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Structural and magnetic properties of erbium doped nanocrystalline Li–Ni ferrites

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Abstract

A series of nanocrystalline $Li_{0.25}Ni_{0.5}Fe_{2.25-x}Er_xO_4$ ($x=0.00$, 0.02, 0.06, 0.08, and 0.10) ferrite powders, having a cubic spinel crystal structure and a low value of coercivity, was synthesized by the sol–gel auto-combustion route. The structure, morphology and magnetic properties of the prepared nanoferrites were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and the magnetic property measurement system (MPMS). A well-defined single phase spinel structure is confirmed in all the samples by X-ray diffraction analysis. The lattice parameters of the samples increase slightly with increasing the erbium content. The crystallite size of the Er-doped samples is smaller than that of pure Li–Ni ferrite, and decrease regularly in the range of 36.0–14.5 nm. It has been observed that the magnetic properties of these ferrites are strongly influenced by the added erbium content. The magnetic measurements indicate that saturation magnetization (M_s) and coercivity (H_c) decrease gradually with the increase of Er content in the lattice.

Keywords: A. Sol–gel processes; Nanostructured materials; X-ray diffraction; Magnetic measurements

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1. Introduction

The substitution of various transition and rare-earth metal ions at different sub-lattices in ferrites has provided interesting magnetic structures and electrical properties. Spinel ferrites are more substantial among others as they have a variety of structures. This is because of the presence of unsatisfied bonds, magnetic dilution and the competition between the various exchange interactions [1–3]. The nanocrystalline Li–Ni soft ferrites have emerged as a remarkable candidate for the microwave applications (phase shifters, isolators and circulators), due to their high resistivity, low eddy current losses, high Curie temperature and magnetic properties [4]. Rare-earth ions have unpaired 4f electrons, and the magnetocrystalline anisotropy in ferrites is associated with the 4f–3d coupling between the rare earth and transition metal ions. Thus, the electromagnetic properties of these ferrites can be improved by doping the appropriate amount of rare-earth ions in place of Fe ions within the Li–Ni spinel lattice [5]. It is known that the preparation methodology used during the synthesis of ferrites is vital because the properties of ferrite particles are directly reliant on the composition and microstructure of the material. Many methods such as the co-precipitation method [6], the sol–gel method [7], the microemulsion method [8], the hydrothermal method [9], the citrate method [10], the combustion method [11], and the microwave-refluxing method [12] have been used during the synthesis of soft ferrites. In the present research, we have engrossed on the preparation of Er-doped Li–Ni ferrite powders by the sol–gel auto-combustion technique. The sol–gel method is a promising technique for the synthesis of nanomaterial because this technique has the benefits of excellent stoichiometry and homogeneity of the products, trace impurities, low processing temperature, and controlled size and morphology of the resulting particles. The effects of doping of the Er content on lattice parameters, crystallite sizes, and magnetic properties are inspected.

2. Experimental details

$Li_{0.25}Ni_{0.5}Fe_{2.25-x}Er_xO_4$ ($x=0.00$, 0.02, 0.06, 0.08, and 0.10) ferrite nanocrystals were synthesized by the sol–gel

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(auto-combustion) technique. First of all, a mixed solution was obtained by dissolving stoichiometric amounts of the relevant metal nitrates (analytically pure grade) and citric acid into deionized water. Even distribution and isolation of the metal ions were accomplished using citric acid. Molar ratio of the nitrates to citric acid was kept as 1:2. In order to enhance the speed of the reaction and to achieve a large surface area of the subsequent particles, the pH of the solution was sustained equal to 7 by the dropwise addition of ammonia solution (base catalyst). The solution was persistently stirred at room temperature until the condensation reaction between the metal nitrates and the citrate was completed and a polymer complex was formed. Then, the temperature of the obtained sol was increased to 80 °C with steady stirring to condensate it into a dried gel. Further increase of temperature up to 280 °C led to the ignition of the dry gel, and a fine ferrite powder was obtained through the burning of the gel in a self-propagating combustion manner. The prepared powders were then sintered for 2 h at 700 °C in order to improve the crystallinity. An X-ray diffractometer (PANalytical X′ pert Pro) with CuKα as a radiation source was used to analyze the phase constitutes of the products. The microstructure and the grain size were studied by field emission scanning electron microscopy (FE-SEM, PHILIPS XL30S FEG) and transmission electron microscopy (TEM, JEOL JEM-2100F). The powders were dispersed in ethanol solution and one droplet of the suspension was placed on the microscopic copper grid, until the solvent was evaporated at room temperature. Magnetic measurements of the powders were carried out using a squid magnetometer MPMS-7 (Quantum Design) under an applied field of 2 T (20,000 Oe) at room temperature.

3. Results and discussion

3.1. Structural and micro-structural studies

The powder X-ray diffraction patterns of Er substituted Li–Ni ferrites sintered at 700 °C are shown in Fig. 1. All the displayed diffractograms exhibited the specific reflections of (Fd3m) cubic spinel structure with no extra peaks. The absence of the additional peaks ensured the formation of single-phase spinel. However, broadening of the diffraction peaks appeared as a result of incorporation of the Er ions within the ferrite lattice. It was observed that the unit cell parameters slightly increased by the increase of erbium content in the Li–Ni spinel lattice, which may be described as the basis of ionic radii. As the ionic radius of Er^{3+} is larger compared to that of Fe^{3+}, the replacement of Fe^{3+} by Er^{3+} in octahedral sites led to an expansion of the unit cell. The change in unit cell parameters with the Er content is shown in Fig. 2, and the values are calculated using the following equation for cubic structure, which are listed in Table 1.

$$a = d(h^2+k^2+l^2)^{1/2} \qquad (1)$$

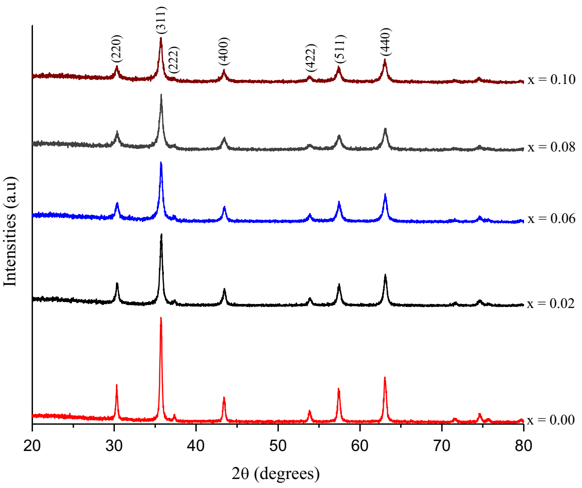

Fig. 1. XRD patterns of $Li_{0.25}Ni_{0.5}Fe_{2.25-x}Er_xO_4$ ferrites sintered at 700 °C.

A similar type of variation was also observed in the lanthanum doped Li–Ni ferrites [13]. The average crystallite size was calculated from XRD line broadening of the (311) diffraction peak by using the Scherrer formula: $D=0.9\lambda/B\cos\theta$, where D is the mean crystallite size, λ is the X-ray wavelength, B is the full peak width at half maximum intensity and θ is the Bragg angle. The variation in average crystallite sizes with the increase of erbium is shown in Fig. 2, and the estimated values are given in Table 1. It has been found that the crystallite size decreased with an increased content of Er in the lattice; similar results were reported throughout the

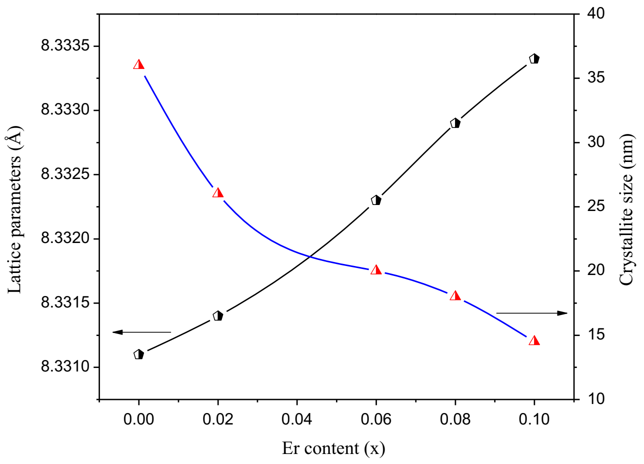

Fig. 2. Dependence of lattice parameters and crystallite size on Er content (x) in $Li_{0.25}Ni_{0.5}Fe_{2.25-x}Er_xO_4$.

Table 1
Lattice parameter, crystallite size, grain size, saturation magnetization and coercivity values of $Li_{0.25}Ni_{0.5}Er_xFe_{2.25-x}O_4$ nanoparticles.

x	Lattice parameters (Å)	Crystallite size XRD (nm)	Grain size SEM (nm)	Saturation magnetization (M_s) (emu/g)	Coercivity (H_c) (Oe)
0.00	8.3311	36.0	–	55.8	152.0
0.02	8.3314	26.0	28.0	45.6	142.2
0.06	8.3323	20.0	23.0	43.2	108.4
0.08	8.3329	18.0	19.0	41.5	75.0
0.10	8.3334	14.5	17.0	40.3	66.1