



Research articles

Cluster-glass-like behavior in zinc ferrite nanograins

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ABSTRACT

Structural and magnetic properties of ZnFe₂O₄ nanograins, prepared by high-energy ball milling and annealed, were systematically studied by X-ray diffraction, ⁵⁷Fe Mössbauer spectroscopy and AC magnetic susceptibility measurements. Disordered spinel-like structure, with a grain size of 12 nm, is established after 200 h of milling. While the 300 K Mössbauer spectrum of the as-milled sample (200 h) displays broad magnetic absorption lines, characteristic of a disordered system, the magnetization data do not show a magnetic phase transition between 4 and 300 K. At low temperatures, the Mössbauer spectra suggest the presence of two distinct ferrite magnetic phases: one attributed to the grain core (crystalline-like phase), with magnetic ordering temperature of about 90 K, and one showing a magnetic hyperfine field distribution; the latter is associated with a chemically disordered phase (grain boundary contributions). Annealing the 200 h sample at 973 K leads to an improvement of atomic ordering of the spinel structure (reduction of cationic inversion) and average grain size of about 17 nm. AC magnetic susceptibility shows a cusp at about $T \approx 30$ K, whilst Mössbauer experiments in the same sample reveal magnetic blocking in the same temperature range. The frequency dependence of susceptibility suggests the formation of a cluster-glass-like state. High temperature susceptibility can be described with a Fulcher law of interacting magnetic clusters.

1. Introduction

Ferrites have thoroughly been studied for the past decades, mainly for their remarkable properties that give them prime importance in better understanding theories of magnetism. Additionally, most ferrites are naturally occurring materials, making them ideal systems for various technological applications [1–5].

Ferrites usually crystallize in a spinel cubic structure [6,7], with two sublattices *A* (tetrahedral) and *B* (octahedral) occupied by 3*d* ions. Therefore, the properties of these materials are strongly dependent on the 3*d*-cation distribution among *A* and *B* sites. This distribution may be modified either by different synthesis methods or by controlled cation substitution. Ion substitution and/or an increase of atomic disorder between the ferrite sites, caused by the different preparation techniques, lead to significant changes in the properties of these materials. Understanding these modifications may lead to further increase the technological potential of ferrites [8–10].

In general, ferrites reveal ferrimagnetic order due to the super-exchange interaction between magnetic *A* and *B* ions. However, in nanostructured materials, due to locally distorted structure and finite size effects [2,4], there are, overall, changes in net magnetization and

magnetic ordering temperature, since surface atoms may have uncompensated magnetic moments. Hence, the grain boundary (surface) contributions, which depend on the preparation method and particle size, may govern the physical properties of ferrites at the nanoscale. Such peculiarities, together with high magnetic permeability, high electrical resistivity and low manufacturing cost, have promoted the extensive use of nanostructured ferrites in several electronic components [1,2,11].

In particular, zinc ferrites (ZnFe₂O₄) show long-range antiferromagnetic ordering below 10 K. All Fe³⁺ ions reside on the octahedral *B* sites with spins coupled antiparallel [4]. However, it has been reported that, on the nanoscale, zinc ferrites may exhibit persistent ferrimagnetic order at temperatures higher than 10 K [12,13]. It is well established that preparation routes and experimental conditions under which these materials are synthesized may result in materials with different magnetic properties. There are many methods employed in the synthesis of ferrites, namely co-precipitation [14], chemical routes [15,16], electrodeposition [17], hydrothermal reaction [18], microwave combustion [19] and high energy ball milling [13,20,21].

The high-energy ball milling method has been used over the last decades in industrial grade processes and it has been employed in the

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preparation of nanostructured ferrites due to its low cost. Very recently the preparational evolution of pure zinc ferrites from its elemental oxide constituents, the structural changes with tunability of cation inversion and its consequences for long-range magnetic properties of nano zinc ferrites have been reviewed [22]. The formation of a defected and inverted metastable state has been studied and its reversibility by heat treatment above 600 K has been demonstrated [23–25]. As outlined in Ref. [22], the modification in cation inversion determines intrinsic magnetic properties of nanograins, including magnetization and Néel temperatures and other local and nuclear magnetic properties. However, the magnetic state and how the magnetic grains are interacting in ZnFe_2O_4 nanocrystalline powders still need a systematic investigation using zero-field time dependent experiments.

Therefore, in this work, we have prepared ZnFe_2O_4 nanograins by milling ZnO and $\alpha\text{-Fe}_2\text{O}_3$ precursors up to 200 h and subsequently annealed at 773 K and 973 K to understand the influence of the annealing temperature on structural and magnetic properties of the nanograins. ^{57}Fe Mössbauer spectroscopy and AC magnetic susceptibility measurements were applied to understand the zinc ferrite formation, exchange interactions among magnetic grains and the suggested magnetic state due to the un-compensated spins of the zinc ferrite spinel structure in nanoscale regime.

2. Experiment

A spinel ferrite system ZnFe_2O_4 was prepared by ball milling from stoichiometric amounts of high purity powder precursors ZnO and $\alpha\text{-Fe}_2\text{O}_3$. The powders, with a total mass of 3g, were milled in a Laermann® Lab Wizz 320, with a ball-to-mass ratio of 3:1. The milling process was initiated with a small amount of the precursor powders, at the defined composition, to cover the milling tools and the walls of the vial, therefore reducing possible contaminations. A more substantial portion of the precursors was then introduced. The milling process was performed with two steel balls (hardness of about 65 HR) occupying 20% of the vial's internal volume.

At pre-defined milling times, part of the powder material was collected for structural and magnetic characterizations. In addition, different parts of the final milled product (200 h of milling) were heat treated in air for 24 h at $T_f = 773$ K and 973 K, respectively. X-ray diffraction (XRD) patterns for all the samples were collected at 300 K using a $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418$ Å) in a Rigaku Ultima IV diffractometer, that was calibrated using a standard graphite crystal. Temperature dependence of ^{57}Fe Mössbauer spectra was measured with a $^{57}\text{Co}:\text{Rh}$ source of about 20 mCi activity in conventional transmission geometry at RT. The spectrometer operates in constant acceleration mode. Each Mössbauer spectrum of the milled or annealed samples was collected during 3–4 days. The isomer shift (IS) values of our data are given relative to $\alpha\text{-Fe}$ at RT. Magnetic properties have been studied using AC magnetic susceptibility measurements that were carried out using an ACMS module from the Physical Properties Measurement System-Evercool II, Quantum Design®. The in phase ($\chi'(T)$) and out-of-phase ($\chi''(T)$) components of the complex AC susceptibility were measured at different frequencies ranging from 10 to 10^4 Hz.

3. Results and discussions

The XRD patterns of the samples milled at various times (t_m) are shown in Fig. 1, including that of the non-milled mixture used as a reference. As can be noticed, the XRD pattern of the precursors (ZnO and $\alpha\text{-Fe}_2\text{O}_3$) displays their characteristic Bragg peaks without measurable traces of contamination. Upon increasing t_m , a new set of diffraction peaks appears superimposed to those of the precursors. These new Bragg peaks match with those of the spinel-like structure of the ZnFe_2O_4 phase. The milling also leads to an increase of the Bragg peak linewidths; an effect that can mainly be associated with grain size reduction.

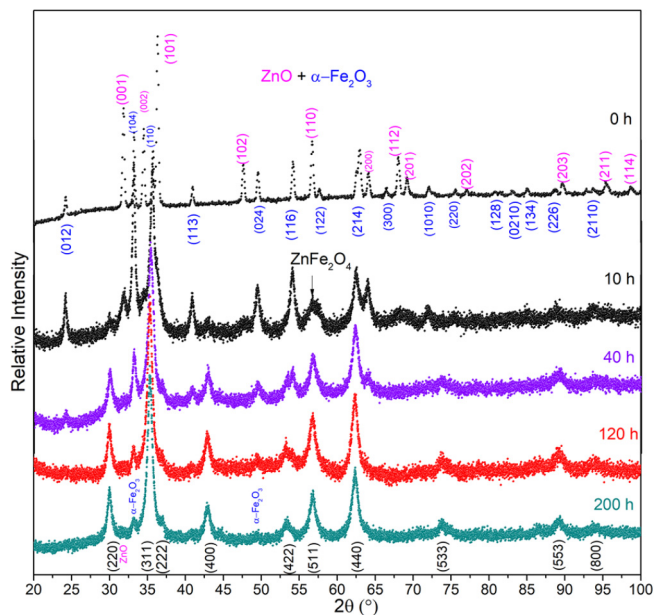


Fig. 1. XRD patterns of the ZnFe_2O_4 samples taken at different milling times (t_m are indicated in the figure). The non-milled powder mixture XRD pattern was also included.

Lattice parameters, grain sizes, internal strain and fraction of the spinel-like structure were obtained for all samples by Rietveld analysis [27]. The zinc ferrite formation can be partially understood when we analyze the area of the XRD patterns for the ferrite phase as a function of t_m , as shown in Fig. 2. It displays a nonlinear behavior, showing a rapid formation of a significant portion of ZnFe_2O_4 up to 90 h of milling. For $t_m > 90$ h, the formation rate is significantly reduced.

The lattice parameter of the ZnFe_2O_4 phase increases for the first 30 h and then remains nearly constant for longer milling times, with a value near to that of the bulk phase, as shown in Fig. 3. The grain size remains nearly constant at about 12 nm after 20 h of milling (figure not shown). Thus, we can infer that when t_m increases, the Gibbs free energy of each phase grows and it gradually favors a Solid State Reaction (SSR), which almost reaches saturation due to the dispersion of the precursor phases in the ZnFe_2O_4 matrix.

Therefore, to reduce contamination from the milling tools and also

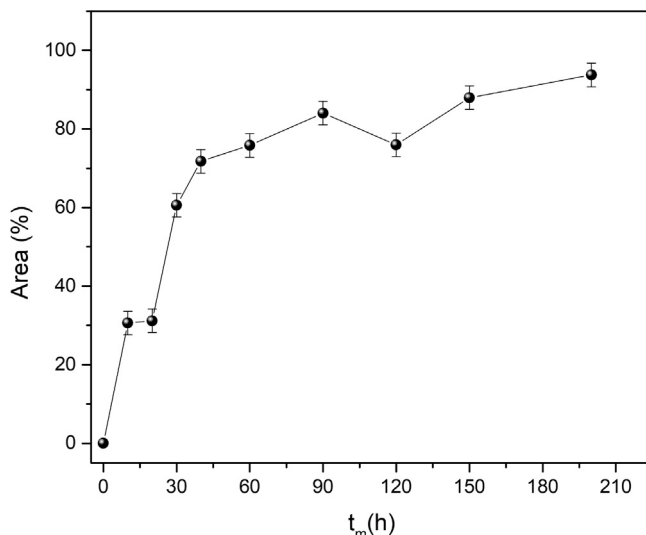


Fig. 2. Relative zinc ferrite (ZnFe_2O_4) phase area obtained from the XRD analysis as a function of milling time t_m .

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