Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 4521–4527

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Temperature induced evolution of structure/microstructure parameters and their correlations with electric/magnetic properties of nanocrystalline Nickel ferrite

Milica Vucinic-Vasic[a,*], Marko Boskovic[b], Aleksandar Antic[a], Goran Stojanovic[a], Milan Radovanovic[a], Martin Fabian[c], Cedomir Jovalekic[d], Miodrag B. Pavlovic[e], Bratislav Antic[b]

[a]Faculty of Technical Sciences, University of Novi Sad, Trg D. Obradovica 6, 21000 Novi Sad, Serbia
[b]The "Vinča" Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522, 11001 Belgrade, Serbia
[c]Institute of Geotechnics, Slovak Academy of Sciences, 043 53 Košice, Slovakia
[d]Insitute for Multidisciplinary Studies, University of Belgrade, Kneza Viseslava 1, 11001 Belgrade, Serbia
[e]Faculty of Electrical Engineering, University of Belgrade, POB 3554, 11000, Belgrade, Serbia

Received 22 May 2013; received in revised form 25 August 2013; accepted 29 August 2013
Available online 7 September 2013

Abstract

Nickel ferrite nanoparticles were annealed in order to find dependence of electric/magnetic properties on crystallite size. The following correlations of crystallite size with physical parameters were found: (a) lattice parameter decreases with the increase in size and it reaches value for bulk counterpart approximately for crystallites bigger than 7 nm, (b) ac electrical resistivity at room temperature increases with the increase in crystallite size, (c) for crystallites of ~7 nm or smaller electrical resistivity have maximum value at 50 °C, (d) the real part of permittivity at selected frequency generally decreases with the increase in crystallite size and (e) magnetization increases with the increase in crystallite size. Deviation of stoichiometry, cation polyvalence, and cation redistribution with annealing are the main factors that influence physical properties of Nickel ferrite nanoparticles.

Keywords: B. Grain size; C. Electrical properties; C. Magnetic properties; D. Ferrite

1. Introduction

For years now, ferrites in the form of nano powders and thin films have been arousing great interest in scientific community. The reason is their applicability in modern technology and the fact that they often serve as modal systems in the research of new phenomena in basic sciences. It is well known that properties of materials at nano scale depend on a number of factors such as composition, shape, size, surface morphology, anisotropy, inter-particle interactions, etc. [1]. Ferrites with spinel structure are traditionally divided into two different ideal types of structures, normal and inverse. Normal spinel ferrites are described by the formula $(M)[Fe]_2O_4$, where (M) and [Fe] represent the tetrahedral and octahedral sites occupied by metal and iron ions, respectively. Bulk $NiFe_2O_4$ has an inverse spinel structure with Ni^{2+} ions occupying half of the octahedral sites and Fe^{3+} ions occupying tetrahedral and half of the octahedral sites $(Fe)[NiFe]_2O_4$. Mixed spinel structure, with Ni^{2+} ions distributed in both tetrahedral and octahedral sites in different ratio, was found for nanocrystalline $NiFe_2O_4$ [2,3].

Electrical and magnetic properties of nanocrystalline ferrites depend on the nature of the ions, their charges and their distribution between tetrahedral and octahedral sites, as well as on microstructure parameters – predominantly on crystallite size. The main mechanism of conductivity in spinels is hopping of electrons among cations in different valence states distributed over octahedral 16d sites [4]. Stoichiometric nickel ferrite is generalized as Mott insulator modal system [5]. There are papers reporting some deviation from stoichiometry [6] and, on the other hand there are papers claiming formation of stoichiometric nanosized nickel ferrite [7]. However, it is doubtful

*Corresponding author. Tel./fax: +381 21635 0770.
E-mail address: milicavv@uns.ac.rs (M. Vucinic-Vasic).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.08.127

whether a nanosized stoichiometric nickel ferrite can be produced. It is known that the electrical properties of bulk $NiFe_2O_4$ are closely related to a small deficiency of oxygen [8]. Deviation from stoichiometry results in polyvalence of iron ions (+2, +3) which leads to a marked lowering of activation energy of conduction electrons [8], and the resistivity of nickel ferrites therefore depends on the concentration of ferrous (Fe^{2+}) ions. From magnetic point of view, properties of nanomaterials are significantly modified in comparison with the bulk counterparts. Depending on the particle size, Ni-ferrite can exhibit ferrimagnetism, superparamagnetism or paramagnetism [9,10]. Ni-ferrite nanoparticles with size above 15 nm and bulk counterpart show ferrimagnetism, while smaller nanoparticles are superparamagnetic. Paramagnetism is found in noncrystalline Ni-ferrites [9,10].

It is known that synthesis procedure determines structural and microstructural characteristics of materials. Hence, there are numerous papers oriented toward development of new procedures and the improvement of existing ones [11]. Lazarevic at al. reported soft mechanochemical synthesis of Nickel ferrite nanoparticles using hydroxides and carbonates as starting compounds [12]. One of the Nickel ferrite samples investigated by Lazarevic at al. [12] was selected and used in present research. In order to obtain samples with different crystallite size, as-prepared sample was annealed at 300, 500 and 700 °C.

The objective of this work was to determine microstructure of nickel ferrite nanoparticles by combining X-ray diffraction line broadening analysis and transmission electron microscopy method, and afterwards to find relations between microstructure and, structural, electric and magnetic properties.

2. Experimental

High energy ball milling (HEBM) was used for preparation of Nickel ferrite nanoparticles. Mixtures of crystalline powders, $Ni(OH)_2$ and $Fe(OH)_3$, were milled in air atmosphere in planetary ball mill (Fritsch Pulverisette 5). A hardened-steel vial of 500 cm^3 volume, filled with 40 hardened steel balls with a diameter of 13.4 mm, was used as the milling medium. The mass of the powder was 20 g and the balls-to-powder mass ratio was 20:1 [12]. As-prepared sample (S0) was annealed at 300, 500 and 700 °C for 3 h. The obtained samples were denoted S300, S500 and S700, according to annealing temperatures.

For the collection of the X-ray powder-diffraction (XRPD) data a Brucker D8 Advance X-ray powder diffractometer was used. The diffractometer was equipped with a Cu-tube. The generator was set-up at 40 kV and 40 mA. The divergence and receiving slits were 0.3° and 0.1 mm, respectively. The scanning range was 15–115° in 2θ, with a step of 0.05° and a scanning time of 35 s per step.

Transmission electron microscopy (TEM) images were obtained using a thermoionic 200 kV Tecnai T20 microscope operating at an accelerating voltage of 200 kV.

For electrical measurements the samples were prepared by pressing powders into tablets. A silver paste was used to connect sample with short lead copper wires in order to put the tablet into a HP-16047 A test fixture. The material was stimulated with an AC source and the actual voltage across the material was monitored. Data equivalent to the real and imaginary parts of complex electrical quantities are measured as a function of the frequency of the applied electric field by using the impedance spectroscopy technique. Impedance analyzer HP-4194A was used in the frequency range from 100 Hz to 40 MHz at three different temperatures: room temperature, 50 °C and 70 °C. A personal computer with in-house developed software tool was used for the control of the whole measurement process and for acquisition of measured data. Electrical properties reported here – resistivity, dielectric permittivity, and loss tangent were derived by knowing the geometrical dimensions of the sample tablet and by measuring its capacitance and parallel resistivity.

Magnetic measurements were performed using an MPMS XL-5 SQUID magnetometer. Magnetization vs. field, $M(H)$, was measured at room temperature up to field of 5 T. Zero-field-cooled (ZFC) and Field-cooled (FC) magnetization $M(T)$ was measured in

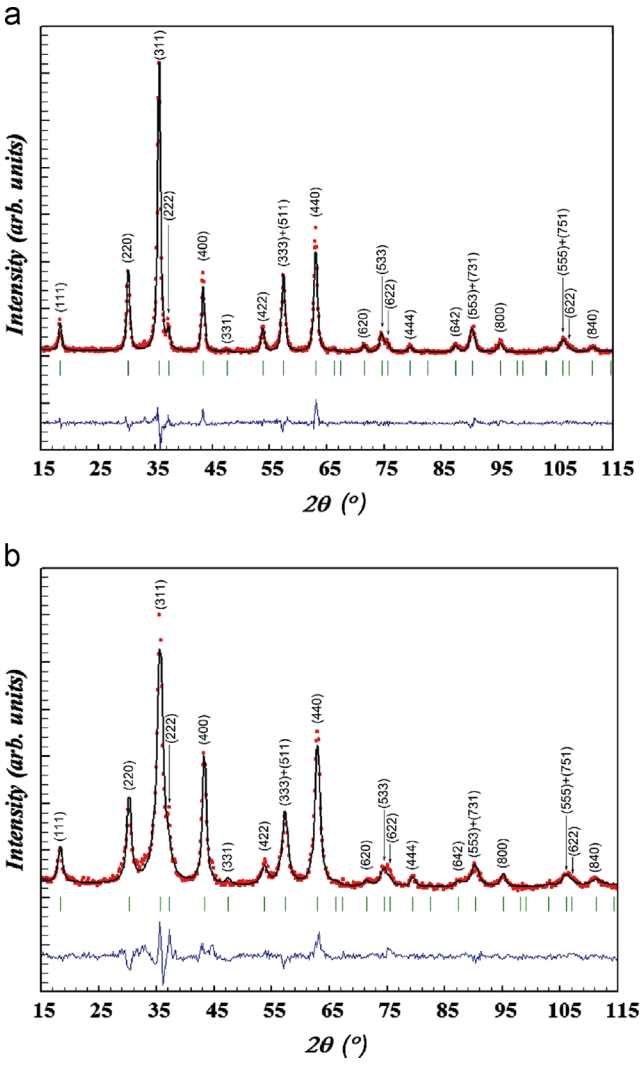

Fig. 1. Result of the Rietveld refinement for as-prepared (S0) (a) and annealed nickel ferrite (S700) (b). Dots denote observed step intensities; the line represents the corresponding calculated values. The difference curve between observed and calculated values is given at the bottom.