 4c). The diffraction patterns of those compounds were observed by X-ray measurement after heating to 1500 K.

Conclusions

Magnetization measurements and TG-DTA measurements were performed for MgFe₂O₄ (Mg-ferrite) nanoparticles encapsulated in amorphous SiO₂. Magnetization values varied with the annealing or quenching conditions. It was clarified that some of the Mg ions positioned themselves at the A sites of the spinel structure as a result of quenching. The magnetization values varied with the heat treatment. However, the precise ratio of site distribution was not clear. Mössbauer measurements are needed to determine the ion distribution in this system. Ferromagnetic nanoparticles are expected to be useful as magnetic materials and in biomedical applications.

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