Physica B: Condensed Matter 534 (2018) 76–82

Contents lists available at ScienceDirect

Physica B: Condensed Matter

journal homepage: www.elsevier.com/locate/physb

Effect of doping rare earths on magnetostriction characteristics of $CoFe_2O_4$ prepared from spent Li-ion batteries

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ARTICLE INFO

Keywords:
Spent Li-ion batteries
Rare earth
Cobalt ferrite
Magnetic materials
Magnetostriction

ABSTRACT

Recovering spent Li-ion batteries is beneficial to the economy and environment. Therefore, this study synthesized nanoparticles of cobalt ferrite doped with different rare earth ions (Nd, Ce, and Pr) by a sol-gel auto-combustion method using spent Li-ion batteries. The effect of the different doping elements on grain sizes, structure, magnetic and magnetostrictive properties, and strain derivative were confirmed by X-ray diffraction, scanning election microscopy, vibrating sample magnetometer, and a magnetostrictive coefficient measuring system. Substitution of a small amount of Fe^{3+} with RE^{3+} in $CoRE_xFe_{2-x}O_4$ ($x = 0.025$, 0.05, and 0.1) had a large effect on magnetostrictive properties and strain derivative, which was improved compared with pure cobalt ferrite at low magnetic field. The maximum strain derivative ($d\lambda/dH = -1.49 \times 10^{-9}\ A^{-1}\ m$ at $18\ kA\ m^{-1}$) was obtained for Nd, $x = 0.05$. Changes in the magnetostriction coefficients and strain derivatives were correlated with changes in cation distribution, microstructure, and magnetic anisotropy, which depended strongly on RE^{3+} substitution and distribution in the spinel structure.

1. Introduction

Li-ion batteries have become very popular energy sources for mobile applications, such as cell phones, hybrid and electric vehicle, etc., and the demand will increase further with ongoing development of the hybrid electric vehicle industry. Rapid development of Li-ion batteries has brought convenience to people's life, but they have only 2–3 years life, which has led to increasing battery scrap generation, which must be recycled for sustainable development of the economy and environment. Li-ion batteries contain a lot of valuable metal resources, such as cobalt, iron, copper, and nickel, which means spent Li-ion batteries have significant residual value. Therefore, many studies have considered recycling spent Li-ion batteries [1–7].

Magnetostriction materials have been intensively studied and reported since they were discovered. Joule found that magnetostrictive materials can transform energy between magnetic and elastic states in 1842. The alloy based magnetostrictive smart material Terfenol-D has been applied in many fields, such as ultrasonic generation, stress sensing, and vibration control. Recently, cobalt ferrite ($CoFe_2O_4$) has been widely studied to overcome some alloy material drawbacks of high cost, poor mechanical properties, and low magnetocrystalline anisotropy [8,9]. Therefore, using spent Li-ion batteries to prepare cobalt ferrite not only provides cost-effective and easily accessible raw materials, but also alleviates resource shortage.

Crystalline cobalt ferrite is $(Co_x^{2+}Fe_{1-x}^{3+})[Co_{1-x}^{2+}Fe_{1+x}^{3+}]O_4$, where x is the fraction of tetrahedral sites (A-sites) occupied by Co^{2+} ions. Thus, crystalline $CoFe_2O_4$ has a mixed spinel structure, related to preparation conditions and heat treatment procedures [9–11]. The Co^{2+} ions tend to occupy octahedral sites (B-sites) and the concentration at the B-sites has a strong influence on $CoFe_2O_4$ performance. Therefore, changing the cation distribution by substituting Co^{2+} or Fe^{3+} with different metal ions, such as Mn, Ca, Al and Ni, will influence cobalt ferrite magnetic and magnetostrictive properties, which have been widely studied [12–15].

The magnetostriction strain coefficient (λ) and strain sensitivity ($d\lambda/dH$) under an applied magnetic field are important factors for cobalt ferrite applications, and enhancing their values is a significant research direction for many applications. Introducing a small amount of rare earth (RE) ions into the spinel lattice to modify the structure and improve magnetostrictive properties of cobalt ferrite has attracted much attention. The 4f electron shells (from 0 (La) to 14 (Lu)) and magnetic moments (from 0 (La) to 10.6 μ_B (Dy)) of the RE ions have spin-orbit coupling to the angular momentum. Doping RE ions into the spinel cobalt ferrites can cause 3d-4f coupling, which determines large magnetocrystalline anisotropy and magnetic behavior. Substituting RE

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https://doi.org/10.1016/j.physb.2018.01.036
Received 19 September 2017; Received in revised form 15 January 2018; Accepted 16 January 2018

elements with large ionic radii for the smaller ionic radii Fe^{3+} within $CoFe_2O_4$ can modify cell parameters, average crystallinity, and grain, which will modify magnetic and magnetostrictive properties [16,17].

Previous studies have synthesized cobalt ferrite with spent Li-ion batteries using the sol-gel hydrothermal method and different metal ions substitution for Co^{2+} or Fe^{3+} using sol-gel auto-combustion [18–20]. However, magnetostrictive properties and strain derivative require further improvement for practical applications. The current study used three different Lanthanide ions with different ionic radii and magnetic moments to modify cobalt ferrite, and compared and contrasted the influence of the RE elements on the final assembly properties. Significant improvement in strain sensitivity was achieved at low doping levels in sintered RE doped cobalt ferrites.

2. Experimental details

A series of RE doped cobalt ferrite samples, $CoRE_xFe_{2-x}O_4$ (RE = Ce, Pr and Nd; x = 0.025, 0.05 and 0.1) were obtained by sol-gel auto-combustion using spent Li-ion batteries collected from mobile phones for raw materials. Cathode materials ($LiCoO_2$) were separated from the spent batteries and dissolved in nitric acid solution containing a small amount of hydrogen peroxide. Precipitations containing Co^{2+} and Fe^{3+} were generated by adjusting the pH with ammonia, then filtered and redissolved in nitric acid to obtain the mixed solution [21]. $Co(NO_3)_2{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$ and $RE(NO_3)_3{\cdot}6H_2O$ were added to the mixed solution to adjust Co^{2+}, Fe^{3+}, and RE^{3+} ion concentrations, respectively, in accordance with the stoichiometry. Citric acid was added to the mixed solution at a 1:1 ratio of metal ion concentration to citric acid and the mixture was constantly stirred at 60 °C until completely dissolved. The final solution pH was adjusted to 6.5 using ammonia at the same temperature to obtain a solution, which was then heated to 80 °C, stirred using a magnetic stirrer to form a gel, and transferred to an air dry oven at 100 °C for 48 h. Approximately 2 mL alcohol was added to the dried sample and ignited, until it was completely burnt to ashes, then ground into power. Full details of the method are available in our previous literature [18,20].

X-ray diffraction (XRD, D8-advance, BRUKER, Karlsruhe, Germany) with monochromatic graphite showed that these samples had characteristics consistent with cobalt ferrite. Microstructures of the sintered samples were obtained by field emission scanning electron microscopy (FESEM, SUPRA-40, Carl Zeiss, Jena, Germany). Then the samples were mixed with 8%–10% polyvinyl alcohol (PVA) and pressed into the desired shape: cylindrical, 10 × 20 mm diameter × length using a uniaxial hydraulic press at 12 MPa. The pressed compacts were sintered at 1450 °C for 6 h with heating/cooling rate 5 °C/min. The magnetostrictive properties of final pure and doped cobalt ferrite samples were investigated by a JDM-30 magnetostrictive coefficient measuring system.

3. Results and discussions

Fig. 1a–c shows X-ray diffraction patterns for pure and doped cobalt ferrite with different RE contents. These were characterized at room temperature with sweep speed interval 0.02° and 20°–80° (2θ) angular extension. The diffraction peaks are sharp and correspond to a cubic spinel ferrite structure (JCPDS, No. 22-1086). Impurity peaks (marked "*" in Fig. 1) were observed in Pr and Nd doped cobalt ferrite ($REFeO_3$) and Ce doped cobalt ferrite (CeO_2) (JCPDS, No. 34-0394). The orthoferrite phase was not observed for Ce doped cobalt ferrite, which may be due to the higher CeO_2 refractory temperature. These effects were consistent with previous studies [17,22,23]. Impurity peaks were considered to be RE^{3+} partial replacement of Fe^{3+} into the spinel lattice, due to limited solubility, which caused excess RE^{3+} ions to accumulate on the grain boundaries and form a secondary phase. Average $CoRE_xFe_{2-x}O_4$ particle size (d_{XRD}) was calculated from full width at half maximum (FWHM) of the XRD peaks with maximum intensity using Scherrer's formula, as shown in Table 1,

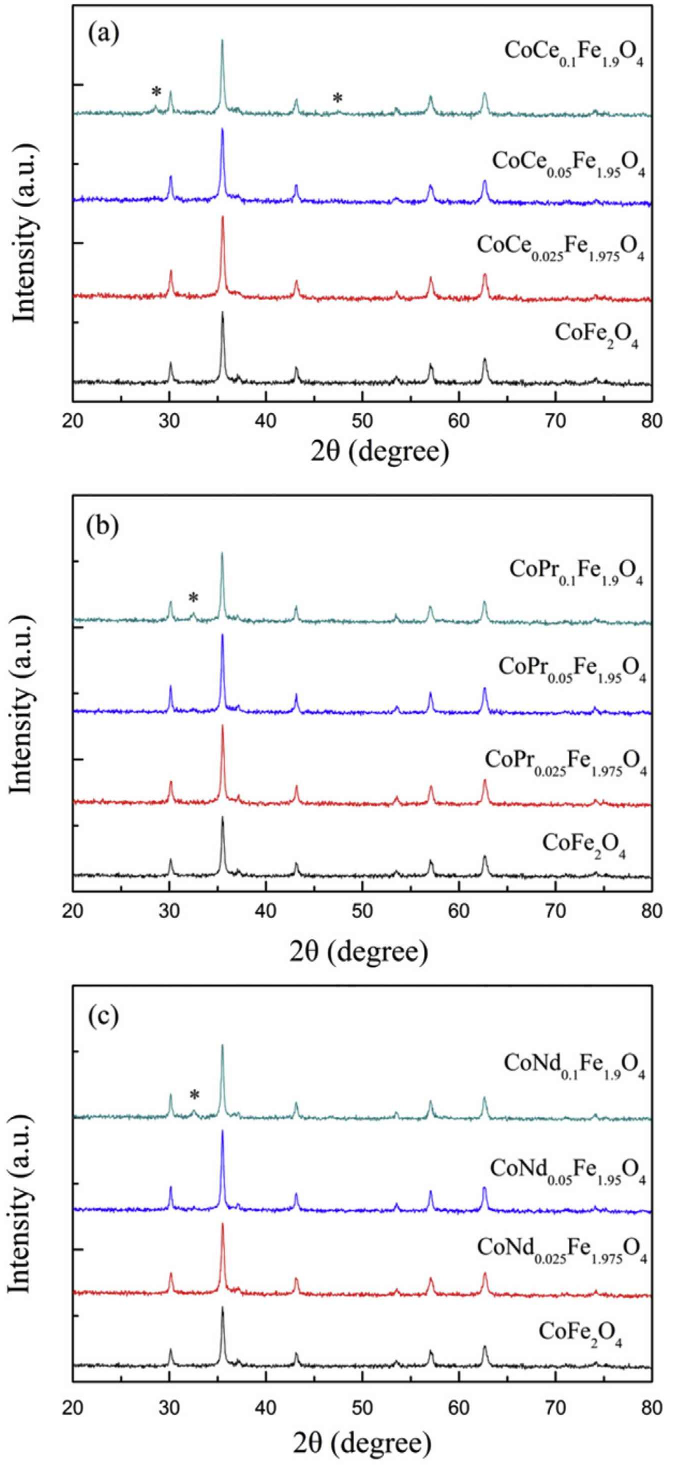

Fig. 1. XRD patterns for (a) $CoCe_xFe_{2-x}O_4$, (b) $CoPr_xFe_{2-x}O_4$ and (c) $CoNd_xFe_{2-x}O_4$ (x = 0.025, 0.05, and 0.1).

$$d_{XRD} = k\lambda/\beta\cos\theta \tag{1}$$

where d_{XRD} is the average crystallite size; k = 0.9 is the Scherrer constant; λ = 1.5406 Å is the radiation wavelength; β is the half width of the relevant diffraction peak; and θ is the Bragg angle.

The lattice parameter, a, for $CoRE_xFe_{2-x}O_4$ can be expressed as

$$a = \lambda\left(h^2 + k^2 + l^2\right)^{1/2} \Big/ 2\sin\theta \tag{2}$$