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Observation on magnetic variation for low concentration of bismuth and samarium doped Ni−Co ferrites

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Abstract

Samarium and bismuth are doped in lower concentration in $Ni_{0.7}Co_{0.3}Fe_{2-x}R_xO_4$ (x = 0, 0.02, 0.04, 0.06) (R = Sm or Bi) and are prepared using ceramic route and sintered at 1150 °C for 4 h. X-ray diffraction confirms the cubic structure without any distortion for higher ionic radii ions in the spinel structure. High strain is observed for $Ni_{0.7}Co_{0.3}Fe_{1.98}Bi_{0.02}O_4$ among investigated samples. Field-emission scanning electron microscope (FE-SEM) confirms the doping of bismuth and samarium in expected ratio for R_x−Ni−Co ferrites. Low concentration doping effects were characterized using spectroscopic techniques, by which four primary bands were noted from Fourier transform infrared (FTIR) and Raman spectroscopy. Saturation magnetization decreases for lower concentrated ions, substituted in Ni−Co ferrites, saturation magnetization shows increase in higher concentration, attributing to changes that occur due to exchange interactions. Coercivity increases with the increase in samarium but decreases with bismuth substitution.

Keywords: Ferrites; Magnetic properties; Spectroscopic techniques; Rare earth

1. Introduction

Ferrites have many important technological applications and magnetism is subjected to intense research. In ferrites, the choice of rare earth ions substitution shows noticeable effects on several factors, such as crystallite size/grain size or magnetic properties. Presence of rare earth ions in octahedral sites or tetrahedral sites of ferrite system has the ability to be in anti-parallel in the sub-lattices that result in lower particle size, causing super paramagnetism [1,2] or spin chanting effects [3,4]. Anisotropy effect variation, caused due to 4f-3d coupling between metals and rare earth ions, plays an important role in determining the magnetization behavior [5]. Magnetization variation that is observed in ferrites, is expressed in terms of M−H loops, magnetic variation further depends on the nature of defects also. Defects that hinder domain wall motions, further depend on the size of the grain [6]. Defects in ferrite system, substituted with rare earth ions, show strain instigating effects in the electrical and magnetic properties in ferrites [7,8]. Rezlscue et al. studied rare earth doped Ni−Zn ferrite explaining the

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flattening effect on permeability and shift of Curie temperature [9,10]. Kolekar investigated gadolinium doped Cd–Cu ferrite, which shows the composition dependence on force constant calculated from spectroscopic absorption bands, attributed to the changes that are observed in cation–oxygen bond distances [11]. Dysprosium doped $Ni_{0.8}Co_{0.2}Fe_{2-x}Dy_xO_4$ ferrite [12] and $Ni_{0.5}Zn_{0.5}Fe_{2-x}Bi_xO_4$ [13] showed effective reduction of properties such as saturation magnetization, coercivity, dielectric constant and tan delta for increase in rare earth doping. A closer review of literature clarifies the modification of structural and magnetic properties of bismuth doped ferrites. When bismuth is substituted, creation of Bi^{5+} or Bi^{3+} replacing Iron (Fe) ions in lower quantity may not alter the spinel structure but may cause significant changes in magnetic properties [14]. Similarly, samarium replacing iron resulted in satisfactory results in improving permeability and higher magnetic properties when compared to undoped ferrites [15]. Therefore, it is fascinating to study the magnetic properties and their effects for higher ionic radii in lower concentration in Ni–Co ferrites. The aim of current work is to evaluate the effects of composition dependence of rare earth metal Samarium and post transition metal Bismuth (Bi) in $Ni_{0.7}Co_{0.3}Fe_{2-x}R_xO_4$ ferrite.

2. Experimental techniques

Polycrystalline $Ni_{0.7}Co_{0.3}Fe_{2-x}R_xO_4$ ceramics were prepared using conventional solid state sintering technique. Raw materials Nickel oxide, Cobalt oxide, ferric oxide in stoichiometry proportional of samarium oxide and bismuth oxide of AR grade were thoroughly mixed and calcined in powder form at 900 °C for 3 h. The powders were again grinded and sintered at 1150 °C for 4 h to obtain $Ni_{0.7}Co_{0.3}Fe_{2-x}R_xO_4$ (for x = 0.02, 0.04, 0.06). The XRD phase was examined by using Bruker D8 SSS X-ray diffraction diffractometer (XRD) using Cu-Kα radiation. The morphology of the surfaces was observed with Carlzeiss ultra-55 field-emission scanning electron microscope (FE-SEM/EDAX). The FTIR measurements were performed with Bruker, Germany Model: Vertex 70. Magnetic measurements were carried out using a 9 T PPMS based VSM (Quantum Design).

3. Results and discussion

X-ray analysis shows the absence of R_2O_3 phase in Ni–Co ferrite besides observing spinel phase, shown in Fig. 1(a) & (b). XRD pattern shows well defined

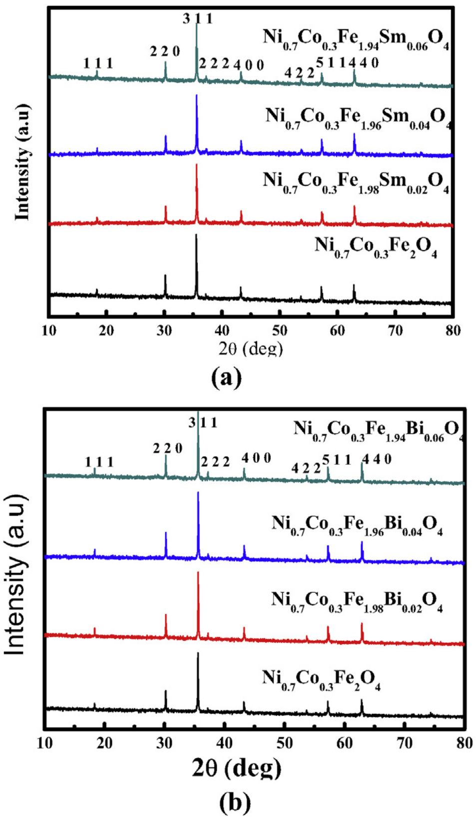

Fig. 1. (a). XRD pattern for Sm doped Ni–Co ferrite. (b). XRD pattern for Bi doped Ni–Co ferrite.

formation of single phase spinel patterns and the intensities of XRD patterns were well matched with those of JCPDS (ICDD: 80-0072). Decrease of 311 peak with increased in ionic radii such as samarium or bismuth, is observed and full width half maxima (FWHM) of the peaks suggest the presence of micron size crystallites. Ionic radius of bismuth (Bi^{3+} = 1.03 Å and Bi^{5+} = 0.76 Å) and samarium (Sm^{3+} = 0.958 Å) are larger than iron (Fe^{2+} = 0.64 Å) occupied octahedral sites, which are evident from peak (220) and (422). The increase in intensity peak at 220 suggests the occupation of higher ionic ions at octahedral sites, and also promotes shrinking of volume and cause strain. The effect of doping on strain depends on the variation of FWHM that shows initial increase and then decrease of strain, as shown in Fig. 2. Comparison between $Ni_{0.7}Co_{0.3}Fe_{2-x}Bi_xO_4$ & $Ni_{0.7}Co_{0.3}Fe_{2-x}Sm_xO_4$ shows larger strain in bismuth doped samples when compared with samarium substituted ferrites, as shown in Fig. 2. Ahmed observed the increase of FWHM with increase in rare earth dopant that results in decreased crystallite

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