Effect of Fe Substitution on Structural and Magnetic Properties of NiCr$_2$O$_4$

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At room temperature, the normal oxide spinel NiCr$_2$O$_4$ is tetragonally distorted and crystallizes in the $I4_1$/amd space group due to cooperative Jahn-Teller ordering driven by the orbital degeneracy of tetrahedral Ni$^{2+}$. The ferrimagnetic Curie temperature ($T_C$) for NiCr$_2$O$_4$ is 74 K. The magnetic moments of NiCr$_2$O$_4$ are composed of a ferrimagnetic (longitudinal) and an antiferromagnetic (transverse) component. Exchange interaction between the magnetic cations influences the overall magnetic properties of the compound. Present work focuses on the modification of structural and magnetic properties upon substituting Fe at Cr site in NiCr$_2$O$_4$ with the motivation of changing the magnetic exchange interaction. In order to do so, single phase Ni(Cr$_{0.5}Fe_{0.5}$)$_2$O$_4$ samples were prepared by co-precipitation techniques, while controlling the pH of precipitation. Upon Fe substitution, crystal structure was not affected much contrary to the earlier reports. In order to determine the oxidation state of each elements X-ray photoelectron spectroscopy (XPS) was performed. $T_C$ was found to increase dramatically above 300 K, confirmed both from temperature and field dependent dc-magnetization studies.

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1. Introduction

NiCr$_2$O$_4$ and NiFe$_2$O$_4$ ferrimagnets crystallizes into normal and inverse spinel structures respectively with magnetic Ni$^{2+}$ ion occupying tetrahedral site in the former and octahedral site in the latter [1, 2]. Cr$^{3+}$ ion occupy the octahedral site in case of NiCr$_2$O$_4$ [1]. For NiFe$_2$O$_4$ half of Fe$^{3+}$ ions occupy tetrahedral site and the rest occupy octahedral site [2]. Thus, structurally both these compounds are quite different.

NiCr$_2$O$_4$ has cubic structure with space group $Fd\bar{3}m$ above 310 K and is a promising magneto-dielectric material [3]. Below 310 K, orbital degeneracy on tetrahedral Ni$^{2+}$ promotes cooperative Jahn-Teller distortion of NiCr$_2$O$_4$, lowering the average structural symmetry from cubic to tetragonal ($I4_1/amd$) [4, 5]. Further, magnetostructural coupling induces a distortion of NiCr$_2$O$_4$ from tetragonal to orthorhombic symmetry at the Néel temperature ($T_N \approx 65$ K) [6, 7]. A second distortion within the orthorhombic structure occurs in the region of 30 K, with significant anomalies observed in both magnetic susceptibility and heat capacity measurements [8]. Neutron diffraction studies confirm the ordering of the longitudinal ferrimagnetic component at 60 K, and the ordering of the transverse antiferromagnetic component at 30 K [1]. Specific heat measurements demonstrate two additional anomalies other than 310 K, one near 70 K and the other at 29 K both due to magneto-structural coupling [9]. In case of NiFe$_2$O$_4$ ferrimagnetism originates from the magnetic moment of anti-parallel spins between Fe$^{3+}$ ions at tetrahedral sites and Ni$^{2+}$ ions at octahedral sites [2]. The ferrimagnetic Curie temperature $T_C$ of NiFe$_2$O$_4$ is 878 K [10]. Therefore, considering the distinct properties of NiCr$_2$O$_4$ and NiFe$_2$O$_4$, it will be most interesting to investigate the subsequent modification in structure and the magnetic properties when substituting the Cr site in NiCr$_2$O$_4$ with Fe.

2. Experimental methods

Ni(Cr$_{0.5}Fe_{0.5}$)$_2$O$_4$ powders were synthesized by chemical co-precipitation techniques, using stock solutions of 0.5 M of nickel nitrate (Ni(NO$_3$)$_2$·6H$_2$O), ferric nitrate (Fe(NO$_3$)$_3$·9H$_2$O) and chromium nitrate (Cr(NO$_3$)$_3$·9H$_2$O). The desired amounts of nitrates in solution form were mixed thoroughly in a beaker using a magnetic stirrer. Diluted aqueous ammonia (30%) solution was added to the nitrate mixture for precipitation. Addition of aqueous ammonia was continued until the pH of the solution reached a value of 9.8. The precipitates were filtered, then washed several times – initially with distilled water, followed by acetone and then with methanol. Finally, the precipitated powders were dried and crushed to powder using an agate mortar and pestle. In order to remove the volatile impurities and to obtain a good crystallinity the samples were calcined at 900°C for 2 hours in a tubular furnace.

Structural characterizations of these samples were carried out utilizing X-ray diffraction (XRD) techniques,

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The sample was cooled in zero applied magnetic field and cooled (parallel to cubic for temperature dependent magnetization \(M\) measurements) were carried out in both zero field cooled \((M_{ZFC})\) and field cooled \((M_{FC})\) conditions. For the \(M_{ZFC}\) measurements the sample was cooled in zero applied magnetic field and then magnetization measurements as function of temperature \((T)\) were taken on heating the sample in a specified probing magnetic field. The \(M_{FC}\) measurements were done by cooling the samples in an applied probing magnetic field and then magnetization measurements as function of temperature was carried out on heating the sample in the same probing field. \(M_{ZFC}\) and \(M_{FC}\) measurements were performed using two probing fields, 0.1 T and 0.5 T, as shown in Fig. 2(a) and (b), respectively. The bifurcation in \(M_{ZFC}\) and \(M_{FC}\) magnetization suggests a \(T_C\) value that exceeds 300 K.

3. Results and discussion

The crystalline structure of \(\text{Ni(Cr}_{0.5}\text{Fe}_{0.5})_2\text{O}_4\) powder sample was determined to be a cubic spinel of \(Fd\bar{3}m\) space group with lattice parameter \(a = 8.301(9)\ \text{Å}\) by Rietveld refinement as shown in Fig. 1. The relatively low value of \(\chi^2 = 1.06\), Bragg \(R\) factor of 9.94% and \(R_f\)-factor of 10.3% suggests a relatively good fit. This is evident from the small variance in difference curve also shown in Fig. 1. The position coordinates used in the simulated XRD spectra were \(\text{Ni}\ (x = 0.125, y = 0.125, z = 0.125), \text{Cr}\ (x = 0.5, y = 0.5, z = 0.5), \text{Fe}\ (x = 0.5, y = 0.5, z = 0.5)\) and \(\text{O}\ (x = 0.25436, y = 0.25436, z = 0.25436)\). In the present case for \(x = 0.5\), the peaks corresponding to the reflections \((222)\) and \((400)\) are not fitted well, suggesting incomplete structural phase transition to the cubic phase, although Barman and Ravi \([14]\) reported a structural phase transformation from tetragonal to cubic for \(x = 0.1\).

![Fig. 1. Rietveld analysis of powder-diffraction pattern of \(\text{Ni(Cr}_{0.5}\text{Fe}_{0.5})_2\text{O}_4\) measured at 300 K using a single phase space group \(Fd\bar{3}m\).](image)

In order to explore the magnetic properties, temperature dependent magnetization \((M)\) measurements were carried out in both zero field cooled \((M_{ZFC})\) and field cooled \((M_{FC})\) conditions. For the \(M_{ZFC}\) measurements the sample was cooled in zero applied magnetic field and as a fit of the XPS data were performed using XPSSpeak4.1 software package \([13]\).

![Fig. 2. \(M_{ZFC}\) and \(M_{FC}\) magnetization as a function of temperature for the \(\text{Ni(Cr}_{0.5}\text{Fe}_{0.5})_2\text{O}_4\), with a probing field of (a) 0.1 T and (b) 0.5 T.](image)

To confirm the ferrimagnetic \(T_C\), magnetization as a function of applied magnetic field was measured at 3 K, shown in Fig. 3. The irreversibility in \(M(H)\) suggests the persistence of ferrimagnetism. Upon heating the sample to 300 K a similar hysteresis in \(M(H)\) was observed (inset of Fig. 3), corroborating the \(M(T)\) results. Park et al. \([15]\) substituted Fe at Cr site with \(x = 0.15\) and observed the transition temperature to be 250 K, while Barman and Ravi \([14]\) found the enhancement of \(T_C\) from 73 K for \(x = 0\) to 187 K for \(x = 0.15\). Present results indicate that increasing the Fe concentration from \(x = 0.1\) to 0.5, the ordering temperature increase drastically when compared to the magnetic behaviour of the host \(\text{NiCr}_2\text{O}_4\).
P. Mohanty, A.R.E. Prinsloo, C.J. Sheppard, W.D. Roos

3+ oxidation state [16]. Fig. 4c shows the Fe\(^{2+}\) sublevels approximately 9.6 eV, suggesting a Cr in the oxidation state [16]. Fig. 4b depicts the Cr\(^{2+}\) core levels with the energy separation between the sub levels (Fig. 4(a)) doublet were found to be 853.1 eV \(^{2p1/2}\) and 870.3 eV \(^{2p3/2}\), respectively, resulting in a difference in binding energy of 17.2 eV, thus indicating that Ni is in the 2+ oxidation state [16]. The calculated moment for Ni(Cr\(^{0.5}_{0.5}\)Fe\(^{0.5}_{0.5}\))\(^2\)O\(_4\) is \(10\mu_B\) [18]. However, the measured saturation magnetization of the Ni(Cr\(^{0.5}_{0.5}\)Fe\(^{0.5}_{0.5}\))\(^2\)O\(_4\) at 0.1 T is approximately 6 emu/g, corresponding to a moment of 0.25 \(\mu_B\), indicating that the moments are not aligned parallel [18]. The higher moment in Ni(Cr\(^{0.5}_{0.5}\)Fe\(^{0.5}_{0.5}\))\(^2\)O\(_4\) is associated with the increases in \(T_C\) when comparing it with NiCr\(_2\)O\(_4\) [10].

4. Conclusions

Ni(Cr\(^{0.5}_{0.5}\)Fe\(^{0.5}_{0.5}\))\(^2\)O\(_4\) samples were prepared by chemical co-precipitation techniques and calcined at 900°C, resulting in a cubic phase. This was confirmed by Rietveld analysis of the XRD data, showing a slight mismatch in the calculated pattern indicating incomplete tetragonal to cubic phase transformation. The ferrimagnetic transition temperature, \(T_C\), was found to be above 300 K, higher than that reported values for the \(x \sim 0.15\) [15] and 187 K for \(x \sim 0.1\) [14]. For this compound the XPS studies indicated that the oxidation state of Ni is 2+, while that of Cr and Fe are 3+. Although both Cr and Fe has a 3+ oxidation state, Fe has a greater number of unpaired \(d\) electrons compared to Cr, therefore a higher moment is expected for the Ni(Cr\(^{0.5}_{0.5}\)Fe\(^{0.5}_{0.5}\))\(^2\)O\(_4\) than for NiCr\(_2\)O\(_4\). The calculated moment for Ni(Cr\(^{0.5}_{0.5}\)Fe\(^{0.5}_{0.5}\))\(^2\)O\(_4\) is \(10\mu_B\) [18].

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In order to understand oxidation state of the elements, XPS studies were carried out. In Fig. 4 high resolution core level photoelectron spectra of (a) Ni \(^{2p}\), (b) Cr \(^{2p}\), (c) Fe \(^{2p}\) and (d) O \(^{1s}\) are shown. The binding energies of the Ni \(^{2p}\) (Fig. 4(a)) doublet were found to be 853.1 eV \(^{2p1/2}\) and 870.3 eV \(^{2p3/2}\), respectively, resulting in a difference in binding energy of 17.2 eV, thus indicating that Ni is in the 2+ oxidation state [16]. Fig. 4b depicts the Cr \(^{2p}\) core levels with the energy separation between the sub levels approximately 9.6 eV, suggesting a Cr in the 3+ oxidation state [16]. Fig. 4c shows the Fe \(^{2p}\) core levels with the energy separation between the sub levels approximately 13.1 eV, confirming 3+ oxidation state of Fe [16]. Fig. 4(d) depicts the O \(^{1s}\) core level spectra. The asymmetry around 531 eV is a result of the contribution of two Gaussian peaks demarcated as Oa and Ob. The Ob peak is assigned to the hydroxyl groups, chemisorbed oxygen, and organic oxygen on the surface whereas Oa represents the lattice oxygen atoms [17]. Chemical synthesis often results such Ob region.
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