

Remarkable influence of Ce⁴⁺ ions on the electronic conduction of Ni_{1–2x}Ce_xFe₂O₄

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The effect of Ce⁴⁺ substitution in NiFe₂O₄, with the chemical formula Ni_{1–2x}Ce_xFe₂O₄ (0 ≤ x ≤ 0.25), is presented in this paper. The Ce⁴⁺ ion increases the DC resistivity of the NiFe₂O₄. The dielectric constant (ϵ') decreases with frequency as well as with composition. Infrared spectroscopy is employed to determine the local symmetry in crystalline solids and to shed light on the ordering phenomenon. The band frequency ν_1 decreases slightly with increasing Ce⁴⁺ concentration, whereas ν_2 remains almost constant. © 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

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Ferrites with a spinel structure are a technologically important class of magnetic oxides due to their magnetic properties, high electrical resistivity and low eddy current and dielectric losses [1]. All of these properties of ferrites are strongly dependent on various parameters, including chemical composition, dopant, method of preparation and distribution of cations [2–7].

Out of the many existing ferrite compounds, NiFe₂O₄ has been the subject of most research activity because it has helped us gain a fundamental understanding of magnetic ordering and its potential applications. Nickel ferrite, including substituted nickel ferrite, is one of the most versatile and technologically important soft ferrite materials because of its ferromagnetic properties, low conductivity and, thus, lower eddy current losses, high electrochemical stability, catalytic behavior, etc. It crystallizes in an inverse spinel structure and exhibits tunable conducting behavior. In the inverse spinel structure, the tetrahedral (A) sites are occupied by Fe³⁺ ions and the octahedral sites [B] are occupied by divalent metal ions (M²⁺) and Fe³⁺ in equal proportions. The crystal structure of spinel ferrite possesses two sublattices, namely tetrahedral (A) and octahedral [B]. Various cations can be incorporated into the spinel lattice to alter the properties of ferrite. For example, the substitution of divalent or

trivalent cations modifies the properties of nickel ferrite. Cerium is especially interesting because of its variable electronic structure. It is also finding use in making permanent magnets, catalysts, etc., and has also been substituted into such materials as Mn–Zn [8], YIG [9], Fe–K [10], Zn–Co ferrites [11] and Mg–Ti ferrite [12].

The substitution of cations like cerium (Ce⁴⁺) into a nickel matrix may produce very interesting electrical properties. Thus, considering all the facts discussed above, we decided to study cerium substitution in nickel ferrite in small concentrations for its electric properties.

A set of six samples with the chemical formula Ni_{1–2x}Ce_xFe₂O₄ (x = 0.0, 0.05, 0.10, 0.15, 0.20 and 0.25) were prepared by a solid-state reaction process [6]. The samples were powdered for X-ray investigation. Part of the powder was examined with a Phillips X-ray diffractometer (Model 3710) using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). The DC resistivity of the samples was measured using a two-probe method in which silver paste was used as a contact material. The samples were firmly fixed between two electrodes to produce good surface contact. An auxiliary heater was used to heat all of the investigated samples. The temperature was measured using a chromel–alumel thermocouple. The frequency-dependent dielectric measurements were carried out on a HIOKY 3532-50 LCR meter at room temperature in the frequency range from 100 Hz to 1 MHz. Infrared (IR) spectra were recorded in the range 350–800 cm^{–1} at room temperature with an IR spectrometer (Bruker).

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The X-ray powder diffraction patterns of all the compositions of $\text{Ni}_{1-2x}\text{Ce}_x\text{Fe}_2\text{O}_4$ are presented in Figure 1. The Bragg reflection peaks of all the samples are sharp, narrow and intense, indicating high crystallinity and fine grain size in the produced samples. The X-ray diffraction patterns show the formation of cubic spinel structures, with the appearance of characteristic peaks representing cerium-based secondary phases in the compositions with higher concentration of cerium ($x = 0.20$ and 0.25). Similar reports indicating the phases of cerium in XRD have been published previously [8]. All peaks other than the cerium-based peaks at higher concentrations of cerium in the XRD pattern match well with the characteristic reflections. At higher percentages of Ce^{4+} substitution ($x \geq 0.20$), the lattice could not accommodate all of the Ce^{4+} ion, resulting in the segregation of secondary phases in the lattice for $x \geq 0.20$. The solubility of Ce^{4+} in NiFe_2O_4 was hence substantially lower for $x \geq 0.20$. Because of the larger ionic radius of Ce^{4+} (1.01 Å) in comparison to that of Ni^{2+} , the centrosymmetric face-centered cubic (fcc) structure might have been distorted at higher concentrations. Also, an orthorhombic second phase appears along with the first original spinel phase. The lattice parameter for the second phase still increased with ion concentration, which led us to conclude that the spinel lattice is not compressed by the inter-granular second phase [13].

The variations in ρ with $1000/T$ for all the compositions of the ferrite system $\text{Ni}_{1-2x}\text{Ce}_x\text{Fe}_2\text{O}_4$ are presented in Figure 2. Resistivity decreases continuously with increasing temperature, revealing the semiconducting nature of the prepared sample. The plot shows two distinct regions, corresponding to ferrimagnetic and paramagnetic regions. The slope is observed to change at a particular temperature. This temperature is designated the Curie temperature of the sample. The change in the slope of temperature vs. resistivity is attributed to a change in the conduction mechanism. The conduction at lower temperature, which happens to be below the Curie temperature range, is due to the hopping of electrons between Fe^{2+} and Fe^{3+} ions, whereas at higher temperatures, i.e. above the Curie temperature, it is due to polaron hopping. The activation energies increase

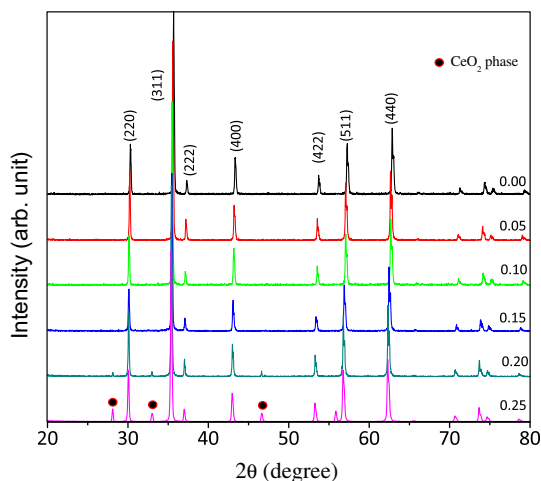


Figure 1. XRD patterns of $\text{Ni}_{1-2x}\text{Ce}_x\text{Fe}_2\text{O}_4$.

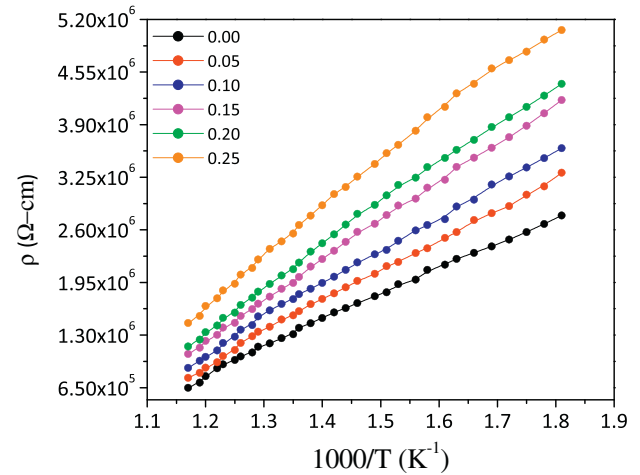


Figure 2. Variations in DC resistivity with Ce content x .

from 0.444 to 0.583 eV. The activation energy obtained in the present work was observed to increase with increasing Ce content x . The calculated activation energies are greater than 0.4 eV, which clearly suggests that the conduction is due to polaron hopping [7]. The hopping probability depends not only on the separation between the ions involved but also on the activation energy. The activation energy of each sample in the measured temperature range can be determined by the temperature dependence of the DC resistivity. The activation energy in the paramagnetic region is greater than that in the ferrimagnetic region and is in agreement with the theory of Irkhin and Turov [14]. The conduction mechanism in ferrites can be explained on the basis of the Verwey–de Boer [15] mechanism, involving electron exchange between the ions of the same element, which are present in more than one valance state and distributed randomly over crystallographic equivalent lattice sites. The number of such ions depends upon the sintering conditions and the reduction of the Fe^{3+} and Fe^{2+} ions at elevated temperatures.

The frequency dependence of the dielectric constant (ϵ') for all the samples was studied at room temperature. The observed variation of the dielectric constant with frequency for all compositions is shown in Figure 3. The dielectric constant decreased with increasing frequency from 100 Hz to 5 MHz, showing typical dielectric dispersion behavior. The decrease in the dielectric constants was rapid at lower frequencies and slower at higher frequencies. The low-frequency dispersion in ferrites is observed due to a space-charge effect. The decrease in the dielectric constant with frequency can be understood on the basis of Koops's theory [16], which considers the dielectric structure as an inhomogeneous medium of two layers of the Maxwell–Wagner type [17]. In this model, the dielectric structure is assumed to consist of good-conducting grains that are separated by poorly conducting grain boundaries [18]. It was found that for ferrites the dielectric permittivity is directly proportional to the square root of conductivity. Therefore, the grains have higher values of conductivity and permittivity, while the grain boundaries have lower values. At lower frequencies, the grain boundaries are more effective in terms of conductivity and permittivity

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