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#### Enhanced Magnetodielectric response in Dy modified NiCr<sub>2</sub>O<sub>4</sub>

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#### Abstract

The chemically synthesized high purity spinel Ni $Cr_{2-x}Dy_xO_4(x=0, 0.1)$  samples have been characterised using magnetic and dielectric measurements in presence of high magnetic field. Crystal and magnetic structure of the samples have been determined by analysing neutron diffraction data recorded between temperature of 6 K and 300 K. NiCr<sub>2</sub>O<sub>4</sub> crystallizes in tetragonal phase with the space group of I41/amd whereas  $NiCr_{1.9}Dy_{0.1}O_4$ crystallizes in the mixed phase of cubic (space group of  $Fd\overline{3}m$ ) and tetragonal phases at room temperature. An additional phase of  $DyCrO_3$  with orthorhombic structure has been found in the Dy doped compound. The lattice parameter a increases and the c decreases in tetragonal structure with the substitution of Dy in Cr site. Both the samples show superlattice reflection peak indicating the presence of long range AFM ordering (transverse component) below 40 K. But the saturation magnetization slightly increases after Dy doping. An anomaly observed near Curie temperature in  $\varepsilon'(T)$  of NiCr<sub>2</sub>O<sub>4</sub> and NiCr<sub>1.9</sub>Dy<sub>0.1</sub>O<sub>4</sub> demonstrates the contribution of coupling between ferroelectricity and ferrimagnetism in the compounds. A linear correlation between the difference in dielectric constant and the field dependent squared magnetization for both the samples has been observed. The spin-spin interactions are most likely responsible for the observed magnetodielectric (MD) effect due to the magnetodielectric hysteresis in both parent and doped samples. Interestingly the MD% is found to increase with Dy doping.

# *Keywords:* Spinel, Antiferromagnetism, Neutron diffraction, Magnetodielectric, Ferrimagnetism.

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An important class of materials, namely, magnetodielectric materials that exhibit neither spontaneous polarization nor gratify the symmetry constraints for magnetodielectric effect; but nevertheless exhibit some kind of coupling between magnetization and dielectric properties in magnetic insulators, depending upon the localized spin configuration and the dielectric properties can be controlled by the magnetic field or conversely the magnetic polarization can be controlled by the electric field. The dielectric constant in magnetodielectric materials is modulated by an applied magnetic field depending on the spincharge coupling. The magnetodielectric coupling is often mediated by lattice dynamics [1]. The identification of the mechanism for strong spin-charge coupling for producing large magnetically induced shift of dielectric constant is a big challenge in the study of magnetodielectric materials. Many group of materials such as charge ordered  $LuFe_2O_4$  [2], EuTiO<sub>3</sub> [3], orthoferrites, orthochromites, MnF<sub>2</sub> [4], MnO [4], and Tb<sub>3</sub>Fe<sub>5</sub>O<sub>12</sub> [5], and different charge ordered manganites etc. are the examples of magnetodielectric materials. Magnetodielectric measurement provides the information about the nature of the magnetic exchange interaction in different frustrated magnets like  $Dy_2Ti_2O_7$  [6],  $Tb_2Ti_2O_7$  [7]. The magneto-dielectric coupling is suggested to originate from the electric and magnetic order coupling for ferroelectric frustrated LuFe<sub>2</sub>O<sub>4</sub> [8].

The materials MCr<sub>2</sub>O<sub>4</sub> (M = Mn, Co and Ni) are ferrimagnetic spinels, in which the  $M^{2+}$  cations occupy the tetrahedral (A) sites and the Cr<sup>3+</sup> cations occupy the octahedral (B) sites. Above 310 K NiCr<sub>2</sub>O<sub>4</sub> shows fully ordered and stoichiometric cubic spinel structure with *Fd3m* space group. The non-Jahn-Teller active Cr<sup>3+</sup> 3d<sup>3</sup> ions preferentially occupy B-sites because of its strong crystal field stabilization of the half occupied nondegenerate  $t_{2g}$  states and empty  $e_g$  states and Ni<sup>2+</sup>3d<sup>8</sup> ( $e_g^4 t_{2g}^4$ ) occupy the tetrahedral site [9]. But in cubic phase the fully occupied low-energy *e* levels and triply degenerate  $t_2$  levels of tetrahedral crystal field are responsible for potentially unstable structure of NiCr<sub>2</sub>O<sub>4</sub>. Below 310 K NiCr<sub>2</sub>O<sub>4</sub> is tetragonally deformed spinel structure by removing the orbital degeneracy [10], where c/a>1. The Jahn-Teller active Ni<sup>2+</sup> ions are responsible for the deformation in this system [9]. The coupling between spin and lattice degrees of freedom in NiCr<sub>2</sub>O<sub>4</sub> suggests this compound for a promising magnetodielectric material. Magnetodielectric properties in normal spinel NiCr<sub>2</sub>O<sub>4</sub> was first reported by Mufti *et al.* [11]. They have reported the change in slope in dielectric constant at 75 K and 31 K and the change in dielectric constant under the applied magnetic field. The polarization of 13  $\mu$ C m<sup>-2</sup> is observed by Maignan *et al.* [12].

Tomiyasu and Kagomiya performed the neutron diffraction study to describe the magnetic structure of NiCr<sub>2</sub>O<sub>4</sub>[13]. They showed that the combined long range order ferrimagnetic and antiferromagnetic components exist in NiCr<sub>2</sub>O<sub>4</sub>. The antiferromagnetic ordering occurs at lower temperature (temperature with a superlattice structure) of 31 K and the ferrimagnetic ordering occurs at relatively higher temperature (Curie temperature) below 74 K. Suchomel *et al.* investigates the magnetostructural coupling in NiCr<sub>2</sub>O<sub>4</sub> by employing the high resolution temperature dependent powder X-ray diffraction, magnetic susceptibility, and heat capacity measurements [14]. They also propose that a structural transition occurs from tetragonal by symmetry lowering in orthorhombic NiCr<sub>2</sub>O<sub>4</sub> at lower temperature magnetic transition of 30 K.

It has been shown in many cases that the rare-earth magnetic ordering plays an important role to achieve magnetodielectric coupling [15 -17]. Some spinel structures by the substitution with rare-earth ions like Dy, Er, Sm, Nd etc. lead to a structural distortion by inducing lattice strain in the material and significantly modify the magnetic and electrical properties in the materials. The doping of Dy (10.5  $\mu_B$ ) in NiCr<sub>2</sub>O<sub>4</sub> assures to manipulate the magnetic coupling. The *f* electron orbital contribution to the magnetic coupling is supposed to control the isotropic and anisotropic properties in the systems. NiCr<sub>2</sub>O<sub>4</sub> is known to have magnetostriction. Substitution of rare earth ions in the different spinel systems may lead to the structural distortion via strain [18, 19]. Dy exhibits large anisotropy and large magnetostriction values (linear strain 7500×10<sup>-6</sup> at 20 K) [20]. So it is interesting to study the effect of Dy doping in NiCr<sub>2</sub>O<sub>4</sub> system on the dielectric and consequent magnetodielectric properties.

In the present work we have carried out a detail investigation and analysis of the temperature and magnetic field dependent dielectric properties of the polycrystalline parent compound of NiCr<sub>2</sub>O<sub>4</sub> and Dy doped NiCr<sub>2</sub>O<sub>4</sub> system. We have demonstrated the linear correlation between the difference in dielectric constant and the field dependent squared magnetization for both the samples and have also discussed about the relation between the magnetodielectric properties and magnetostructural coupling in both NiCr<sub>2</sub>O<sub>4</sub> and Dy doped NiCr<sub>2</sub>O<sub>4</sub> compounds.

### 2. Experimental details

Polycrystalline samples of NiCr<sub>2-x</sub>Dy<sub>x</sub>O<sub>4</sub> (x=0, 0.1) have been synthesized by chemical sol-gel reaction route. The starting materials are Dy<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Ni (NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O, and citric acid. Stoichiometric amount of raw materials are dissolved into minimum amount of nitric acid and distilled water to make a clear solution. The solution is then heated at

180°C following stirring the solution continuously. The finally obtained black fluffy powder is ground and sintered at 1050°C in air for 4 hours to produce the polycrystalline manganites. The pellet (10 mm in diameter) form of as calcined powder is prepared and finally sintered at 1100°C for 4 hours.

The volume fractions of different phases and crystallographic details have been determined from the neutron diffraction study. The temperature dependent magnetization measurement and the magnetic hysteresis loop measurements up to  $\pm$  6 T magnetic field at various temperatures have been performed with the help of a superconducting quantum interference device (SQUID, Quantum Design) magnetometer. Neutron diffraction data has been collected at different temperatures on the PD2 diffractometer ( $\lambda = 1.2443$ Å) at Bhabha Atomic Research Centre, Mumbai, India. Rietveld refinements were carried out using Fullprof program. The dielectric constant and magneto-dielectric response has been measured with the help of a LCR meter (HIOKI Japan, model - 3532-50) employing a cryogen free closed cycle helium refrigeration variable temperature cryostat fitted in a superconducting magnet system with a maximum magnetic field of 8 Tesla (Cryogenics Ltd. U.K.,

8TCFMVTI).

### 3. Results and discussion

### 3.1. Powder Neutron diffraction study

#### **3.1.1.** Crystallographic structure

Figure 1 (a) and Fig. 1 (b) shows the neutron diffraction pattern of parent NiCr<sub>2</sub>O<sub>4</sub> and NiCr<sub>1.9</sub>Dy<sub>0.1</sub>O<sub>4</sub> samples, respectively at 300 K. For the parent compound the detail Rietveld refinements of the neutron diffraction pattern confirms tetragonal centro-symmetric structure with the space group of *I*4/*amd* whereas a coexistence of tetragonal (volume fraction 8%) and cubic structure (volume fraction 86%) with space group of Fd-3m is observed in the case of Dy doped NiCr<sub>2</sub>O<sub>4</sub>. Additionally, an orthorhombic phase of DyCrO<sub>3</sub> having a small volume

fraction of 6 % is observed in Dy doped sample. On lowering the temperature the volume fraction of the tetragonal structure increases to 80% at 6 K. The presence of DyCrO<sub>3</sub> depends on the synthesis condition. Due to the higher ionic radius for Dy ions as compared to Cr the secondary phases are formed at the grain boundary for higher concentration of Dy doped samples. The substitution of Cr by Dy results in a small distortion in the system. Ni takes 16*h* site and O occupies 4*a* site. Both Cr and Dy are distributed in 8*d* site. With the substitution of Cr by rare-earth Dy the lattice parameter *a* is found to increase while the lattice parameter *c* decreases within the tetragonal structure. For both parent and Dy doped sample *a* is found to increase and *c* is found to decrease with increase in temperature. As a result tetragonal distortion increases with lowering of temperature below 300 K. Table 1 shows the structural parameters obtained from the refinement of the neutron diffraction pattern at 6 and 300 K temperature for both the samples.

A structural change is observed in NiCr<sub>2</sub>O<sub>4</sub> due to the deformation in NiO<sub>4</sub> tetrahedra. When Dy is doped in NiCr<sub>2</sub>O<sub>4</sub>, the deformation of NiO<sub>4</sub> may cause the structural change. The mean bond angle O-Ni-O in NiO<sub>4</sub> polyhedra for NiCr<sub>2</sub>O<sub>4</sub> and Ni<sub>1.9</sub>Dy<sub>0.1</sub>Cr<sub>2</sub>O<sub>4</sub> has been listed in Table 1 at both 6 and 300 K. For ideal NiO<sub>4</sub> tetrahedra all bond angles are near 109.5°. But in the tetragonal phase two O-Ni-O bond angles are observed in a distorted tetrahedron due to orbital ordering for both samples.

### 3.1.2. Magnetic structure

Figure 2(a) and (b) shows the neutron diffraction pattern of parent and Dy doped sample at 6K. On lowering of temperature below 100K, enhancement in the intensity of the low angle fundamental reflection (101) is observed below Curie temperature confirming the ferrimagnetic like ordering below this temperature. On further lowering of temperature below 30K superlattice reflections (110) (01-1) (marked on the figure by \*) are observed indicating the antiferromagnetic ordering in these samples. The modelling of the magnetic structure was

done in a manner similar to that reported by Tomiyasu *et al.* [19]. The superlattice reflection (110) near 19.6° representing the transverse antiferromagnetic superlattice reflections is indexed by the propagation vector (001). K. Tomiyasu *et al.* also reported earlier the Neutron diffraction studies of NiCr<sub>2</sub>O<sub>4</sub> and showed the enhancement of superlattice (110) reflection below 30 K [19].

The space group of *I*41/*amd* of tetragonal crystal structure has been used to demonstrate the magnetic structure of the samples. The moments of the transverse component of A and B sublattices are oriented along *z* and *x* directions. The moments corresponding to the longitudinal antiferromagnetic superlattice reflections of A sublattice orient along *x* direction for both parent and Dy doped samples at 6 K. It is observed that the moments for tetrahedral site of ferrimagnetic component increases with Dy doping, but the moments for octahedral sites remain constant. The moment for tetrahedral site of antiferromagnetic component for octahedral site decreases at 6 K. The net moment for the antiferromagnetic component decreases from 1.2 to -0.6  $\mu_B$ . Figure 3 shows the temperature dependent magnetic moment at tetrahedral and octahedral site for the sample *x*=0.1.

### 3.2. Magnetic properties study

Figure 4 (a) and 4 (b) show the temperature dependent magnetization under zero field cooled (ZFC) and field cooled (FC) conditions at different applied magnetic field for x=0.0 and 0.1 samples, respectively. With increasing applied magnetic field from 100 Oe to 6 T, T<sub>ferri</sub> shifts towards higher temperature and become broad for both the samples. For x=0.0 sample as shown in the Fig. 4 (a) both FC and ZFC magnetization increases downward at lower temperature even at higher applied magnetic field of 1 T and 6 T. The lower inset of Fig. 4 (a) shows the enlarge view of FC magnetization at lower temperature in the applied magnetic field of 1 T for x=0.0. On the other hand for x = 0.1 sample at higher magnetic field

of 1 and 6 T the FC and ZFC magnetization is observed to increase in upward direction towards lower temperature. The increase of magnetization at lower temperature towards upward direction indicates the existence of ferromagnetic component at low temperature. The suppression of antiferromagnetic component at low temperature is also observed from neutron diffraction study for x = 0.1 sample. The temperature derivative of ZFC magnetization as a function of temperature has been plotted to understand the phase transition for the samples as shown in the inset of Fig. 4 (a) and (b) for x=0.0 and 0.1, respectively. The magnetic transition near 14 K may be attributed to the paramagnetic response of the Dy<sup>3+</sup> ordering. For all the samples the low temperature magnetic transition is not affected for higher applied magnetic field. Near 67 and 71 K temperatures an anomaly in ZFC and FC curves as well as in inverse susceptibility curves is observed for x=0.0 and 0.1 samples, respectively. Kagimiya and Tomiyasu describe the development of ferrimagnetic component in the material near the temperature (T<sub>ferri</sub>) of 74 K using neutron diffraction experiments [13]. Ishibashi and Yasumi observed another low temperature anomaly in thermomagnetic measurement at 31 K [21]. Tomitasu and Kagomiya reported this temperature to the onset of the ordering of canted antiferromagnetic component of the magnetic structure of  $NiCr_2O_4$ [13]. For the Dy doped samples same type of anomalies are observed near 33 K. Interestingly this anomaly is not affected by Dy doping. At higher temperature above T<sub>ferri</sub> a magnetic transition is observed in case of Dy doped NiCr<sub>2</sub>O<sub>4</sub> samples. We have detected the secondary phases of  $DyCrO_3$  as investigated from the neutron diffraction analysis. The high temperature magnetic transition  $T_{antiferro}$  (139.4 K for x=0.1) above  $T_{ferri}$  is attributed to the canted antiferromagnetic ordering due to the Cr<sup>3+</sup> spins in DyCrO<sub>3</sub> [22]. It is interesting to notice that the high temperature magnetic transition  $T_{antiferro}$  is absent in the thermomagnetic curve under higher applied magnetic field.

The effective paramagnetic moment  $p_{\rm eff}$  of the samples has been determined by the Curie-Weiss law,  $\chi = C/(T - \Theta_{CW})$  (where C is Curie-Weiss constant and  $\Theta_{CW}$  is the Curie-Weiss temperature) in the paramagnetic region of dc susceptibility for the samples. For quenched orbital contribution the spin only effective moment ( $\mu_s = 2\sqrt{S(S+1)}$ ) for Ni<sup>2+</sup> is 2.83  $\mu_B$ . The spin only effective moment for Dy<sup>3+</sup> is 10.5  $\mu_B$ . The experimental values of  $p_{eff}$ are observed to increase with increase in Dy content as listed in Table 2. The expected effective paramagnetic moments for the samples are listed in the Table 2. The theoretical values are slightly greater than the experimentally determined values of 5.74 and 6.41  $\mu_B$  per formula unit obtained from the fitting parameter in the paramagnetic regime using Curie-Weiss law for x=0.0, 0.10 samples, respectively. The incomplete removal of frustration may cause the comparatively low value of  $p_{\rm eff}$  than the expected moment. The distortion leads to the removal of frustration and therefore a long range order appears. The introduction of magnetic ions  $Dy^{3+}$  having higher magnetic moment of 10.5  $\mu_B$  in place of  $Cr^{3+}$  having comparatively low magnetic moment leads to increase the magnetic moment with increasing Dy contents. The decreasing magnitude of  $\Theta_{CW}$  with increasing Dy content reveals the decreasing antiferromagnetic A-B interactions.

Néel-type ferrimagnetic temperature decreases with increase in Dy doping. The frustration index is estimated by rearranging the Curie-Weiss equation as follows:

$$\frac{C}{\chi \Theta_{CW}} = \frac{T}{\Theta_{CW}} - 1$$

Figures 4 (c) and 4 (d) show the plot of  $C/(\chi |\Theta_{CW}|) - 1$  as a function of  $(T/\Theta_{CW})$  for the x=0.0 and 0.1 samples, respectively. The linear dependence of magnetization with the magnetic field at higher temperature for the samples suggests that NiCr<sub>2</sub>O<sub>4</sub> is paramagnetic above 70 K and NiCr<sub>1.9</sub>Dy<sub>0.1</sub>O<sub>4</sub> is paramagnetic above 150 K. At the paramagnetic regime the

fitted straight line passed through the origin indicates the ideal Curie-Weiss behavior. The negative deviation from the ideal line normally results in uncompensated antiferromagnetism whereas the positive deviation from the straight line reveals the pure compensated antiferromagnetic interactions. As shown in the Figs. 4 (c) and 4 (d), the samples exhibit negative deviation from ideal line indicating uncompensated antiferromagnetism or ferrimagnetism. The negative value of  $\Theta_{CW}$  as well as the low saturation magnetization for the samples indicates the existence of non-collinear ferrimagnetic ordering in the samples. To indicate which compound is more frustrated we have calculated the frustrated index of both the parent and Dy doped samples. The frustrated index is defined as  $f = \Theta_{CW} / T_N$ . The value of frustration index *f* is listed in the Table 2. It is observed that all the samples are frustrated and *f* decreases with increasing Dy content. The reduction of *f* with increasing *x* indicates the most stabilization in Dy doped sample. The higher value of *f* indicates that pure NiCr<sub>2</sub>O<sub>4</sub> is magnetically more frustrated.

Figure 5 (a) shows the M-H hysteresis loops for x=0.0 at different temperatures. The linear dependence of magnetization on the applied magnetic field above 70 K for x=0.0 sample reveals the paramagnetic ordering. The coercive field grows below the ferromagnetic ordering temperature for x=0.0 sample. The suppression of magnetization hysteresis loop and the linear increase of magnetization with applied magnetic field above 2.7 T are observed for x=0.0 sample. It is interesting to notice that the linear increase of magnetization starts at relatively higher applied magnetic field for x=0.1 sample. The linear increase of magnetization is observed to be  $0.3 \mu_B$  per formula unit. But the expected magnetization value by taking the collinear ferromagnetic configuration in NiCr<sub>2</sub>O<sub>4</sub> is 2.4  $\mu_B$ . According to Kagimiya and Tomiyasu, the magnetic structure possibly consists of

longitudinal ferromagnetic and transverse antiferromagnetic sublattices [13]. The linear magnetization at higher field occurs due to the contribution of the slightly canting spins.

Figure 5 (b) shows the M-H hysteresis loops for x=0.0 and 0.1, respectively at 5 K. The saturation magnetization is observed to increase with increase in Dy content. With increasing Dy doping the initial field of saturation magnetization shifts to higher field due to the presence of antiferromagnetic ordering requiring higher magnetic field to saturate. The saturation magnetization increases with increase in Dy content below  $T_N$  may be due to the continuous rotation of Dy<sup>3+</sup> ions with canted Cr<sup>3+</sup> ions.

### 3.3. Dielectric and magnetodielectric properties

NiCr<sub>2</sub>O<sub>4</sub> is known to have magnetostriction. Substitution of rare earth ions in the different spinel systems may lead to the structural distortion via strain [18,19]. Dy exhibits large anisotropy and large magnetostriction values [20]. So it is interesting to study the effect of Dy doping in NiCr<sub>2</sub>O<sub>4</sub> system on the dielectric and magnetodielectric properties.

To investigate the effect of changes of spin and lattice structure between 71 and 30 K on the magnetodielectric effect we have performed a careful study of applied magnetic field and temperature dependent dielectric and magnetodielectric properties of NiCr<sub>2</sub>O<sub>4</sub> and NiCr<sub>1.9</sub>Dy<sub>0.1</sub>O<sub>4</sub> systems. Temperature dependent dielectric constant  $\varepsilon'$  of NiCr<sub>2</sub>O<sub>4</sub> shows the anomalies near 30 K and near the ferrimagnetic Curie temperature of 72 K as shown in Fig. 6 (a). Figure 6 (b) shows the derivative of the dielectric permittivity with respect to temperature of Dy doped sample. Three shallow minima are observed near 30, 71, and 139 K as shown in the Fig. 6 (b). The existence of dielectric anomaly near the magnetic and structural transition temperature is a clear indication of the correlation between structural, magnetic, and dielectric properties in the system. The slight change in dielectric permittivity near 71 K may be attributed to the magnetostriction properties of NiCr<sub>2</sub>O<sub>4</sub>.

 $NiCr_{1.9}Dy_{0.1}O_4$  occurs due to the contribution of the orthorhombic  $DyCrO_3$ . The structural and magnetic changes near 30 and 72 K have been investigated from neutron diffraction analysis and magnetic study.

The magnetodielectric measurements have been carried out by measuring the change in dielectric constant under applied magnetic field. The magnetodielectric effect is denoted as  $MD\% = (\epsilon'(H) - \epsilon'(0)) \times 100/\epsilon'(0)$  where  $\epsilon'$  is the dielectric constant. We have measured the isothermal field dependent dielectric permittivity which shows a parabolic dependence on the applied magnetic fields near magnetic transition temperature. The dielectric profile depends on the applied magnetic field as shown in the Fig. 7. For NiCr<sub>2</sub>O<sub>4</sub> at 30 K maximum MD% of 0.045% is obtained with the existence of a hysteresis in MD% profile whereas the MD% is observed to increase in NiCr<sub>1.9</sub>Dy<sub>0.1</sub>O<sub>4</sub>. For Dy doped NiCr<sub>2</sub>O<sub>4</sub> maximum MD% of 0.22% is observed at 30 K. Figure 7 (c) and (d) show the magnetodielectric effect and square of magnetization for NiCr<sub>1.9</sub>Dy<sub>0.1</sub>O<sub>4</sub> at different temperatures of 50 and 90 K, respectively. In order to understand magnetodielectric effect the parabolic dependence of isothermal field dependent dielectric constant measurements have been performed. The thermodynamic potential in a ferroelectromagnetic system in the framework of Ginzburg-Landau theory is defined as [23]

 $\Phi = \Phi_0 + \alpha P^2 - PE + \alpha' M^2 - MH + \gamma P^2 M^2$ 

where  $\Phi$  is the thermodynamic potential;  $\alpha$ ,  $\alpha'$ , and  $\gamma$  are temperature dependent magnetodielectric coupling coefficients; *M* and *P* represent magnetic and electric polarization, respectively; E and H denote electric and magnetic field, respectively. The relative change in MD% with the change in magnetic field trace the curve similar to square of magnetization vs. magnetic field behaviour for the samples at 30 K. The agreement between MD% and the square of magnetization behaviour suggest that the magnetodielectric coupling

is originated from the term  $\gamma P^2 M^2$  of Ginzburg-Landau in the samples, as was earlier proposed by Mufti *et al.* [11]. So the spin mediated magnetodielectric response is significant in the samples. In order to demonstrate the magnetodielectric coupling effect one should consider the spin-orbit coupling ( $\lambda$ . S. L, where L is orbital angular momentum and S is the total spin) of Ni<sup>2+</sup>. In case of NiCr<sub>2</sub>O<sub>4</sub>, Ni<sup>2+</sup> cation exhibit larger spin orbit coupling constant of - 315 cm<sup>-1</sup> resulting in high magnetodielectric coupling [24]. DyCrO<sub>3</sub> shows the ferroelectricity and the magnetocapacitance effect. So the MD% can be affected by the DyCrO<sub>3</sub> phase in Dy doped NiCr<sub>2</sub>O<sub>4</sub>. To understand the details of magnetodielectric response further investigation is required in single crystals of NiCr<sub>2</sub>O<sub>4</sub>.

#### 4. Summary

In summary, both magnetic, dielectric and magnetodielectric properties have been seen to increase with the substitution of Dy for Cr in NiCr<sub>2</sub>O<sub>4</sub>. The antiparallel alignment of Cr and Dy spin is confirmed from neutron diffraction studies. The AFM moments in A site and B site are perpendicular to each other and therefore non collinear. The grown of tetragonal structure possibly takes place by expansion of the lattice parameter *a* (plotted as  $\sqrt{2}$ ) but contraction of *c* for the distortion due to the substitution of Cr by rare-earth Dy. The Dy modified sample shows higher magnetic moment and reveals the decreasing antiferromagnetic A-B interactions after Dy doping in NiCr<sub>2</sub>O<sub>4</sub>. The frustration index *f* indicates the Dy doped sample as the most stabilized one and it may be due to the removal of frustration after distortion by doping effect. The existence of dielectric anomaly near magnetic and structural transition temperature is a clear indication of the correlation between structural, magnetic, and dielectric properties in the samples. The MD% has been enhanced may be due to the large magnetostriction value of Dy. Further investigation is required to understand the details of the improved magnetodielectric response in the Dy modified NiCr<sub>2</sub>O<sub>4</sub>.

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#### Table 1

Structural parameters obtained from the neutron diffraction pattern at 6 and 300 K temperatures for x=0.0 and 0.1 of spinel NiCr<sub>2-x</sub>Dy<sub>x</sub>O<sub>4</sub> samples.

	<i>x</i> =0		<i>x</i> =0.1			
	6K	300K	6K		300K	
	I4/amd	I4/amd	I4/amd	Fd-3m	I4/amd	Fd-3m
a (Å)	5.7712	5.8315	5.7908	8.3180	5.865	8.3176
b (Å)	5.7712	5.8315	5.7908	8.3180	5.865	8.3176
c (Å)	8.5491	8.4096	8.5275	8.3180	8.347	8.3176
$V(Å^3)$	284.74	285.98	285.95	575.52	287.12	575.4321
Vol. fraction			80	14	8	86
(%)						
Ni-O (Å)	1.954	1.955	1.965	1.864	1.919	1.968
O-Ni-O (°)	116.8	115.9	116.2	116.4	116.7	117.49
	112.9	110.9	112.1	109.5	113.3	112.53

#### Table 2.

Comparison between the Curie Weiss temperature, Curie Weiss constant, effective paramagnetic moment, frustration index, theoretical value of moment, saturation magnetization for x=0.0 and x=0.1 samples.

Sample	Θ <sub>CW</sub>	C	<b>p</b> <sub>eff</sub>	f	Theoretical value (µ <sub>B</sub> )	Saturation magnetization at 5 K ( $\mu_B$ )
<i>x</i> =0.0	-286.7	4.216	5.74	3.98	6.16	0.30
<i>x</i> =0.1	-187.2	5.255	6.41	1.34	6.89	0.44

MAT

### **Figure Captions**

**Figure 1.** Rietveld refined neutron diffraction pattern for (a) x=0.0 (b) x = 0.1 measured at 300 K. The tick marks (from top to bottom) indicate the position of reflections for tetragonal, cubic and DyCrO<sub>3</sub> phases.

**Figure 2.** Rietveld refined neutron diffraction pattern for (a) x=0.0 (b) x = 0.1 measured at 6 K. The tick marks (from top to bottom) for x=0 sample indicate reflections corresponding to tetragonal phase, propagation vector k=(001) and k=(000). The tick marks (from top to bottom) for x= 0.1 sample indicate reflections corresponding to tetragonal phase, propagation vector k=(000), k=(001), cubic phase and DyCrO<sub>3</sub>.\\

Figure 3. Temperature dependent magnetic moments at tetrahedral (A) and octahedral (B) sites for x=0.1 sample.

**Figure 4.** (a) ZFC and FC magnetization under the applied magnetic field of 100 Oe, 1 and 6 T for x=0.0. Upper inset shows dM<sub>FC</sub>/dT curves under the applied magnetic field of 100 Oe. Lower inset shows the enlarge view of FC magnetization at lower temperature in the applied magnetic field of 1 T for x=0.0. (b) Temperature dependent ZFC and FC magnetization at different applied magnetic field for x=0.1 sample. Inset shows dM<sub>FC</sub>/dT curves under the applied magnetic field of 100 Oe. (c) Normalized inverse susceptibility showing ideal Curie-Weiss paramagnetism for x=0.0 (d) Normalized inverse susceptibility showing ideal Curie-Weiss paramagnetism for x=0.1 sample. Inset shows temperature dependent inverse susceptibility for x=0.1.

Figure 5. (a) M-H hysteresis loops at different temperatures for x=0.0. (b) Comparison between M-H hysteresis loops measured at 5 K for x=0.0 and x=0.1 samples. Figure 6. (a) Temperature dependent dielectric permittivity of x=0.0 at 10 kHz. (b) Temperature dependent dielectric permittivity of x=0.1 collected at 10 kHz shows three dielectric anomalies near 30, 71, and 140 K. The derivative of dielectric permittivity as a function of temperature shows maxima near 30, 71, and 140 K.

**Figure 7.** The squared field-dependent magnetization plotted against the field-dependent dielectric permittivity data collected at (a) 30 K for x=0.0 and (b) for x=0.1. Field-dependent changes in the dielectric constant correlate with trends in the field-dependent squared magnetization for x=0.1 at (c) 50 K and (d) 90 K.



Figures

Figure 1. P. R. Mandal *et al*.



Figure 2. P. R. Mandal et al.



Figure 3. P. R. Mandal et al.



Figure 4. P. R. Mandal *et al*.



Figure 5. P. R. Mandal et al.

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Figure 6. P. R. Mandal et al.



Figure 7. P. R. Mandal *et al*.

- NiCr<sub>2</sub>O<sub>4</sub> crystallizes in tetragonal phase with the space group of I41/amd whereas NiCr<sub>1.9</sub>Dy<sub>0.1</sub>O<sub>4</sub> crystallizes in the mixed phase of cubic (space group of Fd<sup>3</sup>m) and tetragonal phases at room temperature.
- Both the samples show superlattice reflection peak indicating the presence of long range AFM ordering (transverse component) below 40 K.
- The saturation magnetization slightly increases after Dy doping.

C

- An anomaly observed near Curie temperature in ε' (T) of NiCr<sub>2</sub>O<sub>4</sub> and NiCr<sub>1.9</sub>Dy<sub>0.1</sub>O<sub>4</sub> demonstrates the contribution of coupling between ferroelectricity and ferrimagnetism in the compounds.
- The spin-spin interactions are most likely responsible for the observed magnetodielectric (MD) effect due to the magnetodielectric hysteresis in both parent and doped samples. Interestingly the MD% is found to increase with Dy doping.