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Influence of Cr³⁺ substitution on the electrical and magnetic properties of Ni_{0.4}Cu_{0.4}Zn_{0.2}Fe₂O₄ nanoparticles

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Abstract

The Ni_{0.4}Cu_{0.2}Zn_{0.4} ferrites with different concentrations of Cr³⁺ were synthesized at a low temperature (450°C) using sol-gel auto-combustion method. The X-ray diffraction analysis of the samples confirms the formation of a single-phase cubic spinel structure. The lattice constant decreases from 8.331 to 8.253 Å with an increase in Cr³⁺ substitution. Bulk density decreases from 4.95 to 4.71 gm/cm³ whereas porosity increases from 9.34% to 14.76% with an increase in Cr³⁺ substitution. Transmission electron microscopy was adopted to determine the particle size. Particle size decreases from 19 to 13 nm with the addition of Cr³⁺ ions. Saturation magnetization, coercivity, and other hysteresis parameters were measured using a vibrating sample magnetometer at room temperature with a maximum magnetic field of 8 kOe. Magnetization decreases from 62 to 48 emu/g, whereas coercivity increases from 65 to 180 Oe. The direct current (DC) resistivity increases from 3.62 × 10⁶ to 4.21 × 10⁶ Ω cm with Cr³⁺ content x. The dielectric constant (ε') decreases with increasing concentration of Cr³⁺ ions.

Keywords: Ferrite nanoparticles, Electrical properties, Magnetic properties

Background

Nanoferrite materials eclipse, captivating properties that are analogous to or preferential to those of their bulk counterparts, as they demonstrate extraordinary magnetic properties such as single-domain behavior, superparamagnetism, and diminished magnetization. Ni-Cu-Zn comes under the umbrella of soft ferrites and is chemically symbolized by MFe₂O₄. For the sake of sharp perusal and to exploit the potential and possibilities associated with nanomaterials, the main aim is to invent well-defined, monodisperse structures of predictable mensuration, superiority, and morphology through an ingenious synthesis. Ni-Cu-Zn ferrites are well-established soft magnetic materials for multilayer chip inductor (MLCI) applications because of their high electrical resistivity, hard mechanical properties, high Curie temperature, and environmental stability. Recently, studies have been carried out on the Ni-Cu-Zn ferrite nanoparticles [1,2] though no studies of Cr³⁺

substitution in the Ni-Cu-Zn ferrite are reported. The present work is focused on the Cr³⁺ substitution in the Ni-Cu-Zn ferrite to check their modified properties for MLCI application. In this paper, we have reported our results of Cr³⁺ substitution in Ni-Cu-Zn ferrite nanoparticles with the chemical formula Ni_{0.4}Cu_{0.4}Zn_{0.2}Cr_xFe_{2-x}O₄ (x = 0.0 to 1.0 in steps of 0.25). The samples were synthesized at a low temperature using sol-gel method.

Methods

The powders were synthesized using the sol-gel auto-combustion method. AR grade citric acid (C₆H₈O₇·H₂O), nickel nitrate (Ni(NO₃)₂·6H₂O), copper nitrate (Cu(NO₃)₂·3H₂O), zinc nitrate (Zn(NO₃)₂·6H₂O), chromium nitrate (Cr(NO₃)₃·9H₂O), and iron nitrate (Fe(NO₃)₃·9H₂O) were dissolved in distilled water to obtain a mixed solution. The molar ratio of metal nitrates to citric acid was 1:3. The prepared powders of all the samples were annealed at 450°C for 4 h to obtain the final product. The detailed synthesis process was discussed in our earlier publications [3,4]. X-ray diffraction patterns of the samples were examined using a Philips X-ray diffractometer (model 3710; PANalytical B.V., Almelo, The Netherlands) with

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CuK α radiation ($\lambda = 1.5405 \text{ \AA}$). The magnetic measurements were performed at room temperature using a commercial PARC EG&G VSM 4500 vibrating sample magnetometer (Princeton Applied Research Corporation, Oak Ridge, TN, USA). The magnetic hysteresis loops were measured at room temperature with maximum applied magnetic fields of 0.8 T. Particle sizes were estimated by transmission electron microscopy (TEM). Direct current (DC) resistivity of all samples was measured using a two-probe method. The dielectric constant (ϵ') was measured as a function of frequency using a LCR-Q meter (model Hioki 3532-50, Hioki, Cranbury, NJ, USA).

Results and discussion

The X-ray diffraction (XRD) patterns of the $\text{Ni}_{0.4}\text{Cu}_{0.4}\text{Zn}_{0.2}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ spinel ferrite system with $x = 0.0$ to 1.0 in steps of 0.2 are shown in Figure 1. All of the Bragg peaks of the XRD patterns are broad and do not contain any extra peaks other than the cubic spinel phase. The X-ray diffraction analysis of these samples reveals the formation of a single-phase cubic spinel structure.

The lattice constant values were obtained for every sample using XRD data with an accuracy of $\pm 0.002 \text{ \AA}$ and are listed in Table 1. The decrease in the lattice constant is related to the difference in the ionic radii of Fe^{3+} and Cr^{3+} . In the present ferrite system, Fe^{3+} ions (0.67 \AA) are replaced by the relatively small Cr^{3+} ions (0.64 \AA). It can be seen from Table 1 that the X-ray density increases with increasing Cr content. The variation of the X-ray density with x is opposite to that of the lattice constant with x because the X-ray density is inversely proportional to the lattice constant. Further, the

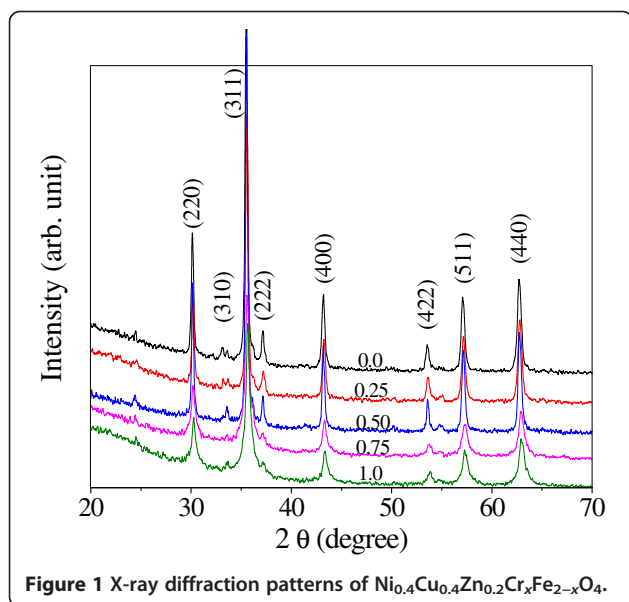
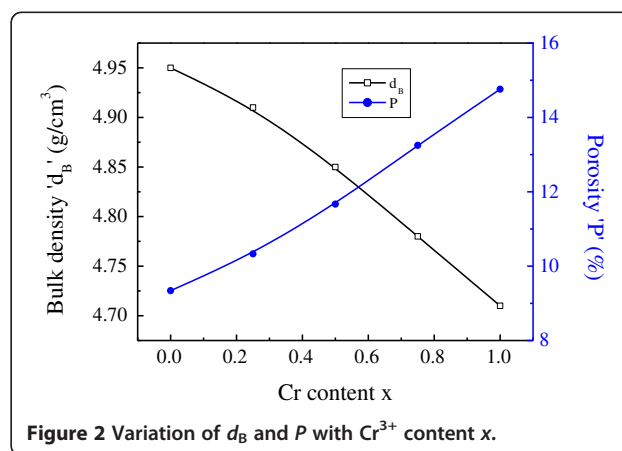
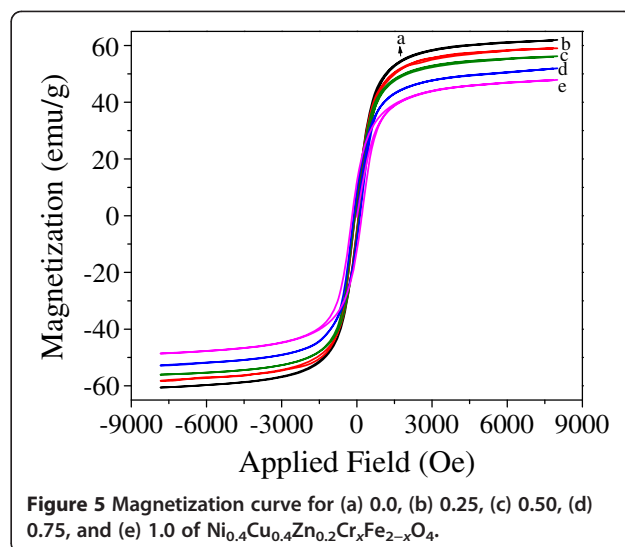
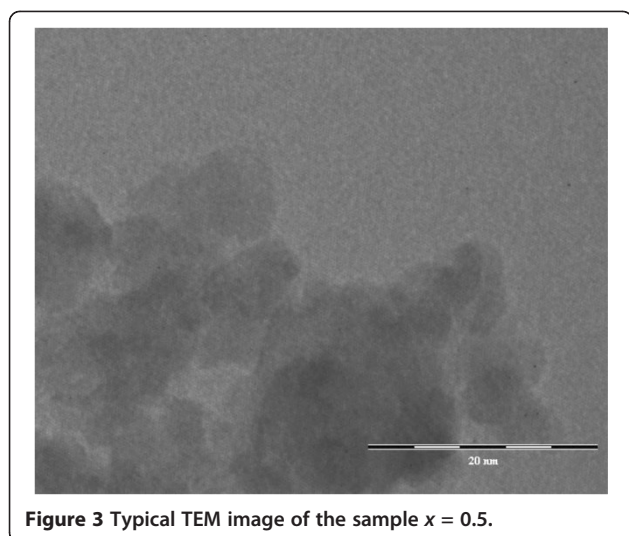


Table 1 Lattice constant (a), X-ray density (d_x), calculated magnetic moment (n_B) and resistivity (ρ) of $\text{Ni}_{0.4}\text{Cu}_{0.4}\text{Zn}_{0.2}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$

Composition (x)	a (\AA)	d_x (gm/cm^3)	n_B	$\rho \times 10^6$ ($\Omega \text{ cm}$)
0.0	8.331	5.460	2.64	3.62
0.25	8.312	5.475	2.50	3.72
0.50	8.293	5.491	2.36	3.95
0.75	8.272	5.510	2.19	4.07
1.0	8.253	5.525	2.01	4.21

molecular weight of Cr^{3+} ions is 51.94, whereas the molecular weight of Fe^{3+} ions is 55.93. Therefore, as the Cr^{3+} ions in the present case replace Fe^{3+} ions, the molecular weight of the system continues to decrease with every substitution of Cr^{3+} ions. This results in the decrease of the X-ray density of the sample. The bulk density (d_B) of the specimens was determined using Archimedes' method. The variation of the bulk density with Cr content x is shown in Figure 2. The bulk density was found to decrease with increasing Cr^{3+} content. In the present series, both the molecular weight of the $\text{Ni}_{0.4}\text{Cu}_{0.4}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$ spinel ferrite and the volume of the unit cell decrease with increasing Cr^{3+} substitution, but the rate of the decrease of the molecular weight is more than that of the volume. Therefore, the bulk density decreases with Cr^{3+} substitution in the present case, which leads to an increase in porosity (P) (Figure 2). It is clear from Figure 2 that the sample density decreases and the porosity increases with increasing Cr^{3+} content. The increase in porosity may be due to the decrease in crystallite size, which increases the grain boundaries of the crystallite and, accordingly, the porosity. TEM was adopted to determine the particle size. Figure 3 shows the typical TEM pattern for $x = 0.5$. Particle size decreases from 19 to 13 nm with the addition of Cr^{3+} ions (Figure 4). The specific surface area (S) was calculated from the diameter of the particle in nanometers and the measured density.





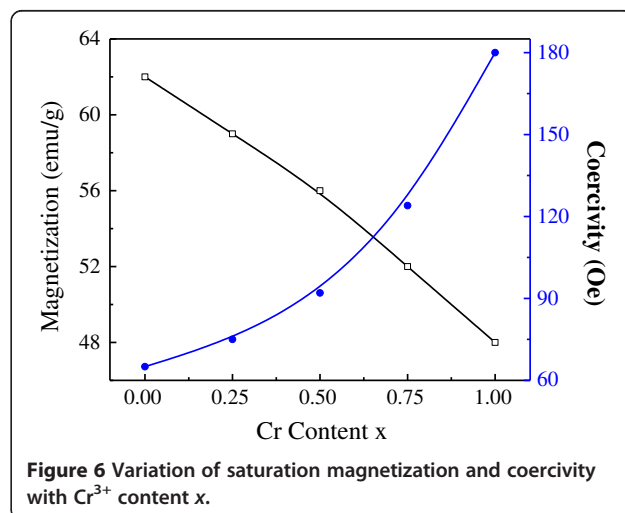
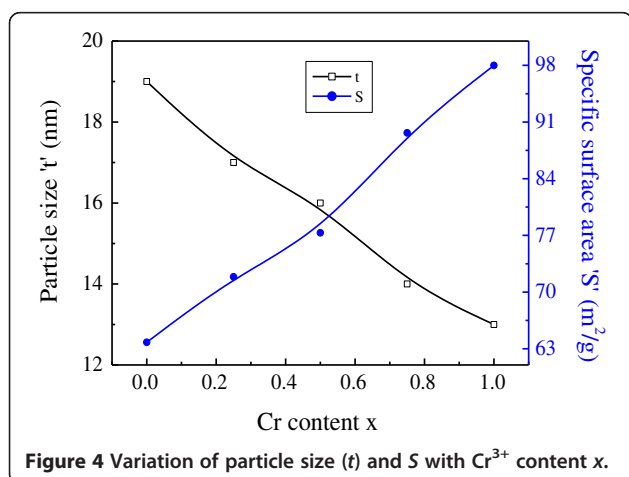
The variation of surface area with Cr content x is shown in Figure 4. S increases with increasing Cr^{3+} content. The increase in S is due to the decrease in crystallite size.

The introduction of Cr^{3+} ions into the Ni-Cu-Zn ferrite greatly affects its magnetic properties. Figure 5 shows the plots of the hysteresis loops for $\text{Ni}_{0.4}\text{Cu}_{0.4}\text{Zn}_{0.2}\text{Cr}_x\text{Fe}_{2-x}\text{O}_4$ specimens. It is observed from Figures 5 and 6 that the saturation magnetization decreases with an increase in Cr^{3+} substitution. The decrease in magnetization is explained by the A-B interaction. In the present case, Cr^{3+} ions of low magnetic moment values ($3\mu_B$) replace Fe^{3+} ions of high magnetic moment ($5\mu_B$). The magnetic moment in ferrite is mainly due to the uncompensated electron spin of the individual ions and the spin alignments in the two sublattices, which are arranged in an antiparallel fashion. In a spinel ferrite, each ion at the A site has 12 B-site ions as nearest neighbors. According to Neel's molecular field model [5], the A-B super-exchange interaction predominates the intrasublattice A-A and B-B

interactions. Therefore, the net magnetic moment is given by the sum of the magnetic moments of the A and B sublattices. The magneton number (n_B) was calculated using the formula:

$$n_B = \frac{M_W \times M_S}{5}, 585 \quad (1)$$

where M_W is the molecular weight of the composition and M_S is the saturation magnetization. It is observed from Table 1 that the magneton number decreases with an increase in Cr^{3+} substitution. It is clearly observed from Figure 6 that the coercivity (H_C) increases as the Cr^{3+} content increases, similar to porosity. Porosity affects the magnetization process because the pores work as a generator of a demagnetizing field. As the porosity increases, a higher field is needed to push the domain



wall, increasing H_C . Also, the saturation magnetization M_S is related to H_C through Brown's relation [6]:

$$H_c = \frac{2K_1}{\mu_0 M_S} \quad (2)$$

According to this relation, H_C is inversely proportional to M_S , which is consistent with our experimental results.

Figure 7 shows the variation of ϵ' with frequency at room temperature. It can be seen from Figure 7 that as the frequency increases, the dielectric constant decreases exponentially. The decrease in dielectric constant is rather sharp at a low-frequency region; as frequency increases, it remains almost constant for all the compositions under investigation. The variation of the dielectric constant with frequency reveals dispersion due to the Maxwell-Wagner-type interfacial polarization and is in agreement with Koop's phenomenological theory [7-9]. The polarization decreases with an increase in frequency and attains a constant value beyond a certain frequency limit. The decrease in dielectric constant with frequency indicates that the mechanism of polarization process in ferrite is similar to that of the conducting process. By electronic exchange, $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^-$, one obtains the local displacement of electron in the direction of the applied electric field. This displacement determines the polarization of the ferrite. The n-type charge transfer in the presently investigated ferrites is due to the hopping of electrons from Fe^{2+} to Fe^{3+} ions according to $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+} + e^-$, while the p-type charge transfer exists in Ni ions according to $\text{Ni}^{2+} + h \leftrightarrow \text{Ni}^{3+}$.

DC resistivity of all samples was measured using a two-probe method. It is observed that DC resistivity shows a linear decrease with temperature (figure not shown here). This variation is explained by the location

of the cations in the spinel ferrite. An increase in resistivity is observed with an increase in Cr^{3+} concentration (Table 1). The observed increase in resistivity can be understood by considering the hopping mechanism, $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$. The increase in Cr^{3+} ions at the B site leads to replacement of Fe^{3+} ions at B site, leading to a decrease of ferrous ions formed. Though the Cr^{3+} ions do not participate in the conduction mechanism, they limit the degree of $\text{Fe}^{2+} \leftrightarrow \text{Fe}^{3+}$ transfer, thereby obstructing electron hopping and resulting in an increase in resistivity.

Conclusions

Nanocrystalline Cr^{3+} substitution into the Ni-Cu-Zn was successfully prepared using sol-gel auto-combustion technique. It is observed that the lattice parameter decreases with the Cr^{3+} doping, which is explained on the basis of the smaller ionic radii of the Cr^{3+} ion than the Fe^{3+} ion. The decrease of saturation magnetization with increasing Cr^{3+} content occurs because the replacement of Fe^{3+} by Cr^{3+} ions weakens the sublattice interaction and lowers the magnetic moments of unit cells. The real and imaginary part of the dielectric are explained in light of the electron hopping mechanism and space charge polarization discussed by the Maxwell-Wagner model and Koop's phenomenological theory. The hopping of electrons between Fe^{3+} and Fe^{2+} as well as the hole hopping between Ni^{3+} and Ni^{2+} are found to be responsible for the conduction mechanism.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

All authors provided the same contributions in this article. All authors read and approved the final manuscript.

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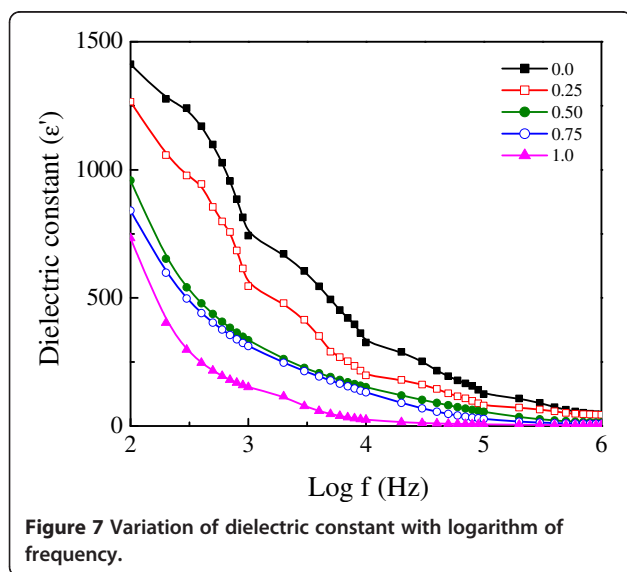
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