Magnetic and electrical properties of Cr substituted Ni nano ferrites
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Received 1 July 2017; Received in revised form 10 August 2017; Received in revised form 7 November 2017; Accepted 4 December 2017

Abstract
Nano-ferrites with composition NiCrFe2−xO4 (where x = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0) were synthesized through citrate-gel auto combustion technique at moderately low temperature. X-ray analysis shows cubic spinel structure single phase without any impurity peak and average crystallite size in the range 8.5–10.5 nm. Magnetic properties were measured using a vibrating sample magnetometer at room temperature in the applied field of ±6 KOe. The obtained M-H loop area is very narrow, hence the synthesized nano ferrites are soft magnetic materials with small coercivity. Magnetic parameters such as saturation magnetization (Ms), coercivity (Hc), remanent magnetization (Mr) and residual magnetization were measured and discussed with regard to Cr3+ ion concentration. Electrical properties were measured using two probe method from room temperature to well beyond transition temperature. The DC resistivity variation with temperature shows the semiconductor nature. Resistivity, drift mobility and activation energy values are measured and discussed with regard to composition. The Curie temperature was determined using DC resistivity data and Loria-Sinha method. The observed results can be explained in detail on the basis of composition.

Keywords: Ni-Cr ferrites, citrate-gel method, XRD, magnetic properties, electrical properties

I. Introduction
Ferrites with general formulae of MFe2O4 are immense magnetic ceramics and better than pure metals due to their high electrical resistivity and lower cost [1,2]. Ferrites show the fascinating electrical and magnetic properties in the nanocrystalline form compared with those of bulk form. This is because of the cation distribution over tetrahedral and octahedral sites, which has a significant effect on the electrical and magnetic behaviour [3]. Hence, the cation distribution is distinctly different from ferrite nanoparticles compared to the bulk ferrites [4]. Accordingly, the ferrite nanoparticles are technically important promising materials due to various applications in electronics [5,6].

Nickel ferrite has an inverse spinel structure with Ni2+ in octahedral site and Fe3+ equally distributed among octahedral and tetrahedral sites [7]. These ferrites are very important materials designed for electronic devices, such as telecommunication tools, permanent magnets, magnetic media used in computers, recording devices and electronic and microwave devices because of their low eddy current losses and good magnetic properties [8].

The properties of ferrites are also dependent on preparation method, chemical composition and type of substituent [9]. Among several methods such as sol-gel route [10], co-precipitation [11], hydrothermal method [12] and reverse micelle technique [13] etc., the citrate-gel auto combustion method is one of the most attractive preparation methods for synthesis of nanosized ferrite particles. The reasons are low annealing temperature, short preparation time, good stoichiometry control and the production of ultrafine particles with a narrow size distribution. Divalent or trivalent substituted nickel nano ferrites are extensively used as magnetic materials in a wide range of technological applications [14].

The electrical and magnetic properties of the nano-
sized ferrites play a vital role in different fields and they are dependent on several factors [15]. Substitution of Fe$^{3+}$ with trivalent cations like Al$^{3+}$ and Cr$^{3+}$ is necessary to accomplish specific objectives like increase of resistivity and saturation magnetization decreases [16]. Several researchers have presented the influence of trivalent substitutions to improve their electrical and magnetic properties [17,18]. To the best of our knowledge, the electrical and magnetic properties of Cr$^{3+}$ substituted nickel nano ferrite has not yet been investigated in detail. Therefore, in the present work, Cr substituted nickel nano ferrites of different compositions have been prepared by the citrate-gel auto combustion method. Further, the electrical properties of Cr substituted nickel nano ferrites have been investigated as a function of temperature, while the magnetic properties have been investigated as a function of composition at the room temperature.

II. Experimental procedure

2.1. Sample preparation

Cr-substituted Ni ferrites, having the general formula NiCr$_x$Fe$_{2.5}$O$_4$ (where $x = 0.1, 0.3, 0.5, 0.7, 0.9$ and $1.0$), were synthesized by using citrate-gel auto combustion method. In a typical experiment, analytically grade nickel nitrate (Ni(NO$_3$)$_2$·$6$H$_2$O, 99% pure, AR Grade), chromium nitrate (Cr(NO$_3$)$_2$·$3$H$_2$O, 99% pure, AR Grade), ferric nitrate (Fe(NO$_3$)$_3$·$9$H$_2$O, 99% pure, AR Grade) and citric acid (C$_6$H$_8$O$_7$·$2$H$_2$O, 99% pure, GR Grade) were dissolved in sufficient amount of deionized water in stoichiometry proportions. To maintain the pH of the solution at 7, ammonia (NH$_3$), which acts as the precipitating agent was added to the solution kept under constant stirring. The resulting solution was then heated at 80°C until it transformed into wet gel. Then the gel was ignited in a self-propagating combustion manner to form a fluffly loose powder. The as-burnt ferrite powders were pulverised in agate mortar and calcined in muffle furnace at 700°C for 5 h. The calcined ferrite powders were again ground in agate mortar to obtain a fine ferrite powder.

2.2. Materials characterization

The structural characterization was done by a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation source ($\lambda = 0.15405$ nm) between the Bragg angles $20^\circ$ to $80^\circ$ in steps of $0.04^\circ$/s. The average crystallite size was calculated using the Scherrer formula for the high intensity $311$ peak [19]. The morphology and average crystallite size were characterized by TEM (Tecnai-12, FEI, Netherlands).

Magnetic properties were determined from the obtained hysteresis loops by using vibrating sample magnetometer (VSM) GMW 3473 in the range ±$6$ kOe applied field at room temperature. From the obtained hysteresis loops, the saturation magnetizations ($M_s$), remanent magnetization ($M_r$), coercivity ($H_c$) were determined and magnetic moment ($\mu_B$) was calculated using the relation [20]:

$$\mu_B = \frac{M_r \cdot M_s}{5585}$$  \hspace{1cm} (1)

where $M_s$ is the molecular weight of each composition. The anisotropy constant ($K$) was calculated by using the relation [21]:

$$H_c = \frac{0.98K}{M_s}$$  \hspace{1cm} (2)

For electrical measurements, the prepared samples were pressed into a circular disc shaped pellets (~$10$ mm diameter and ~$2$ mm thickness) and these pellets were sintered at 400°C for 4 hours. The prepared pellets are silver coated on both sides and air dried to have good ohmic contact. The DC resistivity was measured as a function of temperature by using the two-probe method [22]. The relationship between resistivity and temperature may be expressed as [23]:

$$\rho = \rho_0 \cdot \exp \left(\frac{\Delta E}{k_BT}\right)$$  \hspace{1cm} (3)

where $\rho$ is the DC electrical resistivity at temperature $T$, $k_B$ is the Boltzmann constant and $\Delta E$ is the activation energy. The drift mobility of the charge carriers is calculated from the electrical resistivity data by the following equation [24]:

$$\mu = \frac{1}{n \cdot e \cdot \rho}$$  \hspace{1cm} (4)

where $n$ is the number of charge carriers, $e$ is the charge of electron, $\rho$ is the resistivity at a given temperature.

III. Results and discussion

3.1. Structural properties

X-ray diffraction patterns of the mixed NiCr$_x$Fe$_{2.5}$O$_4$ nano ferrite system are shown in Fig. 1. The appearance of the (111), (220), (311), (400), (511), (440) and (533) planes corresponding to the cubic spinel structure, matches with the standard reference data PDF# 862267 for nickel ferrites (NiFe$_2$O$_4$) from the international centre for diffraction data (ICDD) and all the samples have shown cubic spinel structure being single phase [25]. The average crystallite size is in the range of 8.5 nm to 10.5 nm. Micrographs of NiCr$_{0.3}$Fe$_{1.7}$O$_4$ and NiCr$_{0.7}$Fe$_{1.3}$O$_4$ nano ferrite are represented in Figs. 2 and 3. Micrographs point out the nanostructure environment with the crystallite size in nanometre range.

3.2. Magnetic properties

$M$-$H$ hysteresis loops

The hysteresis loops are obtained for all samples in the range ±$6$ kOe applied field at room temperature using VSM. The obtained hysteresis loops are illustrated
in Fig. 4. The loop area is very narrow therefore the samples present soft ferrite nature with small coercivity [26]. Hence it is clear that Cr substitution in Ni ferrites has enhanced soft magnetic performance. So these materials may be desirable for transformers to minimize the energy dissipation with the alternating fields associated with AC electrical applications. Several magnetic parameters, such as saturation magnetization ($M_s$), coercivity ($H_c$), remanent magnetization ($M_r$) and residual magnetization ratio ($M_r/M_s$), are directly extracted from hysteresis curves. The magnetic moment ($\mu_B$) and anisotropy constant ($K$) were determined from the saturation magnetization and coercivity data and reported in Table 1.

**Saturation magnetization and coercivity**

Microstructure of the materials and composition greatly influence the magnetic properties of soft ferrites. In the prepared sample, magnetization comes from the interchange of domain walls movement, spin rotation and a sum of exchange interactions between A-site and B-site of the ferrite [27]. From the hysteresis loops, it is observed that the Ni-Cr nano ferrites have lower saturation magnetization and coercivity due to the small grain size [28].

The saturation magnetization ($M_s$) decreases from 4.49 to 2.97 emu/g with increase of Cr$^{3+}$ concentration in Ni nano ferrites (Table 1 and Fig. 5). It may be explained with low magnetic moment Cr$^{3+}$ ions ($\sim 3 \mu_B$) being substituted in place of higher magnetic moment...
Table 1. Magnetic properties (saturation magnetization $M_s$, remanent magnetization $M_r$, residual magnetization ratio $M_r/M_s$, magnetic moment $\mu_B$, coercive field $H_c$ and anisotropy constant $K$) of NiCr$_x$Fe$_{2-x}$O$_4$ nano ferrite system

<table>
<thead>
<tr>
<th>$x$</th>
<th>Crystallite size [nm]</th>
<th>$M_s$ [emu/g]</th>
<th>$M_r$ [emu/g]</th>
<th>$M_r/M_s$</th>
<th>$\mu_B$</th>
<th>$H_c$ [Oe]</th>
<th>$K$ [emu/Oe]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>8.96</td>
<td>4.49</td>
<td>0.51</td>
<td>0.113</td>
<td>0.188</td>
<td>136.2</td>
<td>624.5</td>
</tr>
<tr>
<td>0.3</td>
<td>10.36</td>
<td>4.29</td>
<td>0.47</td>
<td>0.110</td>
<td>0.179</td>
<td>126.0</td>
<td>551.4</td>
</tr>
<tr>
<td>0.5</td>
<td>7.95</td>
<td>4.15</td>
<td>0.39</td>
<td>0.094</td>
<td>0.172</td>
<td>116.6</td>
<td>493.9</td>
</tr>
<tr>
<td>0.7</td>
<td>8.55</td>
<td>3.99</td>
<td>0.24</td>
<td>0.060</td>
<td>0.165</td>
<td>63.0</td>
<td>256.3</td>
</tr>
<tr>
<td>0.9</td>
<td>8.84</td>
<td>3.67</td>
<td>0.35</td>
<td>0.095</td>
<td>0.151</td>
<td>79.2</td>
<td>296.2</td>
</tr>
<tr>
<td>1</td>
<td>9.26</td>
<td>2.97</td>
<td>0.44</td>
<td>0.150</td>
<td>0.122</td>
<td>106.1</td>
<td>321.9</td>
</tr>
</tbody>
</table>

The remanent magnetization ($M_r$) and residual magnetization ratio ($M_r/M_s$) values are given in Table 1. Remanent magnetization ($M_r$) varies between 0.24 emu/g and 0.51 emu/g with the residual magnetization ratio ($M_r/M_s$) values between 0.060 and 0.150 with Cr$^{3+}$ ion concentration. The low value of residual magnetization ratio implies on the isotropic nature of the prepared ferrite samples. The low values of the remanent magnetization ($M_r$) can be accredited to the low saturation magnetization as well as the nanosized characteristics [31]. Materials with such low residual magnetisation could be used for low inductance cores and coils [32].

3.3. Electrical properties

DC resistivity variation with temperature

The DC resistivity variation with temperature for NiCr$_x$Fe$_{2-x}$O$_4$ nano ferrite system is shown in Fig. 7. It is observed that the resistivity linearly decreases with increase in temperature due to the hopping of electrons, which indicates the semiconductor nature [33]. In the present system the conduction process can be explained by the Verway and Boer mechanism [34]. During the sintering process a small amount of Fe$^{3+}$ and Ni$^{3+}$ ions are formed and electron exchange occurs between Fe and Ni ions, which can be represented as:

$$\text{Ni}^{2+} + \text{Fe}^{3+} \leftrightarrow \text{Ni}^{3+} + \text{Fe}^{2+}$$

(5)

The conduction at low temperature (i.e. $<400$ K) is
Electrical resistivity increases from $3.17 \times 10^6 \Omega \cdot \text{cm}$ to $6.79 \times 10^6 \Omega \cdot \text{cm}$ and the drift mobility decreases from $7.73 \times 10^{-11} \text{cm}^2/\text{V} \cdot \text{s}$ to $6.69 \times 10^{-11} \text{cm}^2/\text{V} \cdot \text{s}$ with the increase of Cr$^{3+}$ ion concentration in Ni nano ferrite as evidenced in Table 2. It may be due to the hopping of electrons between Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ ions [34]. In the spinel structure the Ni$^{2+}$ ions occupy octahedral (B) sites, Fe$^{3+}$ ions are occupying both the octahedral (B) and tetrahedral (A) sites and the Cr$^{3+}$ ions occupy the octahedral (B) sites [37]. The conduction mechanism in ferrites depends on the hopping of electrons between Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ at the octahedral (B) sites. Compared with B-B sites, the hopping of electrons is less probable between A-B sites and does not exist between A-A sites. Therefore only Fe$^{3+}$ ions are present at A-sites while Fe$^{2+}$ ions are created during the process and occupy B-sites [38]. However, Cr$^{3+}$ ions occupy octahedral (B) site and as a result they decrease the Fe$^{3+}$ ions at the B-sites. In turn, Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ ions polaron hopping happens [39,40]. Hence, increase in resistivity with increasing Cr$^{3+}$ ion concentration. Similar trend observed in Co-Cr nano ferrite was previously reported [41]. The decrease in the drift mobility with composition is due to the fact that samples with higher resistivity have lower mobility and vice versa. Similar results observed in Co-Cr ferrites by Naeem Ashiq [42]. This shows that the investigated materials could be a good choice for high frequency applications.

**Activation energy variation with composition**

Activiation energy could be calculated from the slope of $\ln(\rho \cdot T)$ with inverse temperature shown in Fig. 7. The computed activation energy values are presented in Table 2. Activation energy values are higher in the paramagnetic region as compared to the ferrimagnetic region. It can be attributed to the spin disordered states of the paramagnetic region and the spin ordered states of the ferrimagnetic region [43]. These results suggest that the change in the magnetic ordering has an effect on the conduction process [44]. On the other hand, the activation energy values indicate the slow polaron hopping conduction mechanism in ferrites.

The activation energy ($\Delta E$) of each sample is presented in Table 2 and plotted in Fig. 9. It shows that activation energy ($\Delta E$) increases with the increase of Cr$^{3+}$ ion concentration. It may be due to the increase in resistivity with the increase in Cr$^{3+}$ ion concentration, because activation energy acts in similar way to DC resistivity and drift mobility

The variation of electrical resistivity and drift mobility with Cr$^{3+}$ concentration are shown in Fig. 8. Electrical resistivity increases from $3.17 \times 10^6 \Omega \cdot \text{cm}$ to $6.79 \times 10^6 \Omega \cdot \text{cm}$ and the drift mobility decreases from $7.73 \times 10^{-11} \text{cm}^2/\text{V} \cdot \text{s}$ to $6.69 \times 10^{-11} \text{cm}^2/\text{V} \cdot \text{s}$ with the increase of Cr$^{3+}$ ion concentration in Ni nano ferrite as evidenced in Table 2. It may be due to the hopping of electrons between Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ ions [34]. In the spinel structure the Ni$^{2+}$ ions occupy octahedral (B) sites, Fe$^{3+}$ ions are occupying both the octahedral (B) and tetrahedral (A) sites and the Cr$^{3+}$ ions occupy the octahedral (B) sites [37]. The conduction mechanism in ferrites depends on the hopping of electrons between Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ at the octahedral (B) sites. Compared with B-B sites, the hopping of electrons is less probable between A-B sites and does not exist between A-A sites. Therefore only Fe$^{3+}$ ions are present at A-sites while Fe$^{2+}$ ions are created during the process and occupy B-sites [38]. However, Cr$^{3+}$ ions occupy octahedral (B) site and as a result they decrease the Fe$^{3+}$ ions at the B-sites. In turn, Fe$^{3+} \leftrightarrow$ Fe$^{2+}$ ions polaron hopping happens [39,40]. Hence, increase in resistivity with increasing Cr$^{3+}$ ion concentration. Similar trend observed in Co-Cr nano ferrite was previously reported [41]. The decrease in the drift mobility with composition is due to the fact that samples with higher resistivity have lower mobility and vice versa. Similar results observed in Co-Cr ferrites by Naeem Ashiq [42]. This shows that the investigated materials could be a good choice for high frequency applications.

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**DC resistivity and drift mobility**

The activation energy ($\Delta E$) of each sample is presented in Table 2 and plotted in Fig. 9. It shows that activation energy ($\Delta E$) increases with the increase of Cr$^{3+}$ ion concentration. It may be due to the increase in resistivity with the increase in Cr$^{3+}$ ion concentration, because activation energy acts in similar way to DC resistivity and drift mobility.

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**Table 2. Electrical properties of NiCr$_2$Fe$_{2-x}$O$_4$ nano ferrite system (activation energy in para region $E_p$, activation energy in ferro region $E_f$ and activation energy $\Delta E$)**

<table>
<thead>
<tr>
<th>$x$</th>
<th>Resistivity [(\Omega \cdot \text{cm})]</th>
<th>Drift mobility (\mu_d) [(\text{cm}^2/\text{V} \cdot \text{s})]</th>
<th>Activation energy [eV]</th>
<th>Curie temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>$3.17 \times 10^6$</td>
<td>$7.73 \times 10^{-11}$</td>
<td>0.41</td>
<td>0.24</td>
</tr>
<tr>
<td>0.3</td>
<td>$4.10 \times 10^6$</td>
<td>$7.55 \times 10^{-11}$</td>
<td>0.52</td>
<td>0.32</td>
</tr>
<tr>
<td>0.5</td>
<td>$4.64 \times 10^6$</td>
<td>$7.42 \times 10^{-11}$</td>
<td>0.63</td>
<td>0.39</td>
</tr>
<tr>
<td>0.7</td>
<td>$5.06 \times 10^6$</td>
<td>$7.29 \times 10^{-11}$</td>
<td>0.72</td>
<td>0.44</td>
</tr>
<tr>
<td>0.9</td>
<td>$5.84 \times 10^6$</td>
<td>$6.84 \times 10^{-11}$</td>
<td>0.79</td>
<td>0.48</td>
</tr>
<tr>
<td>1.0</td>
<td>$6.79 \times 10^6$</td>
<td>$6.69 \times 10^{-11}$</td>
<td>0.85</td>
<td>0.51</td>
</tr>
</tbody>
</table>
between Fe
tering into octahedral sites hinder the electron hopping
increase in activation energy imply that the Cr ions en-
electrical resistivity, as reported by others [45,46]. This
increase in activation energy imply that the Cr ions en-
suppression into paramagnetic phase at the temperature
values of activation energies and vice versa [47].
correspondingly, the sample with higher resistivity has higher
2
change in slope. This indicates transformation from fer-
curie temperature are shown in Table 2 and Fig.
with those recognised as the magnetic transition tem-
formation of Fe
3
of the Curie temperature. Similar behaviour was already
observed for the trivalent substitution in nano ferrite
1.0) was synthesized using citrate-gel auto combustion
method. X-ray diffraction pattern confirms the forma-
tions lowering electrical conduc-
C. The Curie temperature is de-
terminated by an overall strength of the exchange inter-
action between A and B sublattice. When the replace-
ment of Fe
3
ion with Cr
3
ions are replaced by para-
magnetic Cr
3
ions [39]. The Curie temperature is de-
termined by an overall strength of the exchange inter-
action between A and B sublattice. When the replace-
ment of Fe
3
ion with Cr
3
ions increases, the magneto-
tization decreases in B-sublattice without disturbing the
A-sublattice. This leads to a decrease in the A-B inter-
actions (Fe
3
←O
2
←Fe
3
) which results in the decrease of the Curie temperature. Similar behaviour was already
observed for the trivalent substitution in nano ferrite system [48,49]. The Curie temperatures obtained from DC resistivity measurements were in good agreement with those recognised as the magnetic transition temperature (789 to 642 K) from the Loria-Sinha method (gravity method) as reported in Table 2.

IV. Conclusions

NiCr
x
Fe
2−x
O
4
(where \( x = 0.1, 0.3, 0.5, 0.7, 0.9, 1.0 \) was synthesized using citrate-gel auto combustion method. X-ray diffraction pattern confirms the forma-
tion of the cubic spinel structure single phase without any impurity peaks with the crystallite size in the range of 8.5 to 10.5 nm. The obtained hysteresis loops confirm that the prepared Ni-Cr nano ferrites are soft magnets with narrow loop area and small coercivity. Hence, these materials may be desirable for transformers to minimize the energy dissipation. The DC resistivity variation with
temperature shows the semiconductor nature of the ma-
terial. The increase in the resistivity and decrease in the drift mobility with Cr
3
ion concentration were ascribed to the electron hopping between Fe
3
↔ Fe
2+
ions. This shows that materials may be good choice for high fre-
quence applications. The sample with higher resistivity has higher values of activation energy for conductivity and vice versa. The measured Curie temperatures from DC resistivity were in good agreement with those obtained as magnetic transition temperatures from Loria-Sinha method.

Acknowledgement: The authors are grateful to Head, Department of Physics, Osmania University, Hyderabad for providing the facility to synthesis of samples. One of the authors (KVK) is grateful to Dr. B. Balu Naik, Principal JNTUH College of Engineering, Sultanpur, Pulkal (M), Sangareddy District and the author (RS) is grate-
ful to Dr. G. Durga Sukumar Principal, Vignan Institute of Technology & Science, Yadadri-Bhuvnanagiri (Nalgonda).

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