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Preparation and Magnetic Properties of Zn-Doped Fe₃O₄ Magnetic Colloid

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Abstract. Fe₃O₄ magnetic colloids were produced by co-precipitating a Fe⁺³, Fe⁺², and Zn²⁺ containing solution with a NaOH solution at 70°C. Analyses results indicated that the Zn content of the Fe₃O₄ colloids was always less than the solution’s Zn content. The difference was found to be the smallest when the colloid was precipitated at pH=10. The σₙ values of the Fe₃O₄ colloid significantly improved by adding an appropriate amount of Zn ions and precipitating it at an optimum pH value, pH=10. The optimum Zn ion content was 6.18 at%, which was corresponded to Zno(Fe₂⁺,Zn⁺⁺)Fe₃O₄. At this composition the colloid’s σₙ value was 94 emu/g, and increased by more than 34% of pure Fe₃O₄ colloid’s σₙ value. By theoretical calculation the σₙ should increase 27.8%.

INTRODUCTION

Investigators have synthesized magnetite colloid by the chemical coprecipitation method to prepare magnetic fluid since 1966[1-3]. An appropriate amount Zn ion in the colloids may increase the colloid’s σₙ value because adding Zn ion increases the unbalanced magnetic moment between the spinel’s A site and the B site. In this study, we investigate the effects of Zn ion on the σₙ value of Fe₃O₄ magnetic colloids to test whether or not adding Zn ions can increase the colloid’s magnetic properties and what the optimum amount of Zn ion is.

EXPERIMENTAL

Fe₃O₄:Zn magnetic colloids were produced by the chemical co-precipitation method, i.e. mixing an acidic solution containing 0.1 M FeCl₃·4H₂O, 0.2 M FeCl₃·6H₂O, an appropriate amount of ZnCl₂·4H₂O, with a sufficient volume of 0.1 M NaOH alkali solution at 70°C, and then centrifuging them from the mixed solution. TEM, XRD, EDX, and VSM analyses were performed to measure the particle size, structure, chemical composition, and magnetic properties of the Fe₃O₄:Zn magnetic colloids.

RESULTS AND DISCUSSION

X-ray diffraction analysis results in Figure 1 reveal that a high pH value of the co-precipitated solution favored the formation of Fe₃O₄ colloids. At pH=10, well crystallized spinel phase was formed and no other phase was detected. Zn ion formed a solid solution with Fe₃O₄. EDX analysis of Zn ion content in Fe₃O₄ colloids (Figure 2) reveals that Zn ion content in Fe₃O₄ colloid was always less that in the original solution because Zn has a higher solubility in this pH range than either Fe²⁺ or Fe³⁺ ions. For an initially fixed Zn ion content of 6.91 at% (8 wt%) in the solution, the Zn ion content in the Fe₃O₄ colloids ranged from 2.87 at% at pH=5 to a maximum value of 6.71 wt% at pH=10. Later, it gradually declined to 6.32 wt% at pH=12. The difference between the Zn ion in the colloid and in the original solution was the smallest at pH=10 because of the Zn ion’s amphibous property. At a fixed pH=10 in the precipitated solution, Figure 3 shows the relationship between Zn content in the solution before co-precipitation and Zn content in the Fe₃O₄ colloid. Zn ion content in the Fe₃O₄ colloid is always less than that in the original solution. Electron micrographs reveal that the colloid particles were spherical with a diameter less than 100Å.
Because the $\sigma_a$ value of Fe$_3$O$_4$:Zn colloids was found to be optimal when they were produced at pH=10, Fe$_3$O$_4$:Zn colloids were produced at pH=10 for various Zn contents. Figure 4 reveals that the $\sigma_a$ values of the Fe$_3$O$_4$ colloids significantly improved by adding an appropriate amount of Zn ions, e.g. ranging from 70 emu/g at Zn=0 at% to a maximum of 94 emu/g at Zn=10.97 at%. The optimal Zn content of the Fe$_3$O$_4$:Zn colloid is Zn=6.18 at% where the $\sigma_a$ value of the colloid is 34% more than the $\sigma_a$ values of the colloids without adding the Zn ion.

6.18 at% of Zn ion in the Fe$_3$O$_4$:Zn colloid implies that, initially, Fe$^{3+}$ is 31.27 at% and Fe$^{3+}$ is 62.55 at% in this colloid. However, adding Zn$^{2+}$ ion replaces Fe$^{3+}$ ion and causes a 6.18 at% surplus of Fe$^{3+}$ in the spinel structure. The fact that x-ray analysis in Figure 1 indicates that the Fe$_3$O$_4$:Zn colloid is a single phase solid solution, suggests that the surplus Fe$^{3+}$ must be somewhere in the spinel structure. The Fe$^{3+}$ was apparently oxidized to Fe$^{2+}$ by dissolving oxygen in the solution and became part of the spinel because, at pH=10, free Fe$^{2+}$ is unstable and quite easily oxidized. If such a fact is true, the subsequent spinel formula of the Fe$_3$O$_4$:6.18 at% Zn colloid is as follows: (Zn$_{0.818}$Fe$_{0.182}$O$_4$). This formula's net magnetic moment, as calculated from its individual magnetic moments, is 5.112 $\mu$; meanwhile, the net magnetic moment of pure Fe$_3$O$_4$ is 4 $\mu$. Adding 6.18 at% Zn ion to Fe$_3$O$_4$ increases the $\sigma_a$ value of Fe$_3$O$_4$ by 27.8%, which is slightly different from the experimental value of 34%. The optimum $\sigma_a$ value of Fe$_3$O$_4$:Zn colloid is that the spinel's A site is occupied by 18.54 at% of Zn ion, which is quite different from the other members of the ferrite family where the optimum $\sigma_a$ value occurs when the spinel's A site is occupied by 50 at% of Zn ion. Some Hc values were found in the Fe$_3$O$_4$:Zn colloids (Figure 4), implying that the colloids contain some larger particles which are beyond super-paramagnetic range and are therefore ferrimagnetic. Moreover, Figure 4 indicates that the Hc value of the Fe$_3$O$_4$:Zn colloids gradually decrease with the Zn ion content.

References