Magnetic and Optical Properties of Fe_3O_4 Nanoparticle Ferrofluids Prepared by Coprecipitation Technique

K. T. Wu, P. C. Kuo, Y. D. Yao, and E. H. Tsai

***Abstract*—Nanometer size Fe_3O_4 particles were fabricated by chemical coprecipitation technique. The particle shape and size are affected by the PH value of the reactive solutions. The ferrofluids were fabricated with the Fe_3O_4 particles as magnetic particles, ammonium oleate as surfactant, and de-ionized water as solvent. Optical transmission of Fe_3O_4 nanoparticle ferrofluids was investigated as a function of incident optical wavelengths between 450 and 750 nm and applied magnetic fields up to 150 Oe. In general, for samples with lower PH value, the particles are small and agglomerate together, however, for samples with higher PH value, the particles are larger and distributed uniformly. Samples precipitated with higher PH value show larger variation of the transmittance (ΔT). This can be understood by our transmission electron microscope and X-ray diffraction pattern studies. The behavior of agglomeration for samples with lower PH value relates to the smaller variation of the optical transmission to the magnetic field.**

***Index Terms*—Chemical coprecipitation, Fe_3O_4, nanoparticle ferrofluid.**

I. Introduction

In recent years, research associated with magnetic fluids have received wide attention, and show a rich variety and complexity in physical phenomena [1]–[9]. Ferrofluids have been extensively applied to audio voice coil-damping, inertia-damping apparatuses, bearings, stepping motors, and vacuum seals etc. [10]. There are many chemical methods to prepare magnetic fluid. In this investigation, we successfully fabricated nanometer size Fe_3O_4 ferrofluids by a chemical coprecipitation technique, and report the magnetic and optical properties of this fluid.

II. Experiments

Fe_3O_4 nanoparticles were prepared by a chemical coprecipitation technique. The starting materials were $FeCl_2$, $FeCl_3$, and NaOH. The $FeCl_2$ and $FeCl_3$ solutions were prepared by adding $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 7H_2O$, into de-ionized water and stirring to complete dissolution. The NaOH solution is prepared by dissolving NaOH into de-ionized water. These solutions prepared with various concentrations were mixed together by stirring. The reaction temperature is kept at 70 °C and the reaction time is one hour [11]. The final PH values of these mixed solution were varied between 12 and 14. The chemical reaction can be expressed as:

$$FeCl_2 + 2FeCl_3 + 8NaOH \rightarrow Fe_3O_4 + 8NaCl + 4H_2O.$$

The NaCl is separated from the precipitant of this reaction by washing and centrifuging it with de-ionized water several times leaving Fe_3O_4. The Fe_3O_4 nanoparticle ferrofluids were fabricated using nanometer size Fe_3O_4 particles as magnetic particles, ammonium oleate as surfactant, and de-ionized water as solvent. The weight ratio of (magnetic particle : ammonium oleate : de-ionized water) is 2.0 : 0.6 : 97.4.

The crystal structure of the particles is investigated by x-ray diffraction. The particle shape, size, and morphology are observed by a transmission electron microscope (TEM). The optical transmission of the ferrofluids has been investigated as a function of incident optical wavelengths between 450 and 750 nm and applied magnetic fields up to 150 Oe. The magnetic field is parallel to the incident light.

III. Results and Discussion

The quality of the precipitated Fe_3O_4 nanoparticles is mostly affected by the reaction temperature and the PH value of the reactive solution. According to [11], the reaction temperature affects the particle size, phases, and reaction time. For temperatures below roughly 60 °C, the final precipitates will be dominated by either α-FeOOH or γ-FeOOH. The particle shape of α-FeOOH is long and rodlike, and its color is yellow; for γ-FeOOH particle, its shape is lath and vein-like, and its color is orange. For temperatures above roughly 60 °C, the final precipitates are dominated by Fe_3O_4, its shape is granular and its color is black. In this study, the reaction temperature is always kept at 70 °C in order to get good quality of Fe_3O_4 particles. The x-ray diffraction pattern of the final precipitates is shown in Fig. 1. From this figure it is clear, single phase Fe_3O_4 for all the final precipitates.

We find that samples with PH < 13.9, the particles are smaller and agglomerated, however, for samples with PH > 13.9, the particles will become spherical and larger but still in the nanometer range with uniform distribution. The saturation magnetization of these Fe_3O_4 nanoparticles is roughly 52 emu/g. Fig. 2 shows the transmission electron microscopy (TEM) image of the Fe_3O_4 nanoparticles for samples with

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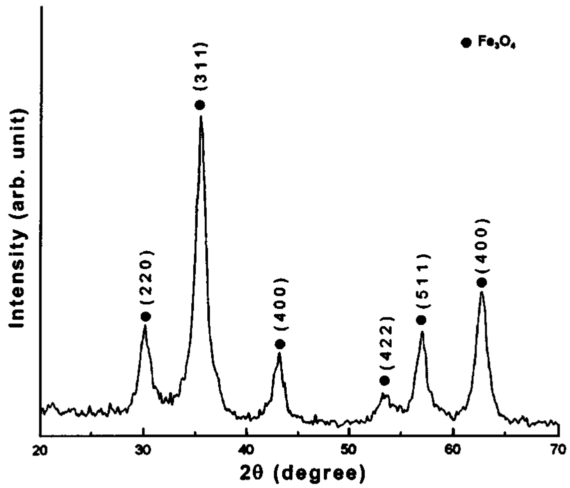

Fig. 1. X-ray diffraction patterns of the final precipitates.

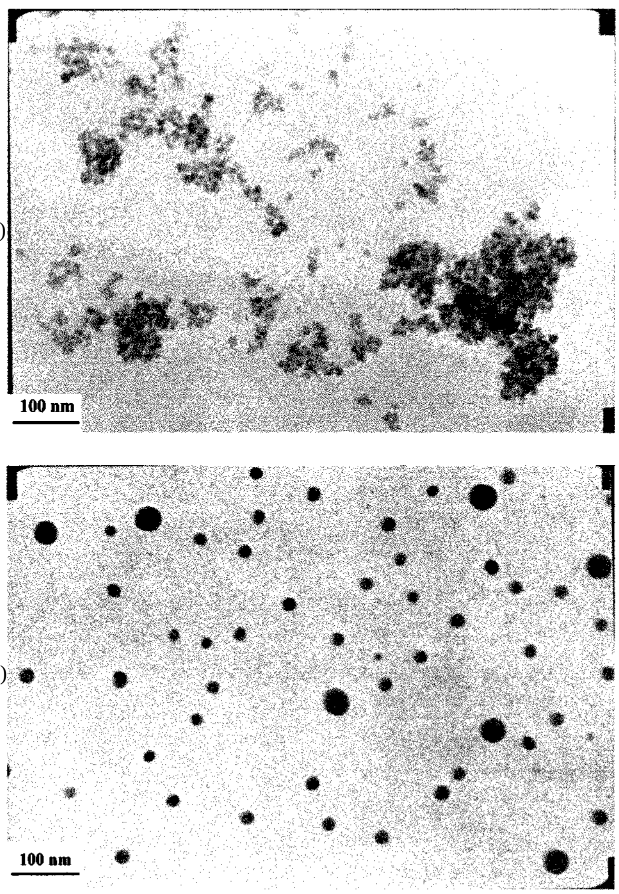

Fig. 2. TEM image of Fe_3O_4 nanoparticles for samples with (a) PH = 12.49 and (b) PH = 13.98.

(a) PH = 12.49, and (b) PH = 13.98. It shows clearly that samples with higher PH value exhibit better distribution and with particles in spherical shape. Optical transmission of the Fe_3O_4 nanoparticle ferrofluid sealed in a 4 cm × 1 cm rectangular glass cell with a thickness of 100 um has been investigated as a function of incident optical wavelengths between 450 and 750 nm and applied magnetic fields up to 150 Oe. In general, the optical transmission of a Fe_3O_4 ferrofluid increases with

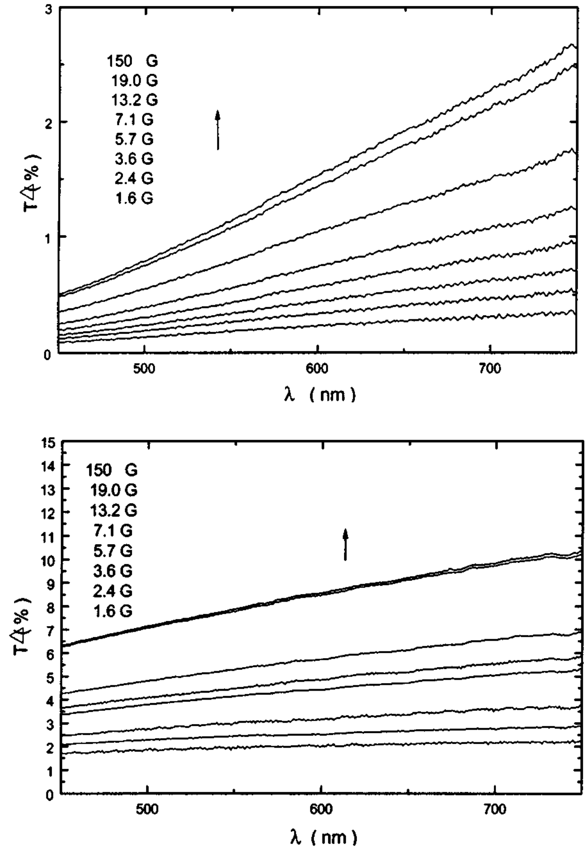

Fig. 3. ΔT versus wavelength for samples with (a) PH = 12.49 and (b) PH = 13.98.

increasing wavelength of incident visible light between 450 and 750 nm.

Fig. 3 shows the variation of the transmittance ΔT as a function of wavelength with an applied magnetic field of 1.6, 2.4, 3.6, 5.7, 7.1, 13.2, 19.0, and 150 Oe for samples with (a) PH = 12.49 and (b) PH = 13.98.

In general, samples precipitated with higher PH value show larger variation of the transmittance (ΔT). Our experimental data show that ΔT is almost the same for applied magnetic field increasing from 23 to 150 Oe. In Fig. 3(a), ΔT varies from roughly 0.5 to 2.7% with increasing incident wave length from 450 to 750 nm for samples with PH value of 12.49 under magnetic field of 150 Oe. From Fig. 3(b), ΔT varies from roughly 6.3 to 10.4% with increasing incident wave length from 450 to 750 nm for samples with PH value of 13.98 under magnetic field of 150 Oe. This can be understood by our X-ray diffraction pattern and transmission electron microscope studies; i.e., the behavior of agglomeration for samples with lower PH value relates to the smaller variation of the optical transmission to the applied magnetic field.

The variations of the transmittance of the samples as a function of the applied field with incident wavelength at 600 nm are depicted in Fig. 4. The ΔT increases rapidly for samples with PH > 13.9. This is related to the homogeneous separation and spherical shape of the nanometer size magnetic particles. However, the variation of ΔT is very small for samples with PH < 13.9. Below roughly 20 Oe, ΔT increases with increasing applied magnetic field; but, ΔT is almost the same for magnetic

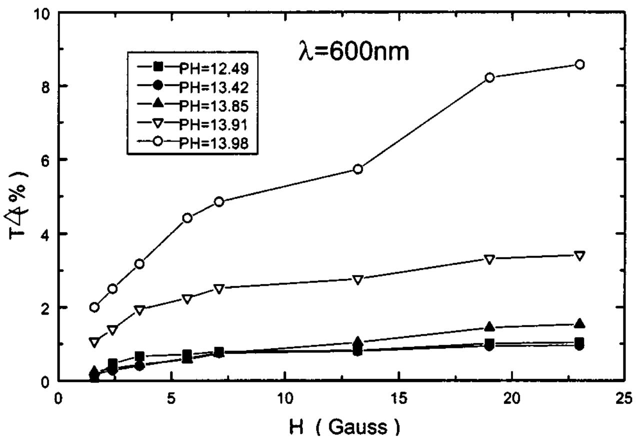

Fig. 4. The variation of the transmittance of the samples as a function of the applied field with incident wavelength at 600 nm.

fields between roughly 20 and 150 Oe, so that it is not plotted in Fig. 4.

In summary, nanometer size Fe_3O_4 ferrofluids have been successfully fabricated by chemical coprecipitation technique. Optical transmission of Fe_3O_4 nanoparticle ferrofluids have been investigated as a function of incident optical wavelengths between 450 and 750 nm and applied magnetic fields up to 150 Oe. For samples with lower PH value, the particles are small and agglomerate together, however, for samples with higher PH value, the particles are larger and distributed quite uniformly. Samples precipitated with higher PH value show larger variation of the transmittance (ΔT). These magnetic and optical properties of nanoparticle ferrofluids may present some potential applications, such as magnetic induced optical sensors.

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