Microelectronic Engineering 126 (2014) 158–164

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Fabrication and magnetic properties of electrospun $Ni_{1-x}Cu_xFe_2O_4$ nanofibers

Orapan Saensuk [a], Santi Maensiri [c], Atipong Bootchanont [c], Ekaphan Swatsitang [a,b,*]

[a] Materials Science and Nanotechnology Program, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
[b] Integrated Nanotechnology Research Center and Department of Physics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand
[c] School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

ARTICLE INFO

Article history:
Received 1 November 2013
Received in revised form 4 July 2014
Accepted 11 July 2014
Available online 18 July 2014

Keywords:
$Ni_{1-x}Cu_xFe_2O_4$
Nanofibers
Electrospinning technique
Magnetization
XANES

ABSTRACT

Nickel copper ferrite $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5) nanofibers were successfully fabricated by electrospinning technique. The obtained nanofibers were calcined at a temperature of 600 °C, with a heating and cooling rate of 1 °C/min for 3 h. Samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), X-ray absorption near edge structure (XANES) and vibrating sample magnetometer (VSM). The diameters of the as-spun nanofibers as shown by SEM images are in the range of 360.95 ± 20–511.79 ± 25 nm and reduced to 73.60 ± 15–87.52 ± 18 nm after calcination. All calcined samples have a spinel ferrite structure as revealed by XRD and TEM. Crystallite size were calculated from the XRD peaks using Scherrer's equation and found to increase from 18.46 to 30.78 nm with increasing Cu content. XANES results confirm the substitution of Cu cations on both of the octahedral and tetrahedral sites. The magnetization measurements reveal that the $Ni_{1-x}Cu_xFe_2O_4$ nanofibers exhibit soft ferromagnetic behavior with decreasing magnetization from 37.71 to 15.10 emu/g and increasing coercivity from 50.90 to 144.66 Oe as the Cu content is increased.

1. Introduction

Spinel ferrites of the general chemical formula, MFe_2O_4, (where M = Co, Ni, Mn, Mg, Zn, etc.) are widely investigated due to their wide range of applications from a simple function device such as a small permanent magnet to sophisticated electronic devices [1]. Some interesting applications of these materials are in computer peripherals, telecommunications equipment, permanent magnets, electronic and microwave devices, magnetic media used in computers, recording devices and magnetic cards. In these ferrites, the electrical and magnetic properties can be diversified by modification of their crystal structure with the replacement of Fe cations by different transition metals. Moreover, these properties depend also on the processing conditions of different preparation methods, which can yield products of different morphology and size [2].

Recently, a number of physical and chemical methods such as, mechanical milling [3], electro-deposition [4], hydrothermal reaction [5], oxidative precipitation [6], sol–gel [7], and electrospinning [8–10] have been attempted to produce nano-size ferrites.

Among these ferrites, pure and doped Ni-ferrites, $Ni_{1-x}M_xFe_2O_4$ (M = Co, Mn, Mg, Cu, Zn and etc.) with inverse spinel structure have been intensively studied due to their capability for use in electronic devices because of their large permeability at high frequency, very low magnetocrystalline anisotropy, remarkably high electrical resistivity, low eddy current and dielectric losses, mechanical hardness, chemical stability and cost effectiveness [11–13]. For example, Co-Ni ferrites are suitable for high-frequency electronic device applications in the telecommunications field [12]. Other than these, pure and doped Cu-ferrites, $Cu_{1-x}M_xFe_2O_4$ (M = Co, Mn, Mg, Ni, Zn and etc.) of a cubic form are of interest to researchers due to being stable at temperature higher than 400 °C [14] and having been found useful as a catalyst for environment measurements, gas sensors, and hydrogen production [15]. The interest in the study of these ferrites, especially $Ni_{1-x}Cu_xFe_2O_4$, has increased, as can be seen from the vast increase in reports distributed by many research groups [16–20]. Hoquea et al. [16] reported the investigation of the crystal structure, porosity and compressive strength of $Ni_{1-x}Cu_xFe_2O_4$ along with scanning electron microscopy (SEM) in order to study the effect of composition and microstructure on the magnetic properties, and the initial

* Corresponding author at: Materials Science and Nanotechnology Program, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand. Tel.: +66 43 203166; fax: +66 43 202374.
E-mail address: ekaphan@kku.ac.th (E. Swatsitang).

http://dx.doi.org/10.1016/j.mee.2014.07.010
0167-9317/

magnetic permeability and saturation magnetization were found to be maximal for a composition of $x = 0.2$. Doha et al. [17] reported the preparation of $Ni_{1-x}Cu_xFe_2O_4$ nanopowders using the coprecipitation method with ultrasound irradiation. In their study, a single phase of $Ni_{1-x}Cu_xFe_2O_4$ nanopowders was obtained with grain sizes between 20 and 30 nm. The maximum value of saturation magnetization was obtained for $x = 0.5$. Azadmanjiri et al. [18] reported the synthesis of $Ni_{1-x}Cu_xFe_2O_4$ nanopowders using the sol–gel auto-combustion method. The phase purity of the samples was checked by XRD and IR spectroscopy. Msomi and Moyo [19] studied the magnetic properties of $Ni_{1-x}Cu_xFe_2O_4$, prepared by the usual ceramic method using VSM technique. A single phase formation of the compound was confirmed by XRD. The coercive field (H_c) was found to increase with the reduction in grain size. Patil and Chougule [20] synthesized $Ni_{1-x}Cu_xFe_2O_4$ using the standard ceramic method. The XRD results confirmed the formation of a cubic single-phase ferrite. The Cu content was found to have a significant influence on the electromagnetic properties.

However, the synthesis of $Ni_{1-x}Cu_xFe_2O_4$ in nanofibrous form has not yet been studied, so it is of interest to investigate the properties of this material, because one dimensional nanofibers have unique properties such as a high aspect ratio which can result in a high permeability compared to their bulk counterparts of the same volume and have a higher ferromagnetic resonance frequency due to their shape anisotropy [21,22]. In addition, the nanofibrous form of ferrite materials can enhance high density magnetic recording [23]. Moreover, the porous nature and high surface area of nanofibers have advantages over nanoparticles as, for example, an anode of a Li-ion battery made of $NiFe_2O_4$ nanofibers can assist the electrochemical reaction since electrolyte can easily access into the anode and the empty space of pores can accommodate the volume change during the conversion reaction, resulting in a high discharge capacity [24].

The aim of this work was to prepare $Ni_{1-x}Cu_xFe_2O_4$ ($x = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.5) nanofibers by electrospinning technique using metal nitrates of Ni, Cu and Fe as starting materials. This technique is employed due to its simplicity; the obtained fibers have large surface-to-volume ratio, dimensional stability, and good crystalline orientation which will promote the enhancement of the magnetic properties [25,26]. The introduction of Cu^{2+} ions into the structure of $NiFe_2O_4$ is expected to modify its structural and magnetic properties. All prepared samples were characterized using SEM, FT-IR, XRD, TEM, XAS and VSM. In order to confirm the oxidation state of Ni, Cu, and Fe ions, the absorption XANES K-edge spectra of Ni, Cu, and Fe are also simulated using the FEFF 8.2 program.

2. Experimental

The preparation of $Ni_{1-x}Cu_xFe_2O_4$ ($x = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.5) nanofibers is similar to the process described in our previous works [8–10]. In a typical procedure, 5.565 g of polyvinyl pyrrolidone (PVP, $(C_6H_9NO)_x$ Mw ≈ 1,300,000, Aldrich) was dissolved in a mixture of ethanol (50 ml), followed by magnetic stirring for 3 h to ensure the dissolution of PVP. A metal nitrate solution was prepared by dissolving $Ni(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}2.5H_2O$, and $Fe(NO_3)_3{\cdot}9H_2O$ (with $1-x{:}x{:}2$ molar ratios) in 10 ml of Dimethylformamide (DMF) followed by continuous magnetic stirring for 3 h. Subsequently, 4 ml of the metal nitrate solution was slowly added into the PVP solution under magnetic stirring at room temperature for 10 h to obtain a well-dissolved solution. This solution was used for electrospinning. The solution was loaded into a plastic syringe equipped with a 22-gauge needle made of stainless steel.

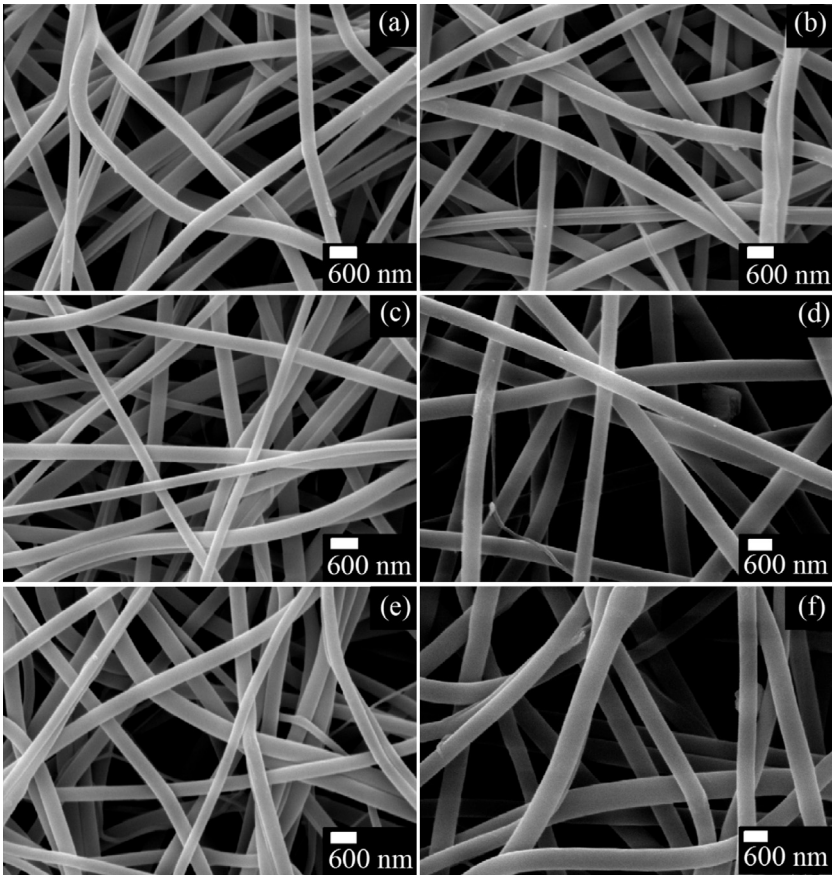

Fig. 1. SEM images of as-spun $Ni_{1-x}Cu_xFe_2O_4$ nanofibers, (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$ and (f) $x = 0.5$.