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Structural and magnetic study of Al^{3+} doped $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ nanoferrites

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ABSTRACT

Nanostructured Al^{3+} doped $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0) ferrites were synthesized via the wet chemical method. X-ray diffraction, transmission electron microscopy, and magnetization measurements have been used to investigate the structural and magnetic properties of spinel ferrites calcined at 950 °C. With the doping of Al^{3+}, the particle size of $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ first increased to 47 nm at $x = 0.4$ and then decreased down to 37 nm at $x = 1$. The main two absorption bands in IR spectra were observed around 600 cm^{-1} and 400 cm^{-1} corresponding to stretching vibration of tetrahedral and octahedral group Fe^{3+}–O^{2-}. Saturation magnetization and hyperfine field values decreased linearly with Al^{3+} due to magnetic dilution and the relative strengths of Fe–O–Me (Me = Fe, Ni, Zn, and Al) superexchanges. The coercive field showed an inverse dependence on ferrite particle size with minimum value of 82 Oe for $x = 0.4$. A continuous drop in Curie temperature was observed with the Al^{3+} substitution. From the Mossbauer spectral analysis and X-ray diffraction analysis, it is deduced that Al^{3+} for $x < 0.4$ has no obvious preference for either tetrahedral or octahedral site but has a greater preference for the B site for $x > 0.4$. In nutshell the study presents detailed structural and magnetic, and Mossbauer analysis of $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ ferrites.

1. Introduction

Due to their various technological applications, NiZn–ferrites have attracted recently considerable research interest [1]. The performance of these materials in the bulk form with grain dimensions in micrometer scales is limited to a few megahertz frequency due to their higher electrical conductivity and domain wall resonance [2,3]. However, the recent technological advances in the electronics industry demand compact ferrite cores to work at higher frequencies [4]. One way to circumvent this problem is by synthesizing the ferrite particles in nanometric scales before compacting them for sintering. When the size of the magnetic particle is smaller than the critical size for multidomain formation, the particle is in a single domain state. Domain wall resonance is avoided, and the material can work at higher frequencies. In addition, it is known that magnetic properties of ferrites are sensitive to preparation technique and their microstructures [5]. The dielectric and magnetic properties of such ferrites depend strongly on preparation methodology and distribution of cations at the tetrahedral (A) and octahedral (B) sites in the lattice [6–9]. Thus any alteration to the cation distribution in ferrites can alter their electrical and magnetic properties. These atomic level changes in ferrites can be engineered via doping the desired level of magnetic [10–12] or non-magnetic atoms for cations such as [13–17], which in turn affect the crystal structure, influence Fe(A)–O–Fe(B) interactions, and eventually alter magnetic properties of the compound. Therefore, the selection of appropriate additives is the key to obtaining high performance ferrites.

In this work, we present the results of systematic doping of non-magnetic Al^{3+} content on the structural and magnetic properties of $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ ferrite synthesized via wet chemical method. Aluminum ions have been proven to have substantial influence on M-Ferrites (M = Al, Co, Mg, Li, etc.), especially increasing resistivity and reducing eddy current losses [18–20]. In addition, the doping of non-magnetic Al^{3+} in NiZn–ferrite not only brings grain refinement but also alters the magnetic properties to a great extent [21]. Based on the earlier studies, Ni:Zn ratio was chosen to be 0.75:0.25 as at this ratio, $NiZnFe_2O_4$ ferrite shows high magnetization with a high degree of spin collinearity at A and B sites [22]. The study highlights the site preference of Al^{3+} in $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ over a wide range of substitution and its influence on the magnetic interaction involved.

2. Experimental

One pot method [23] was used to synthesis $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1). $Ni(NO_3)_2\cdot 9H_2O$, Zn

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Table 1
Stoichiometry of chemicals used in the synthesis of $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$.

x	Weight in g			
	$Ni(NO_3)_2·6H_2O$	$Zn(NO_3)_2·6H_2O$	$Al(NO_3)_3·9H_2O$	$Fe(NO_3)_3·9H_2O$
0.0	0.5453	0.186	0	2.02
0.2	0.5453	0.186	0.188	1.818
0.4	0.5453	0.186	0.375	1.616
0.6	0.5453	0.186	0.563	1.414
0.8	0.5453	0.186	0.750	1.212
1.0	0.5453	0.186	0.938	1.010

$(NO_3)_2·9H_2O$, $Fe(NO_3)_3·9H_2O$, and $Al(NO_3)_3·9H_2O$ were mixed in the stoichiometric amount, as listed in Table 1, in 30 ml of distilled water. The solution was ultrasonicated for 30 min. After ultrasonication, the solution was cooled down to the room temperature and then the pH was adjusted around 6.5 using ammonium hydroxide. The solution was then heated at 110 °C to get rid of the extra water. The dried solid product was heated at 950 °C for 12 h which resulted in a black powder of $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$.

The X-ray diffraction (XRD) patterns were collected by Bruker D8 Advance X-ray diffractometer using Cu Kα radiation. The particle size and morphology were analyzed using transmission electron microscope at 120 keV. The surface area of the synthesized particles was measured using surface area analyzer (Autosorb-I, Quantachrome). The infrared spectra, FTIR, were collected in transmission mode using Thermo IR100 spectrometer in the wave number range 400–4000 cm^{-1} on a compacted sample-KBr pellet. The magnetic properties of the samples were investigated at room temperature (RT) using vibrating sample magnetometer (VSM). RT ^{57}Fe Mossbauer spectroscopy was used to derive hyperfine parameters. The Mossbauer spectrometer (SEE Co.) was calibrated against α-Fe foil. The Mossbauer spectra were analyzed using WMoss software from SEE Co.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD pattern of Al^{3+} doped $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ nanocrystalline ferrites. All the Al^{3+} substituted nickel ferrites of the various compositions show the desired crystalline cubic spinel phase (ICDD: 01-072-6799) along with minor amount of impurity phase NiO. The inset Fig 1, shows that the peak at 35–37° shifts to a lower angle with increasing Al^{3+} doping, which indicates lattice contraction with Al^{3+} substitution. The broader peaks of the spinel phase also suggest the presence of NiZn–ferrite in nanocrystalline form. The lattice parameter and percent composition of ferrite and NiO phase were extracted from the profile fitting of XRD data using TOPAS (Bruker Inc.) and are listed in Table 2. The inset Fig. 1 shows that the lattice parameter "a" linearly decreased at the rate of −0.153 Å per Al^{3+} ion, thus obeying the Vegard's law [24]. The decrease in lattice parameter upon Al^{3+} substitution is due to the smaller ionic radius of Al^{3+} ion (~0.535 Å) with respect to the ionic radius of Fe^{3+} ion (~0.645 Å). From the line-broadening analysis of (3 1 1) peak and using Scherrer's formula [25], the dependence of crystallite size on the Al^{3+} doping in $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ is plotted in the Fig. 2. The crystallite size increases initially with Al^{3+} content up to $x = 0.4$ (47 nm) and then decreases with further addition of Al^{3+} reaching to a value of 37 nm at $x = 1.0$. Similar dependence of crystallite size on Al^{3+} content in $ZnFe_2O_4$ has been reported earlier [26]. The inset Fig. 2 shows TEM images of $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ for $x = 0.0$ and 1.0, cubic shape spinel ferrites. The X-ray density Dx of the samples was determined using the relation [27], $Dx = 8M/(N_A a^3)$, where M is the molecular weight of the composition, N_A is the Avogadro's number, and "a" is the lattice constant. The multiplication factor 8 was used as there are 8 formula units in a unit cell. The X-ray density decreases with the increasing Al^{3+} ion content due to rapid decrease in molecular weight of the sample as compared to the lattice shrinkage, Table 2. The surface area measurement performed using nitrogen absorption using BET method show a correspondence with the particle size, having maximum surface area (7.506 m^2/gm) for particle with minimum particle size for $x = 1.0$.

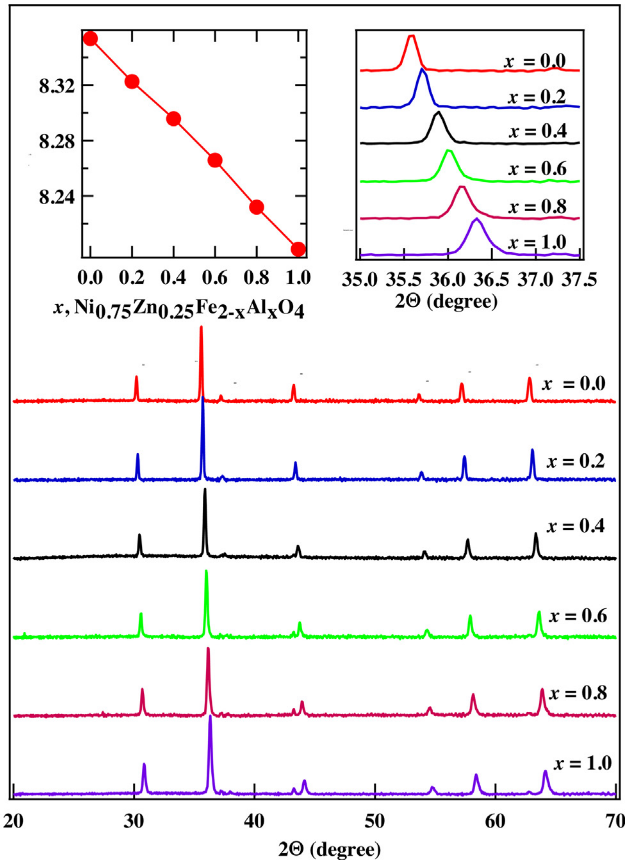

Fig. 1. The X-ray diffraction patterns of the $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ as function of Al^{3+} doping. The inset figure shows lattice parameter of $Ni_{0.75}Zn_{0.25}Fe_{2-x}Al_xO_4$ as a function of Al^{3+} doping.

Table 2
Structural parameters derived from X-ray diffraction pattern refinement.

x	% Composition $NiZnFe_2O_4$	% Composition NiO	"a" (Å)	"a-th" (Å)	Dx (g/cm^3)	Particle size (nm)	Surface area (m^2/gm)
0.0	100	0.00	8.35361 (±89)	8.3328	5.382	42.97	6.467
0.2	92.93	7.07	8.32261 (±51)	8.3038	5.321	46.77	2.140
0.4	96.44	3.56	8.29576 (±63)	8.2732	5.236	46.84	1.439
0.6	95.83	4.17	8.26582 (±60)	8.2437	5.157	43.57	2.358
0.8	96.30	3.70	8.23189 (±46)	8.2177	5.076	38.17	2.803
1.0	93.07	6.93	8.20156 (±111)	8.1927	4.999	37.19	7.506