The role of terbium cation substitution on the magnetic properties of cobalt ferrite nanoparticles

Q1 Tahmineh Sodaee [a,*], Ali Ghasemi [a], Ebrahim Paimozd [a], Andrea Paesano Jr. [b], Akimitsu Morisako [c]

[a] Materials Engineering Department, Malek-Ashtar University of Technology, Shahin Shahr, Iran
[b] Centro de Ciências Exatas, Departmento de Física, Universidade Estadual de Maringá, Brazil
[c] Spin Device Technology Center, Faculty of Engineering, Shinshu University, Nagano 38-8553, Japan

ARTICLE INFO

ABSTRACT

Terbium substituted cobalt ferrite nanoparticles with composition of $CoFe_{2-x}Tb_xO_4$ ($x=0$–0.5 in a step of 0.1) were prepared employing a reverse micelle process. The effect of Tb^{3+} cations substitution on structural and magnetic properties of cobalt ferrite nanoparticles was investigated. X-ray diffraction and field-emission scanning electron microscopy evaluations demonstrated that the single phase spinel ferrites with a narrow size distribution were obtained. Mössbauer spectroscopy was used to determine the site preference of constitutive elements. The results confirm the preference of terbium cations for tetrahedral sites. Vibrating sample magnetometer was employed to probe the magnetic properties of the samples at room temperature. It was found that with an increase in terbium content, the coercive field decreases while the saturation of magnetization increases. Magnetic dynamics of the samples was studied by measuring ac magnetic susceptibility versus temperature. The phenomenological Neel–Brown and Vogel–Fulcher models were employed to distinguish between the interacting or non-interacting system. Results exhibited that there is a strong interaction among fine particles.

Q4 1. Introduction

There is an increasing interest in magnetic ferrite nanoparticles because of their broad applications in several technological fields including permanent magnets, magnetic fluids, magnetic drug delivery, microwave devices, and high density information storage [1,2]. Cobalt ferrite has cubic spinel structure and has been extensively studied because of its interesting magnetic properties. It has been regarded as one of the competitive candidates for a variety of applications in high density magnetic recording media, microwave devices, high sensitivity sensor, and biomedical industries [3–6]. The magnetic properties of cobalt ferrite are dependent on exchange interaction, and how the cations are distributed among the two sublattices. Certainly, the magnetic interactions will vary with the change of cations in chemical composition and with different cation distributions between the tetrahedral and the octahedral sites. Currently, our publications were in the field of synthesizing and magnetic analysis of ferrite nanoparticles [7–12]. Even though studies on the fabrication and the magnetic characteristics of cobalt ferrite nanoparticles substituted with different cations are rapidly expanding [13–18], however to the best of our knowledge, there

is no study concerning the magnetic properties of terbium substituted cobalt ferrite. Terbium is one of the heavy rare earth elements that is paramagnetic at room temperature and above. At low temperatures its magnetic behavior is complex and becomes ferromagnetic. The ferromagnetic rare earth has magnetic moments per atom exceeding that of iron, it might make useful material, although expensive. With this view in mind, current interest is to make terbium substituted cobalt ferrite nanoparticles using the reverse micelle technique.

2. Experimental procedure

$CoFe_{2-x}Tb_xO_4$ ($x=0$–0.5 in a step of 0.1) nanoparticles were prepared by the reverse micelle process. In the preparation of ferrites, two microemulsions with the different aqueous phases were prepared. In the first microemulsions, metal solution was used, however in the second one, ammonium hydroxide was employed. Stock solutions of 0.5 M sodium dioctylsulfosuccinate (AOT) were prepared in isooctane. A metal solution was synthesized using $FeCl_3$, $CoSO_4.7H_2O$, and $Tb(NO_3)_3$ dissolved in water and AOT–isooctane. The second microemulsion was synthesized by mixing ammonia, water, and AOT–isooctane. The second microemulsion was then added to the first one and stirred for 2 h at room temperature. The pH was adjusted to 10.0 throughout the process. After rapid magnetic stirring, ethanol was used to

Q3 Q2 * Corresponding author.
E-mail address: t.sodaee@yahoo.com (T. Sodaee).

extract the surfactant and the organic solvent. The colloidal precipitate was sedimented by centrifuging and washed with ethanol and water. The final nanoparticles were annealed at 400 °C for 4 h, which is much lower than that of traditional ceramic synthesizing temperature (1310 °C).

X-ray powder diffraction was performed by employing Cu$K\alpha$ radiation. Field-emission scanning electron microscopy (FE-SEM) was employed to characterize the morphology and the particle size distribution of the nanoparticles. The Mössbauer spectroscopy (MS) characterizations were performed in the transmission geometry, using a conventional spectrometer, operated in the constant acceleration mode. The Mössbauer spectra were analyzed using a non-linear least-square routine, with Lorentzian line shapes. Vibrating sample magnetometer (VSM) was used to investigate the variation of magnetization with magnetic field at room temperature. The temperature dependence of the magnetic susceptibility of nanoparticles was studied using the Lake Shore magnetic susceptometer model 7000.

3. Results and discussion

3.1. Structural characteristics

The X-ray diffraction patterns of $CoFe_{2-x}Tb_xO_4$ ferrite nanoparticles are presented in Fig. 1. It was found from the patterns that the spinel phases can be formed in all the specimens without the existence of any secondary phases at relatively a low temperature. The Mössbauer spectra of typically prepared ferrite nanoparticles are shown in Fig. 2. A well-resolved six-line pattern of $CoFe_{2-x}Tb_xO_4$ ferrite nanoparticles is mainly attributed to the ferrimagnetic behavior. The ordinary cobalt ferrite shows, as expected, two discrete sextets respective to the iron cations occupying the tetrahedral (A) sites (sextet 1) and the octahedral
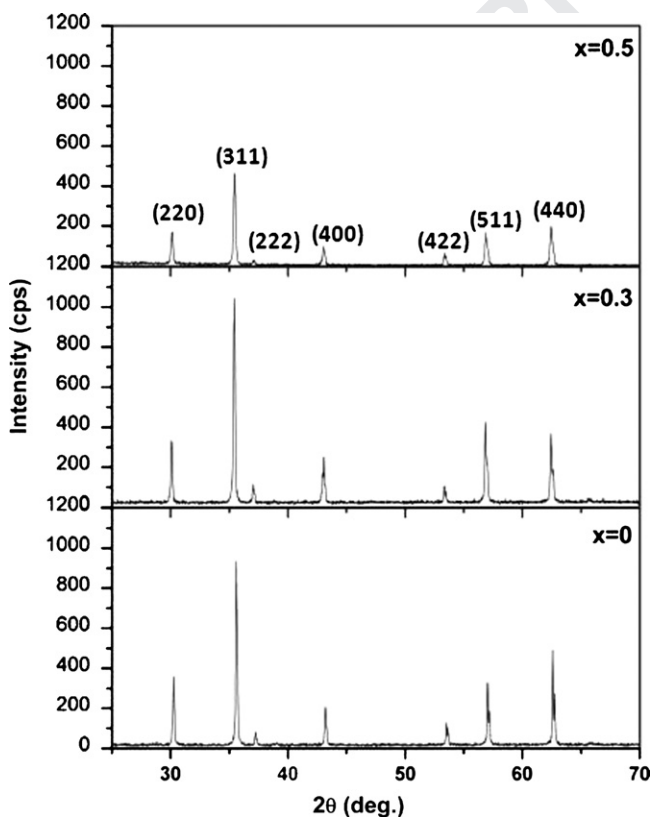

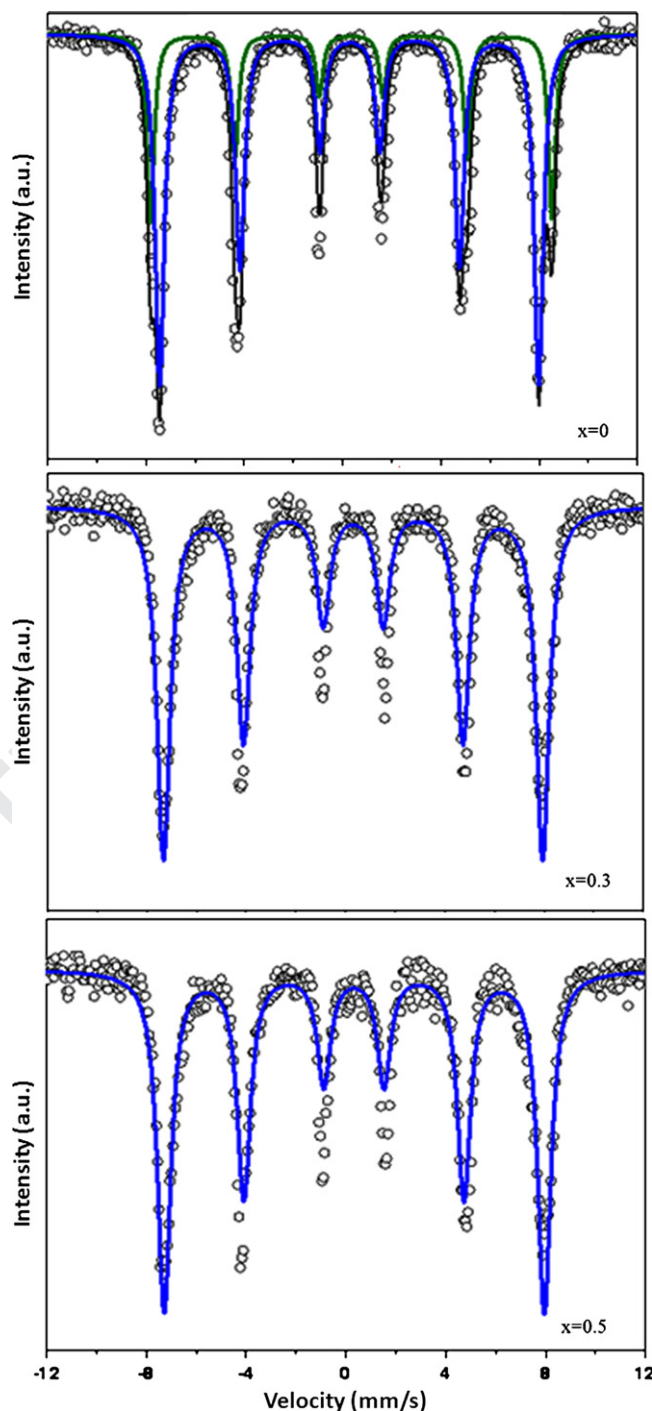Fig. 1. XRD patterns of $CoFe_{2-x}Tb_xO_4$ ferrite nanoparticles.

Fig. 2. Mössbauer spectra of $CoFe_{2-x}Tb_xO_4$ ferrite nanoparticles.

Table 1
Hyperfine parameters for the ferrite samples (IS: isomer Shift; Qs: quadrupole splitting; Γ: linewidth; B_{hf}: hyperfine magnetic field).

Sample	Sitio	δ (mm/s)	QS (mm/s)	Γ (mm/s)	B_{hf} (T)	A (%)
$CoFe_2O_4$	Sextet 1	0.28	−0.02	0.44	47.4	70.3
	Sextet 2	0.34	0.01	0.35	50.6	28.7
$CoFe_{1.7}Tb_{0.3}O_4$	Sextet 1	0.30	0.00	0.64	47.4	100
$CoFe_{1.5}Tb_{0.5}O_4$	Sextet 1	0.31	0.01	0.65	47.2	100

[B] sites (sextet 2). The fitted hyperfine parameters are summarized in Table 1. The isomer shifts reveal that only trivalent iron cations are present in these ferrite nanoparticles. For the $x=0.3$