Production of Co-Ti ferrite nanoparticles for use as agents in hyperthermia treatment

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Abstract. Co-Ti ferrite (Co_1+xTi_xFe_{2-x}O_4, 0.2 ≤ x ≤ 0.5) nanoparticles with average diameters ranging from 6 to 12 nm were produced by using our novel wet chemical method. The crystal structures and magnetic properties of the obtained samples were investigated by X-ray diffraction and superconducting quantum interference device (SQUID) magnetometer measurements. DC magnetization measurements showed that the coercive force $H_c$ and saturation magnetization $M_s$ decreased as the composite parameter $x$ increased. This phenomenon suggests that Ti$^{4+}$ ions located on B-sites weaken the superexchange interaction between A and B sites. For $x = 0.3$, the value of $H_c$ decreased drastically. The AC magnetic susceptibility of these samples was also investigated, and it was concluded that the sample with a diameter of 12 nm and composition given by $x = 0.3$ is the most appropriate sample for use as an agent in hyperthermia treatment.

1. Introduction

Magnetic nanoparticles have attracted much attention in recent years because they have tremendous potential for use not only in magnetic recording media but also in biomedical applications. One of the authors has proposed a novel method for the preparation of magnetic nanoparticles and has reported the magnetic properties of magnetic particles thus obtained [1–6]; further, possibilities of biomedical application have also been demonstrated [7, 8]. We have succeeded in modifying amino groups on the surface of the magnetic nanoparticles and introducing them into the cells. Cell-selective functionalized magnetic particles were also developed. Further, a magnetic material can be utilized in hyperthermia treatment for cancer patients because the material yields thermal energy upon application of an external field.

In this study, Co-Ti ferrite nanoparticles were prepared in order to carry out hyperthermia treatment, and the magnetic properties of these nanoparticles were investigated. Only a few reports on the magnetic properties of Co-Ti ferrite exist in the literature [9–11]. It is known that imaginary part of AC magnetic susceptibility $\chi''$ related temperature increase of magnetic materials by alternative field [12]. The relationship between power dissipation and can be described following equation:

$$P = \Delta U = \mu_0 \pi \chi'' f H^2 \quad (1)$$
This expression shows that $\chi''$ is an important parameter for effective thermal increase. In order to determine the optimum composition, the out of phase component of the AC magnetic susceptibilities $\chi''$ of the nanoparticles were observed.

2. Experiment

Co-Ti ferrite ($\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$) nanoparticles were produced by mixing aqueous solutions of $\text{CoCl}_2\cdot6\text{H}_2\text{O}$, $\text{TiCl}_4$, $\text{FeCl}_2\cdot4\text{H}_2\text{O}$, and $\text{Na}_2\text{SiO}_3\cdot9\text{H}_2\text{O}$. The mole ratio of the prepared reagent was $\text{Co}:\text{Ti}:\text{Fe}:\text{Si} = 1+x:x:2-2x:3$. The obtained precipitates were washed several times with distilled water and dried at approximately 350K in a thermostat. The as-prepared samples were subjected to heat treatment in a furnace in an air environment at annealing temperatures of 1073 K to 1173 K. Each sample was examined by CuK$\alpha$ X-ray powder diffraction ($\lambda = 0.154$ nm). DC magnetization of the samples was measured by using a SQUID magnetometer (Quantum Design, MPMS) in a $\pm 50$-kOe magnetic field at temperatures from 5 to 300 K. The AC magnetic susceptibility of the samples was also measured under a 1-Oe, 100-Hz alternative magnetic field.

3. Results and Discussion

3.1. X-ray diffraction

The X-ray powder diffraction patterns of $\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ samples annealed at two different temperatures are shown in Figure 1 for various sample compositions: $x = 0.2$, 0.3, 0.4 and 0.5. A broad peak corresponding to amorphous SiO$_2$ was observed around $2\theta = 23^\circ$. Moreover, (220), (311), (511), and (440) peaks corresponding to the spinel structure can be clearly observed. The lattice constant increased as the amount of Ti ions increased. This result is consistent with the fact that Fe$^{3+}$ ions with a radius of 0.064 nm were successfully replaced by Ti$^{4+}$ ions with a larger radius of 0.072 nm. The particle size of the spinel phase has been estimated from the broadening of the diffraction peaks by using the Scherrer formula. The diameters of the particles and lattice constants for different compositions are shown in Table 1.

![Figure 1. Powder X-ray diffraction patterns of $\text{Co}_{1+x}\text{Ti}_x\text{Fe}_{2-2x}\text{O}_4$ for various compositions and for particle sizes of 6 nm (a) and 12 nm (b).](image-url)
Figure 2 shows temperature dependence of zero-field-cooled (ZFC) magnetization of various composition $x$, at a particle size of 6 nm (a) and 12 nm (b), under a 100 Oe field. If we define the peak temperature of FC as blocking temperature $T_b$, $T_b$ was found to be between 150 and 310 K, though some samples couldn’t be observed. Above the blocking temperature, the magnetic spins in the particle are supposed to fluctuate with thermal energy. If the $T_b$ is below room temperature, spins behave superparamagnetically at observed room temperature. Figure 3 shows the magnetization curves for Co-Ti ferrite for various compositions and for particle sizes of 6 nm (a) and 12 nm (b). The samples were measured at room temperature under a ±50-kOe field. For both (a) and (b), the coercivity $H_c$ and saturation magnetization $M_s$ decreased as the composition parameter $x$ increased. It is believed that Fe$^{3+}$ ions with 5 $\mu_B$ replace Co$^{2+}$ ions with 3 $\mu_B$ and Ti$^{4+}$ ions as $x$ increases. As a result, the magnetic moment of the particle as well as $H_c$ and $M_s$ decreased. Besides, non-magnetic Ti ions that are supposed to prefer the B site in the spinel structure weaken the superexchange interaction among A-O-B. These disordered magnetic spins causes coercivity drastically. The composition parameter $x$, particle sizes, lattice constants and saturation magnetizations are summarized in Table 1.
3.3. AC magnetic susceptibility

Figure 4 shows the imaginary parts of the AC magnetic susceptibility \( \chi'' \) of the samples; \( \chi'' \) was measured when the samples were placed in a 1-Oe, 100-Hz ac magnetic field at room temperature. The temperature corresponding to the peak \( \chi'' \) shifted toward lower temperatures as the parameter \( x \) increased. This phenomenon reflects the replacement of Fe\(^{3+}\) ions by Ti\(^{4+}\) ions, and due to the replacement, the anisotropy energy in the particle decreased. The peak magnitude of \( \chi'' \) for the sample with a diameter of 12 nm is larger than that for the sample with a diameter of 6 nm. Thus, \( \chi'' \) varies with the particle size. From this result, it is concluded that the sample with a diameter of 12 nm and \( x = 0.3 \) has the highest magnetic susceptibility value at room temperature and that this sample is the most appropriate here and expected for use as an agent in hyperthermia treatment. Power absorption can be estimated from equation (1), if we assume frequency of 100 Hz, alternative field of 100 kOe for the sample of 12 nm (\( \chi'' \) value is 1.39\( \times \)10\(^3\)) at room temperature, \( P = 426 \) Wg\(^{-1}\) could be obtained.

4. Conclusion

Co-Ti ferrite (Co\(_{1+x}\)Ti\(_x\)Fe\(_{2-2x}\)O\(_4\), 0.2 \( \leq x \leq 0.5\)) nanoparticles were produced by using our novel wet chemical method. DC magnetization measurements showed that the coercive force \( H_c \) and saturation magnetization \( M_s \) decreased as the composite parameter \( x \) increased. This phenomenon suggests that Ti\(^{4+}\) ions located on B-sites weaken the superexchange interaction between A and B sites. From the imaginary part of the susceptibility \( \chi'' \) of the nanoparticles, it is concluded that the sample with a diameter of 12 nm and \( x = 0.3 \) has the largest susceptibility at room temperature. This sample is expected to be used as an agent in hyperthermia treatment.

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