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Effect of Ca substitution on some physical properties of nano-structured and bulk Ni-ferrite samples

S.T. Assar*, H.F. Abosheisha

Engineering Physics and Mathematics Department, Faculty of Engineering, Tanta University, Tanta, 31521, Egypt

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ABSTRACT

Nanoparticles of $\text{Ni}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ($x=0.0, 0.02, 0.04, 0.06$ and 0.10) were prepared by citrate precursor method. A part of these samples was sintered at 600°C for 2 h in order to keep the particles within the nano-size while the other part was sintered at 1000°C to let the particles to grow to the bulk size. The effect of Ca^{2+} ion substitution in nickel ferrite on some structural, magnetic, electrical and thermal properties was investigated. All samples were characterized by using X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR) and vibrating sample magnetometer (VSM). A two probe method was used to measure the dc electrical conductivity whereas the photoacoustic (PA) technique was used to determine the thermal diffusivity of the samples. To interpret different experimental results for nano and bulk samples some cation distributions were assumed based on the VSM and XRD data. These suggested cation distributions give logical explanations for other experimental results such as the observed values of the absorption bands in FTIR spectra and the dc conductivity results. Finally, in the thermal measurements it was found that increasing the Ca^{2+} ion content causes a decrease in the thermal diffusivity of both nano and bulk samples. The explanation of this behavior is ascribed to the phonon-phonon scattering.

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1. Introduction

The synthesis and characterization of nanoparticle spinel ferrites represent intense areas of research owing to the expected large number of technological applications over a wide frequency range due to their low cost and high electromagnetic performance. Among the spinel ferrites nickel ferrites which have a reverse spinel crystal structure AB_2O_4 where A sites are occupied by Fe^{3+} ions and B sites are occupied by 1:1 Ni^{2+} and Fe^{3+} ions. The properties of nickel ferrites are greatly affected by the ratio of the constituting ions [1]. To adjust the magnetic properties, some metal ions such as Zn^{2+} [2], Mg^{2+} [3], Cd^{2+} [4], and Li^{1+} [5] may be introduced into the system. It has been currently observed from literature that substituting nonmagnetic divalent or monovalent ions in nickel ferrites may enhance some physical properties and qualify the material for a specific application e.g. to serve as high frequency magnets, transformer cores, low frequency inductors, electromagnetic shields, read/write heads, micro and radio wave absorbers, high-density data storage and biomedical applications [6].

Generally, much work on ferrites has been carried out on microcrystalline ceramics prepared by the standard ceramic technique, involving high-temperature reactions between finely milled oxide (or carbonate) powders followed by shaping and successive pressing and sintering. Such method does not allow controlling fully crystallite size and shape as well as powder properties [7] and has some limitations of obtaining fine particles of the order of nanometers. However, the self-combustion reaction is a promising method for preparation of ferrites. This technique is versatile and does not need sophisticated equipment. It is fast and safe and it enables nano-size particle formation [8].

The aim of the present work is to prepare Ni-Ca ferrite nano and bulk samples and to study the effect of varying the Ca^{2+} ion content in both kinds of samples on their properties. The authors believe that studying these properties may be useful for many promising applications.

2. Experimental

Nanocrystalline $\text{Ni}_{1-x}\text{Ca}_x\text{Fe}_2\text{O}_4$ ($x=0.0, 0.02, 0.04, 0.06$ and 0.10) particles were prepared by citrate precursor method, where, $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ were used as raw materials. All chemicals used were

* Corresponding author.

E-mail addresses: soha_talaat@yahoo.com, s_talat@f-eng.tanta.edu.eg, sohatalaat73@gmail.com (S.T. Assar).

of high grade purity. The details of the preparing method had been reported in a previous work [9]. Different measurements were performed for two groups; one group includes all of the prepared compositions sintered at 600 °C and the other group includes the same compositions sintered at 1000 °C. Moreover, all samples were pressed under a pressure of about 2.6×10^8 N/m² into pellets with 15 mm diameter and about 4 mm thickness for electrical measurements and pellets with 10 mm diameter and less than 1 mm thickness for thermal measurements.

The as-prepared and sintered samples were characterized by X-ray diffraction (XRD) BRUKER-D8 using CuK_α as a target and the incident wavelength $\lambda = 1.5406$ Å radiation. The crystallite sizes D_{311} of the sintered samples were estimated from the full-width at half maximum (FWHM) of the strongest reflection of the planes (3 1 1) using the X-ray diffractometer software program. Also, the particle sizes of only two samples having $x = 0.06$ – one sintered at 600 °C and the other at 1000 °C – were checked up using a transmission electron microscope (TEM) model JEOL JEM-1230. The magnetization measurements were carried out for the sintered samples at room temperature up to a maximum field of 20 kG, by using a vibrating sample magnetometer (VSM), model Lake Shore 7410.

The dc electrical conductivity of the samples was determined as a function of temperature by using the two-probe method. The relationship between the dc conductivity and temperature is the Arrhenius relation [10]:

$$\sigma_{dc} = \sigma_0 \exp(-E/kT) \quad (1)$$

where, σ_0 is a pre-exponential constant, E is activation energy for dc conduction, k is Boltzmann's constant $= 8.617 \times 10^{-5}$ eV K⁻¹ and T is the absolute temperature.

Moreover, the thermal diffusivity α of the sintered samples was estimated by using a home-made experimental setup based on the open photoacoustic cell (OPC) technique. The theory of the PA effect in solid samples illustrated by Rosencwaig and Gersho [11] and the construction of the experimental setup had been previously explained in details [12].

3. Results and discussion

The X-ray diffraction patterns of the samples sintered at 600 °C and 1000 °C and the as-prepared samples are shown in Fig. 1(a–c), respectively. All patterns confirm the formation of the cubic spinel structure of the desired ferrites (ICDD Card No.: 03-065-0380). The peaks become sharp and narrow with increasing the sintering temperature indicating the enhancement of crystallinity in bulk samples than in nanosamples. It can be seen that, only the nanosample of $x = 0.0$ sintered at 600 °C contains a small amount of hematite (Fe₂O₃). At such a temperature, some of the nickel ferrite may undergo oxidation forming an intermediate phase like hematite with a body centered cubic structure (BCC) which does not solve in the spinel structure according to Vladimirtseva and Soltyk [13] who had previously reported that maximum oxidation of spinel phase occurs between 600 and 800 °C. Moreover, it is worth mentioning that all the as-prepared samples contain a very small amount of a second phase of Ni₃Fe. Actually, by sintering the samples at 600 °C, the amount of this phase decreases (in the sample of $x = 0.02$) or disappears (in the other samples) and also it disappears completely in all samples sintered at 1000 °C. This indicates that the resulting heat from the exothermic reaction between oxidant and reductant is not enough to form a pure phase of spinel Ni-Ca ferrite nanoparticles. Therefore, preparing these samples may require calcination at higher temperatures to make the secondary phases (Fe₂O₃, and/or Ni₃Fe) build again into the

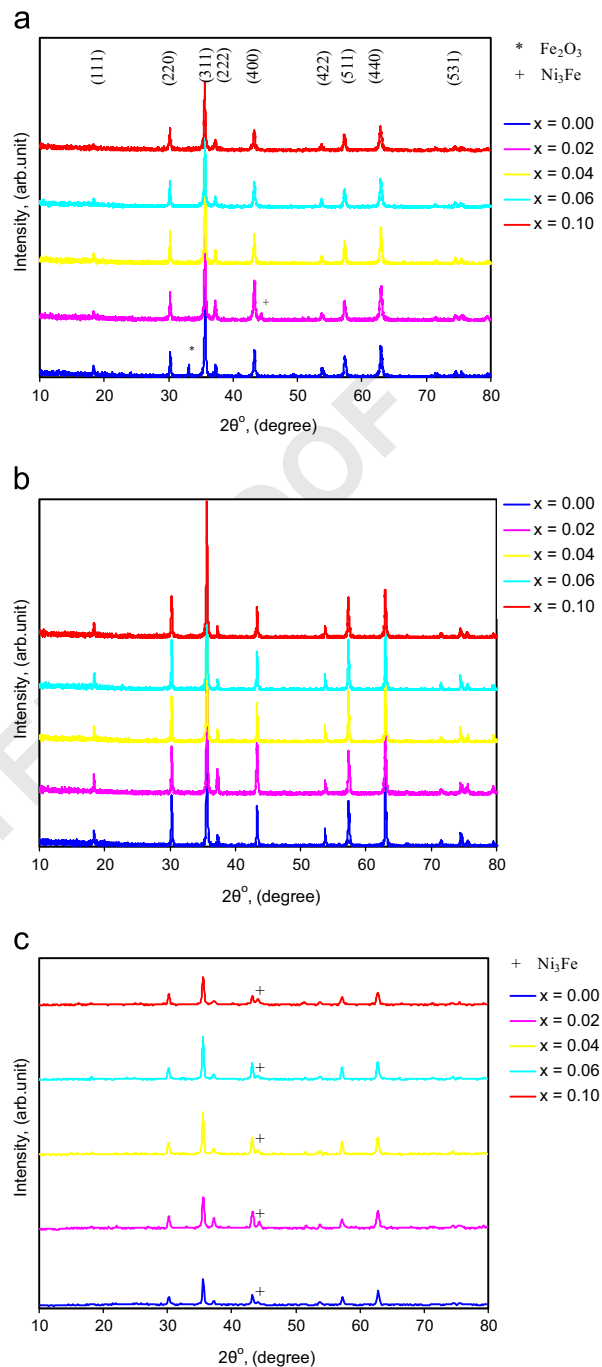


Fig. 1. XRD patterns of (a) the nanosamples sintered at 600 °C, (b) bulk samples sintered at 1000 °C, and (c) the as-prepared samples of Ni_{1-x}Ca_xFe₂O₄.

spinel structure. This behavior had been observed in a previous work [14].

The structural properties of the nanosamples and their bulk counterparts are shown in Table 1. It can be clearly seen that the lattice constant of both nano and bulk samples increases with increasing the concentration of Ca²⁺ ion simply because it has a relatively large ionic radius of (0.99 Å) compared to the other constituents (Ni²⁺ (0.78 Å), and Fe³⁺ (0.67 Å)). Also, it is observed that the lattice constant of the nanosamples is larger than their bulk counterparts. This may be due to the probability of existence of a greater amount of Fe²⁺ ions in the lattice of the nanosamples than in their bulk counterparts. The crystallite sizes of the samples sintered at 600 °C, range from 38.4 to 60.5 nm while those of the samples sintered at 1000 °C become in the bulk scale (> 100 nm)

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