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Sequence of phases in the hydrothermal synthesis of zinc-doped magnetite system

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Abstract

Hydrothermal techniques have been used to synthesize samples of $Zn_xFe_{3-x}O_4$ ($x = 0.0$–1.0) starting with $ZnSO_4{\cdot}7H_2O/FeSO_4{\cdot}7H_2O$ aqueous solution. The sequence of phases, structural and magnetic properties were followed by X-ray diffraction (XRD), Mössbauer spectroscopy and transmission electron microscopy (TEM). Refinement of the XRD spectra yielded the dependence of the lattice parameters of zinc-doped magnetite and zinc ferrite phase as function of the Zn molar concentration x. As well, the particle diameter was derived and represented as a function of Zn content x. As a function of Zn concentration, the phase content of hydrothermally synthesized samples was found to consist of zinc-doped magnetite, goethite and zinc ferrite. Consistent with the XRD results, Mössbauer spectroscopy data indicate the presence of magnetite and goethite at $x \leq 0.2$, magnetite and zinc ferrite at $x \leq 0.9$ and pure zinc ferrite only at high zinc concentrations. The presence of different magnetite phases was confirmed by TEM and particles with a size of 50 nm were identified. Our results show that zinc ferrite is formed at high zinc concentration by the hydrothermal method and an acicular component of goethite–magnetite is obtained at low zinc content.

Keywords: Magnetic materials; Zinc ferrites; Substitutions; Mössbauer spectroscopy; X-ray diffraction

1. Introduction

Magnetite (Fe_3O_4) is an oxide with the inverse spinel structure, which has one Fe^{3+} ion on the tetrahedral A site and two Fe ions, with a total valence of 5+, on the octahedral B site [1]. The fundamental studies on the structure and properties of magnetite-containing systems intensified a few years ago, since the construction of a magnetite-based all-oxide spin valve was proposed [2].

Our group initiated several basic and applied research investigations on pure and substituted magnetite, regarding the occurrence of site and distributed hyperfine magnetic fields in synthetic magnetite [3,4], determination of the recoilless fraction of magnetite and nanomagnetite using our dual absorber method [5], Mössbauer studies of the Verwey transition in cobalt and manganese-doped magnetite [6–10], the evolution of phases during mechanochemical activation in magnetite containing systems [11,12] and conversion electron Mössbauer study of magnetite/nickel and magnetite/chromium multilayers obtained by pulsed laser deposition [13].

In the present study we focus on the hydrothermal synthesis of $Zn_xFe_{3-x}O_4$ ($x = 0.0$–1.0) and follow the sequence of phases using XRD, Mössbauer spectroscopy and TEM.

2. Experimental

The synthesis of nanocrystalline $Zn_xFe_{3-x}O_4$ ($0 \leq x \leq 1$) oxide system has been performed by a hydrothermal route. The starting materials were $ZnSO_4{\cdot}7H_2O$ and $FeSO_4{\cdot}7H_2O$ of analytical grade (Aldrich, 99.99%). Divalent metal hydroxides were co-precipitated from aqueous solutions of zinc and iron(II) sulfates at different molar ratios, using a NaOH (3 M) solution as precipitation agent. The total sulfate concentration was fixed at 0.3 mol dm^{-3}. In order to avoid the uncontrolled iron(II) oxidation, all solutions were prepared in a glove box under nitrogen atmosphere, with double distilled water (previously degassed by removing O_2 and dissolved CO_2 with nitrogen gas). $Zn(OH)_2$ is amphoteric, so that stable zincate ions, ZnO_2^{2-}, are formed in basic solutions [14] at pH values greater than 10, determining a zinc loss in the final samples prepared through the hydrothermal route.

In the present study, metal hydroxides were co-precipitated at pH 9 where the loss phenomenon is minimum. The pH measurements were performed with a Cole-Parmer Benchtop pH-meter and a special electrode (Sure Flow) used for suspensions and viscous samples. The partial iron oxidation was assured by adding a predetermined amount of sodium nitrate to the reaction mixture. The

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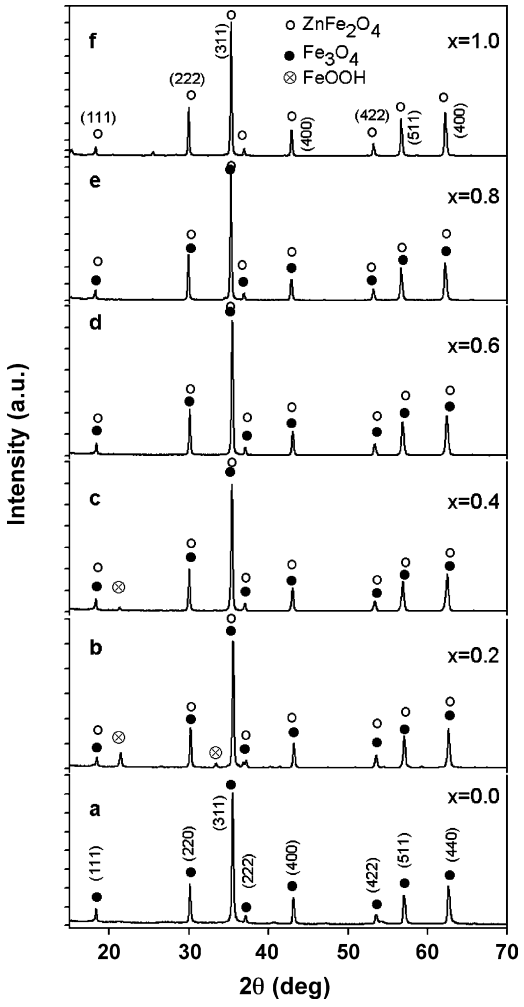

Fig. 1. XRD patterns of the $Zn_xFe_{3-x}O_4$ system: (a) $x = 0.0$; (b) $x = 0.2$; (c) $x = 0.4$; (d) $x = 0.6$; (e) $x = 0.8$; (f) $x = 1.0$.

suspension containing the co-precipitated hydroxides was placed into a 50 ml Teflon lined autoclave and heated at 200 °C for 4 h. The autoclave was naturally cooled to room temperature, the resulting oxide was separated by filtration, washed with distilled water until no SO_4^{2-} anions were detected and finally dried at 105 °C. The nature of the synthetic route does not allow a reliable prediction of the substitution level, such that in this paper we refer to the zinc molar concentration x.

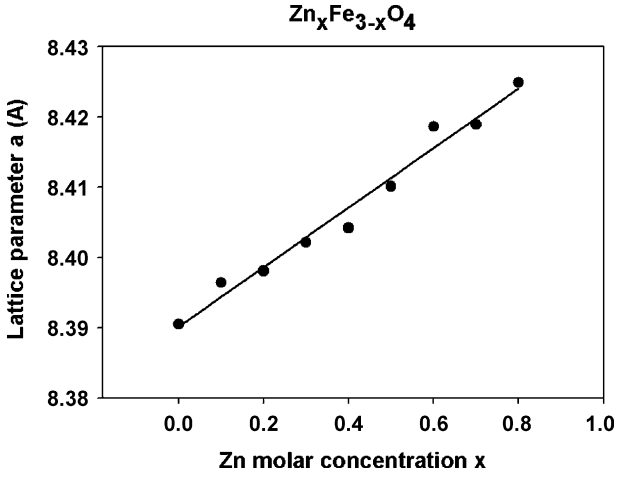

Fig. 2. Lattice parameter of the $Zn_xFe_{3-x}O_4$ system as function of Zn molar concentration x.

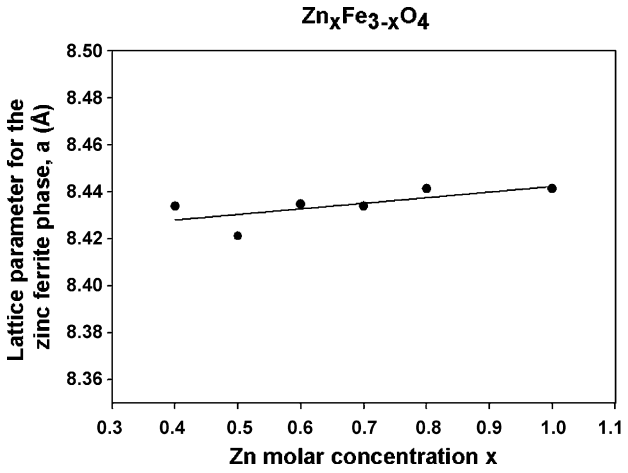

Fig. 3. Lattice parameter for the zinc ferrite phase as function of Zn content x.

The X-ray diffraction spectra were recorded with a Rigaku D-2013 diffractometer with Cu Kα radiation (λ = 1.540598 Å). The Mössbauer spectra were recorded at room temperature using a source of ^{57}Co in Rh matrix and an MS-1200 constant acceleration spectrometer. All spectra were analyzed by nonlinear least-squares fitting using the NORMOS program. The electron microscopy analyses were performed using a JEOL 200 CX microscope.

3. Results and discussion

Fig. 1(a)–(f) displays the XRD patterns of the $Zn_xFe_{3-x}O_4$ system at various levels of zinc content. Refinement of these spectra yielded the identification of various phases present in the zinc-doped magnetite system. Thus, the diffraction peaks in Fig. 1(a) are consistent with the presence of magnetite as starting material. For $x = 0.2$, Fig. 1(b) shows the occurrence of magnetite, goethite and zinc ferrite phases. At $x = 0.4$, Fig. 1(c) indicates that the goethite phase drops drastically. For $x = 0.6$ and 0.8 in Fig. 1(d) and (e) it is apparent that the goethite phase disappears from the phase sequence, leaving a system containing magnetite and zinc ferrite. The zinc ferrite phase remains dominant for $x = 1.0$, Fig. 1(f).

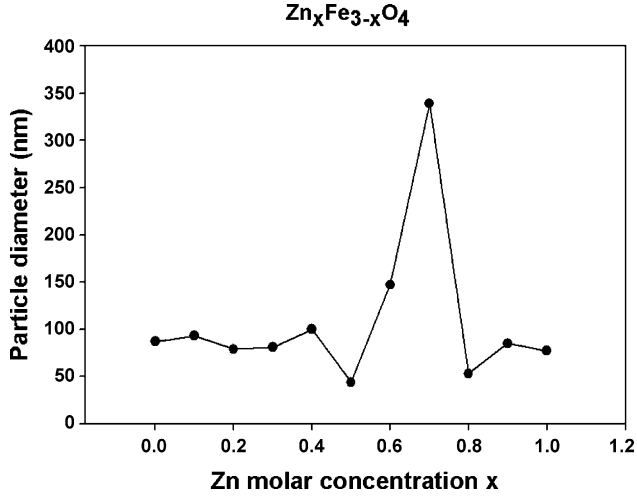

Fig. 4. Particle diameter of the $Zn_xFe_{3-x}O_4$ nanoparticles as function of Zn concentration x.