Journal of Magnetism and Magnetic Materials 391 (2015) 108–115

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Cr-substituted Ni–Zn ferrites via oxalate decomposition. Structural, electrical and magnetic properties

M.A. Gabal [a,*,1], Y.M. Al Angari [a], F.A. Al-Agel [b]

[a] Chemistry department, Faculty of Science, King Abdulaziz University, Jeddah, KSA
[b] Physics department, Faculty of Science, King Abdulaziz University, Jeddah, KSA

ARTICLE INFO

Article history:
Received 22 February 2015
Received in revised form
23 April 2015
Accepted 24 April 2015
Available online 29 April 2015

Keywords:
Cr-substitution
NiZn ferrite
Susceptibility
Hysteresis
Conductivity

ABSTRACT

A series of Cr-substituted Ni–Zn ferrites; $Ni_{0.8}Zn_{0.2}Cr_xFe_{2-x}O_4$ (x=0.0–1.0) were prepared via oxalate decomposition route to characterize the effect of Cr-substitution on structural, magnetic and electrical properties. The prepared powders were characterized using X-ray diffraction (XRD), Fourier transform infrared (FT-IR) and transmission electron microscopy (TEM). XRD indicated single-phase cubic ferrites. The lattice parameters (a_{Exp}) exhibited a gradual decrease with increasing chromium, attributed to the smaller ionic radii of Cr^{3+} substituent. According to the obtained structural data, an appropriate cation distribution was suggested and fortified through FT-IR spectroscopy besides magnetic and electrical measurements. TEM image showed agglomerated cubic crystals with an average size of about 20 nm. Vibrating sample magnetometer (VSM) measurements indicated minimal hysteresis characteristic for soft magnetic material. The decrease in saturation magnetization (M_s) with Cr-substitution was discussed in view of Neel's two sub-lattice model. The change in the coercivity with Cr-content was discussed in view of estimated cation distribution and magnetization values. The obvious fall in the Curie temperature, estimated from molar susceptibility measurements, with increasing Cr-concentrations was assigned to the gradual replacement of Fe^{3+} ions on the octahedral sites by paramagnetic Cr^{3+} ions. ac-conductivity as a function of both frequency and absolute temperature exhibited a semi-conducting behavior. The decrease in conductivity with increasing Cr-content was attributed to the preferential occupation of Cr^{3+} ions by octahedral sites which replacing Fe^{3+} ions and limiting Fe^{2+}–Fe^{3+} conduction.

1. Introduction

Ni–Zn ferrites are soft ferrimagnetic ceramic materials with superior many technological applications due to their high permeability at high frequency, remarkably high-electrical resistivity, low-eddy current loss, and reasonable cost [1,2]. They are commonly used in high frequency transformer cores and inductors, microwave devices, radars, antenna rods, high-speed digital tape or disk recording, etc. [3].

Ni–Zn ferrite is a well-known mixed inverse spinel with unit cell consisting of eight formula units of the form: $(Zn_xFe_{1-x})[Ni_{1-x}Fe_{1+x}]O_4$ [4]. The intrinsic magnetization of the system is thus depending on the inverse and normal phase, i.e., the distribution of cations in the spinel lattice. The cationic substitution induces changes in the structure and texture of the crystal, resulting in significant modifications in the magnetic and electrical properties [5]. The understanding of these changes provides information on which the reliable formulation of ferrites suitable for specific applications can be based.

Few researchers have been reported on the effect of paramagnetic substitution with Cr^{3+} ions on the electromagnetic properties of Ni–Zn ferrites. El-Sayed [6] studied the effect of Cr-substitution in NiZn ferrite on the structure, density, porosity, shrinkage and grain size. The results showed a decreasing trend with increasing Cr-content.

El-Sayed [5] also explained the electrical conductivity of these ferrites in terms of their cation distribution and revealed the predominance of the hopping conduction mechanism.

Costa et al. [3] studied the effect of Cr^{3+} on the morphological and magnetic properties of Ni–Zn ferrites produced by the combustion reaction. The obtained ferrites, with an average crystallite sizes between 21 and 26 nm, exhibited saturation magnetizations in the range of 43–53 emu/g, which showed a gradual decrease with increasing Cr.

Birajdar et al. [7] prepared Cr-substituted Ni–Zn ferrites with

---

[*] Corresponding author.
E-mail address: mgabalabdonada@yahoo.com (M.A. Gabal).
[1] Permanent address: Chemistry Department, Faculty of Science, Benha University, Benha, Egypt.

http://dx.doi.org/10.1016/j.jmmm.2015.04.115
0304-8853/

the formula $Ni_{0.7}Zn_{0.3}Cr_xFe_{2-x}O_4$ ($x=0.0$–0.5) via sol–gel auto-combustion method. The results showed that the bulk density and crystallite size decrease with increasing chromium content whereas porosity and coercivity increase.

The processing methods are known also to affect the different properties of ferrites as they can result in different cation distributions or sizes. Many methods were developed for preparing ferrites [8–11]. To the best of our knowledge, there is no reported results on the preparation of Cr-substituted Ni–Zn ferrites through the thermal decomposition reaction of their respective oxalates.

Devising methods to organize functional magnetic nanostructures for the quest of magnetic materials leads to the production of different properties [12]. In the present study, we will report on the preparation of $Ni_{0.8}Zn_{0.2}Cr_xFe_{2-x}O_4$ ferrites ($x=0.0$–1.0) via oxalate decomposition process. The decomposition route and ferrites formation will be followed using differential thermal analysis-thermogravimetry techniques (DTA-TG). The prepared ferrites will be characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and transmission electron microscopy (TEM) measurements. The magnetic properties will be measured through vibrating sample magnetometer (VSM) and DC-magnetic susceptibility (as a function of magnetic field strength and temperature) measurements. In addition, the electrical properties as a function of frequency and temperature will be also measured. The effect of Cr-substitution and the entire processing method on the structural, magnetic and electrical properties of Ni–Zn ferrites will be estimated and discussed.

2. Experimental procedures

Cr-substituted Ni–Zn nano-crystalline ferrites with a general formula $Ni_{0.8}Zn_{0.2}Cr_xFe_{2-x}O_4$ ferrites ($x=0.0$–1.0) were synthesized by impregnation technique [13–15]. All chemicals were analytical grade and used without any further purification. In a typical experiment, the nickel nitrate $Ni(NO_3)_2\cdot 6H_2O$, zinc nitrate $Zn(NO_3)_2\cdot 6H_2O$, ferric nitrate $Fe(NO_3)_3\cdot 9H_2O$, chromium oxide; Cr_2O_3 and oxalic acid; $H_2C_2O_4\cdot 2H_2O$ were used as starting materials. The respective metal oxalates were prepared through precipitation method in which oxalic acid solution was added under vigorous stirring to metal nitrate solution and the obtained precipitate was collected by filtration followed by drying in oven at 100 °C.

For the preparation of the precursors, stoichiometric ratios of metal oxalates were mixed thoroughly in a mortar using water drops to ensure homogeneity. The obtained dry precursors were calcined in an electric furnace at 1000 °C for 2 h and the obtained powders were stored in a desiccator.

Thermogravimetric (TG) and differential thermal analysis (DTA) of the dried precursor was carried out using Perkin Elmer STA 6000 thermal analyzer up to 1000 °C at a heating rate of 5 °C min^{-1} in air atmosphere.

Structural characterization was carried out on a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (step time 8 s; step size 0.02 °; $2\theta=10$–70 °). The average particle size was calculated using the most intense peak (311) applying the Scherrer formula [14].

FT-IR spectra in the range 300–700 cm^{-1} were recorded using a JASCO FT-IR 310 spectrometer. The powders were mixed with spectral grade KBr as the standard.

TEM studies were carried out using Jeol (JEM-1011 electron microscopy) operated at 100 kV.

Magnetic measurements were performed using the vibrating sample magnetometer (VSM; 9600-1 LDJ, USA) with a maximum applied field of 5 kOe at room temperature.

Dc-magnetic susceptibility were measured using Faraday's method [14]. The measurements were performed as a function of temperature from room temperature up to 800 K and different magnetic field intensities (660, 1010, 1340 and 1660 Oe).

The electrical measurements, viz. ac-conductivity and dielectric measurements were carried out on a Hioki LCR high tester 3531 (Japan) using the two-probe method. The samples in a powdered form were compressed to pellets of 1 cm diameter and about 1 mm thickness using a pressure of 2 t cm^{-2}. The two surfaces were polished and coated with silver paint. The temperature was raised up to 823 K and the frequency was changed in the range (100 Hz–5 MHz).

3. Results and discussion

3.1. Thermal decomposition process and ferrite formation

The thermal decomposition behavior of the oxalate precursor in air, with $x=0.2$ as a representative study, was followed up to ferrite formation. Fig. 1 exhibits the simultaneous DTA-TG curves up to 1000 °C. From the figure, it is clear that the weight loss starts at 123 °C with the release of 1.5% up to 140 °C attributed to the loss of 0.4 water molecules (experimentally calculated = 1.4%). The second weight loss step sets on 165 °C with a steep slope up to 207 °C, exhibiting a weight loss of 17.2% agreed well with the theoretically calculated loss due to the release of remaining water molecules from the precursor. Two endothermic DTA peaks with peaks temperatures at 133 and 189 °C are characterizing these two dehydration steps.

The decomposition process of the formed anhydrous precursor is followed immediately after the dehydration process showing three well-defined TG steps up to 385 °C. These steps are attributed, according to the obtained weight losses and decomposition ranges to the decomposition of ferrous, nickel and zinc oxalates content, respectively [13]. The weight loss of the first step up to about 280 °C amounts to 20.5% agreed well with the theoretically calculated of 20.4% attributed to the decomposition of ferrous oxalate content into iron(III) oxide. The very sharp exothermic DTA peak at 232 °C characterizes well this oxidative decomposition process.

The nickel oxalate content of the precursor decomposed exothermically in the following step showing 11.6% weight loss assigned to the formation of NiO (calculated weight loss = 11.5%). The accompanying exothermic DTA peak at 332 °C is attributed to the oxidation of nickel metal decomposition product [16].

In the last weight loss step, amounts to 2.9%, the zinc oxalate content decomposed to ZnO with the release of CO and CO_2. The closely corresponding exothermic DTA peak at 347 °C is due to the oxidation of CO byproduct to CO_2 [16].

After the complete decomposition of the oxalates content the

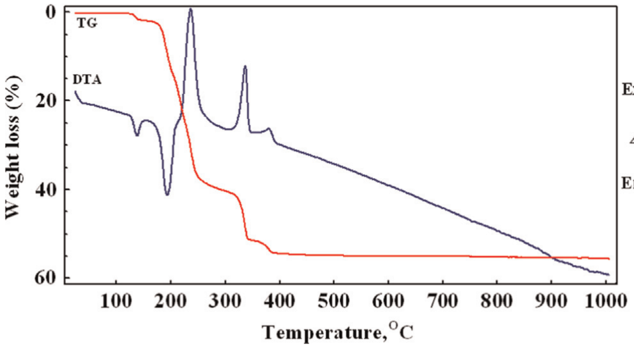

Fig. 1. DTA-TG curves in air of precursor with Cr-content of 0.2. Heating rate = 5 °C min^{-1}.