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Dielectric, electrical transport and magnetic properties of Er^{3+} substituted nanocrystalline cobalt ferrite

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ABSTRACT

Erbium substituted cobalt ferrite ($CoFe_{2-x}Er_xO_4$; $x=0.0$–0.2, referred to CFEO) materials were synthesized by sol-gel auto-combustion method. The effect of erbium (Er^{3+}) substitution on the crystal structure, dielectric, electrical transport and magnetic properties of cobalt ferrite is evaluated. $CoFe_{2-x}Er_xO_4$ ceramics exhibit the spinel cubic structure without any impurity phase for $x \leq 0.10$ whereas formation of the $ErFeO_3$ orthoferrite secondary phase was observed for $x \geq 0.15$. All the CFEO samples demonstrate the typical hysteresis (M–H) behavior with a decrease in magnetization as a function of Er content due to weak superexchange interaction. The frequency (f) dependent dielectric constant (ε') revealed the usual dielectric dispersion. The ε'–f dispersion ($f=20$ Hz to 1 MHz) fits to the modified Debye's function with more than one ion contributing to the relaxation. The relaxation time and spread factor derived are $\sim 10^{-4}$ s and $\sim 0.61(\pm 0.04)$, respectively. Electrical and dielectric studies indicate that ε' increases and the *dc* electrical resistivity decreases as a function of Er content ($x \leq 0.15$). Complex impedance analyses confirm only the grain interior contribution to the conduction process. Temperature dependent electrical transport and room temperature ac conductivity (σ_{ac}) analyses indicate the semiconducting nature and small polaron hopping.

1. Introduction

Ferrites, which are a class of 'magnetic materials', have been the attention of researchers for several decades due to their remarkable applications in high density magnetic recording, magnetic fluids, spintronics, biotechnology, high frequency data storage and gas sensors [1–3]. Cobalt ferrite ($CoFe_2O_4$; CFO), which is the most versatile hard ferrimagnetic material, exhibits unique properties such as high Curie temperature (520 °C), high coercivity (5400 Oe), high magneto-crystalline anisotropy, moderate saturation magnetization (80 emu/g) at 300 K, large Kerr effect and Faraday rotation [4–7]. CFO materials are also utilized in high frequency and power devices especially for electromagnetic interference suppression (EMIS), phase shifters and circulators for mobile phones [8]. In addition, CFO finds application in lithium (Li) batteries and super capacitors [9]. However, the physical, structural, electrical, magnetic and dielectric properties of CFO are sensitive to the method of synthesis, reactive/processing atmosphere, size and morphology of the particles and cation doping in the host crystal structure that substitute for Fe^{3+}/Fe^{2+} ions [9–11].On the other hand, for electrical and electro-magnetic applications, electrical transport, impedance and dielectric properties are quite important [5–13].

The present work was performed on erbium (Er^{3+}) substituted CFO. The objective is to understand the Er-substitution induced effects on the structural, electrical transport, impedance and dielectric properties of CFO. For the purpose, well established sol–gel auto-combustion technique was adopted for synthesis in view its demonstrated suitability for the synthesis of nanocrystalline oxides/ferrites with homogeneous microstructure, narrow size distribution and uniform shape at lower processing temperatures. The reason for undertaking the detailed investigation of Er-substitution is as follows. It is well known that rare earth (RE) ions have unpaired *4f* electrons and the strong spin-orbit coupling therefore substitution of RE ions into spinel ferrite, leads to the presence of *4f* –*3d* couplings, which can also modify the electrical and magnetic properties of spinel ferrites. Rare-earth ion substitution is, therefore, becoming a promising way of improving the dielectric and electromagnetic properties and EMI shielding effectiveness of ferrites [14]. In modern technology, most of the

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electronic gadgets are wireless with higher chip speed indicates the need against the penetration of the radiation through the shield [15]. For significant absorption of the radiation by the shield, the shield should have electric and/or magnetic dipoles, which interact with the electromagnetic field in the radiation. For electric dipoles, the dielectric constant should be sufficiently high. As such, while the magnetic diploes are readily present due the ferromagnetic nature of the cobalt ferrite, enhanced dielectric constant is expected due to the rare earth (Er^{3+}) substitution at the Fe site in the cobalt ferrite. Furthermore, the mechanism of multiple reflections at various surfaces or interfaces in the shield requires a larger surface in the shield [16]. This requirement can be fulfilled by the nanocrystalline materials, which offer exceedingly higher surface-to-volume ratio. Thus, Er substitution coupled with morphology-controlled CFO is expected to offer the possible candidate materials for the shielding applications.

The substitution of RE ions for Fe in Co ferrite leads to the structural disorder and lattice strain [9], which allows tuning the dielectric and electrical properties [11,18]. The overall electrical and magnetic properties of ferrites depend upon the nature of ions, their oxidation states, and their distribution among the tetrahedral and octahedral (B) sites [14]. Er^{3+} is nonmagnetic at room temperature; however, Er^{3+} substitution for Fe^{3+} in CFO induces significant saturation magnetization, which is extremely useful to tailor the properties and performance [14]. Furthermore, in connection with the variation of *f*-shell electron orbital contribution to the magnetic interactions, Er^{3+} can be either isotropic or anisotropic. Therefore, introducing the trivalent rare earth (RE) cations such as Er^{3+} into the inverse spinel ferrite lattice will also induce RE^{3+}–Fe^{3+}interactions, which could modify the corresponding magnetic properties [6,19–21]. As such, a better understanding of the dielectric and transport properties of Er substituted CFO ceramics may be useful to fabricate materials for electromagnetic applications. Furthermore, while the overall attention paid towards Er^{3+} substitution in CFO is meager, there is some controversy related with the composition and crystal structure as a function of Er content [6,19,22–23]. Therefore, the present work on the dielectric and electrical transport properties along with complex impedance spectroscopic analyses of the Er-substituted CFO is expected to further contribute to the current understanding of the RE ion incorporation effects in ferrites.

2. Materials and methods

2.1. Synthesis

Nanocrystalline $CoFe_{2-x}Er_xO_4$ (CFEO; $x=0.0$–0.2) ceramics were synthesized by citrate-nitrate sol–gel auto combustion route, which is advantageous over other conventional methods. For the synthesis of CFEO composition, the analytical reagent (AR) grade nitrates of $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Er(NO_3)_3 \cdot 6H_2O$ and citric acid ($C_6H_8O_7 \cdot H_2O$) were used as raw precursors. Stoichiometric amount of metal nitrates and citric acid with 1:1 ratio were dissolved in deionized water to form citrate-nitrate solution then the liquor ammonia was added drop by drop into the citrate-nitrate solution to adjust the pH (≈ 7). The final solution was continuously stirred on a magnetic stirrer to homogenize the solution and to form the redox mixture of citric acid and metal nitrates for combustion reaction. Then the resultant solution was dehydrated slowly on a hot plate at 80 °C with continuous stirring until the viscous xerogel was formed. On further heating, the temperature of gel increased and at a certain temperature auto-ignition of the gel took place with evolution of gases and the black powder was obtained. To determine the processing temperatures, thermo gravimetric-differential thermal analysis (TG-DTA) was performed on the black powder samples. By considering the results of TG-DTA analysis (not shown here), the samples were finally sintered at 700 °C for 5 h.

2.2. Characterization

Crystal structure of the ceramics was examined using the X-ray diffraction (XRD) unit with CuK_α radiation ($\lambda=1.54178$ Å; D8 Advance, Bruker Inc., Karlsruhe, Germany). Electrical and dielectric measurements were made on the pelletized samples. The magnetic properties of all the samples were investigated at 300 K, using a Vibrating sample magnetometer with a model, Lakeshore-7307. To ensure better Ohmic contact, prior to transport property measurements, the silver paste was painted on to the polished surfaces of the pellet and cured at 100 °C for 3 h. The frequency dependence of dielectric permittivity (ε') and dissipation factor ($\tan\delta$) in the range from 20 Hz to 1 MHz were studied using a precision LCR meter bridge (HP4284 A). AC conductivities were calculated using room-temperature dielectric data. The impedance parameters, namely Z' and Z'' for all the samples, were measured at room temperature in the frequency range from 20 Hz to 1 MHz using a precision LCR meter bridge (HP4284 A). The *dc* resistivity measurements were carried out using two-probe method in the temperature range from room temperature to 500 °C.

3. Results and discussion

3.1. Crystal structure and morphology

The XRD patterns obtained for $CoFe_{2-x}Er_xO_4$ ($x=0.0$–0.2) are shown in Fig. 1. Er-substituted CFO exhibit all the characteristic reflections expected for ferrites. Most intense is the (311) reflection. The XRD data, thus, confirms the formation of a cubic spinel structure, space group *Fd3m* (227). It is evident that the ceramics

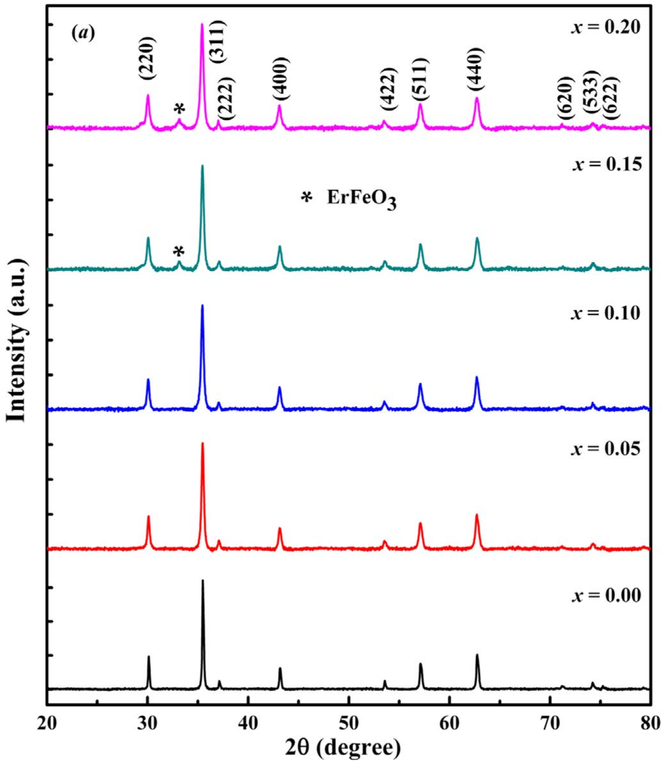

Fig. 1. XRD patterns for $CoFe_{2-x}Er_xO_4$ceramics. The data shown are for variable Er content (x).