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Structure and magnetic properties of manganese–nickel ferrite with lithium substitution

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Abstract

$Li_{0.5x}Mn_{0.4}Ni_{0.6-x}Fe_{2+0.5x}O_4$ ($0.0 \le x \le 0.3$) was obtained by calcining oxalates precursor over 600 °C in air. The precursor and its calcined products were characterized by thermogravimetry and differential scanning calorimetry, X-ray powder diffraction, scanning electron microscopy, and vibrating sample magnetometer. A high-crystallized $Li_{0.5x}Mn_{0.4}Ni_{0.6-x}Fe_{2+0.5x}O_4$ with a cubic structure was obtained when the precursor was calcined at 600 °C in air for 2 h. The specific saturation magnetization of $Li_{0.5x}Mn_{0.4}Ni_{0.6-x}Fe_{2+0.5x}O_4$ depends on the composition and calcination temperature. $Li_{0.1}Mn_{0.4}Ni_{0.4}Fe_{2.1}O_4$ obtained at 600 °C had the highest specific saturation magnetization value, 57.94 emu/g. However, $Mn_{0.4}Ni_{0.6}Fe_2O_4$ obtained at 600 °C had the highest coercivity value, 130.32 Oe.

Keywords: Magnetic properties; Spinel ferrites; Chemical synthesis; Thermal transformation

1. Introduction

Polycrystalline spinel ferrites MFe_2O_4 (M=Cu, Mn, Mg, Zn, Ni, Co, etc.) are widely used in the field of high-density information storage, magnetic separation, ferrofluids, catalysts, drug targeting, magnetic resonance imaging, and gas sensor devices because of their high permeability in the radio frequency region, high electrical resistivity, mechanical strength, and chemical stability [1–14]. The structure of ferrospinels depends on the outer electron configuration and radius of divalent cation, and distribution of cations at the different sites. For example, $ZnFe_2O_4$ is a kind of normal spinel ferrite, $NiFe_2O_4$ is inverse spinel, and $MnFe_2O_4$ and $Mn_{1-x}Zn_xFe_2O_4$ are random spinel. The magnetic moment direction of cations in tetrahedral A-site is opposite to that in octahedral B-site. Therefore, magnetic moment of spinel ferrites can be regulated by distribution of different divalent cations at the different sites and/or univalent cation doping.

Various synthetic approaches have been pursued to prepare spinel $Mn_{1-x}Ni_xFe_2O_4$ and doped $Mn_{1-x}Ni_xFe_2O_4$ with different particle sizes and morphological features, including solid-state reaction at high temperature [15], reverse micelle technique [16], emulsion method [17,18], ceramic technique [19–21], sol–gel combustion method [22,23], solvothermal method [24,25], co-precipitation method [26], hydrothermal method [27], mechanochemical route [28,29], oxalate precursor route [30], citrate precursor method [31,32], etc. In the synthesis of $Mn_{1-x}Ni_xFe_2O_4$, the crystallite diameter, morphology, and crystalline phases of $Mn_{1-x}Ni_xFe_2O_4$ associated with its performances highly depend on the composition, synthesis method, and calcination temperature. Airimioaei et al. [22] synthesized nanocrystalline $Ni_{1-x}Mn_xFe_2O_4$ ($x=0$, 0.17, 0.34, 0.5) by the sol–gel combustion method, followed by calcination at 900 °C for 5 h. The magnetic study shows that the specific saturation magnetization decreases with increasing the Mn addition, from $M_s=50$ emu/g for $x=0$ to $M_s=39$ emu/g for $x=0.50$; coercivity slightly increases with increasing the amount of Mn from ~37.4 Oe to ~53.7 Oe for $x=0$–0.5, respectively. Köseoğlun [27] synthesized spherical $Mn_xNi_{1-x}Fe_2O_4$ ($x=0.2$, 0.4, and

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0.6) nanoparticles by a polyethylene glycol (PEG)-assisted hydrothermal route. The magnetic study at room temperature shows that the zero coercivity and sharp increase in the magnetization of the samples with the applied field, indicating the superparamagnetic nature of the samples. $Mn_{0.6}Ni_{0.4}Fe_2O_4$ had the highest specific saturation magnetization value, 56 emu/g. Although many researchers have made great efforts to obtain a single phase $Ni_{1-x}Mn_xFe_2O_4$ with high performance, facile and scalable synthesis of $Ni_{1-x}Mn_xFe_2O_4$ with high performance at a low cost is still a significant challenge. Therefore, it is highly desirable and necessary to explore new synthetic methods for the preparation of $Ni_{1-x}Mn_xFe_2O_4$ and/or doped $Ni_{1-x}Mn_xFe_2O_4$. To the best of our knowledge, the synthesis of $Li_{0.5x}Mn_{0.4}Ni_{0.6-x}Fe_{2+0.5x}O_4$ by thermal decomposition of oxalates precursor has rarely been reported in previous studies.

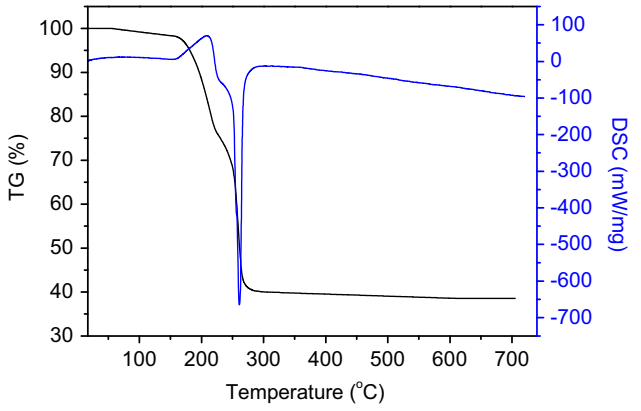

Fig. 1. TG/DSC curves of $Mn_{0.4}Ni_{0.6}C_2O_4$–$2FeC_2O_4 \cdot 8.3H_2O$ at a heating rate of 10 °C/min in air.

This study aims to prepare $Li_{0.5x}Mn_{0.4}Ni_{0.6-x}Fe_{2+0.5x}O_4$ by calcining oxalates precursor in air and study effect of compo sition and calcination temperature on magnetic properties of $Li_{0.5x}Mn_{0.4}Ni_{0.6-x}Fe_{2+0.5x}O_4$. Our results clearly show that the magnetic properties, in particular the specific magnetizations (M_s) and coercivity (H_c), can be precisely tailored by controlling the composition as well as the calcination temperature.

2. Experimental

2.1. Reagent and apparatus

All chemicals used are of reagent-grade purity (purity > 99.9%). The TG/DSC measurements were conducted using a Netzsch Sta 409 PC/PG thermogravimetric analyzer under continuous flow of

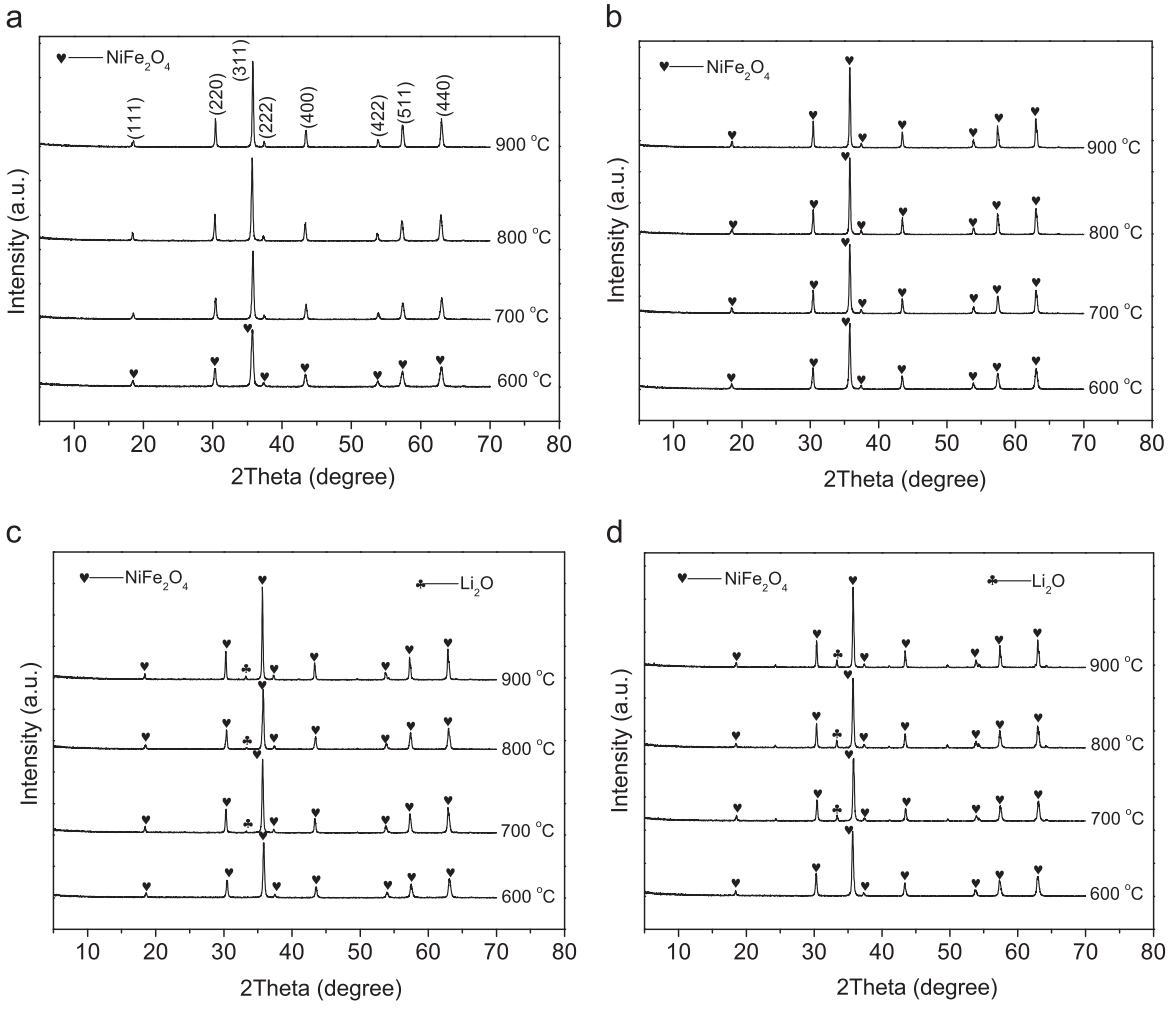

Fig. 2. XRD patterns of $Li_{0.5x}Mn_{0.4}Ni_{0.6-x}Fe_{2+0.5x}O_4$: (a) $Mn_{0.4}Ni_{0.6}Fe_2O_4$, (b) $Li_{0.05}Mn_{0.4}Ni_{0.5}Fe_{2.05}O_4$, (c) $Li_{0.1}Mn_{0.4}Ni_{0.4}Fe_{2.1}O_4$, and (d) $Li_{0.15}Mn_{0.4}Ni_{0.3}Fe_{2.15}O_4$.