



Structural characteristics, electrical conduction and dielectric properties of gadolinium substituted cobalt ferrite



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ARTICLE INFO

Article history:

Received 29 May 2014

Received in revised form 23 July 2014

Accepted 24 July 2014

Available online 4 August 2014

Keywords:

Cobalt ferrite
Gd-substitution
Microstructure
Dielectric relaxation
Electrical conduction

ABSTRACT

Gadolinium (Gd) substituted cobalt ferrites ($\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$, referred to CFGO) with variable Gd content ($x = 0.0\text{--}0.4$) have been synthesized by solid state reaction method. The crystal structure, surface morphology, chemistry, electrical conduction and dielectric properties of CFGO compounds have been evaluated. X-ray diffraction measurements indicate that CFGO crystallize in the inverse spinel phase. The CFGO compounds exhibit lattice expansion due to substitution of larger Gd ions into the crystal lattice. Gd-substitution induced smooth microstructure and particle size reduction is evident in electron microscopy analyses. Frequency dependent dielectric measurements at room temperature obey the modified Debye model with a relaxation time of $\sim 10^{-4}$ s and a spreading factor of 0.244–0.616. The frequency ($f = 20$ Hz–1 MHz) and temperature ($T = 30\text{--}900$ °C) dependent dielectric constant analyses indicate that pure CFO exhibits two dielectric relaxations in the frequency range of 1–10 kHz while Gd substituted CFO compositions exhibit only single relaxation at 1 kHz. The dielectric constant of CFGO is temperature independent up to ~ 550 °C. The dielectric constant increases with $T > 550$ °C. Dielectric constant of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ ceramics is also enhanced compared to pure CoFe_2O_4 due to the lattice distortion upon Gd incorporation. The $\tan \delta$ (loss tangent)– T data reveals the typical behavior of relaxation losses in CFGO. Activation energy of the dielectric relaxation calculated employing Arrhenius equation varies from 0.564 to 0.668 (± 0.003) eV with increasing x values from 0.0 to 0.4. Thermally activated small polaron hopping mechanism is evident in temperature dependent electrical properties of CFGO. The effect of Gd-substitution in CFO is remarkable on the resistivity and, hence, activation energy; both increases with increasing Gd content. A two-layer heterogeneous model consisting of semiconducting grains separated by insulating grain boundaries was able to account for the observed temperature and frequency dependent electrical properties in CFGO ceramics. The results demonstrate that the crystal structure, microstructure, electrical and dielectric properties can be tailored by tuning Gd-content in the CFGO compounds.

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1. Introduction

Ferrites constitute an important group of materials, which exhibit diverse properties and phenomena that are useful for a wide range of scientific and technological applications. Ferrites find application in various fields such as electronics, optoelectronics, magnetics, magneto-electronics, electrochemical science and technology, and biotechnology [1–31]. Spinel structured ferrite materials exhibit remarkable properties which are attractive for electronics and magneto-electronics. High saturation magnetization, large permeability at high frequency, and remarkably high electrical resistivity are some of the key features that facilitate the integration of these materials into solid state electronics and

magneto-electronics [8–10,12–14]. Recently, ferrite materials were also considered to be the potential compounds for electrode application in Li-ion batteries and solid oxide fuel cells. NiFe_2O_4 , CoFe_2O_4 and CuFe_2O_4 were considered to be potential candidates for cathode materials in lithium batteries [23,24]. Among spinel ferrite, cobalt ferrite CoFe_2O_4 (CFO) has attracted remarkable attention and widely studied because of their large magneto-crystalline anisotropy, high coercivity, moderate saturation magnetization, large magnetostrictive coefficient, chemical stability and mechanical hardness [32]. The structure, electrical and dielectric properties of cobalt ferrite (CFO) plays a key role in designing the magnetic, electronic, microwave and electrochemical devices. However, the properties and phenomena of CFO compounds are dependent on microstructure and chemistry, which in turn depend on the synthesis processes and conditions employed for fabrication [29–31,33]. Generally exact chemical composition, firing tempera-

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ture (if any), reactive or processing atmosphere and the ions that substitute $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions dictate the electrical properties of a Co ferrite at room temperature [33,34].

There are eight formula units, or a total of $8 \times 7 = 56$ ions, per unit cell of CoFe_2O_4 . The large oxygen ions which have ionic radius about 1.3 Å are packed quite close together in a face-centered cubic arrangement. And the much smaller metal ions (ionic radii from about 0.7–0.8 Å) occupy the spaces between them [33,34]. The spaces can be divided into two types; one is called a tetrahedral (or A site) and another is known as an octahedral (or B site). A site is called tetrahedral because it is located at the center of a tetrahedron whose corners are occupied by oxygen ions. And in the octahedral site oxygen ions around it occupy the corners of an octahedron [33–36]. Partial substitution of Fe^{3+} by rare earth ion leads to structural distortion in spinel structure [8,12,29] which induces strain and significantly modifies the electrical and dielectric properties. It has been mentioned in the literature that inclusion of Zn, Cu, Co and Cd in ferrites [29,34] increase the dielectric constant due to the formation of excess Fe^{2+} which eventually increase the hopping of electrons between Fe^{2+} and Fe^{3+} .

The impetus for the present work is to study the effect of Gadolinium (Gd) incorporation on the structure, electrical and dielectric properties of Co ferrite. The obvious goal of the work is to examine whether the dielectric constant of these materials can be enhanced compared to pure Co ferrite while retaining their insulating nature. Among many possible ways of engineering the advanced functional materials based on ferrites, doping with different rare-earth (RE) ions is a well-known straightforward and versatile way to tune their desirable structure and physical properties [35]. Depending on the ionic size and concentration, incorporation of RE-ions in spinel ferrites results in an improved dielectric constant, increase in resistivity and a decrease in dielectric and magnetic losses [37–39]. The ionic size of Gd^{3+} ions (0.938 Å) is larger than that of cobalt ions (0.735 Å) and iron ions (0.645 Å). Therefore doping the parent spinel cobalt ferrite with Gd^{3+} ions is expected to induce structural disorder and lattice strain, which will have profound influence on the electrical conduction and dielectric properties of the resulting compounds. The significance of the work presented in this paper on CFGO compounds is twofold. Understanding the effect of Gd-substitution in a wide range of composition ($x = 0.0$ – 0.2) is the first. The existing reports focus on the lower end of Gd-content ($x = 0.0$ – 0.2) and some results reported on structural data of CFGO compounds is not in agreement with each other. Deriving a comprehensive understanding of the structure–property relationship is the second. A specific attention is focused towards understanding the electrical conduction and dielectric properties of CFGO compounds in detail. While attention paid towards the electrical properties of CFGO compounds is meager, the detailed results and analysis presented and discussed in this paper demonstrate that Gd-substitution has a strong influence on the electrical properties of cobalt ferrite. Through the frequency and temperature dependent electrical characterization of CFGO materials, it is shown that two-layer heterogeneous system, where the semiconducting ferrite grains are separated by insulating grain boundaries, accounts for the observed electrical properties. Therefore, the results of the work presented in this paper are expected to substantially contribute towards understanding the effect of rare-earth ion substitution in cobalt ferrites and associated effects on the electrical properties as a function of applied frequency and temperature.

2. Experimental

The CFGO polycrystalline compounds were prepared from 99.99% pure CoO, Fe_2O_3 , and Gd_2O_3 by the solid state reaction method. Powders of the starting materials were ground in an agate mortar and pestle for 2 h in an ethanol medium and

the mixtures were heat treated in air at 1200 °C for 12 h employing controllable furnace with a ramp rate of 10 °C/min for both heating and cooling. Phase identification and crystal structure of the materials synthesized were investigated using X-ray diffraction (XRD) measurements employing a Bruker D8 Discover X-ray diffractometer. Measurements were made at room temperature using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406$ Å). Surface morphology of CFGO compounds was examined by scanning electron microscopy (SEM). Hitachi S-4800 FE-SEM was employed to obtain the secondary electron imaging of the samples. Elemental composition was determined with energy dispersive X-ray spectrometry (EDS). Samples for SEM and EDS analyses were prepared by dispersing the CFGO compound on carbon tape which was pasted on Al grid. Surface imaging analysis was performed using probe electron beam operating at 18 kV. The secondary electrons generated from sample were used for imaging the surface. To measure dielectric and electric properties pellets were made using Die and Carver press. The pellet diameter and thickness were ~ 7.9 mm and 1.5 mm, respectively. Each batch of pellets was pressed in a Carver press at 4.5 tons, sintered at 1300 °C for 12 h. For dielectric measurements, the surfaces of the samples were well polished, rubbed with silver paste as the electrode for the electrical measurements and then heated in a furnace at 93 °C for 2 h in order to get the best performance. A signal of 1 V and frequency in the range of 20 Hz–1 MHz was applied to the circuit using HP precision LCR meter. Before each measurement standard calibration and precaution was taken to remove, any stray capacitance, lead, and contact resistance. Room temperature capacitance, resistance, impedance and dielectric loss were recorded as a function of frequency in the range of 20 Hz–1 MHz. The whole sample assembly then placed in a temperature controlled furnace. The real part (ϵ') and imaginary part (ϵ'') of dielectric constant and AC resistivity (ρ_{ac}) of the samples as a function of temperature were calculated from the capacitance and resistance measurements made on a LCR meter. A simultaneous loss tangent ($\tan \delta$) was also recorded along with the capacitance measurements.

3. Results and discussion

3.1. Crystal structure and lattice parameter

XRD patterns of pure CFO and Gd-substituted CFO (CFGO) are shown in Fig. 1. XRD data indicate that the CFO and CFGO crystallizes in the inverse spinel phase without any impurity phase, which means CFGO crystallizes in inverse spinel phase for initial Gd concentration and secondary phase formation emerges with increasing Gd content. The lattice constant determined from XRD for pure CFO is 8.373 Å, which agrees with that of pure CoFe_2O_4 reported in the literature [3,36]. It is noted that CFGO compounds exhibit lattice expansion, which is dependent on the Gd content. It is obvious that when some of Fe^{3+} ions are substituted by Gd^{3+}

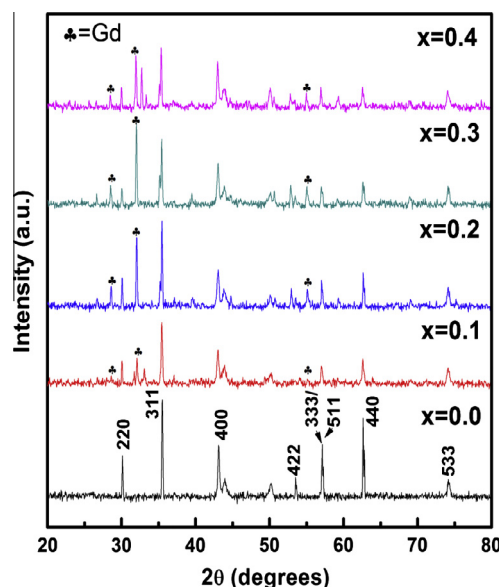


Fig. 1. XRD patterns of $\text{CoFe}_{2-x}\text{Gd}_x\text{O}_4$ (CFGO) compounds as a function of x . The data indicate that pure and Gd-substituted CFO compounds crystallize in inverse spinel structure. As indicated, secondary phase GdFeO_3 peaks appear with increasing Gd content.

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