Effect of Fe Substitution on Structural and Magnetic Properties of $NiCr_2O_4$

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At room temperature, the normal oxide spinel $NiCr_2O_4$ 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 $NiCr_2O_4$ is 74 K. The magnetic moments of $NiCr_2O_4$ 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 $NiCr_2O_4$ with the motivation of changing the magnetic exchange interaction. In order to do so, single phase $Ni(Cr_{0.5}Fe_{0.5})_2O_4$ 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.

1. Introduction

$NiCr_2O_4$ and $NiFe_2O_4$ 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 $NiCr_2O_4$ [1]. For $NiFe_2O_4$ half of Fe^{3+} ions occupy tetrahedral site and the rest occupy octahedral site [2]. Thus, structurally both these compounds are quite different.

$NiCr_2O_4$ 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 $NiCr_2O_4$, lowering the average structural symmetry from cubic to tetragonal ($I4_1/amd$) [4, 5]. Further, magneto-structural coupling induces a distortion of $NiCr_2O_4$ 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 $NiFe_2O_4$ 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 $NiFe_2O_4$ is 878 K [10].

Therefore, considering the distinct properties of $NiCr_2O_4$ and $NiFe_2O_4$, it will be most interesting to investigate the subsequent modification in structure and the magnetic properties when substituting the Cr site in $NiCr_2O_4$ with Fe.

2. Experimental methods

$Ni(Cr_{0.5}Fe_{0.5})_2O_4$ powders were synthesized by chemical co-precipitation techniques, using stock solutions of 0.5 M of nickel nitrate ($Ni(NO_3)_2 \cdot xH_2O$), ferric nitrate ($Fe(NO_3)_2 \cdot xH_2O$) and chromium nitrate ($Cr(NO_3)_3 \cdot xH_2O$). 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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with a Phillips PANanalytical X-pert Pro X-ray diffractometer and using a Cu–K_α radiation. Rietveld refinements of the powder diffraction data were carried out by FULLPROF package [11]. The magnetic measurements on encapsulated powder samples were performed using a 14 T Cryogen Free Physical and Magnetic Measurement System (CRYOGENIC Ltd., UK) with a vibrating sample magnetometer (VSM) insert [12]. X-ray photoelectron spectroscopic (XPS) measurements were carried out at room temperature using Al–K_α radiation (i.e. 1486.71 eV). Fitting of the XPS data were performed using XPSpeak4.1 software package [13].

3. Results and discussion

The crystalline structure of Ni(Cr$_{0.5}$Fe$_{0.5}$)$_2$O$_4$ powder sample was determined to be a cubic spinel of $Fd\bar{3}m$ space group with lattice parameter $a = 8.301(9)$ 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 Rf–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 Ni ($x = 0.125$, $y = 0.125$, $z = 0.125$), Cr ($x = 0.5$, $y = 0.5$, $z = 0.5$), Fe ($x = 0.5$, $y = 0.5$, $z = 0.5$) and 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 $x = 0.1$.
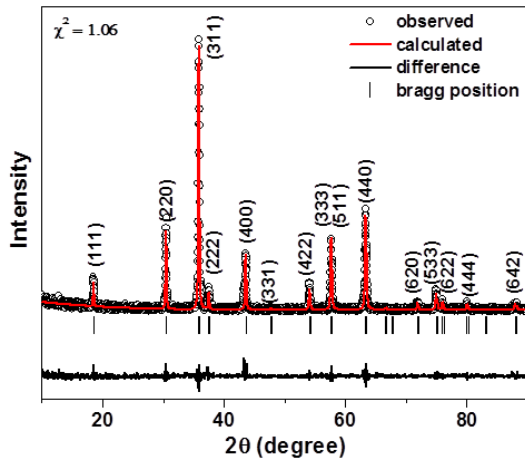

Fig. 1. Rietveld analysis of powder-diffraction pattern of Ni(Cr$_{0.5}$Fe$_{0.5}$)$_2$O$_4$ measured at 300 K using a single phase space group $Fd\bar{3}m$.

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

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.
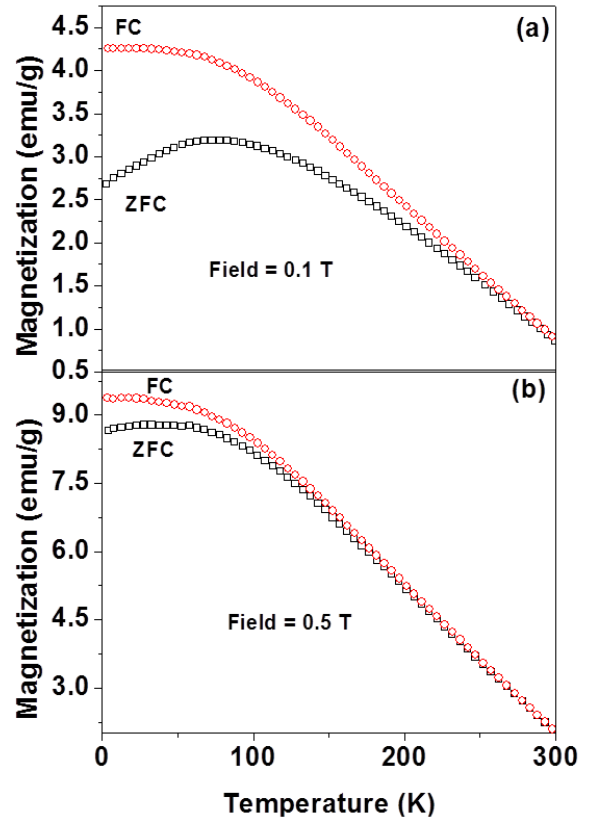

Fig. 2. M_{ZFC} and M_{FC} magnetization as a function of temperature for the Ni(Cr$_{0.5}$Fe$_{0.5}$)$_2$O$_4$, with a probing field of (a) 0.1 T and (b) 0.5 T.

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 $x = 0.1$. 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 NiCr$_2$O$_4$.
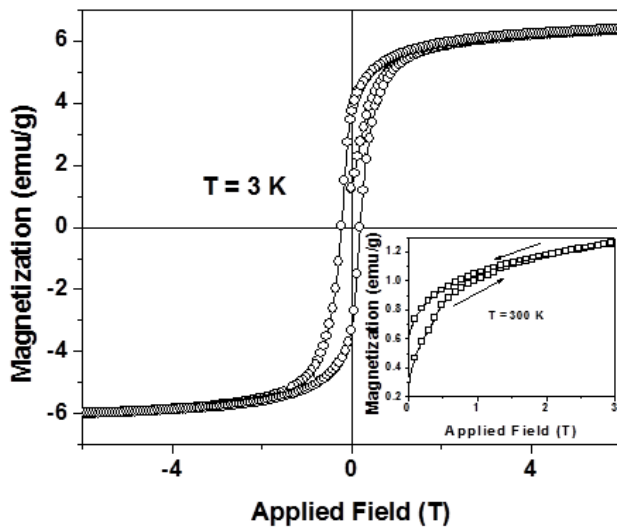
Fig. 3. Magnetic field dependent magnetization measurement for $Ni(Cr_{0.5}Fe_{0.5})_2O_4$ sample measured at 3 K and 300 K (inset), respectively.

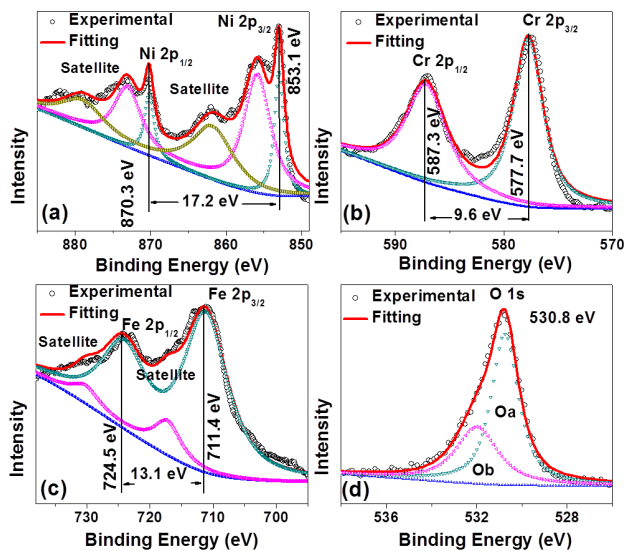Fig. 4. XPS core level spectra related to the following regions of $Ni(Cr_{0.5}Fe_{0.5})_2O_4$: (a) Ni $2p$, (b) Cr $2p$, (c) Fe $2p$, and (d) O $1s$.

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 $(2p_{3/2})$ and 870.3 eV $(2p_{1/2})$, 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 sublevels approximately 9.6 eV, suggesting a Cr in 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.

4. Conclusions

$Ni(Cr_{0.5}Fe_{0.5})_2O_4$ 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 $x = 0.15$ [15] and 187 K for $x = 0.1$ [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 $Ni(Cr_{0.5}Fe_{0.5})_2O_4$ than for $NiCr_2O_4$. The calculated moment for $Ni(Cr_{0.5}Fe_{0.5})_2O_4$ is $10\mu_B$ [18]. However, the measured saturation magnetization of the $Ni(Cr_{0.5}Fe_{0.5})_2O_4$ at 0.1 T is approximately 6 emu/g, corresponding to a moment of 0.25 μ_B, indicating that the moments are not aligned parallel [18]. The higher moment in $Ni(Cr_{0.5}Fe_{0.5})_2O_4$ is associated with the increases in T_C when comparing it with $NiCr_2O_4$ [10].

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