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Neutron diffraction study and magnetic properties of $NiFe_{2-x}Sc_xO_4$

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ABSTRACT

Polycrystalline $NiFe_{2-x}Sc_xO_4$ (x = 0.00, 0.05 and 0.10) compounds were prepared using solid state reaction method. X-ray diffraction measurements revealed that the compounds exhibited cubic inverse spinel phase without any impurity phases. Room temperature neutron diffraction measurements were carried out to determine magnetic structure along with the structural properties. Raman measurements also supported the cubic inverse spinel ferrite structure of the compounds. The gradual shifts in wave numbers of prominent Raman modes indicated that the Sc^{3+} ions replaced Fe^{3+} ions at the B-site. A decrease in saturation magnetization (M_s), Curie temperature (T_c) and anisotropy constant of $NiFe_{2-x}Sc_xO_4$ was observed with an increase of the Sc content.

1. Introduction:

Among the ferrites, Nickel ferrite ($NiFe_2O_4$) has been investigated extensively due to its excellent magnetic and electrical properties, namely, high- frequency permeability, high M_s high T_c and large electrical resistivity [1–4]. Owing of its excellent properties, $NiFe_2O_4$ can also be used in microwave devices which require strong coupling to electromagnetic signal~~s~~. In $NiFe_2O_4$, Fe^{3+} ions occupy the tetrahedral (A) sites, Fe^{3+} and Ni^{2+} ions occupy octahedral (B). Its net magnetic moment per molecule and Curie temperature are 2 μ_B and 858 K, respectively [5]. The substitution of Gd^{3+} ions for Fe^{3+} in $NiFe_2O_4$ resulted higher H_c (coercive field) and M_s, are decreased. [6–7]. In general, it is observed that a partial substitution of Fe^{3+} by rare-earth ion~~s~~ R^{3+} in $NiFe_2O_4$ decreases its M_s and T_c [4,6,8]. It will be interesting to observe the influence of substitution of non-magnetic ion other than rare-earth ion at Fe site in $NiFe_2O_4$ and observe its effect on structural and magnetic properties of nickel ferrite. To the best of our knowledge, there have been no reports on neutron diffraction study of Sc substitution for Fe in $NiFe_2O_4$. Here we reports the effects of partial replacement of Fe^{3+} by non-magnetic Sc^{3+} in $NiSc_xFe_{2-x}O_4$ compounds with x = 0.00, 0.05 and 0.10 and their structural and magnetic properties are studied.

2. Experimental details:

Polycrystalline $NiSc_xFe_{2-x}O_4$ (x = 0.00, 0.05 and 0.10) compounds were prepared by the standard solid state reaction method using high purity NiO, Fe_2O_3 and Sc_2O_3 powders. These powders were mixed and ground in a mortar and pestle for three hour and then calcined at 1200 °C for 12 h. Bruker D8 Advance X-ray powder diffractometer with CuK_α radiation was used to determine the phase purity of the samples. Neutron diffraction measurements were carried out a diffractometer, PD-3 at Dhruva reactor, Trombay. Raman spectra were collected in the range of 200 to 800 cm^{-1} by a laser Raman spectrometer. Nd-YAG laser operating at 532 nm was used for excitation. Infrared spectra were recorded using JASCO FTIR Spectrometer in the range 200–1000 cm^{-1}. Magnetization measurements were carried out with a vibrating sample magnetometer (VSM) at different temperatures.

3. Results and discussions

XRD patterns of $NiSc_xFe_{2-x}O_4$ (x = 0.00, 0.05 and 0.10) compounds are shown in Fig. 1(a). Rietveld refinement is carried out for all the compounds using the Full Prof program. The refined XRD patterns show the formation of single phase cubic inverse spinel structure with $Fd\bar{3}m$ space group without any secondary phases. Variation of the lattice parameter, *a*, with the Sc^{3+} content (x) is determined by the Rietveld method which is found to

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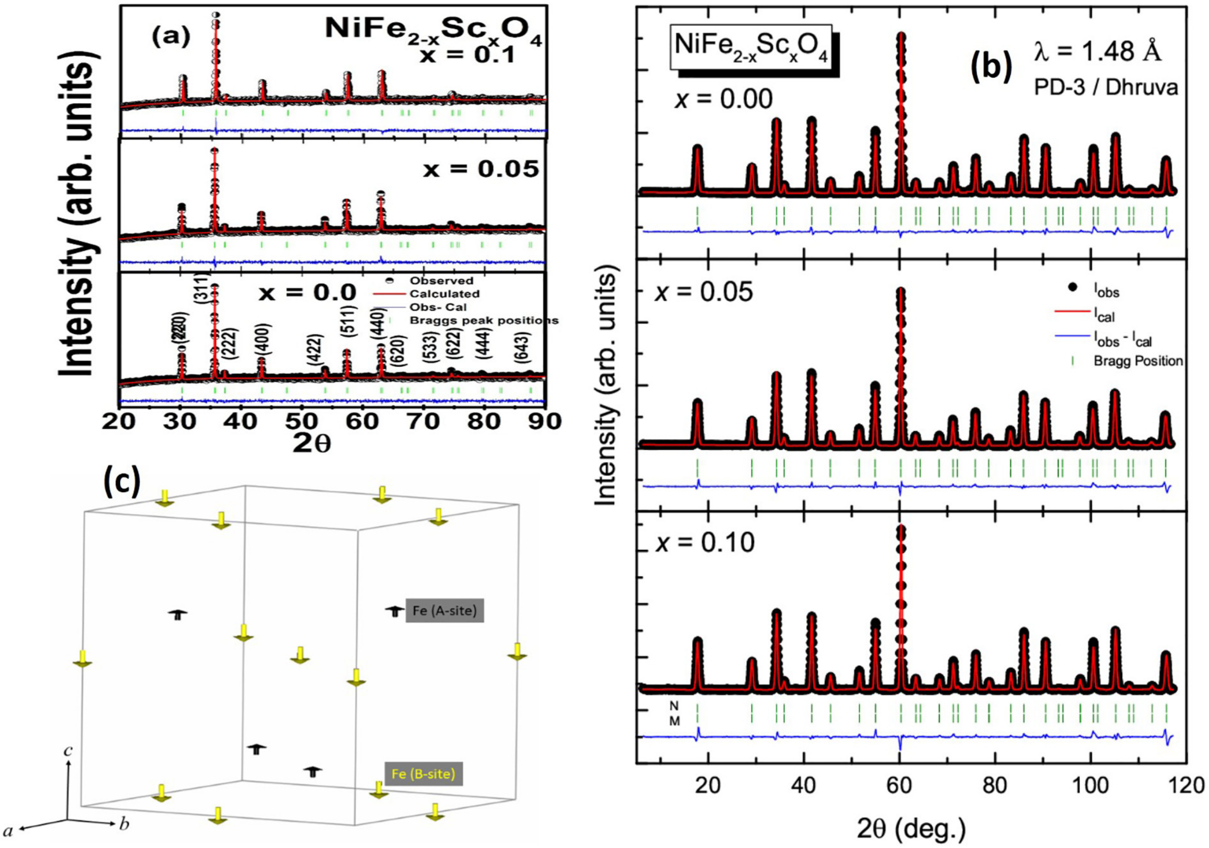

Fig. 1. (a) Rietveld refined room temperature (a) XRD patterns (b) Neutron diffraction patterns for NiFe$_{2\text{-}x}$Sc$_x$O$_4$ (x = 0.00, 0.05 and 0.10) (c) Magnetic structure of NiFe$_2$O$_4$.

increase with x given in table 1. This is expected as the ionic size of Sc^{3+} (0.81 Å) is larger than the ionic size of Fe^{3+} ions (0.64 Å). The increase in lattice parameter with the substitution of Sc^{3+} ions clearly indicates that the substituted ions replace the smaller Fe^{3+} ions [9].

Neutron diffraction (ND) experiments were carried out on powdered NiFe$_{2\text{-}x}$Sc$_x$O$_4$ (x = 0.00, 0.05 and 0.10) samples. Fig. 1(b) shows the Rietveld refinement of the ND data fitted using a structural model used to refine the XRD data. The good agreement between observed and calculated profiles confirms the phase formation and validity of the starting model. ND data also refined for the magnetic structure. The values of the structural refinement and net magnetic moments obtained from the Rietveld refinement are given in Table 1. The magnetic structure of NiFe$_2$O$_4$ is shown in Fig. 1 (c). The magnetic structure comprises of Fe at A-site and Fe and Ni at B site of the AB$_2$O$_4$ spinel structure. The net moment of the B-site comprises of the combined moment of Ni and Fe. It can be clearly seen that the Fe at B-site is substituted by the Sc ion as the moment of B-site and the net moment of the sample decreases with increasing Sc content.

Table 1
Structural parameters of XRD and structural and magnetic structure parameters obtained from the Rietveld refinement of ND of NiFe$_{2\text{-}x}$Sc$_x$O$_4$ (x = 0.00, 0.05 and 0.10).

NiSc$_x$Fe$_{2\text{-}x}$O4	***x* = 0.00**	***x* = 0.05**	***x* = 0.1**
XRD			
a (Å)	8.3375	8.34446	8.35286
V (Å^3)	579.5721	581.026	582.782
χ^2	1.74	1.98	1.90
NPD			
a (Å)	8.33099(2)	8.33907(2)	8.33125(3) Å
V (Å^3)	578.216(3)	579.899(3)	578.269(3) Å
Fe$^{3+(}$A) - O^{2-}	1.8767(9) Å3.4673(9) Å	1.8746(8) Å3.4699(8) Å	1.8866(10) Å3.4693(10) Å
Fe^{3+}/Sc$^{3+(}$B) - O^{2-}	2.0415(9) Å	2.0456(8) Å	2.0361(10) Å
Bragg-R	3.12	2.89	3.13
Rf-factor	1.94	1.79	2.09
Mag-R	5.28	5.37	3.38
χ^2	3.26	2.74	2.44
Rp	5.16	4.96	2.03
Rwp	7.49	6.95	3.57
Rexp	4.15	4.20	2.29
Fe^{3+}(A) μ_B	2.410(27)	2.681(26)	2.568(35)
Fe^{3+}/Ni^{2+} (B) μ_B	3.964(37)	3.766(37)	2.000(53)
Net Moment (μ_B / f. u.)	1.553(32)	1.085(21)	0.568(23)

Raman measurements were carried out on NiFe$_{2\text{-}x}$Sc$_x$O$_4$ (x = 0.00, 0.05 and 0.10) compounds at room temperature in the wave number region 100–800 cm^{-1} as shown in Fig. 2(a). Four Raman active modes (Eg, T2g, A1g (1), A1g (2)) are observed which are typical observations for cubic inverse spinel ferrite structures belonging to$Fd\bar{3}m$ space group [10]. The positions of T$_{2g}$(2) and T$_{2g}$(3) modes, corresponding to FeO$_6$ octahedra, are at 492, 488, 487 and 570, 571, 575 cm^{-1} for x = 0.00, 0.05, 0.10, respectively. A systematic shift in the wave numbers of these modes further confirms that the Sc^{3+} substitutes for Fe^{3+} present in the B-site. Belov et al reported Sc^{3+} ions occupy octahedral position in NiFe$_2$O$_4$ [11].

Fig. 2(b) shows FT-IR spectra of NiFe$_{2\text{-}x}$Sc$_x$O$_4$ (x = 0.00, 0.05 and 0.10) from 400 cm^{-1} to 1000 cm^{-1}. With increase in the Sc^{3+} content, the position of the frequency band show shift towards lower wavenumbers 601.7 cm^{-1}, 596.9 cm^{-1} and 594.0 cm^{-1} corresponding to x = 0.00, 0.05 and 0.10 respectively. The shift could be due to increase in the bond length of tetrahedral sites as frequency of the vibration varies inversely with the bond length.

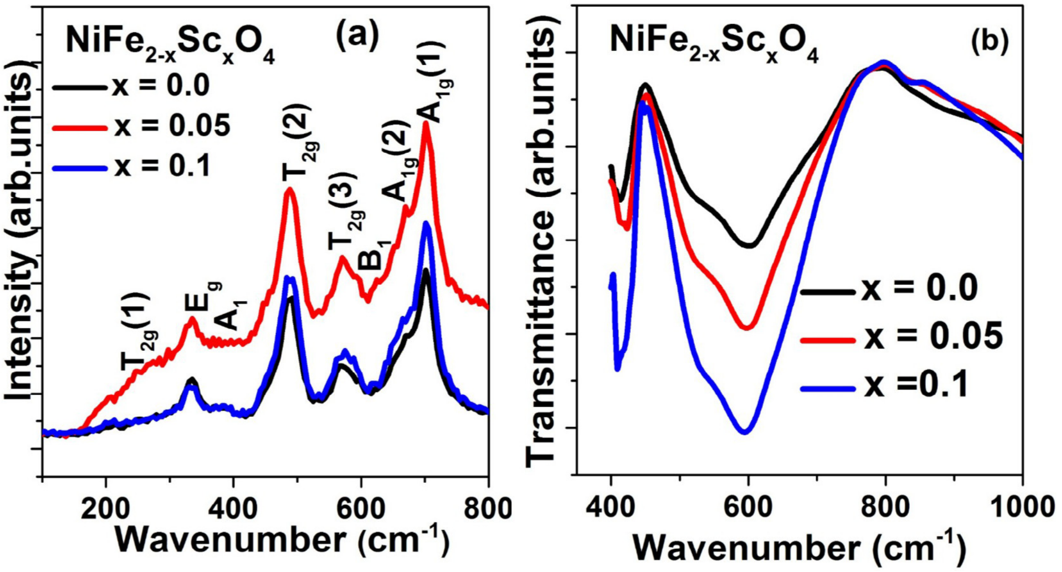

Fig. 2. (a) Room temperature Raman spectra and (b) FTIR spectra of $NiFe_{2-x}Sc_xO_4$ (x = 0.00, 0.05 and 0.10) samples.

Fig. 3(a, b) shows M−H curves of $NiFe_{2-x}Sc_xO_4$ (x = 0.00, 0.05 and 0.10) compounds at 300 K and 5 K. As observed from Fig. 3 (a), M_{max}, the maximum magnetization, increases for all the samples as the temperature decreases from 300 to 5 K while it decreases at a given temperature with the Sc concentration. The magnetization is reduced with nonmagnetic Sc content, similar observation reported in $NiFe_{2-x}Al_xO_4$ [12]. M_{max} for pure $NiFe_{2-x}Sc_xO_4$ is found to be ~ 53.24 emu/gm in agreement with the literature [13]. It is found that the saturation magnetization (Ms) values of $NiFe_{2-x}Sc_xO_4$ (x = 0.00, 0.05 and 0.10) are 53.24, 44.26, and 39.17 emu/gm at 300 K and 57.66, 48.54 and 43.97 emu/gm at 5 K, respectively. *Ms* values are found to decrease with increasing temperature, confirming the ferrimagnetic nature of the investigated compounds .Thus, the magnetic moments of $NiFe_{2-x}Sc_xO_4$ (x = 0.00, 0.05 and 0.10) samples decrease as the occupancy of Sc^{3+} ions (non-magnetic) in the octahedral site increases due to an increase in the Sc concentration. Thus, the partial substitution of magnetic Fe^{3+} ions, by non-magnetic Sc^{3+} ions, leads to a decrease in the B-site moment. The magneto-crystalline anisotropy constant K_1 can be found by fitting M−H data to the following equation, which is the law of approach to saturation (LAS) for cubic anisotropic polycrystalline systems [14].

$$M(H) = M_S - \frac{8K_1^2}{105\mu_0 M_s H^2} + kH$$

where k is the paramagnetic susceptibility. This term, kH, has been neglected in fitting the data as there are no paramagnetic impurities in the samples. The values of K_1 at 300 K for $NiFe_{2-x}Sc_xO_4$ are found to be 2.3×10^4 J/m^3, 1.87×10^4 J/m^3 and 1.4×10^4 J/m^3 for x = 0.00, 0.05 and 0.10, respectively. The reported value of K_1 of polycrystalline $NiFe_2O_4$ is 3.3×10^4 J/m^3 at 300 K [13]. The values of K_1 of $NiFe_{2-x}Sc_xO_4$ at 5 K are 2.7×10^4 J/m^3, 2.14×10^4 J/m^3 and 1.72×10^4 J/m^3 for x = 0.00, 0.05 and 0.10, respectively. According to single ion model, anisotropy in ferrites is due to the localized divalent ions in the octahedral site [13]. The non-zero orbital angular momentum is quantized along the trigonal axis (1 1 1) of the unit cell due to the crystalline fields produced by the oxygen ions and the trigonal field produced by co-cations. May be the O^{2-}-Ni^{2+}–O^{2-} the decreasing bond angles with Sc substitution correlate with smaller magnetic anisotropy values of *K*1. It is suggested that the observed decrease of K_1 in $NiFe_{2-x}Sc_xO_4$ compounds, studied here, is most probably due to a small distortion of the lattice.

Fig. 3(c) shows M vs T curves from which Curie temperatures for $NiFe_{2-x}Sc_xO_4$ compounds are determined. The T_C values of

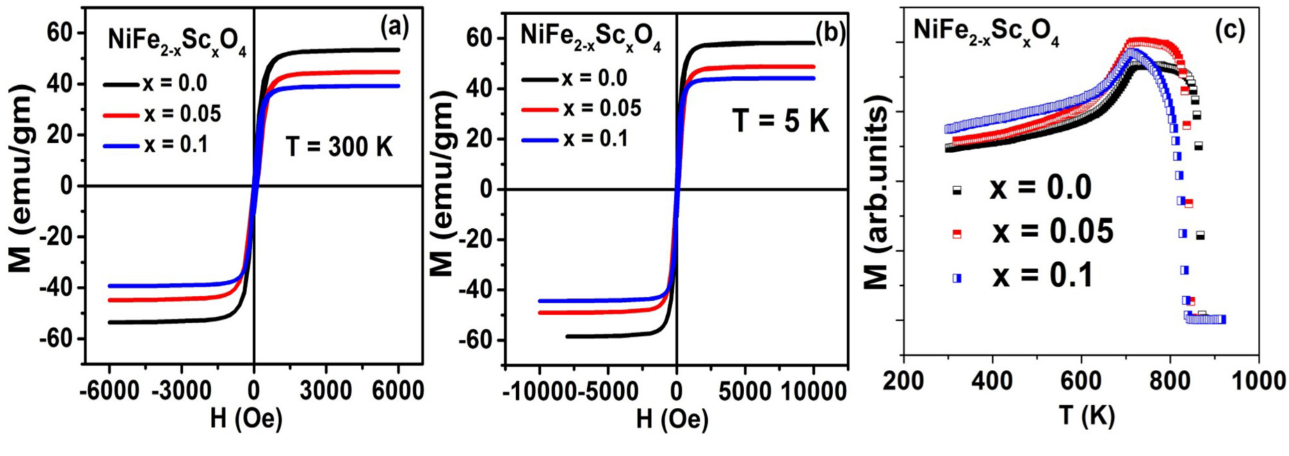

Fig. 3. M vs. H curves (a) at 300 K(b) at 5 K and (c) M vs T curves to determine Curie temperature for each value of x for $NiFe_{2-x}Sc_xO_4$ (x = 0.00, 0.05 and 0.10).

$NiFe_{2-x}Sc_xO_4$ compounds are 871, 851 and 844 K, for x = 0.0, 0.05 and 0.10, respectively. The decrease in T_C value in Sc -substituted nickel ferrites compared to that of pure nickel ferrite is expected due to the reduction of the Fe-Fe interactions at the B site.

4. Conclusions

Polycrystalline single phase $NiFe_{2-x}Sc_xO_4$ (x = 0.00, 0.05 and 0.10) compounds are synthesized and studied in this work. The compounds crystallize in the cubic inverse spinel phase as confirmed by the studies carried out using XRD, ND and Raman spectroscopy. The lattice constant of Sc doped compounds are found to increase because of substitution of larger ionic size of Sc^{3+} ions for Fe^{3+} ions. ND data has been refined also for the magnetic structure. The saturation magnetization (Ms) values of $NiFe_{2-x}Sc_xO_4$, are determined to be 53.24, 44.26, and 39.17 emu g^{-1} for x = 0.00, 0.05 and 0.10, respectively. The M_s Values of $NiFe_{2-x}Sc_xO_4$ compounds are found to decrease with increasing Sc concentration at a given temperature, 300 K or 5 K. Curie Temperature (T_C) value also decreases in Sc -substituted nickel ferrites compared to that of pure nickel ferrite.

CRediT authorship contribution statement

Bhumireddi Sattibabu: Conceptualization, Methodology, Writing - original draft. **T. Durga Rao:** Methodology. **A.K. Bhatnagar:** Writing - review & editing. **V. Satyanarayana Murthy:** . **S. Rayaprol:** Resources, Software. **V. Siruguri:** Resources, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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