Magnetization and self-heating temperature of NiFe₂O₄ nanoparticles measured by applying ac magnetic field

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Abstract. Magnetic and self-heating properties of various size NiFe₂O₄ (7.7-242.0 nm) were evaluated. The self heating temperature of each sample measured by applying ac magnetic field was affected by its magnetic property. The particle size dependence was also explained by the magnetic properties of the samples. At the lower frequency, the self heating was contributed by hysteresis loss. The ac magnetization process was also evaluated and the result could clarify the origin of self-heating. The 7.7 nm particle was heated by relaxation losses by the applied field at higher frequency. The energy efficiency of a magnetic field to generate self heating was analyzed. It was found that the particle of 130.7 nm exhibited the highest temperature rise and heat generation efficiency for the applied field of low amplitude and frequency.

1. Introduction

Magnetic nanoparticles have high potential for cellular labeling, gene delivery and other biomedical applications. They exhibit unique properties, such as conjugation of biological materials, large specific surface area, guidance by magnet and heat dissipation in alternating magnetic fields. Owing to these properties, magnetic particles can be used for various applications such as magnetic separation, magnetic resonance imaging, drug delivery system and hyperthermia [1, 2, 3]. Hyperthermia is a cancer treatment which has fewer side effects than chemotherapy and radiotherapy. The self heating of magnetic nanoparticles in ac magnetic filed is caused by hysteresis loss and relaxation losses [1, 4]. The relaxation losses are caused by the delay in the magnetic moment relaxation. The Brownian relaxation loss and Néel relaxation loss are associated with magnetic moment rotations with the entire particles and within the particles, respectively. It is significant for hyperthermia to use the nanoparticles which induce high temperature rise. Ferrite nanoparticles are suitable materials for biomedical applications because of abundant size range, diversity and chemical stability compared to metal nanoparticles [5]. Many studies are reported on iron oxide nanoparticles, but there are few on other ferrite nanoparticles [6]. In this paper, the self heating properties and magnetic properties of NiFe₂O₄ nanoparticles were studied in order to clarify their heating origins.

2. Experiments
Magnetization curves and self-heating temperature rise of NiFe$_2$O$_4$ nanoparticles in dried powder state with various size were measured. The mean size and deviation of each NiFe$_2$O$_4$ nanoparticle are listed in table 1. The 7.7 nm NiFe$_2$O$_4$ nanoparticle was synthesized by newly modified sol-gel method [7]. The Other nanoparticles larger than 7.7 nm were synthesized by high temperature thermal decomposition [8]. The dc magnetization curves of both of major and minor loops were measured using a vibrating sample magnetometer (VSM) at room temperature with the maximum field of 10 kOe. The ac magnetization curves were also measured with applying a magnetic field of 200 Oe at 100 kHz. The self-heating temperature of the particles of 60 mg was measured by applying ac magnetic field of 50-500 Oe in filed strength. The frequency was also varied from 100 to 800 kHz.

| Sample | Size [nm] |
|--------|-----------|
| Sample 1 | 7.7±1.0  |
| Sample 2 | 24.8±6.3  |
| Sample 3 | 32.8±8.6  |
| Sample 4 | 54.6±12.3 |
| Sample 5 | 86.1±23.2 |
| Sample 6 | 130.7±44.9 |
| Sample 7 | 242.0±72.9 |

3. Results and discussion

3.1 Magnetic properties
The hysteresis loops of the 7.7 nm and 130.7 nm NiFe$_2$O$_4$ nanoparticles measured by the VSM are shown in figure 1. The 7.7 nm sample exhibits superparamagnetic characteristic.

![Figure 1](image.png)

**Figure 1.** The hysteresis loops of 7.7 nm and 130.7 nm NiFe$_2$O$_4$ nanoparticles measured by a vibrating sample magnetometer at room temperature with the maximum applied field of 10 kOe.
Figure 2 shows the size dependence of saturation magnetization, remanent magnetization and coercivity.

The saturation magnetization was determined by the magnetization under applied field of 10 kOe. It is observed that the smaller size particles exhibit smaller saturation magnetization except the 7.7 nm nanoparticle. This reduced magnetization of nanosized magnetic particles is explained by the surface spin disorder which is due to cation redistribution or the formation of spin glass like structure in the near-surface layers [9, 10, 11]. The decrease in particle size causes an increasing proportion of spin disordered surface layer. The existence of non magnetic layer as surface “dead layer” is also discussed [12, 13]. Thus smaller size particles possess lower magnetization. The saturation magnetization of 7.7 nm sample which was prepared by a different synthesizing method from other ferrimagnetic samples was possibly attributed to different crystalline texture. The remanent magnetization was decreased with decreasing the particle size below 100 nm. The coercivity of the nanoparticles was strongly dependent on their size. The coercive force was maximum for the 54.6 nm sample. Similar results on other spinel ferrite nanoparticles have been reported and this tendency is explained by domain structures of single or multi, domain wall pinning and other properties [10, 11, 12].

Minor loops of the magnetization curves were also evaluated. Figure 3 shows the results for the 7.7 nm, 24.8 nm and 130.7 nm NiFe$_2$O$_4$ nanoparticles.

**Figure 2.** Saturation magnetization, remanent magnetization and coercivity of NiFe$_2$O$_4$ nanoparticles indicated as a function of particle size.

**Figure 3.** The minor loops of 7.7 nm, 24.8 nm and 130.7 nm NiFe$_2$O$_4$ nanoparticles measured by a vibrating sample magnetometer at room temperature.
The superparamagnetic sample of 7.7 nm did not exhibit an effective area in its minor loop, which suggested that there was no hysteresis loss. The 24.8 nm sample, second smallest particle, exhibited a certain area of the hysteresis curve. It indicated that the sample was ferromagnetic. The 130.7 nm sample exhibited a larger area.

3.2 Self-heating temperature rise
Figure 4 shows temperature rise of the samples indicated by $\Delta T/\Delta t$ at $t \approx 0$, its initial slope for time dependence, where $T$ and $t$ are the measured temperature and time, respectively. The applied field strength was varied and its frequency was fixed at 10 kHz. It is supposed that only hysteresis loss contributes to the heat generation of the nanoparticles due to the low frequency. The 7.7 nm particle exhibited slight temperature rise because of its superparamagnetic property as shown by the minor hysteresis loop in figure 3. The other ferromagnetic nanoparticles were heated to higher temperature with increasing the applied field strength. The 24.8 nm and 32.8 nm particles have similar temperature rise at the field amplitude above 250 Oe, but the temperature rise of the 24.8 nm particle is lower than that of the 32.8 nm particle below 250 Oe. The reason is that coercivity of the 24.8 nm particle (137 Oe) is smaller than that of the 32.8 nm particle (192 Oe). Hysteresis losses increase gradually with increasing the field strength, and almost saturate according to its saturation magnetization [14]. Due to the smaller coercivity of the 24.8 nm particle, the weaker field strength could open the hysteresis loop of the 24.8 nm particle rather than the 32.8 nm particle. The 54.6 nm particle shows low temperature rise at applied field below 200 Oe and higher heat generation above 200 Oe due to the largest coercivity and large magnetization. The 86.1 nm and 130.7 nm particles show similar temperature rise at magnetic field below 150 Oe. With increasing the field strength, the temperature rise of the 130.7 nm particle exhibits higher than that of 86.1 nm because of the similar coercivity and larger magnetization. The largest particle of 242.0 nm shows the highest temperature rise at small magnetic field below 150 Oe but it saturates immediately. The saturated temperature rise is lower than those of 86.1 nm and 130.7 nm particles due to the small coercivity of around 100 Oe. Figure 5 shows the efficiency of applied energy to generate self heating.
It is determined by the temperature rise divided by $H^2 \times f$, Where $H$ and $f$ are the amplitude and frequency of applied ac magnetic field, respectively.

The energy efficiency of multi domain nanoparticles corresponds to the coercivity, which are 100 Oe, 157 Oe, 145 Oe and 205 Oe for the 242.0 nm, 130.7 nm, 86.1 nm and 54.6 nm particles, respectively. It is reported that alternative magnetic field frequency within the range of 100 kHz to 200 kHz, depending on the body cross-section and tissue conductivity, are recommended for human therapy [14]. In addition, the product of field strength and frequency should be limited to $5 \times 10^9$ A/ms as biocompatible condition [15]. Within the above condition, the magnetic field strength should be below 25 kA/m (314 Oe) at the frequency of 200 kHz, and the highest temperature rise is obtained by the 130.7 nm particle.

Figure 6 shows the dependence of ac field frequency of temperature rise.

**Figure 5.** The energy efficiency of applied magnetic field to generate self heating. The temperature rise was divided by $H^2 \times f$, Where $H$ and $f$ are the amplitude and frequency of applied ac magnetic field, respectively.

**Figure 6.** The dependence of magnetic field frequency of temperature rise. The ac field amplitude was 50 Oe and frequency was varied from 100 to 800 kHz.
The applied field strength was 50 Oe and frequency range was 100-800 kHz. The temperature rise of the 24.8 nm particle was proportional to frequency. It indicated that the self heating of the nanoparticle was originated from hysteresis loss. Other particles of larger size also exhibited proportional characteristic. On the other hand, the 7.7 nm superparamagnetic particle exhibited non-proportional frequency dependence, suggesting that the relaxation losses were responsible for heating. The ac magnetization curves of the 7.7 nm and 24.8 nm nanoparticles were measured as shown in figure 7.

![Figure 7. The ac magnetization curves of 7.7 nm and 24.8 nm NiFe2O4 nanoparticles measured by applying ac magnetic field at 100 kHz at room temperature.](image)

The superparamagnetic 7.7 nm sample exhibited no area for its dc minor hysteresis loop in figure 3. This sample also exhibited no area for its ac minor hysteresis loop at an applied field frequency of 100 kHz. At this lower frequency, the 7.7 nm sample exhibited neither the hysteresis loss nor the relaxation losses. The 24.8 nm sample had a certain area in the ac hysteresis, and the area was consistent to that of dc hysteresis. It means that an ac hysteresis area of the 24.8 nm sample is associated with only hysteresis loss.

Self heating induced by relaxation loss under an ac magnetic field particularly occurs in smaller particles with single domain structure [16]. The Brownian relaxation loss and Néel relaxation loss are associated with magnetic moment rotations with the entire particles and within the particles, respectively. Each relaxation time is given by the following equations: (1), (2) and (3),

\[ \tau_N = \tau_0 \exp\left(\frac{KV_M}{k_B T}\right) \]  
\[ \tau_B = \frac{4\pi \eta R_H^3}{k_B T} \]  
\[ \tau_{eff} = \frac{\tau_N \tau_B}{\tau_N + \tau_B} \]

where \( \tau_0 \) : the Brownian relaxation time, \( \tau_N \) : the Néel relaxation time, \( \tau_0 = 10^{-9} \) s, \( K \) : the anisotropy constant, \( V_M \) : the volume of particle, \( k \) : the Boltzmann constant, \( T \) : the temperature, \( \eta \) : the viscosity, \( R_H \) : the radius of the particle and \( V_H \) : the hydrodynamic particle volume. The heat dissipation by relaxation loss is given by the following equation,
\[ P = \pi \mu_0 \chi_0 H^2 f \frac{2\pi f \tau_{\text{eff}}}{1 + (2\pi f \tau_{\text{eff}})^2} \]  

(4)

where \( \chi_0 \) is the ac magnetic susceptibility. From calculations using (1)-(4) and the anisotropy constant \( K = -5.1 \times 10^4 \) as the bulk value \[17\], NiFe\(_2\)O\(_4\) nanoparticles of 4-12 nm is expected to have power dissipation by relaxation loss under ac magnetic field. This agrees with the experimental result that only the 7.7 nm particle induces self heating by relaxation loss. As the samples were in dried powder state, Néel relaxation loss was dominant in this study.

4. Conclusion

Magnetic properties and heating properties of NiFe\(_2\)O\(_4\) nanoparticles with different sizes of 7.7-242.0 nm were studied. The 7.7 nm particle exhibited superparamagnetism in the VSM measurement. It was not heated by applying an ac magnetic field with relatively lower frequency at 10 kHz. The samples of larger size which exhibited ferromagnetic in the VSM measurement were heated by in an ac field due to hysteresis loss. The energy efficiency of a magnetic field to generate self heating was analyzed. The 130.7 nm nanoparticle was heated most efficiently within the excitation condition considering human safety. At higher frequency of the applied field, The 7.7 nm particle was heated and frequency dependence of its temperature rise suggested that the heating was originated from Néel relaxation loss.

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