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Cation distribution and microwave absorptive behavior of gadolinium substituted cobalt ferrite ceramics

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ABSTRACT

In the first step, gadolinium substituted cobalt ferrite nanoparticles with composition of $CoFe_{2-x}Gd_xO_4$ (x = 0–0.05 in a step of 0.01) were synthesized by a hydrothermal technique and without subsequent annealing. X-ray diffraction and field-emission scanning electron microscopy evaluations exhibited that single phase spinel ferrites with narrow size distribution were achieved. The EDS analysis confirmed that the applied process for fabrication of $CoFe_{2-x}Gd_xO_4$ nanoparticles is a proper process for the synthesis of spinel cobalt ferrites with homogeneity in composition. Mössbauer spectroscopy was utilized to distinguish the site preference of constitutive elements. A well-resolved doublets pattern of ferrite nanoparticles is mainly attributed to the superparamagnetic behavior. The results of magnetic hysteresis revealed that the gadolinium substituted cobalt ferrite nanoparticles exhibit superparamagnetic trend at a room temperature. The zero field cooled magnetization curves of gadolinium substituted cobalt ferrite nanoparticles showed that with an increase in gadolinium content, the blocking temperature increases. Fitting the experimental data of susceptibility with the Neél-Brown model expresses that there are powerful interactions between nanoparticles of gadolinium substituted cobalt ferrite and the Neél-Brown model was not operate for such ferrites. In the second step, the gadolinium substituted cobalt ferrite nanoparticles were annealed and the structural characteristics, magnetic properties and microwave absorptive behavior were evaluated. The Mössbauer spectras show a well-resolved six-line pattern of ferrite nanoparticles which is mostly imputed to the ferrimagnetic treatment. The magnetic hysteresis loops at a room temperature confirmed that the coercive field increased from 802 Oe for x = 0 to 965 Oe for x = 0.02 and then at higher contents, decreased. The magnetic hysteresis curves of $CoFe_{1.98}Gd_{0.02}O_4$ for fields applied parallel and perpendicular to the sample axis, expresses high value of magnetocrystalline anisotropy field of 13 kOe which exhibits that the resonance frequency can be shifted to higher frequency. Consequently the microwave absorber can be covered a wide-band of electromagnetic waves in the X-band.

1. Introduction

Among spinel ferrites, cobalt ferrite has unique features such as comparatively large coercivity, high magnetocrystalline anisotropy, and moderate saturation of magnetization. Therefore, cobalt ferrite is a hard magnetic material. It has tremendous potential utilizations in technological fields containing high sensitivity sensor, microwave devices, biomedical industries, and high density magnetic recording media [1–9]. lately, our researchs was in the field of preparation and magnetic features of cobalt ferrite nanocrystals [10–16].

In last years, remarkable consideration has been focused on the size of magnetic ferrite nanoparticles because the alteration of the size of particles may be a main way for controlling its magnetic features. The magnetic features of ferrites correlate closely with its size particles. Below a critical diameter, the coercivity is zero. Such particles are called superparamagnetic.

Recent expansions in microwave absorber technology have resulted in materials that can impressively decrease the reflection of electromagnetic signals, and have proper physical operation [17,18]. There is a wide variety of absorber materials that can be applied for low and high frequency applications [19–23]. Therefore, evaluation of the microwave absorptive behavior is vital and important, not to mention the novel scientific features that accompany them.

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Expanding new techniques for the fabrication of cobalt ferrite nanoparticles with fine particles and studying their distinguished properties is of remarkable interest. Various methods have been expanded to prepare nanocrystalline cobalt ferrite including co-precipitation, hydrolysis method, mechanical alloying, and sol-gel process [24–27]. Synthesis of ferrite nanoparticles within hydrothermal has illustrated the ability to control the morphology, size distribution, chemical stoichiometry, and cation occupancy [28]. The magnetic features of cobalt ferrite are subordinate on exchange interaction, and how the cations are distributed between the two sublattices. Surely, the magnetic interactions will modify with the change of cations in chemical composition and with different cation distribution among the tetrahedral and octahedral sites.

Even though studies on the fabrication and magnetic features of gadolinium substituted cobalt ferrite nanoparticles are quickly developing, however to the best of our knowledge no studies about the synthesis and magnetic features of gadolinium substituted cobalt ferrite nanoparticles with superparamagnetic treatment have been reported. Likewise, there is no perusal concerning the microwave properties of gadolinium substituted cobalt ferrite. With this view in mind, in the first step, we attempted to prepare gadolinium substituted cobalt ferrite superparamagnetic nanoparticles using a hydrothermal technique. In this paper we have successfully synthesized gadolinium substituted cobalt ferrite nanoparticles with superparamagnetic treatment by a hydrothermal technique. Our experiments demonstrate that the particle size of ferrite nanocrystals are very fine. In the second step, the gadolinium substituted cobalt ferrite nanoparticles were annealed and the structural characteristics, magnetic properties and microwave absorptive behavior were evaluated. We discussed the effect of gadolinium cations substitution on the size of particles, crystal structure, cation distribution, magnetic features, and microwave absorbing characteristics of $CoFe_2O_4$ nanoparticles. The reported absorption and reflection loss reveal that synthesized nanoparticles are suitable candidates for electromagnetic wave absorber at microwave frequencies.

2. Materials and methods

The preparation of gadolinium substituted cobalt ferrite nanoparticles with composition of $CoFe_{2-x}Gd_xO_4$ ($x = 0–0.05$ in a step of 0.01) were accomplished by a hydrothermal process. In the first step, in a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ (Merck, 99.99%), $Fe(NO_3)_3 \cdot 9H_2O$ (Merck, 99.999%), and $Gd(NO_3)_3 \cdot 6H_2O$ (Fluka, 99.99%) were separately dissolved in deionized water. The amounts of the nitrates were estimated in order to obtain the same atomic ratio of Co:Fe:Gd present on $CoFe_{2-x}Gd_xO_4$. The solutions were then blended and stirred at a room temperature. The final solution that includes the metal ions was kept under stirring while 40 ml of 2 M NaOH solution was joined drop wise into it. It was then stirred, and moved to an autoclave system. It was put into an oven for thermal treatment at 160 °C. By finishing the thermal treatment, the powder was sedimented from the solution by centrifugation, and dried at

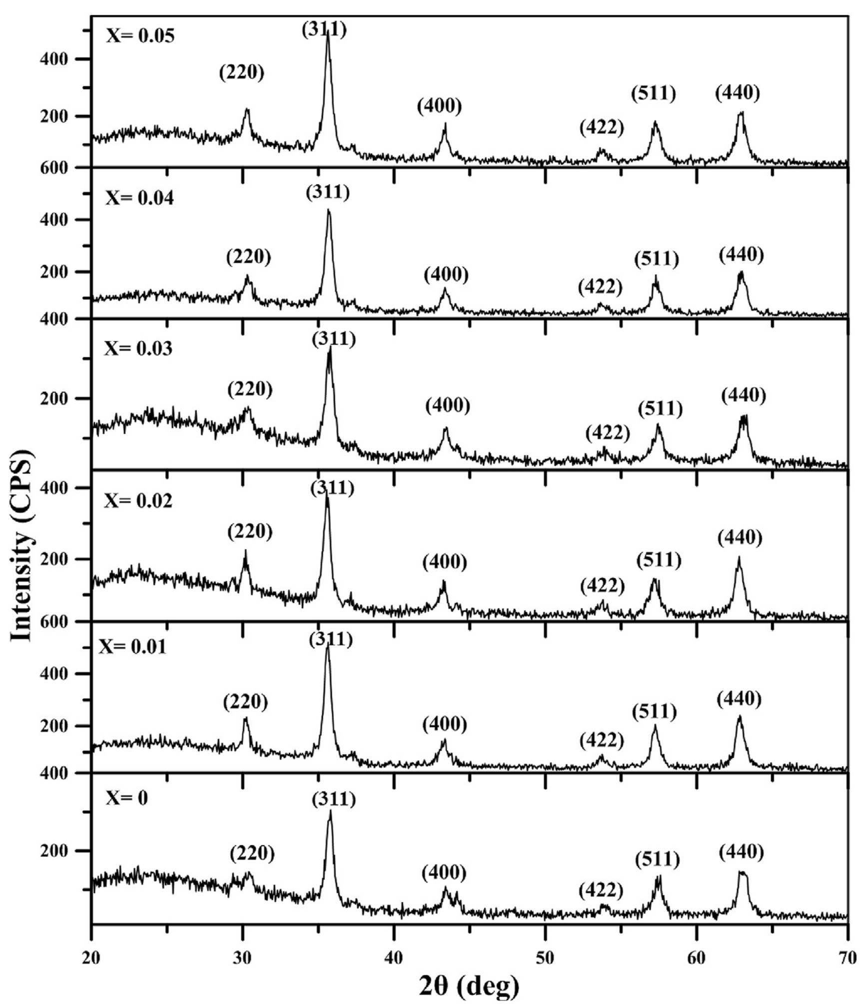

Fig. 1. X-ray diffraction patterns of as-synthesized $CoFe_{2-x}Gd_xO_4$ ferrite nanoparticles.