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Sol–gel auto-combustion synthesis of $Ni_{0.5}Zn_{0.5}Fe_2O_4/(SiO_2)_x$ (x = 10, 20, 30 wt.%) nanocomposites and their characterizations

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Abstract

A nitrate–citrate–silica gel was prepared from metallic nitrates, citric acid and tetraethoxysilane (TEOS) by sol–gel process, and it was further used to synthesize $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposites by auto-combustion. The obtained $Ni_{0.5}Zn_{0.5}Fe_2O_4/(SiO_2)_x$ (x = 10, 20, 30 wt.%) samples were characterized by IR, ^{29}Si CP/MAS NMR, XRD, TEM, EPR and impedance analyzer measurements. Particle size of these composites was calculated from Scherrer's formula, and that decreased with increasing SiO_2 content. The content of TEOS in the starting solution affects the interaction between NiZn ferrite and silica, and then determines the particle size, dielectric properties and the EPR properties (ΔH_{PP}, g factor, N_S and T_2) of the as-synthesized powder.

Keywords: D. EPR

1. Introduction

Magnetic properties of crystalline materials dispersed in a non-magnetic matrix, either porous or not, have been studied in ferrite/SiO_2 [1–3], ferrite/resin [4,5], ferrite/polymer [6,7] and ferrite/forsterite system [8]. These types of composite, if formed from nanoparticles, enhance their magnetic

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properties as compared with the magnetic materials obtained by conventional processes [9–11]. 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. Thus, dispersed nanocrystals often possess limited particle agglomeration and narrow grain size distribution under the space confinement effects. In addition, the morphologies, particle size distribution and crystal structures for the nanocrystals can be controlled by changing the compositions of the matrixes, concentration and treatment conditions [12].

NiZn 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 [13,14]. Many synthetic approaches have been employed to prepare magnetic nanocrystals [15–17]. 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 process has the advantages of inexpensive precursors, a simple preparation method, homogeneous and a resulting nano-sized powder. The synthesis has been used to create different ceramic systems [18,19].

In this paper, we focus on the synthesis of $Ni_{0.5}Zn_{0.5}Fe_2O_4/(SiO_2)_x$ (x = 10, 20, 30 wt.%) nanocomposites by a sol–gel auto-combustion technique. The spectroscopic characterization of the formation processes of NiZn ferrite/SiO_2 nanocomposite are studied using FTIR, ^{29}Si CP/MAS NMR and XRD. Moreover, the interaction between silica and NiZn ferrite is observed through FTIR, ^{29}Si NMR and EPR spectra. The dielectric properties and EPR parameters like peak-to-peak linewidth (ΔH_{PP}), g factor, spin number (N_S) and spin–spin relaxation time (T_2) properties of $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ synthesized with different TEOS content are described in detail. Furthermore, they were compared with the ferrites prepared by SiO_2 powder-doped NiZn ferrite nanocomposites [20].

2. Experimental

2.1. Preparation of NiZn ferrite/SiO_2 composite

Analytical grade nickel nitrate, zinc nitrate, iron nitrate, citric acid and TEOS were used as raw materials to prepare $Ni_{0.5}Zn_{0.5}Fe_2O_4/SiO_2$ nanocomposite material. The ferrite powder was synthesized as follows. The initial molar ratio was Ni:Zn:Fe = 1:1:4. First, 2.0g $Ni(NO_3)_2{\cdot}6H_2O$, 2.05g $Zn(NO_3)_2{\cdot}6H_2O$ and 11.12g $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 20 ml of ethanol, and then 10, 20 and 30 wt.% of TEOS and H_2O in a molar ratio of 1:4 was added into the solution. The molar ratio of all nitrates together to citric acid was 1:1. About 1 wt.% of *p*-toluenesulfonic acid monohydrate was added into the solution. This is expected for an acid-catalyzed system, which is susceptible to polymeric termination by reactions with water or alcohol, and would favor formation of small oligomers, possibly due to the breakdown of the silica network. The entire mixture was thoroughly stirred for 24 h at room temperature. Then, the mixed solution was poured into a teflon dish and heated 12 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. For the samples dried gel with 10, 20, 30 wt.% SiO_2, the notations A_1, A_2, A_3, were designated, and for samples NiZn ferrite/10, 20, 30 wt.% SiO_2, the notations B_1, B_2, B_3.