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Co-precipitation of a Ni–Zn ferrite precursor powder: Effects of heat treatment conditions and deagglomeration on the structure and magnetic properties

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Abstract

A Ni–Zn ferrite precursor powder was synthesized by co-precipitation upon adding ammonia to an aqueous solution of the precursor iron, nickel, and zinc nitrate salts. The powder was calcined at a range of temperatures (200–1200 °C) and the crystalline phase evolution was assessed by X-ray diffraction coupled with Rietveld refinement. Intermediate phases ($NiFe_2O_4$ and Fe_2O_3) with increasing crystallinity coexisted in the system up to 1000 °C. The required $Ni_{0.8}Zn_{0.2}Fe_2O_4$ phase could only be attained at 1200 °C. The magnetic properties measured using a vibrating sample magnetometer revealed high magnetization saturation level (∼59 emu/gm) above 400 °C. The coercivity showed a steady decrease with increasing heat treatment temperature, leading to a change from a hard to soft magnetic state. The BET specific surface area and the SEM morphology were found to be dependent on calcination temperature, atmosphere (air or N_2) and on the milling procedure.

Keywords: Magnetic materials; Chemical syntheses; Ni–Zn ferrites; Surface properties; Rietveld refinement

1. Introduction

Ni–Zn ferrite with the spinel structure is a versatile technological material due to its high-resistivity and low-Eddy current losses, and is particularly suitable for high-frequency applications. Ni–Zn ferrites have been commercially used in applications including recording heads, antenna rods, loading coils, microwave devices and the telecommunication field.[1,2] In the typical ion configuration for Ni–Zn bulk ferrites (for low Zn concentration), Ni and Zn ions occupy B-site and A-site positions respectively. The incorporation of divalent zinc into the A-site leads to a substantial increase of the magnetization in the ferrimagnetic state, from 2.34 μ_B per formula unit in pure Ni ferrite to 3.65 μ_B per formula unit in 20% substituted Zn ferrite.[3]

The microstructure and magnetic properties of Ni–Zn ferrites are highly sensitive to composition, sintering conditions, grain size, the nature and amount of any additives and impurities and the preparation methodology. Therefore, the chemical composition and processing methods are critical factors that determine the physical properties of ferrites. Recently, many publications have reported various “bottom up” preparation techniques based on wet-chemical reactions to obtain ferrite powders. The most popular are: sol–gel methods,[4–6] microemulsion[7] hydrothermal-microwave[8] and hydrothermal synthesis,[9–11] and co-precipitation.[12–14] The wet chemical synthesis of highly reactive powders has proved to be one of the most effective routes to decrease the reaction temperature to obtain ferrites. Co-precipitation and sol–gel methods produce homogeneous, fine and reproducible precursor ferrite powders, i.e., metal oxides are

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firstly obtained by chemical synthesis without ferrite formation and, subsequently, high temperatures are needed to promote their chemical reaction to form different kinds of ferrites.[10,12,15] From the thermal dynamics viewpoint, it is well established that densification is enhanced by using fine-grained powders exhibiting high surface free energy. However, increased diffusion activity on strongly curved surfaces is a feature of an individual particle only, whereas the densification activity describes the interaction of a multitude of particles, and the high surface of particles is also a strong driving force for agglomeration. The formation of agglomerates resulting in inhomogeneous pore size distribution may considerably retard densification and increase the average grain size of sintered bodies.[16]

The synthesis of ferrites by using "top-down" methods, such as high energy mechanical milling, has been also reported.[17–20] This means that besides deagglomerating the starting component precursor powders, the milling energy might also induce the formation of new crystalline phases and change the surface characteristics of the ferrite powders. The effects of morphological/chemical changes occurring during milling on the dispersion ability of ferrite powders have not been reported so far. Thus, the present study aims at synthesising Ni–Zn ferrite particles in two steps: chemical co-precipitation of corresponding precursor oxides and their chemical reaction at high temperature. The precursor powder mixture heat treated at 400 °C was selected to evaluate the effects of other physical treatments (milling/atmosphere of heat treatment) on the crystalline phase assembly, the physical characteristics of the powders, including the magnetic properties. This temperature (400 °C) represented a good compromise between incipient magnetic properties and a low degree of powder agglomeration.

2. Experimental procedure

The synthesis of the ferrite precursor powder was performed by the co-precipitation method using high-purity nickel nitrate hexahydrate [$Ni(NO_3)_2{\bullet}6H_2O$, Sigma Aldrich, Germany], zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$, Sigma Aldrich, Germany] and iron nitrate nonahydrate [$Fe(NO_3)_3{\bullet}9H_2O$, Sigma Aldrich, Germany] as starting materials. Ammonia solution (ammonium hydroxide solution, ca 25% NH_3, Sigma Aldrich, Germany) was also used as precipitating agent. The cationic reagents corresponding to 0.25 mol of $Ni_{0.8}Zn_{0.2}Fe_2O_4$ ferrite were weighted separately, dissolved in a beaker containing about 0.9 L of de-ionized water and then transferred to a volumetric borosilicate glass flask, adding the necessary water to complete the total volume of 1 L. This cationic solution was heated to 80 °C under continuous mechanical stirring, and then ammonia solution was slowly added to set the pH at around 9.5. The synthesis conditions (temperature, pH and mechanical stirring) were kept constant for 2 h in order to complete the reaction. The precipitated powder was filtered and washed twice with distilled water and then dried at 80 °C for 48 h.

The thermal behaviour of the dried powder from room temperature up to 1200 °C was assessed by DTA/TG analysis (SETARAM, Labsys, Caluire, France) using a heating rate of 10 °C/min. Based on the results observed, powder samples were then calcined at 200, 300, 400, 600, 800, 1000 and 1200 °C for 1 h, to study the effects of heat treatment on crystalline phase evolution. Heat treatments were carried out in a Thermolab furnace with a heating rate of 5 °C/min to achieve the preset temperature, followed by a dwelling time of 1 h and then cooled to room temperature at the rate of 5 °C/min. A calcination temperature of 400 °C was then selected to study the effects of the heat treatment atmosphere and deagglomeration method of the powders on their properties. This temperature represented a good compromise between the incipient magnetic properties and a low degree of powder agglomeration. Accordingly, powder samples were treated as follows: (i) air atmosphere; (ii) air atmosphere + hand deagglomeration in a mortar; (iii) air atmosphere + planetary milling for 4 h in ethanol; and (iv) air atmosphere + planetary milling for 4 h in ethanol, followed by calcination in nitrogen atmosphere at 400 °C for 1 h; (v) the same as (iv) + hand deagglomeration in a mortar. Sample codes and the respective experimental conditions used are presented in Table 1.

Table 1
Samples' codes and respective post synthesis procedures for NiZn ferrite powders obtained by co-precipitation.

Sample code	Preparation conditions
Sample 1	NiZn ferrite calcined at 400 °C in air before milling
Sample 2	Sample 1 after deagglomeration in a mortar
Sample 3	Sample 1 planetary milled in ethanol
Sample 4	Sample 3 heat treated again at 400 °C but in N_2 atmosphere

Qualitative and quantitative analysis of crystalline phases in the resultant Ni–Zn ferrite powders were determined by X-ray diffraction (XRD) analysis using a conventional Bragg–Brentano diffractometer (Philips PW 3710, Eindhoven, Netherlands) with Ni-filtered Cu-K_α radiation. X-ray diffraction data were recorded in 2θ range = 5–100° (step size 0.02° and 6 s of counting time for each step). The phase fractions were extracted by Rietveld-RIR (reference intensity ratio) refinements, using GSAS software and EXPGUI. The background was successfully fitted with a Chebyshev function with a variable number of coefficients depending on its complexity. The peak profiles were modeled using a pseudo-Voigt function with one Gaussian and one Lorentzian coefficient. Lattice constants, phase fractions, and coefficients corresponding to sample displacement and asymmetry were also refined.

The specific surface area was determined by the nitrogen adsorption BET method using a Surface Area Analyzer (Gemini, Micromeritics, USA). Density and particle size distribution of the powders were measured by using helium gas picnometer (Accupyc Quantachrome, Florida, USA) and laser scattering analyser (Coulter LS 230, Buckinghamshire, UK), respectively. Scanning Electron Microscopy (SEM, Hitachi S-4100, Tokyo, Japan) was used to analyse the shape and state of agglomeration of Ni–Zn ferrite particles treated under different conditions. Magnetization measurements were made on a Vibrating Sample Magnetometer (VSM, Cryogenics, UK) at room temperature using a field up to 10 T.