Low Temperature Synthesis of MgFe$_2$O$_4$ Soft Ferrite Nanocrystallites

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ABSTRACT

Single phase soft ferrite nanocrystallites could be synthesized by various methods. Most of the methods start from preparation of powder or they are high temperature synthesis. We have tried to synthesize MgFe$_2$O$_4$ nanocrystallites at low temperature to improve their properties. MgFe$_2$O$_4$ magnetic particles with crystallite size (~ 7.4nm) were successfully synthesized below 200°C by auto- combustion assisted sol-gel method with the control of pH value and hydrolysis conditions. The pH dependent combustion nature has been studied by thermal analysis (DTA and TG) of the dried gel. The formation of single phase cubic spinel was confirmed by XRD analysis. The morphology of the powder was characterized by FESEM. It represents a soft agglomerated structure composed of magnetically interacting ultrafine crystallites. These nanocrystallites synthesized at low temperature improved electrical and magnetic properties and the results discussed.

Keywords: MgFe$_2$O$_4$ nanocrystallites, sol-gel auto-combustion, pH modification, ion occupation

1. INTRODUCTION

Ferromagnetic iron oxides, γ-Fe$_2$O$_3$, Fe$_3$O$_4$, spinel and hexaferrites are technologically important materials for data storage and transmission. Due to their optical, electrical, magnetic, mechanical and catalytic properties, the study of these metal oxides has attracted the attention of materials scientists[1]. Magnesium ferrites are the most versatile of the ferrites and allied compounds with widespread application in microwave devices. These materials exhibit low saturation magnetization, high resistivity and uniform and reproducible characteristics[2].

The ferrite particles in nano-regime could provide more advantages over the bulk ferrites with reminiscent change of physical properties and low temperature environment is the key parameter for the synthesis of nanoparticles[3]. Recently, more attention was focused on the Auto-Combustion assisted Sol- Gel method as that soft solution method is a promising route to synthesize nanocrystallites in simple, fast and economical way [4, 5, 6, 7]. MgFe$_2$O$_4$ nanocrystallites were prepared through sol-gel auto-combustion method by Y. Huang et al.[8]. The ferrite precursor was decomposed

around 400°C without pH modification. The hydrolysis of cations and inorganic polymerization govern by the pH value of aqueous solution are of fundamental importance in this synthesis. Hence, an attempt was made to synthesize MgFe$_2$O$_4$ nanocrystallites and to observe some of its characteristics through the Auto-Combustion assisted Sol- Gel method under the control of the pH value of aqueous solution and hydrolysis conditions.

2. MATERIALS AND METHOD

In this study, samples with the formula MgFe$_2$O$_4$ were synthesized via the Auto-Combustion assisted Sol- Gel method. The energy to form the ferrite nanocrystallites is provided by oxidation-reduction process of thermal precursor and fuel in the Sol-Gel auto-combustion proces[9]. Metal nitrates were employed in this process as they have a dual role of being a soluble cation sources and the oxidant[10]. Citric acid was used with 2 important roles: the fuel for the combustion reaction and as a chelating agent to form complexes with metal ions, preventing the precipitation of hydroxilated compounds[11].

The starting materials were analytical reagent grade oxides: Ferric nitrate nanohydrate $Fe(NO_3)_3.9H_2O$ (Wako 99.0%), Magnesium nitrate hexahydrate $Mg(NO_3)_2.6H_2O$ (Wako 98.0%) and Citric acid $C_6H_8O_7$ (Wako 98.0%). Aqueous solution of metal ions and chelating agent were prepared with distilled water. The molar amount of metal nitrate to citric acid was 1:1. The pH value was modified by adding ammonia solution (28%) drop wise under constant stirring to reach to 7. After the solution was evaporated on a hot plate at a water-bath temperature 60°C to form a sticky gel, the temperature was increased to 80°C in order to obtain a condensed gel. When the gel was formed, the temperature was increased to ~200°C. A large amount of gases (CO_2, H_2O, N_2) librated and auto-combustion occurred giving rise to a dark brown ferrite powder.

The X-ray diffraction patterns for all the samples were recorded on a SRA (M18XHF) X-ray diffractometer. Transmission Electron Microscopy analysis was performed by JEOL JEM2010F and magnetization curve under applied magnetic field was obtained by PPMS. Thermogravimetry (TG) and simultaneous differential thermal analysis (DTA) of the precursor powder were performed by TG-DTA 2000S (Japan).

3. RESULTS & DISCUSSION

3.1 X-ray Analysis

The XRD spectrum of the $MgFe_2O_4$ nanocrystallites after combustion is shown in Fig. 1. The XRD analysis confirmed the formation of single-phase $MgFe_2O_4$ cubic spinel, showing well defined reflection of allowed planes. The crystallite size after combustion at 200°C estimated by the Debye-Scherrer formula[12] was 7.4nm. The peak broadening in the XRD spectrum again confirmed the formation of the nano-size crystallites.
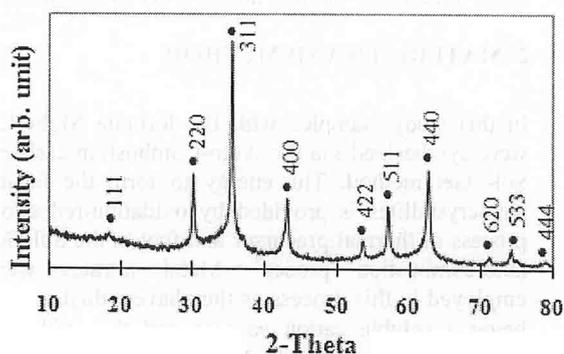

Figure 1. The XRD spectrum of the $MgFe_2O_4$ as-burnt powder

3.2 Morphological Analysis

To evaluate the morphology of the as-burnt powder, high resolution and low resolution images of Transmission Electron Microscopy were taken and shown in Fig. 2(a) and (b) respectively.
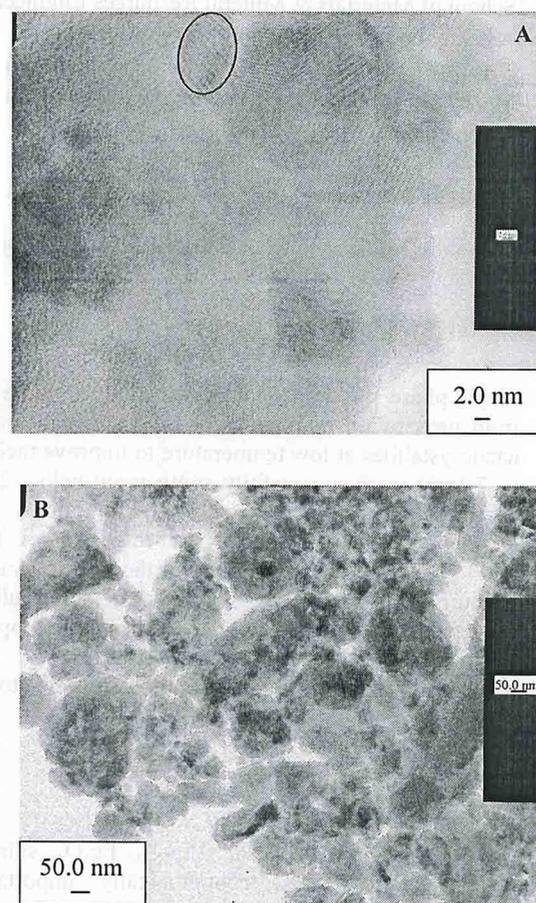

Figure 2. (A) High resolution TEM and (B) Low resolution TEM images of the as burnt powder

It was determined that the crystallite size to be ~7 to 8 nm which agrees with the calculated value by the Debye-Scherrer formula. Relatively low hydrolysis temperature and low combustion temperature could produce nanocrystallite magnetic ferrite in single step.

As they are magnetic ferrite crystallites, the particles are agglomerated and composed of nanocrystallites held together by magnetic interaction[13] as illustrated in Fig. 2 (b).

3.3 TG/DTA Analysis

The dried gel precursors were also characterized by TG/DTA at a heating rate 10°C/min until 500°C under O_2 flow at 100ml/min. The thermal decomposition of the precursor, citric acid and NH_4NO_3 are shown in Fig. 3(A) and (B).
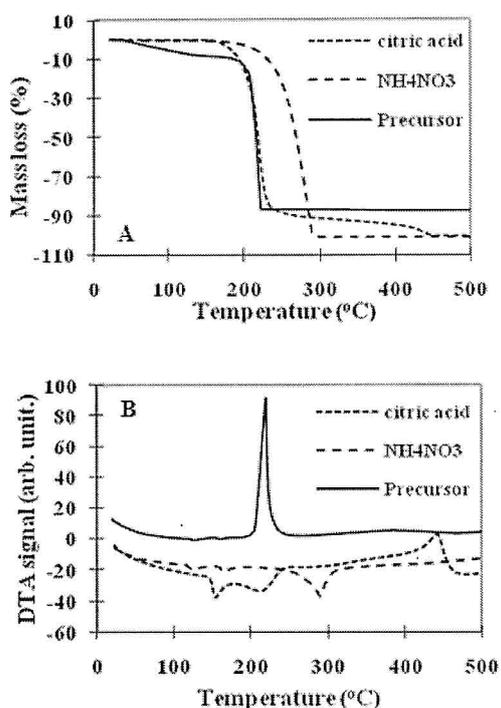

Figure 3. (A) TG & (B) DTA plots of the precursors, citric acid and NH_4NO_3

In aqueous chemistry, the degree of condensation varies with different legend types and the formation of legends in turn depends on the pH region[14]. As the pH value of the aqueous solution was modified to 7, better condensation process during hydrolysis provided single step decomposition to form the nanocrystallites. The weight loss for precursor occurs in two steps. In fact, O-H groups, carboxyl group and NO_3^{3-} ions exist in the dried gel[15]. The first weight loss represents the water vaporization of O-H groups. In the second step, a large weight loss represents the decomposition of carboxyl, NO_3^{3-} ions and NH_4NO_3, and at the same time, auto-combustion occurred. The decomposition of NH_4NO_3 supplied oxygen to accelerate the combustion reaction[16].

As the decomposition of NH_4NO_3 is endothermic process as shown in the DTA curve in Fig. 3 (B), the combustion temperature is decreased and the amount of heat generated in the combustion process is also decreased. Therefore, the decomposition of NH_4NO_3 favours the formation of small crystallite size in this synthesis.

On these basic, we have proposed a chemical reaction as in Eqn (1).

$$Mg(NO_3)_2 + 2Fe(NO_3)_3 + 3C_6H_8O_7 + 3.5O_2 \longrightarrow MgFe_2O_4 + 4N_2 + 18CO_2 + 12H_2O \quad (1)$$
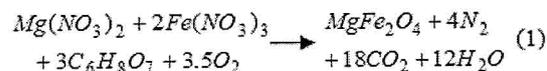
3.4 Magnetic Properties

The spin of the A and B sites ions oppositely magnetize sublattices A and B, with a resultant magnetic moment equal to the difference between those of A and B site ions[17]. It has been experimentally observed that the value of saturation magnetic moment for the B lattice (M_B) is greater than that of the A lattice (M_A), so that the resultant saturation magnetization (M_s) can be written as in Eqn (2),

$$M_s = |M_B - M_A| \quad (2)$$

The value of n_B (saturation magnetization per formula unit in Bohr magneton) can be obtained from the resultant hysteresis loop, by using the following equation[18].

$$n_B = \frac{MW \times Ms}{5585} \quad (3)$$

Where, MW is the molecular weight of the compound and M_s is the saturation magnetization.
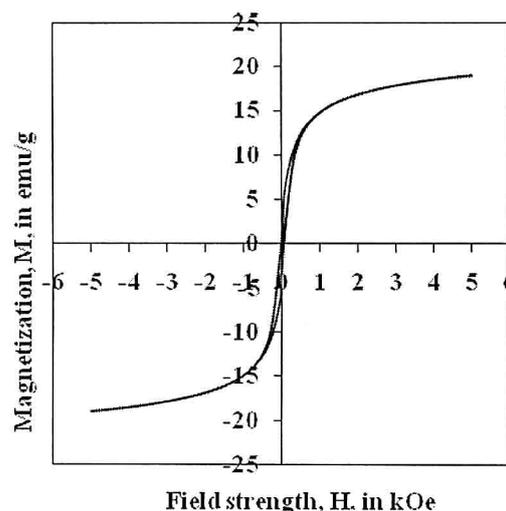

Figure 4. The magnetization curve of the as-burnt powder under applied magnetic field of ± 5 kOe

The magnetic properties were calculated from the magnetization curve and are shown in Table 1. It was found that the magnetic properties had improved compared to those synthesized by conventional ceramic method in our previous work.

Table 1. The value of satuation magnetization M_s, remanent magnetization M_r, the magneton number n_B and coerceivity H_c for the as-burnt powder

Synthesis	M_s emu/g	M_r emu	H_c Oe	n_B μ_B
Sol-Gel	46.32	18.94	2.14	0.68
Conventional	31.06	22.76	2.85	0.82

The estimated ratio of Mg^{2+} ions in A site and B site[19] was calculated from magnetic moment and presented in Eqn 4 and Eqn 5.

A site: $(Mg^{2+}_{0.068} Fe3^+_{0.932})$ (4)

B site: $[Mg^{2+}_{0.932} Fe^{3+}_{1.068}]$ (5)

The detail observation for magnetization mechanism of those as-synthesized nanocrystallites is under progress.

4. CONCLUSIONS

$MgFe_2O_4$ nanocrystallites (~7.4 nm) were successfully synthesized by the auto-combustion assisted sol-gel method under the control of the pH value of aqueous solution and hydrolysis conditions. Single step decomposition of nitrate–citrate had occurred around 200°C by pH modification of the aqueous solution at 7. The magnetic properties can be improved compared to those synthesized by conventional ceramic method. Clear understanding of the decomposition process of citrate-nitrate precursor has been developed in this study.

5. ACKNOWLEDGEMENTS

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