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Substitution effect on structural, electrical and magnetic properties of $NiFe_{2-2x}Al_xCr_xO_4$ ($x = 0–0.6$) nano-crystalline ferrites via oxalate precursor route

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ABSTRACT

This manuscript reports on the structural, magnetic and electrical properties of Al–Cr co-substituted nickel ferrites; $NiAl_xCr_xFe_{2-2x}O_4$ ($0.0 \le x \le 0.6$), synthesized via oxalate decomposition route. The decomposition process was monitored using DTA-TG techniques, and the obtained ferrites were characterized using XRD, FT-IR, VSM, AC-magnetic susceptibility and electrical properties measurements. The single-phase structure was confirmed using XRD and FT-IR spectroscopic measurements. With increasing Al–Cr substitution, the obtained saturation magnetizations, via VSM measurements, showed a gradual decrease while coercivity exhibited a steady increase. The electrical properties as a function of temperature and frequency showed a semiconducting behavior with conductivity decreasing by increasing substitution, which enhances the use of these materials in microwave devices applications.

1. Introduction

The interest of scientists and researchers toward ferrites materials with spinel structure arises from the interesting theoretical as well as technological applications in many fields, such as satellite communication, memory devices, computer components, antenna rod, transformers, etc. [1].

$NiFe_2O_4$ is an inverse spinel ferrite taken to be collinear ferrimagnet [2], where degree of inversion depends on the cooling rate and heat treatment. It has been the subject of many investigations under different treatment [3–5].

The effect of Cr-substitution in $NiFe_2O_4$ has received a lot of attention. Fayek and Ata Allah [6] reported that Cr^{3+} content occupy the octahedral sites for a maximum of $x = 0.6$, and the excess Cr^{3+} replaces the Fe^{3+} at the tetrahedral site. Mössbauer measurements [7] showed well-resolved magnetic spectra for the tetrahedral and octahedral sites, which suggest that as Cr substitution increases, the system slowly converted into a normal spinel structure. Singh et al. [8] synthesized spinel-type ternary ferrites with composition $NiFe_{2-x}Cr_xO_4$ ($0 \le x \le 1$) by a precipitation method. The samples were characterized using IR, XRD, BET surface area, and XPS techniques. Singhal et al. [9] have investigated the cation distribution in chromium substituted nickel ferrites, prepared by aerosol route, using XRD, magnetic and Mössbauer spectral studies. Chromium-substituted nickel ferrites synthesized through oxalate precursors [10] showed a decrease in the magnetic properties with increasing Cr content.

In Al-containing ferrites, aluminum ions are preferred to occupy both tetrahedral (A) and octahedral [B] sites depending on the amount of Al, which will affect the amount of iron ions in the two sites [1]. $NiFe_{2-x}Al_xO_4$ ferrites were prepared by the conventional ceramic method and were characterized by X-ray diffraction, scanning electron microscopy, and magnetic measurements [11]. Nano-crystalline Al-doped nickel ferrites have been synthesized by sol–gel auto-ignition method, and the effect of magnetic dilution on the structural and magnetic properties has been studied [12]. The structural and electrical properties of $NiFe_{2-x}Al_xO_4$, synthesized through co-precipitation method, were discussed as a function of Al substitution [1].

In the literature, there are very few works dealing with Al and Cr co-substituted $NiFe_2O_4$. Chhaya et al. [13] studied crystal structure and the magnetic properties of the mixed spinel $NiAl_xCr_xFe_{2-2x}O_4$ ($x = 0.0–0.9$) using XRD, Mössbauer spectroscopy and magnetic susceptibility measurements.

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Polycrystalline Al and Cr co-substituted disordered spinel series $NiAl_xCr_xFe_{2-2x}O_4$ ($0.1 \le x \le 0.9$) were prepared through solid-state method and studied by XRD, magnetization and electrical resistivity measurements [14].

The aim of the present study is to prepare single-phase nano-crystalline $NiAl_xCr_xFe_{2-2x}O_4$ ferrites ($0.0 \le x \le 0.6$) through the thermal decomposition of their corresponding metal oxalates. The oxalate decomposition reaction was followed using thermal analysis techniques (DTA-TG). The structural characterization was investigated using XRD and FT-IR techniques. The magnetic properties were measured using vibrating sample magnetometer (VSM) and DC-magnetic susceptibility techniques. The electrical properties as a function of temperature and frequency were also characterized. The effect of the magnetic dilution on the electrical and magnetic properties was discussed. To the best of our knowledge, no systematic investigations of the structural, magnetic and electrical properties of Al and Cr co-substitution of $NiFe_2O_4$ are reported in the literature. In addition, the entire preparation method seems to be novel for the preparation of these types of ferrites.

2. Experimental

2.1. Synthesis of ferrites

Nano-crystalline ferrites of the general formula $NiAl_xCr_xFe_{2-2x}O_4$ ($0.0 \le x \le 0.6$) were synthesized through thermal decomposition process. AR grade $FeSO_4{\cdot}7H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ and $H_2C_2O_4{\cdot}2H_2O$ were used as supplied for the preparation of individual metal oxalates; $FeC_2O_4{\cdot}2H_2O$ and $NiC_2O_4{\cdot}2H_2O$ through coprecipitation method [15]. The impregnation technique, previously described [16,17], was then used for the preparation of ferrites precursors. In this process, stoichiometric amounts of metal oxalates along with Al_2O_3 and Cr_2O_3 are weighed and thoroughly mixed in a porcelain mortar using drops of bi-distilled water. After drying the wet precursors in an electrical oven, they were annealed in a muffle furnace at 1000 °C for 2 h under static air atmosphere.

2.2. Techniques

Differential thermal analysis-thermogravimetry (DTA-TG) measurements were investigated in air atmosphere using a Shimadzu DT-60 thermal analyzer. The experiments were carried out at a heating rate of 5 °C min^{-1} up to 1000 °C.

The powder X-ray diffraction (XRD) analysis of the calcined precursors were conducted at room temperature using a D8 Advanced diffractometer, Bruker AXS, using Cu Kα1 radiation (λ = 0.15406 nm).

FT-IR spectra were measured in the range of 1000–200 cm^{-1} using a Jasco FTIR 310 spectrometer.

The hysteresis measurements at room temperature were performed using a vibrating sample magnetometer (VSM-9600M) with a maximum applied field of 5 kOe.

The DC-magnetic susceptibility measurements were carried out using Faraday's method [10,16]. The measurements were performed up to 850 K as a function of different magnetic field intensities (1010, 1340 and 1660 Oe).

The temperature dependence of electrical properties as a function of frequency (100 Hz–5 MHz) was measured by a Hioki 3531 LCR bridge using the two-probe method [10]. The samples were palletized, and the two surfaces of each pellet (1 cm in diameter and about 1 mm in thickness) are polished, coated with silver paste and checked for good conduction. A K-type thermocouple was used to measure the sample temperature with accuracy better than ±1 °C.

3. Results and discussion

3.1. Precursor decomposition and ferrite formation processes

The thermal decomposition process of the entire precursors, up to ferrite formation, was monitored in air using DTA-TG measurements. Typical DTA-TG curves of the precursor with $x = 0.2$ at heating rate of 5 °C min^{-1} are shown in Fig. 1. From the figure, it is clear that the decomposition proceeds through three defined steps giving a total weight loss of 54.4% at 343 °C. According to the accompanied DTA peaks behavior, the first step can be attributed to the dehydration of the precursor contents whereas the following steps can be assigned to the decomposition of the oxalate contents. The dehydration step showed an experimental weight loss of 19.0% agrees well with the theoretically calculated one of 18.9% attributed to the loss of 5.2 water molecules from nickel and iron oxalate contents. Two endothermic DTA peaks are found to characterize this dehydration process. According to the obtained endothermicity, these peaks at 162 and 189 °C can be assigned to the loss of water content from nickel oxalate and iron oxalate, respectively. The second step follows immediately after the dehydration step, showing a weight loss of 20.9% at 255 °C. This weight loss agrees well with calculated weight loss of 20.7% attributed to the decomposition of ferrous oxalate content into Fe_2O_3. This oxidative decomposition reaction is accompanied by a sharp exothermic DTA peak at 231 °C due to the oxidation of ferrous oxalate in the oxidizing atmosphere which is followed, immediately by the oxidation of the decomposition products with the evolution of CO_2 [15]. The decomposition products are thermally stable up to 310 °C and then decomposed exothermically in the third step with a weight loss of 14.6%. This weight loss can be assigned to the decomposition of nickel oxalate content into NiO with the oxidation of the decomposition products into CO_2 [18] (calc. weight loss = 14.5%). The DTA curve exhibits a sharp exothermic peak at 334 °C, due to oxidative decomposition of nickel oxalate, followed by another weak broad exothermic one, which can be attributed to the oxidation of the residual CO. At this stage, only oxides due to iron(III), Ni(II), Al(III) and Cr(III) are only present and no further weight loss change can be observed up to 1100 °C. The broad endothermic DTA peak starting at 1000 °C can be assigned to the beginning of the ferrite formation [10]. Accordingly, this temperature can be taken as the minimum calcination temperature for ferrites formation.

3.2. Structural properties

3.2.1. X-ray diffraction

X-ray diffraction patterns of calcined precursors at 1000 °C are shown in Fig. 2. Analysis of these patterns confirms the complete formation of spinel cubic structure with plains reflections of (1 1 1),

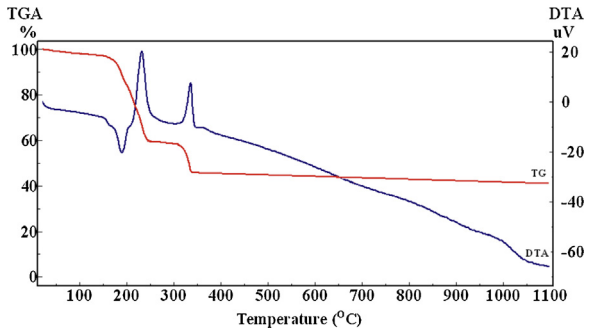

Fig. 1. DTA-TG curves in air of precursor with Al–Cr content of 0.2. Heating rate = 5 °C min^{-1}.