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The characterization of nanosized $ZnFe_2O_4$ material prepared by coprecipitation

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The nanosized $ZnFe_2O_4$ material was synthesized using the coprecipitation method from Zn^{2+} and Fe^{3+} cations in a boiling aqueous medium. The results of TG/DSC, XRD, SEM, TEM and VSM analysis show that the $ZnFe_2O_4$ material prepared after annealing at 600 °C had tetragonal structure, a size of 20 – 50 nm, $H_c < 70$ Oe, $M_r < 0.5$ emu/g and $M_s \sim 2.5$ emu/g.

Keywords: sol-gel synthesis, nanopowders, zinc ferrite, magnetic properties.

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1. Introduction

Currently, nanomaterials, especially magnetic materials, have a wide range of relevant application to the manufacture of appliances such as generator transformers, electrical motors, and digital detectors. Among many kinds of magnetic substances, ferrite nanoparticles, spinel AB_2O_4, have been studied not only because of their high magnetic permeability, but also their appropriate magnetic saturation and resistance for reducing the Foucault current effect, as well as prolonging the life of devices [1–5].

It is worth considering that there are numerous means for synthesizing nanoparticles, for instance, co-precipitation, sol-gel, and coordination. The advantage of these methods is undoubtedly the low crystallization temperature, whereas the traditional ceramic method requires a much higher temperatures to create the desired product. Another advantage is that they can also enhance the homogeneity and purity of target materials [3, 6–11].

According to studies [7–9], some methods, such as sol-gel, gel combustion or coordination, have been used to prepare spinel AB_2O_4 nanoparticles (A is Co, Ni, Zn and B is Fe). However, the single crystallization in these strategies depends on many elements: temperature and time for annealing, pH, molar fraction of gel agents and metallic cations, actual gelling temperature. In addition, there are no scientific reports associated with synthesis of $ZnFe_2O_4$ nanoparticles by coprecipitation from zinc(II) hydroxide and iron(III) hydroxide because $Zn(OH)_2$ is completely dissolved in excessive alkaline solution (e.g. NaOH, NH_3).

In this paper, the coprecipitation was utilized through the hydrolysis stage of Zn^{2+} and Fe^{3+} cations in boiling water [9, 10], before the addition of ammonia solution as the precipitating reactant, which helped the target solution attain the proper pH to synthesis and characterization of either crystal morphology or magnetization of $ZnFe_2O_4$ nanoparticles. The Zn^{2+} and Fe^{3+} cations were hydrolyzed in boiling water, and then the solution was cooled in order to produce stable precipitates and inhibit the agglomeration of nanoparticles [9, 10, 12].

2. Experimental

2.1. Chemicals and equipment

$Fe(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, NH_3 25 % ($d = 0.91$ g·ml^{-1}), deionized water, filtered paper were used in the experiments. $Fe(NO_3)_3{\cdot}9H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ were mixed in the molar ratio of Zn^{2+}:Fe^{3+} = 1:2 and they were then dissolved in water prior to precipitation.

Additional equipment included 100 ml, 250 ml, 500 ml flasks, pipette, burette, magnetic stirrer, stir bar, electric stove, furnace, crucible, pH meter.

2.2. Synthesis of $ZnFe_2O_4$ nanoparticles

The mixture consisting of $Zn(NO_3)_2$:$Fe(NO_3)_3$ = 1:2 was carefully added in a dropwise manner to a flask of boiling water (to > 90 °C). It was stirred until the obtained solution became brown-red and this color remained unchanged when the solution was cooled at room temperature. Next, a 5 % NH_3 solution was carefully added to this system until its pH reached the range of 9.0 – 9.2, followed by a continuous stir of the solid separating from solution for 30 minutes. The precipitate was filtered and washed with water prior to being dried at room temperature for about 3 days. Finally, the precursor was milled and annealed in an aerobic atmosphere at different temperatures with the heating rate of 10 °C/minute for the investigation of crystallization and evaluation of phase components.

2.3. Techniques

To determine the desired temperature for single phase $ZnFe_2O_4$ formation, the sample was analyzed thermally by Labsys Evo (TG-DSC 1600 °C) under a nitrogen atmosphere with a heating rate of 10 °C/minute, from room temperature to 1100 °C.

XRD patterns were obtained using a D8-ADVANCE (Germany) with CuK_α radiation (wavelength of 0.154056 nm), $2\theta = 10 - 70$ °, step size of 0.03 °/min. The average size (nm) of crystal was calculated by the Scherrer equation: $D_{hkl} = \dfrac{k \times \lambda}{\beta_{hkl} \times \cos\theta}$, where β_{hkl} was peak width-full width at half maximum (FWHM-radian), θ was the corresponding diffraction angle (degree), $k = 0.89$.

The microstructure and morphological images were recorded by Scanning Electron Microscopy (SEM) in FESEM S4800 HITACHI (Japan) and Transmission Electron Microscopy (TEM) in JEOL-1400 (Japan).

The magnetic properties of samples were studied at room temperature by a Vibrating Sample Magnetometer (VSM) in MICROSENE EV11 (Japan).

3. Results and discussion

Thermogravimetric analysis (TGA) (Fig. 1) demonstrated a weight loss of 18.51 % during calcination from room temperature to 1100 °C. This was 4.49 % less than the predicted weight loss based on stoichiometry of chemical reaction (23.0 %) due to the steam and CO_2 adsorption of the sample.

These weight losses occurred mainly from 30 – 500 °C, corresponding to the endothermic peaks in the DSC curve, namely at 116.31 °C and 159.71 °C because $Zn(OH)_2$ and $Fe_2O_3{\cdot}nH_2O$ underwent decomposition. From

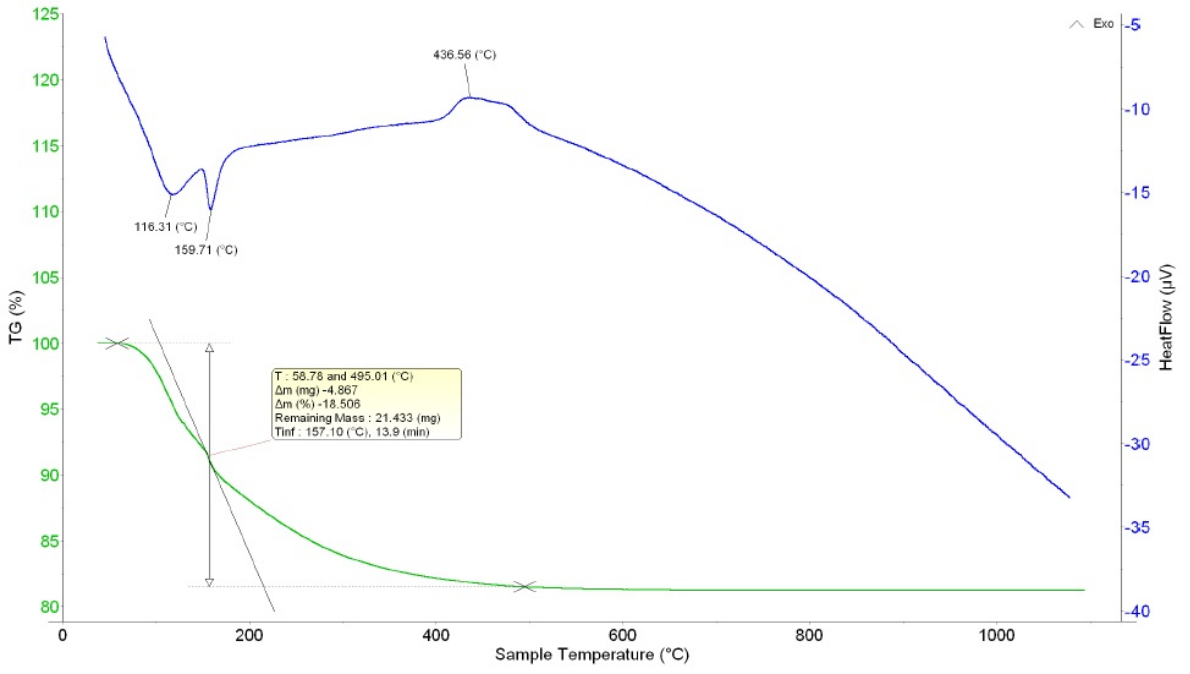

FIG. 1. TG-DSC curves of precusor

300 °C to 600 °C a slight weight loss was recorded and levelled off when the temperature approached 600 °C. Therefore, samples were annealed from 600 °C to investigate the formation of the $ZnFe_2O_4$ phase. The XRD patterns at different temperatures were shown in Figs. 2 and 3.

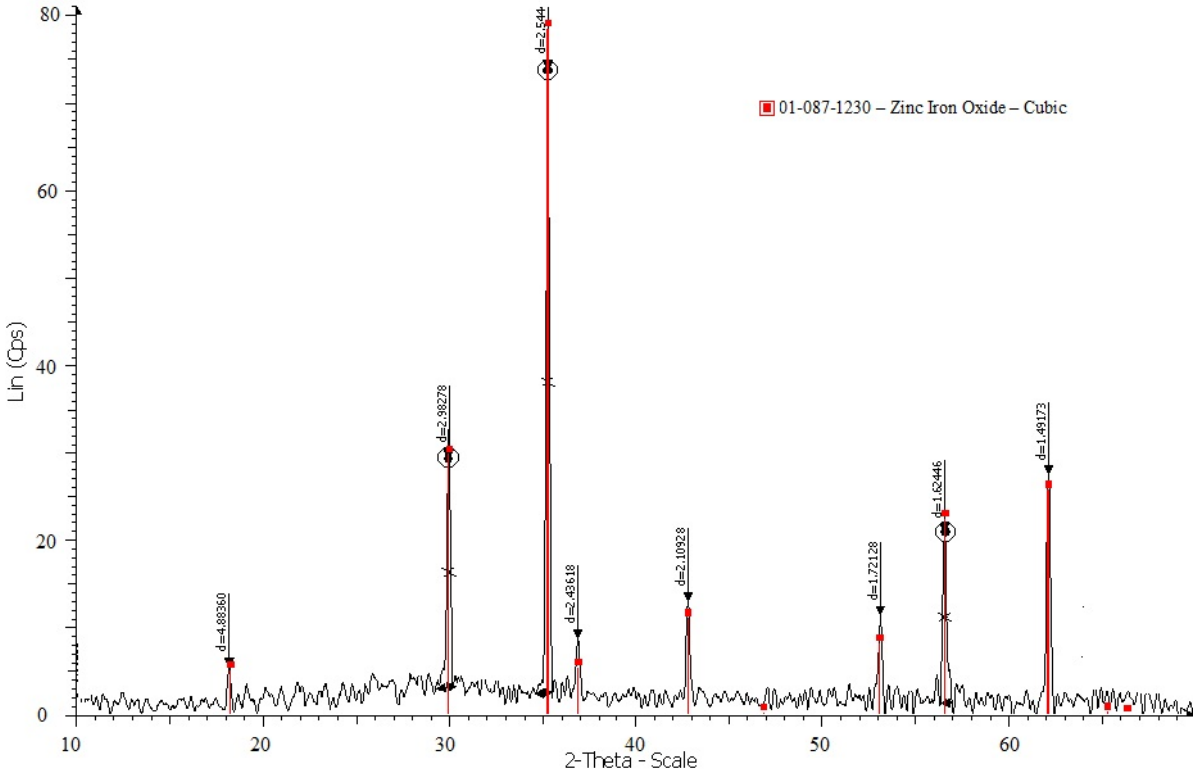

FIG. 2. XRD pattern of $ZnFe_2O_4$ annealed at 800 °C for 2 h in comparison with standard pattern (red bars)

XRD patterns of $ZnFe_2O_4$ annealed at 600 °C, 700 °C and 800 °C for 2 h matched well to standard ones (No. 01-087-1230), which involved the $ZnFe_2O_4$ crystal in cubic structure and led to the conclusion that no other phases existed in the annealed samples. However, the increases in peak intensity as well as the narrowness in the peak width indicated that the crystallization at high temperature was better than the low temperature one. This was confirmed by the growth in the crystal size according to the Scherrer equation (Table 1).

TABLE 1. The magnetic properties of $ZnFe_2O_4$ annealed samples

Annealing temperature, °C	Grain size based on Debye-Scherrer equation, nm	M_r, emu/g	M_s, emu/g	H_c, Oe
600	33.99	0.435	2.507	69.83
700	36.29	0.218	2.306	60.59
800	38.67	0.152	1.617	37.35

SEM and TEM images of sample annealed at 700 °C illustrated that the size of target grains ranged from 30 – 50 nm, which was confirmed by XRD data. Moreover, the agglomeration of particles was observed in these images (Fig. 4).

The magnetic investigation of samples annealed at a variety of temperatures (Fig. 5 and Table 1) showed that residual magnetism M_r values, the saturation magnetization M_s and magnetic coercivity H_c all decreased when the annealing temperature was increased. This means that at higher temperatures, the growth in grain size may decrease the strength of the compound's magnetic properties. For instance, the magnetic coercivity value was calculated by equation [1]:

$$H_c(\mathrm{Oe}) = A/d + D, \tag{1}$$

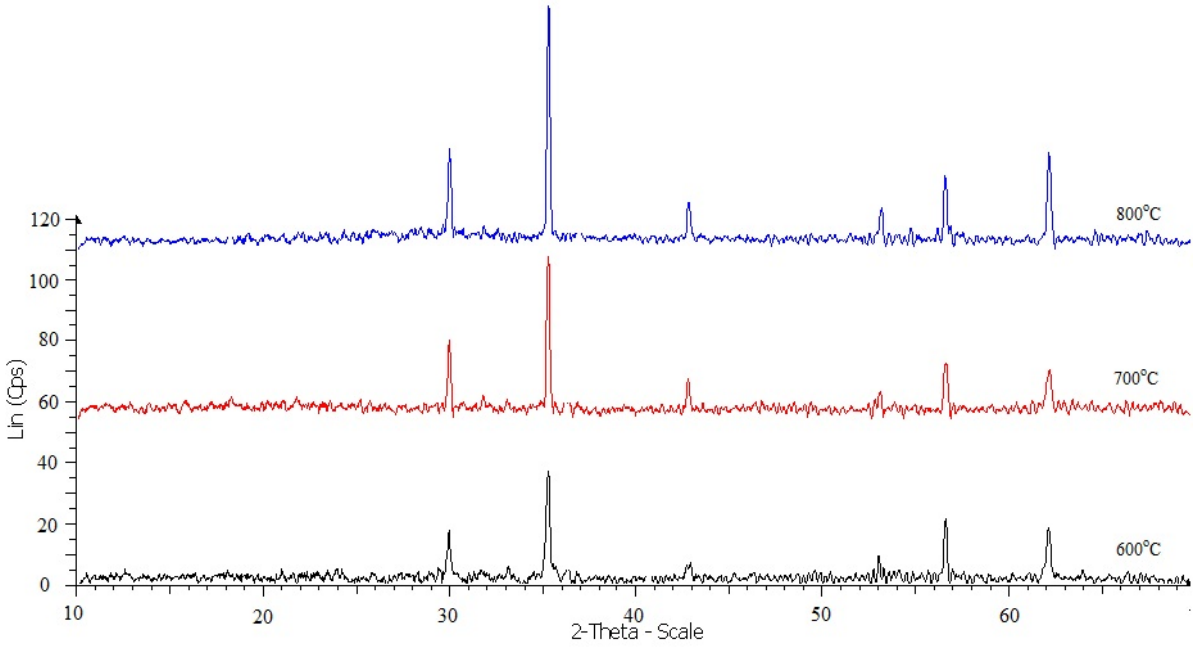

FIG. 3. XRD patterns of $ZnFe_2O_4$ annealed at 600 °C, 700 °C and 800 °C for 2 h

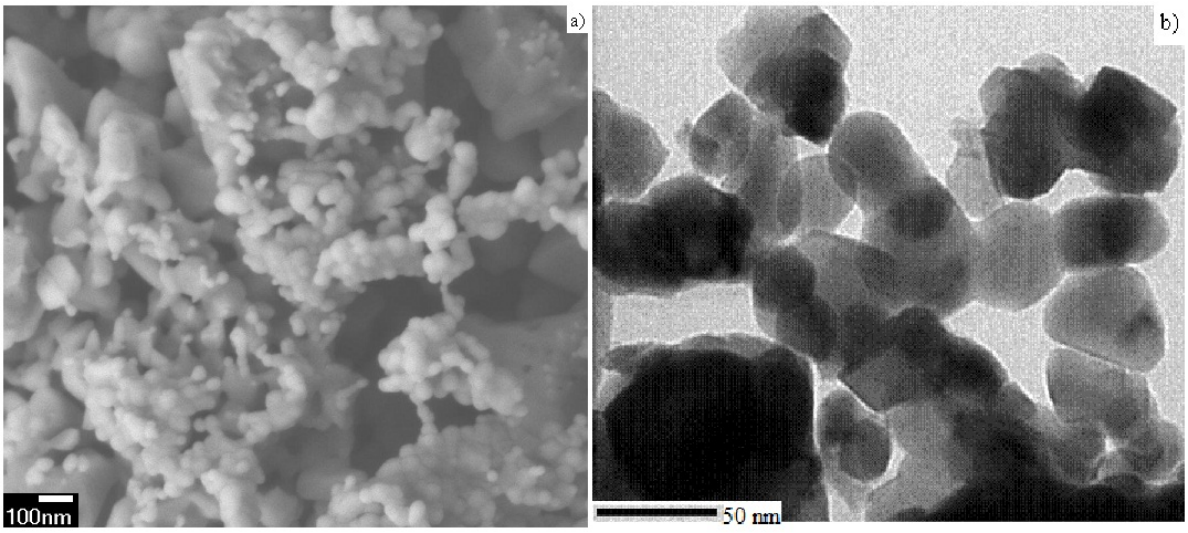

FIG. 4. SEM (a) and TEM (b) images of $ZnFe_2O_4$ sample annelaed at 700 °C ($t = 2$ h)

where A, D were factors depending on concentration of impurities; d was the particle diameter.

$ZnFe_2O_4$ nanoparticles prepared by coprecipitation had small M_r and H_c at 1500 Oe, and magnetization did not meet the saturation state (narrow hysteresis loop and ongoing curve). This proved not only the soft magnetic properties of the target material, but also the superparamagnetism which can be applied to the manufacture of magnetic cores.

4. Conclusion

$ZnFe_2O_4$ nanoparticles were prepared by coprecipitation using NH_3 after hydrolyzing cation solution in boiling water. Single phase $ZnFe_2O_4$ material was produced when the precursor was annealed aerobically from 600 °C. The cubic structure of $ZnFe_2O_4$ crystal ranged from 30 – 50 nm in size. H_c, M_r, M_s were small and dropped when the grain size increased.

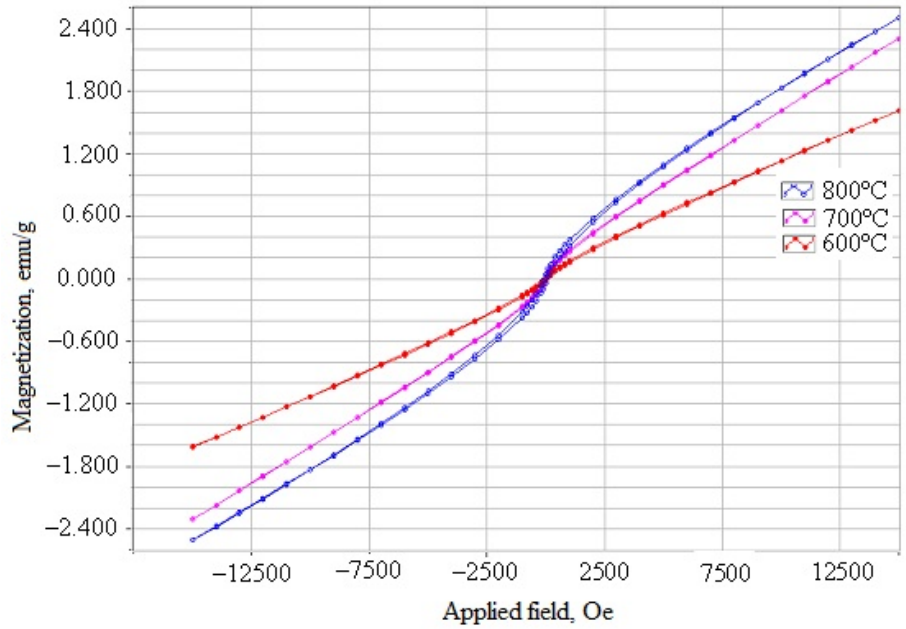

FIG. 5. The magnetic hysteresis curve of $ZnFe_2O_4$ annealed samples

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