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Effect of complexant/fuel on the chemical and electromagnetic properties of SiO_2-doped Ni–Zn ferrite

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Abstract

The $Ni_{0.5}Zn_{0.5}Fe_2O_4$/10 wt.% SiO_2 nanocomposites were grown at low temperature using different aqueous solution methods. The sol–gel auto-combustion method used involved complexing agents such as glycine, hydrazine and citric acid in aqueous medium that functioned as a fuel, decomposed the metal complexes at low temperature. FTIR, ^{29}Si CP/MAS NMR, XRD, EPR, SQUID and impedance analyzer measurements were studied the effect of complexant/fuel on the chemical and electromagnetic properties of SiO_2-doped Ni–Zn ferrite. The complexing agents in the starting solution influenced the magnetic interaction between Ni–Zn ferrite and silica, and then affected the particle size. Further, the complexing agent type had a direct effect on the EPR parameters (ΔH_{PP}, g-factor, N_S and T_2), SQUID parameters (M_s, M_r and H_c) and dielectric properties (dielectric constant and loss) of the as-synthesized powder.

Keywords: Complexing agent; Fuel; Ferrite; Silica; EPR

1. Introduction

Ni–Zn ferrites are one of the most versatile magnetic materials for general use, which have many applications in both low and high frequency devices and play a useful role in many technological applications such as microwave devices, power transformers in electronics, rod antennas, read/write heads for high speed digital tape, etc., because of their high resistively, low dielectric losses, mechanical hardness, high Curie temperature and chemical stability [1–4]. The amorphous matrixes have been shown to play an important role in retarding the motion of the particles as well as the grain growth during the formation of nanocrystals. In addition, the electromagnetic properties of composite are affected not only by the compositions, additives and annealing conditions but also by the raw materials [5,6].

Many synthetic approaches have been employed to prepare magnetic nanocrystals [7–10]. The sol–gel auto-combustion technique is a novel way with a unique combination of the chemical sol–gel process and the combustion process. The synthesis has been used to create different ceramic systems [11,12]. The success of the process is due to an intimate blending among the constituents using a suitable fuel or complexing agent (e.g., citric acid, urea, glycine, etc.) in an aqueous media and an exothermic redox reaction between the fuel and an oxidizer (i.e., nitrates) [13]. The powder characteristics like crystallite size, surface area, extent and nature of agglomeration are primarily governed by enthalpy or flame temperature generated during combustion, which itself is dependent on nature of the fuel and fuel-to-oxidant ratio [14].

Chelating ligands, which contain carboxylate groups or aliphatic amine groups, are essential in the water-soluble complex precursor synthesis route. Citric acid (containing carboxylate groups), glycine (containing carboxylate and aliphatic amine groups) and hydrazine (containing aliphatic amine groups) were often used before in the synthesis of metallic oxides. Such types of complexing agent can effectively complex metal ions of varying ionic sizes, which helps in preventing their selective precipitation to maintain compositional homogeneity among the constituents. On the other

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hand, these can also serve as a fuel in the combustion reaction, being oxidized by nitrate ions. In our previous papers [15–17], SiO_2-doped Ni–Zn ferrite nanocomposites were prepared using sol–gel auto-combustion method. Many initial synthesis conditions such as silica content, calcinations temperature, solution pH and fuel-to-oxidant ratio have been varied in order to determine the optimal conditions for synthesizing the material. In this study, the effects of complexing agent on the evolution of crystalline phase and the characteristics of composites have been investigated in detail.

2. Experimental

2.1. Preparation of Ni–Zn ferrite/SiO_2 composite

Analytical grade nickel nitrate, zinc nitrate, iron nitrate, fuel and silica powder were used as raw materials to prepare $Ni_{0.5}Zn_{0.5}Fe_2O_4$/10 wt.% SiO_2 nanocomposite. The initial molar ratio was Ni:Zn:Fe = 1:1:4. First, 2.0 g $Ni(NO_3)_2{\cdot}6H_2O$, 2.05 g $Zn(NO_3)_2{\cdot}6H_2O$, and 11.12 g $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 60 ml of deionized water, then 10 wt.% of SiO_2 powder (Aerosil 200; <100 nm) and the fuel, such as citric acid, glycine and hydrazine were added into the solution. The molar ratio of nitrates to fuel was 1:1. A small amount of ammonia was added to the solution to adjust the pH value to about 5. The entire mixture was thoroughly stirred for 6 h at 70 °C. Then, the mixed solution was poured into a teflon dish and heated 24 h at 60 °C and 3 h at 100 °C under a vacuum to obtain a dried gel. When ignited at any point, the dried gel burnt in a self-propagating combustion manner until all the gels were burnt out completely to form a loose powder.

2.2. Characterization of Ni–Zn ferrite/SiO_2 composite

Thermogravimetric (TG) and differential thermal analysis (DTA) of the gel precursor were carried out by Perkin-Elmer TGA-2 at heating rate of 10 °C/min under air. The phase identification of the as-burnt powder was performed using X-ray diffraction (XRD; SIEMENS D5000) with Cu Kα radiation. Average grain sizes (D) were determined from the XRD peaks using Scherrer's formula as well as by a PHILIPS CM-200 transmission electron microscopy (TEM). Infrared spectra (IR) of the as-burnt powder were recorded on a Bomem DA 3.002 spectrophotometer from 400 to 4000 cm^{-1} by the KBr pellet method. The solid-state ^{29}Si NMR spectra of the gel precursor were determined using a Bruker MSL-400 with the cross-polarization combined with magic angle spinning (CP/MAS). The ^{29}Si CP/MAS NMR provides a unique way to follow the structure of silica network and the magnetic interaction between iron(III) and silica. The electron paramagnetic resonance (EPR) spectra of the composites were recorded on a Bruker EMX-10 spectrometer operating at X-band (ν = 9.6 GHz) with 100 kHz field modulations. DPPH (g = 2.0036) was used as a field marker. The EPR spectra were recorded at variable temperatures (200–400 K) using variable temperature controller. Magnetization measurements were performed in fields of up to 5 T using a Quantum Design SQUID magnetometer (Model MPMS5). The dielectric parameters were measured with an HP4291B impedance analyzer from 1 MHz to 1 GHz.

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the TG-DTA curves, which display the formation temperature of the Ni–Zn ferrite/SiO_2 and the pyrolysis processes of gel precursors grown by the organic acid-assisted aqueous method. Different combustion reactions were observed during the pyrolysis of these chelating precursors due to the different compositions used. The TGA curves show a slowly weight loss profile for citric acid sample and hydrazine sample as compared with glycine sample. The initial weight loss which occurred in the temperature range 40–150 °C was mainly due to the dehydration, which is accompanied by endothermic peaks below 150 °C in the DTA curve. The weight loss in the temperature range 150–260 and 260–400 °C was due to the decomposition of nitrate and carbonate, respectively, corresponding to the exothermic peak at 234 and 294 °C in the DTA curve of citric acid sample [15]. However, the exothermic peak for hydrazine sample is shifted to 263 and 350 °C.

From the TG-DTA curve of the glycine sample, it can be seen that a fast weight loss profile takes place at the

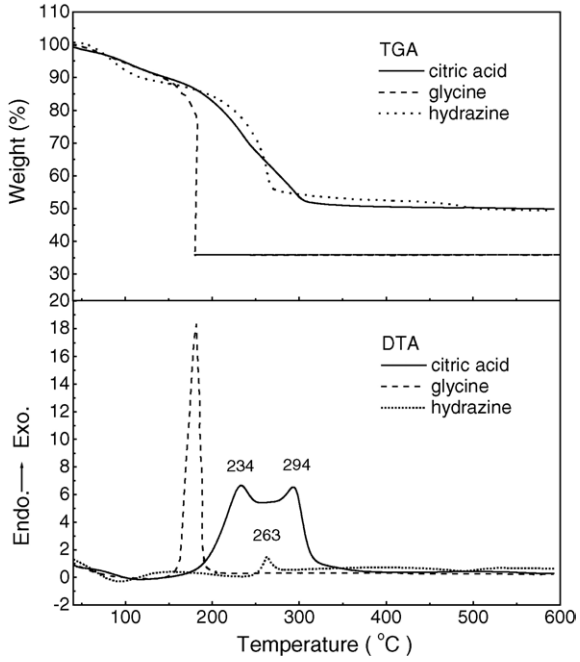

Fig. 1. TGA and DTA curves of the dried gel obtained for different complexing agent under air at the heating rate 10 °C/min.