Nuclear Instruments and Methods in Physics Research B 375 (2016) 71–78

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

# Positron annihilation and magnetic properties studies of copper substituted nickel ferrite nanoparticles

Z. Kargar [a,*], S.M. Asgarian [a], M. Mozaffari [b]

[a] Physics Department, College of Science, Shiraz University, Shiraz, Iran
[b] Department of Physics, Faculty of Science, University of Isfahan, Isfahan 81746-73441, Iran

ARTICLE INFO

*Article history:*
Received 6 January 2016
Received in revised form 7 March 2016
Accepted 20 March 2016
Available online 31 March 2016

*Keywords:*
Ni–Cu ferrite
Nanoparticle
Positron annihilation lifetime spectroscopy
Coincidence Doppler broadening spectroscopy

ABSTRACT

Single phase copper substituted nickel ferrite $Ni_{1-x}Cu_xFe_2O_4$ ($x = 0.0$, 0.1, 0.3 and 0.5) nanoparticles were synthesized by the sol–gel method. TEM images of the samples confirm formation of nano-sized particles. The Rietveld refinement of the X-ray diffraction patterns showed that lattice constant increase with increase in copper content from 8.331 for $x = 0.0$ to 8.355 Å in $x = 0.5$. Cation distribution of samples has been determined by the occupancy factor, using Rietveld refinement. The positron lifetime spectra of the samples were convoluted into three lifetime components. The shortest lifetime is due to the positrons that do not get trapped by the vacancy defects. The second lifetime is ascribed to annihilation of positrons in tetrahedral (A) and octahedral (B) sites in spinel structure. It is seen that for $x = 0.1$ and 0.3 samples, positron trapped within vacancies in A sites, but for $x = 0.0$ and 0.5, the positrons trapped and annihilated within occupied B sites. The longest lifetime component attributed to annihilation of positrons in the free volume between nanoparticles. The obtained results from coincidence Doppler broadening spectroscopy (CDBS) confirmed the results of positron annihilation lifetime spectroscopy (PALS) and also showed that the vacancy clusters concentration for $x = 0.3$ is more than those in other samples. Average defect density in the samples, determined from mean lifetime of annihilated positrons reflects that the vacancy concentration for $x = 0.3$ is maximum. The magnetic measurements showed that the saturation magnetization for $x = 0.3$ is maximum that can be explained by Néel's theory. The coercivity in nanoparticles increased with increase in copper content. This increase is ascribed to the change in anisotropy constant because of increase of the average defect density due to the substitution of $Cu^{2+}$ cations and magnetocrystalline anisotropy of $Cu^{2+}$ cations. Curie temperature of the samples reduces with increase in copper content which can be explained based on Néel's theory.



## 1. Introduction

Spinel ferrites are used widely in engineering and technology [1,2] because of their high resistivity and negligible eddy current loss. One of the most important class of spinel ferrites is Ni-ferrite. A high magnetic permeability and a low hysteresis loss are two very useful factors of the ferrite in many applications [1]. In the bulk form, half of $Fe^{3+}$ ions in nickel ferrite occupy tetrahedral sites and the other half and $Ni^{2+}$ ions occupy the octahedral sites. This arrangement is called the inverse spinel [3]. To improve or to change properties of the nickel ferrite, many procedures have been carried out such as the reduction of particle size to nanoscale [4] and substitution of different amount of various cations in spinel structure [5]. Substitution of nickel with various amount of copper in bulk and nanoparticle $NiFe_2O_4$ to obtain improved magnetic properties, high frequency response and high resistance has been reported in several papers [6–9]. When particle size is made to be nanosize, anomalous variation in properties of ferrites are observed [10]. Also it is found that distribution of vacant and void type defects plays role in altering the properties of nanomaterial and magnetic nanoparticles [11–13]. Hence determination of type and concentration of defects at Ni-Cu ferrite nanoparticles as well as the effect of $Cu^{2+}$ content on the distribution of defects in the Ni-ferrite can be used to investigate the change of the electronic and magnetic properties of Ni–Cu ferrite nanoparticles.

Positron annihilation spectroscopy (PAS) is a nondestructive and sensitive technique for investigation of defects, voids and vacancies in various materials. The three different experimental techniques used in positron annihilation measurements are positron annihilation lifetime spectroscopy (PALS), Doppler broadening spectroscopy (DBS) and angular correlation of annihilation

* Corresponding author.
*E-mail address:* kargar@susc.ac.ir (Z. Kargar).

http://dx.doi.org/10.1016/j.nimb.2016.03.041
0168-583X/

radiation (ACAR) [14]. Positron annihilation lifetime spectroscopy (PALS) is the most commonly used technique in positron annihilation spectroscopy for determination of type and concentration of the defects in different materials such as ceramics, polymers and metals [15–18]. Coincidence Doppler broadening spectroscopy (CDBS) measurements with two detectors (for background reduction) can be used to obtain informations about atoms surrounding the defect and the type and concentration of the open volume defects in materials [19,20].

In this research, we synthesized $Ni_{1-x}Cu_xFe_2O_4$ ($x$ = 0.0, 0.1, 0.3 and 0.5) nanoparticles by sol–gel method. The evolution of vacancy type defects due to substitution of copper ions in Ni-ferrite are studied using PAS. Then the magnetic properties of prepared samples are measured at room temperature and the effect of $Cu^{2+}$ substitution on magnetic properties are investigated. An effort has been made to find up a possible correlation between magnetic properties and the defects concentration in the prepared samples.

## 2. Experimental details

In this work copper substituted nickel ferrite $Ni_{1-x}Cu_xFe_2O_4$ ($x$ = 0.0, 0.1, 0.3 and 0.5) nanoparticles were prepared by the sol–gel method. The weighted stoichiometric amounts of $Fe(NO_3)_3.9H_2O$, $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$ (with minimum purities 99%) and $C_6H_8O_7.H_2O$ all from Merck Co. were used as starting materials. The nitrates were dissolved in distilled water individually and then the solutions were mixed. The citric acid ($C_6H_8O_7.H_2O$) was added to the nitrates solution to adjust molarity at 2. The whole solution was stirred for 30 min at room temperature on a magnetic stirrer without heating until it formed a uniform sol. Then, the sol was heated on a hot plate up to 120 °C under constant stirring to transform into a gel. The gels were dried at 100 °C in an oven for 48 h. The dried gels were ground and annealed at 300–600 °C temperatures for 2 h in the air to achieve single phase samples.

The X-ray diffraction profiles of samples were recorded using Cu K$\alpha$ radiation with Ni filter on a Bruker D8ADVANCED X-ray diffractometer that operated at 40 kV and 40 mA. The data with step size $2\theta = 0.02^\circ$ and counting time 1s for the angular range $2\theta = 16 - 90^\circ$ were recorded. X-ray data were analyzed for lattice constant and cation distribution using the Rietveld refinement method employing Material Analysis Using Diffraction (MAUD) program, 2.54 version [21]. For instrumental broadening correction, a Quartz standard was used. The average crystallite size was obtained using the Scherrer equation [22]. The morphology and size of the samples were observed by a transmission electron microscopy (TEM), Zeiss – EM10C model.

Positron annihilation lifetime spectra were recorded using a slow-fast gamma-gamma coincidence spectroscopic set-up using two identical plastic scintillator detectors fitted with photomultiplier tubes. The time resolution of this set-up measured with a $^{60}Co$ source was 250 ps at full width at half maximum (FWHM) of the spectrum. A positron source of about 15$\mu$Ci activity was prepared by depositing and drying $^{22}NaCl$ on a 7 μm thick Mylar foil and covering with identical foil. It covered from two sides with adequate amount of nanoparticles to guarantee the annihilation of all positrons within nanoparticles. More than $1.5 \times 10^6$ counts were collected for each measurement and the resulting spectra were analyzed using the Pasqual [23] programs. The lifetime of positron annihilation in source and Mylar foil were measured as 300 ps and 1500 ps with measurements on annealed defect-free Al samples and the source correction to source and Mylar foil was carried out. The spectra of all the samples were fitted with reasonable variances between 0.95 and 1.08. Coincidence Doppler broadening spectroscopy (CDBS) measurements of samples were performed with a high purity Ge (HPGe) detector (40% efficiency, with a resolution of 1.2 keV at 611.6 keV of $^{137}Cs$) and a NaI(Tl) scintillator placed in collinear geometry with the Ge detector.

Magnetic measurements were performed using a Vibrating Sample Magnetometer (VSM) at room temperature. Curie temperatures of the samples were determined using a Faraday balance that recording M-T curves in the presence of a permanent magnet.

## 3. Result and discussion

### 3.1. X-ray and Rietveld refinement studies

Fig. 1 illustrates the X-ray diffraction (XRD) patterns of the $Ni_{1-x}Cu_xFe_2O_4$ nanoparticles (where $x$ = 0.0, 0.1, 0.3 and 0.5) and the calculated profiles with MAUD programs. Also the subtracted profiles are displayed in Fig. 1. As can be seen all the samples are single phase and have spinel structure.

The Rietveld method is a powerful technique for determination of the structural details of powders from diffraction patterns [24,25]. The quality of refinement is judged by the R factors ($R_{wp}, R_b$ and $R_{exp}$) and "goodness of fit" $\sigma$. The $R_{wp}$ is the weighted-profile R value which verifies the quality of structural refinement. The final $R_{wp}$ should approach the statistically expected R value, $R_{exp}$ which represents the quality of the data or the counting statistics. The ratio between $R_{wp}$ and $R_{exp}$, $\sigma = \frac{R_{wp}}{R_{exp}}$ is defined as "goodness of fit". In the best qualified fitting, $\sigma$ should approach unity. $R_b$, the Bragg-intensity R value is used to evaluate the improvement in the structural model [26]. It is calculated based on the observed and the calculated integrated Bragg intensities. A small value of $R_b$ indicates that the model is reproducing the crystallographic observations well [27]. The various R factors are listed in Table 1. The $\sigma$ (goodness of fit) is the most important parameter for judging the quality of a Rietveld refinement [25,26,28]. This parameter is very close to unity as given in Table 1. Also, the difference between the observed and the calculated patterns is another way to judge the goodness of the Rietveld refinement [28]. As it is seen from Table 1 and Fig. 1, a very good Rietveld refinement of the X-ray diffraction patterns was achieved.

The results of the structural Rietveld refinement of the XRD patterns for all samples are listed in Table 2. Because of larger radius of copper ion (0.57 Å for A site and 0.72 Å for B site) than that of

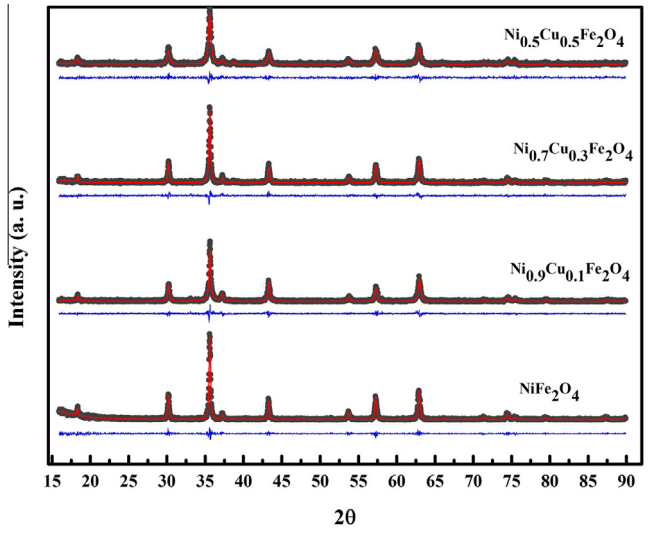


**Fig. 1.** XRD patterns of the synthesized nanoparticles (points) along with the calculated profile (solid line). The bottom lines illustrate the subtracted patterns.