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# Syntheses of tabular cobalt ferrite crystal using non-equilibrium crystallization conditions

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**Abstract.** Cobalt ferrite $CoFe_2O_4$ tabular crystals were synthesized via two-step coprecipitation using non-equilibrium crystallization conditions by supplying a solution of $CoCl_2•6H_2O$ and $FeCl_3•6H_2O$ and a solution containing NaOH at a later crystallization stage. Mean particle size of ~16.5 nm $CoFe_2O_4$ primary particles synthesized by coprecipitation showed non-oriented structure. Effect of heat treatment temperature on the microstructures of the final $CoFe_2O_4$ crystal was examined, orderly arranged plate-like tabular $CoFe_2O_4$ crystals were formed under calcination at 800 °C. Magnetic hyspersis loops measured at 300 and 5 K indicated the anisotropy in the tabular crystals.

## Introduction

Ferrite $MFe_2O_4$ (M = Co, Ni, Zn, Mn, et al.) with spinel structure is widely used for microwave absorbers and high-frequency electronics, owing to its high Curie temperature, relatively high saturation magnetization, strong magnetostrictive effect, high diffusion anisotropy and good stability as well [1−3]. Moreover the recent years have witnessed an unprecedented use of soft ferrite in the preparation of composite multiferroic materials (e.g., $BaTiO_3/CoFe_2O_4$ [4], $Pb(Zr,Ti)O_3/NiFe_2O_4$ [5], et al) which have great potential application for storage units. Several syntheses methods applied to soft ferrite particles have been used including conventional ceramic method [6], coprecipitation [7], sol-gel [8] and combustion reaction method [9]. The microstructure and processing for each are quite different.

Synthesis of soft ferrite with a tabular crystal microstructure attracts special attention [10−15]. Tabular particles can yield thinner coatings and facilitate to prepare multilayer thin films. Particles with tabular structure exhibit better properties such as dispersing and microwave absorption capabilities. And tabular or plate-like particles provide template for grain grow oriented to form textured polycrystalline ceramics. Taking the advantage of anisotropy of single crystal, the $d_{33}$ coefficient of lead-free piezoelectric material $(Na_{0.84}K_{0.16})_{0.5}Bi_{0.5}TiO_3$ with textured structure can be optimized [16]. Magnetic materials' properties such as magnetostrictive can be also enhanced by forming textured structures [17]. The prospect application of soft ferrite and the advantages of tabular particles suggest that it is worthwhile to investigate the possibility of synthesis tabular spinel ferrite particles.

Two-step coprecipitation method using non-equilibrium crystallization conditions was an effective method to synthesis plate-like particle crystals which had been used by Zhao et al. [18] to synthesis Mg-Al-layered double hydroxides (LDH). In the present work, cobalt ferrite $CoFe_2O_4$ crystal with tabular structure was synthesized by the two-step coprecipitation method, effect of processing parameters such as concentration of solutions and heat-treatment temperature on formation of the $CoFe_2O_4$ crystal was studied, and the materials' microstructure and magnetic properties was investigated.

## Experimental procedure

$CoFe_2O_4$ tabular particles were synthesized using non-equilibrium crystallization conditions via two-step coprecipitation. The preparation procedure is shown in Fig. 1. In the first step, $CoFe_2O_4$ primary particles were synthesized by coprecipitation method as the following process: At first, according to the Co/Fe ratio of 1:2, 0.267 mol/L $CoCl_2$ and 0.533 mol/L $FeCl_3$ aqueous solutions were prepared. 6 mol/L NaOH aqueous solution was also prepared as an oxidizer and pH adjuster. The NaOH solution was heated to 80 °C in a water bath, and source solutions of Co and Fe were added into the NaOH at the same time with stirring. Precipitation generated immediately. The precipitation was washed, filtered, dried, grinded and calcinated at 500 °C for 2 h to form $CoFe_2O_4$ nano-particles.

In the second step, tabular $CoFe_2O_4$ crystal was synthesized via the superposition of the $CoFe_2O_4$ basic cell on the interface of the primary particles. At first, aqueous suspension of primary particles was prepared and heated to 95 °C. Then solution of NaOH and source solutions of Co and Fe were added slowly and independently into the suspension with stirring, and the concentration of metal ions in the suspension were kept over-saturated during the synthesis process. The molar ratio of $CoCl_2$ to primary $CoFe_2O_4$ was 0.4. The reaction products in the non-equilibrium crystallization conditions resulted in the recrystallization of $CoFe_2O_4$. The dried reaction products were calcinated to obtain $CoFe_2O_4$ crystals with final structure. Various calcination temperatures were tested.

The heat analysis of the formation of $CoFe_2O_4$ primary particles and final tabular crystals were conducted at a differential scanning calorimetry analyzer and a thermal gravimetric analyzer (Diamond TG/DTA, PerkinElmer Instruments). A Philips CM-12 field-emission transmission electron microscope (TEM) was used to examine the particle sizes and distributions of the primary particles. The nanoparticles were dispersed on holey carbon grids for TEM observation. Materials' magnetic hysteresis loops at 300 K and 5 K were measured with a vibrating sample magnetometer (VSM) (Lake Shore) and a Quantum Design MPMS-XL superconducting quantum interference device (SQUID), respectively.

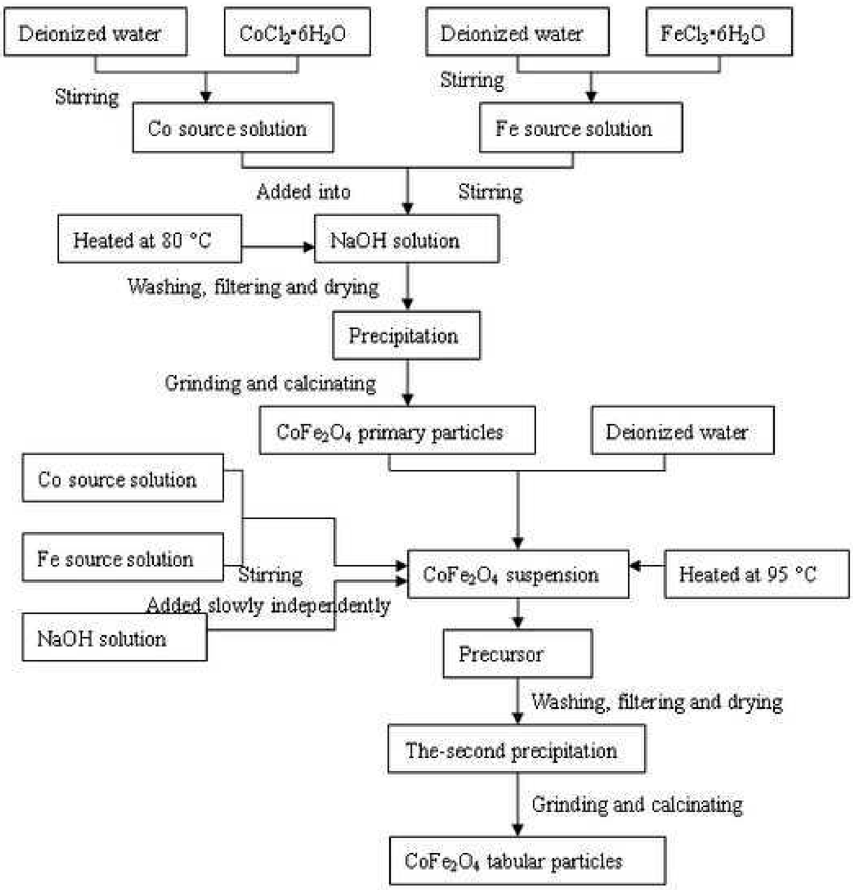


Fig.1 Flow chart for the synthesis of $CoFe_2O_4$ using two-step coprecipitation method

**Results and discussions**

Coprecipitation method is an effective approach to the synthesis of superfine particles of composite oxide included at least two metal ions elements. It was used in this study to prepare $CoFe_2O_4$ primary particles with $CoCl_2$ and $FeCl_3$ as Co and Fe source and NaOH as the base and pH adjuster, respectively. The source solution of metal ions was added into NaOH solution so that nucleation of grains happened. At first, metal ions reacted with the base to generate hydroxides, NaOH, $Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3$, $Co^{2+} + 2OH^{-} \rightarrow Co(OH)_2$, as the solution was heated at 80 °C, the hydroxides decomposed to corresponding oxides, $2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$, $Co(OH)_2 \rightarrow CoO + H_2O$. By calcinated at a high temperature, the oxides reacted to generate crystallize particles with final composition, $Fe_3O_4 + CoO \rightarrow CoFe_2O_4$. The heat analysis of the formation of primary particles from the dried precitation was conducted, as shown in Fig. 2. As the temperature increased to 150 °C, TG curve showed the weight of the precipitation decreased rapidly and then did not changed, combined with an endothermic peak in the DTA curve. This attributed to the evaporation of water including free water and water existed in hydroxides. Above 150 °C, the weight did not changed evidently, while a rather wide exothermic peak with summit at around 500 °C was observed. This stage corresponded to the crystallization process of primary $CoFe_2O_4$ particles. Fig. 3 exhibited the micro-morphology of the synthesized primary $CoFe_2O_4$ particles measured by TEM, particles took on spherical or square shape without preferred orientation. Size histograms obtained from TEM images fitted to a log-normal distribution. The average particles size was 16.5 nm.

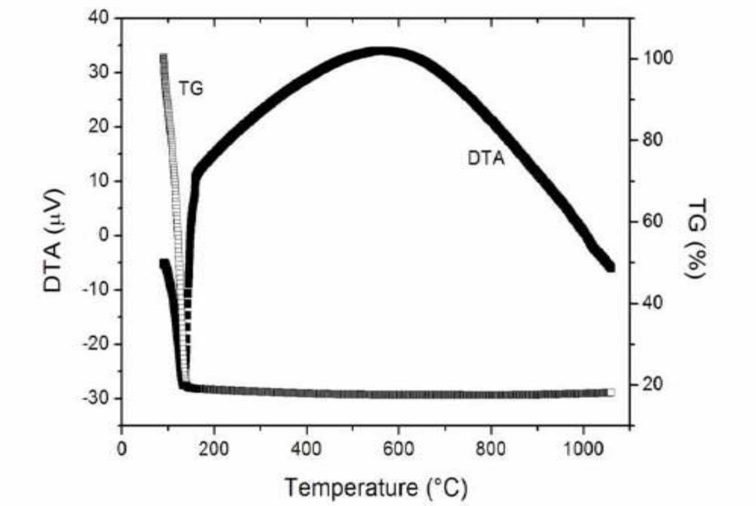


Fig.2 TG-DTA analysis of the formation of primary $CoFe_2O_4$ particles using coprecipitation method

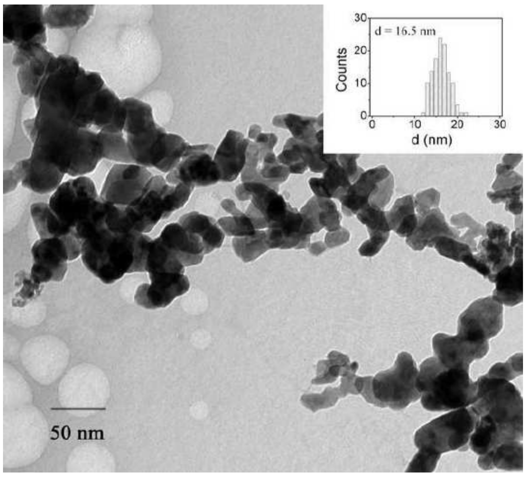


Fig.3 TEM image of the primary $CoFe_2O_4$ particles. Insets: log-normal size distributions

Tabular $CoFe_2O_4$ particles were synthesized via regrowth of grains on the interface of the primary crystals using non-equilibrium crystallization conditions. The rate of generating of new grain nuclear was slower than that of regrowth of grains when reaction happened in conditions of low temperature and high concentration [18−21]. Therefore the controlling of high temperature and slow adding speed was the key to synthesize large size crystals using non-equilibrium crystallization conditions. To investigate the formation process of large size $CoFe_2O_4$ crystals, TG-DTA curves of the-second precipitation were measured, as shown in Fig. 4. The TG curve was similar to that of Fig. 2. The weight of precipitation decreased as temperature increased to ~150 °C and then kept steady. However the DTA curve showed much difference. Beside an exothermic peak at ~400 °C, two peaks at temperature of ~700 and ~800 °C were also observed. This phenomenon indicated the oriented growth of crystals along the primary $CoFe_2O_4$ particles at above temperatures. Fig. 5 showed the micro-morphology of the regrown $CoFe_2O_4$ crystals. regrown crystals calcinated at 700 °C for 2h (Fig. 5a-b) partly took on tabular shape while non-oriented particles existed. Orderly arranged plate-like tabular $CoFe_2O_4$ crystals were formed under calcination at 800 °C.

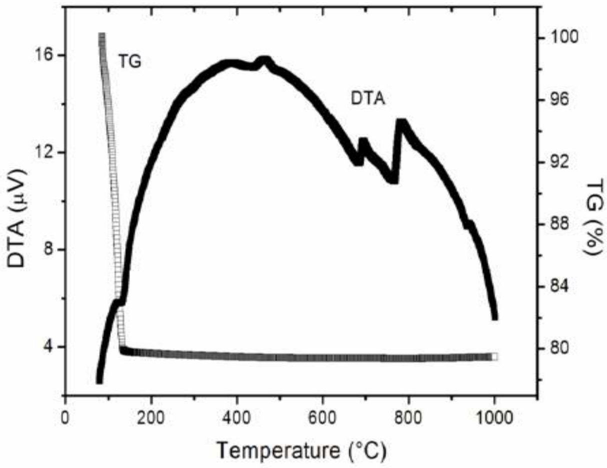


Fig.4 TG-DTA analysis of formation of tabular $CoFe_2O_4$ particles using two-step coprecipitation method

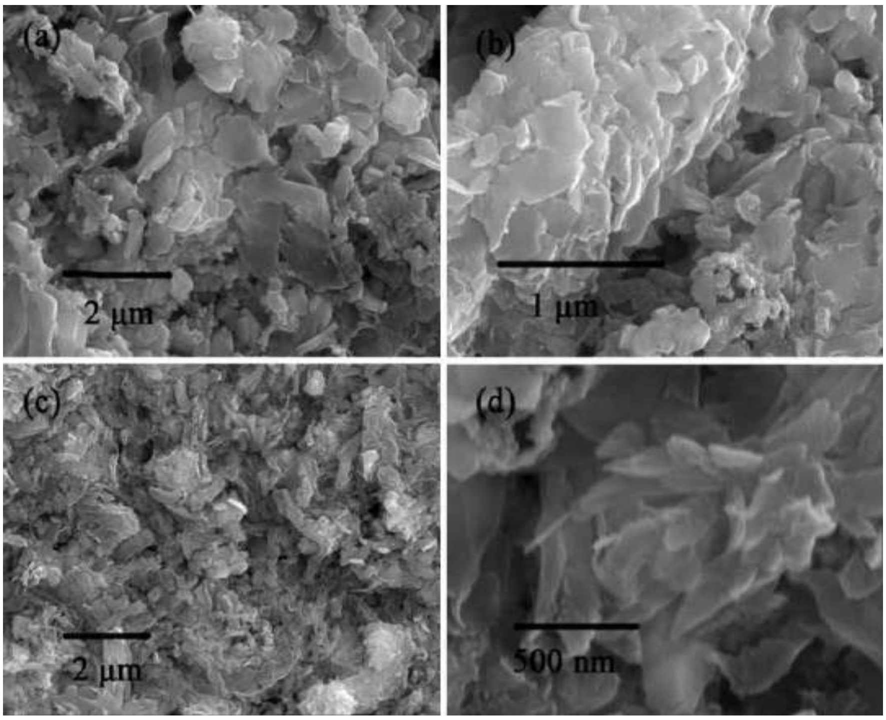


Fig.5 SEM image of tabular $CoFe_2O_4$ particles: (a)−(b) heat treated at 700 °C for 2 h, (c)−(d) heat treated at 800 °C for 2 h

The magnetic hysteresis loops of the tabular $CoFe_2O_4$ crystals calcinated at 800 °C were measured, as shown in Fig. 6 and Fig. 7. Hysteresis loop measured at room temperature (300 K) (Fig. 6), evident ferromagnetic properties were observed, values of saturation magnetization $M_s$, remnant magnetization $M_r$ and coercive field $H_c$ were 53.6, 17.4 emu/g and 572.1 Oe, relatively. Hysteresis loop measured at 5 K (Fig. 7) took on a wide shape like hard magnetic materials. Relative values of $M_s$, $M_r$ and $H_c$ were 68.2, 57.3 emu/g and 12 400 Oe. The difference between magnetic hysteresis loops measured at 300 and 5 K indicated the anisotropy of the tabular $CoFe_2O_4$ particles.

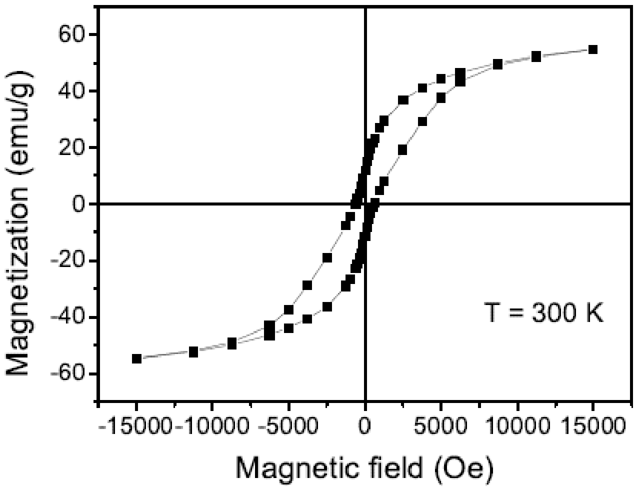


Fig.6 Magnetic hysteresis loop of tabular $CoFe_2O_4$ particles measured at 300 K

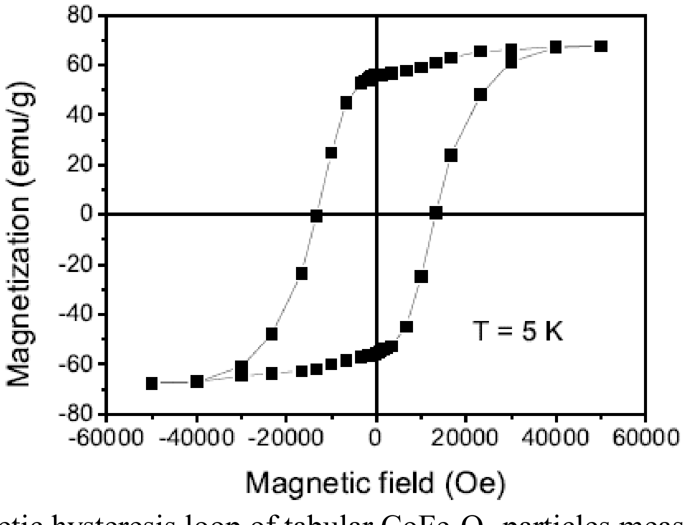


Fig.7 Magnetic hysteresis loop of tabular $CoFe_2O_4$ particles measured at 5 K

## Conclusions

Cobalt ferrite spinel $CoFe_2O_4$ tabular crystals were synthesized via two-step coprecipitation using non-equilibrium crystallization conditions by supplying a solution of $CoCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ and a solution containing NaOH at a later crystallization stage. Mean particle size of ~16.5 nm $CoFe_2O_4$ primary particles synthesized by coprecipitation took on a spherical or square shape and showed non-oriented structure. Tabular $CoFe_2O_4$ crystal was synthesized via the superposition of the $CoFe_2O_4$ basic cell on the interface of the primary particles. The controlling of high temperature and slow adding speed was the key to synthesize large size crystals using non-equilibrium crystallization conditions. Effect of heat treatment temperature on the microstructures of the final $CoFe_2O_4$ crystal was examined, orderly arranged plate-like tabular $CoFe_2O_4$ crystals were formed under calcination at 800 °C for 2 h. Magnetic hysteresis loops measured at 300 and 5 K indicated the anisotropy in the tabular crystals.

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