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Enhanced magnetodielectric response in Dy modified $NiCr_2O_4$

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ABSTRACT

The chemically synthesized high purity spinel $NiCr_{2-x}Dy_xO_4$ ($x = 0, 0.1$) samples have been characterized using magnetic and dielectric measurements in presence of high magnetic field. Crystal and magnetic structure of the samples have been determined by analyzing neutron diffraction data recorded between temperature of 6 K and 300 K. $NiCr_2O_4$ 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 $Fd\bar{3}m$) 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 $NiCr_2O_4$ and $NiCr_{1.9}Dy_{0.1}O_4$ 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.

1. Introduction

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 spin-charge 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], $EuTiO_3$ [3], orthoferrites, orthochromites, MnF_2 [4], MnO [4], and $Tb_3Fe_5O_{12}$ [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 magnetodielectric coupling is suggested to originate from the electric and magnetic order coupling for ferroelectric frustrated $LuFe_2O_4$ [8].

The materials MCr_2O_4 (M = Mn, Co and Ni) are ferrimagnetic spinels, in which the M^{2+} cations occupy the tetrahedral (A) sites and the Cr^{3+} cations occupy the octahedral (B) sites. Above 310 K $NiCr_2O_4$ shows fully ordered and stoichiometric cubic spinel structure with $Fd3m$ space group. The non-Jahn–Teller active Cr^{3+} $3d^3$ 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 $Ni^{2+}3d^8$ ($e_g^4 t_{2g}^4$) 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 $NiCr_2O_4$. Below 310 K $NiCr_2O_4$ is tetragonally deformed spinel structure by removing the orbital degeneracy [10], where $c/a > 1$. The Jahn–Teller active Ni^{2+} ions are responsible for the deformation in this system [9]. The coupling between spin and lattice degrees of freedom in $NiCr_2O_4$ suggests this compound for a promising magnetodielectric material. Magnetodielectric properties in normal spinel $NiCr_2O_4$ was first reported by Mufti et al. [11]. They have reported the

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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 μC m^{-2} is observed by Maignan et al. [12].

Tomiyasu and Kagomiya performed the neutron diffraction study to describe the magnetic structure of $NiCr_2O_4$ [13]. They showed that the combined long range order ferrimagnetic and antiferromagnetic components exist in $NiCr_2O_4$. 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 $NiCr_2O_4$ 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 $NiCr_2O_4$ 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 μ_B) in $NiCr_2O_4$ 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. $NiCr_2O_4$ 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^{-6} at 20 K) [20]. So it is interesting to study the effect of Dy doping in $NiCr_2O_4$ 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 $NiCr_2O_4$ and Dy doped $NiCr_2O_4$ 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 $NiCr_2O_4$ and Dy doped $NiCr_2O_4$ compounds.

2. Experimental details

Polycrystalline samples of $NiCr_{2-x}Dy_xO_4$ ($x = 0, 0.1$) have been synthesized by chemical sol–gel reaction route. The starting materials are Dy_2O_3, Cr_2O_3, Ni $(NO_3)_3{\cdot}6H_2O$, 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 h 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 h.

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 ±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

Fig. 1(a) and (b) shows the neutron diffraction pattern of parent $NiCr_2O_4$ and $NiCr_{1.9}Dy_{0.1}O_4$ 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 $NiCr_2O_4$. Additionally, an orthorhombic phase of $DyCrO_3$ having a small volume fraction of 6% is observed in Dy doped sample. On lowering the temperature the volume fraction of the tetragonal

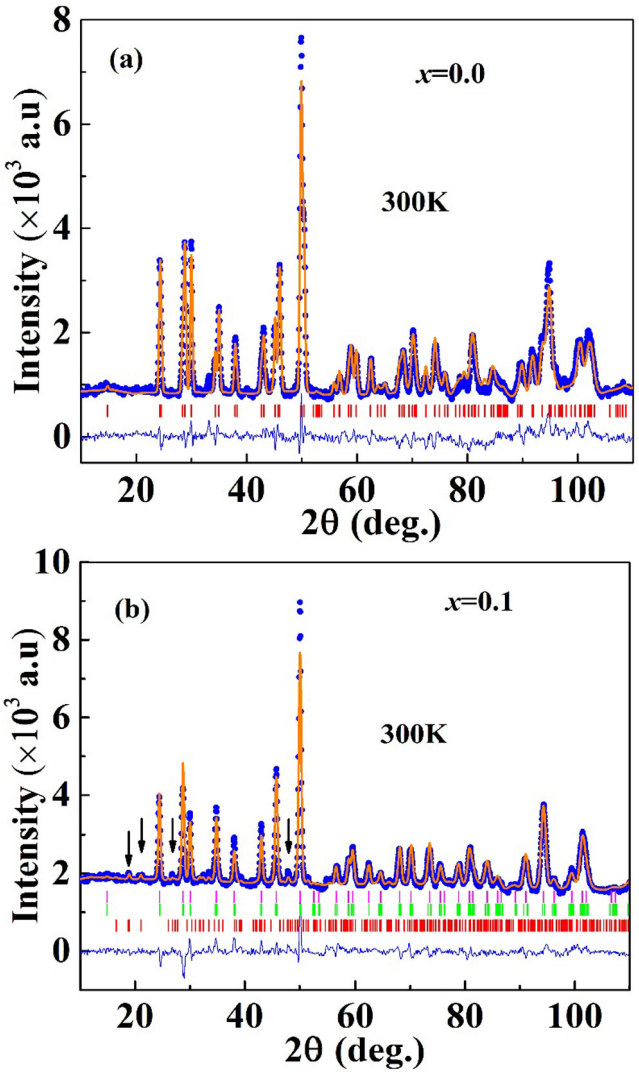

Fig. 1. Rietveld refined neutron diffraction pattern for (a) $x = 0.0$ (b) $x = 0.1$ measured at 300 K. The tick marks (from top to bottom) indicate the position of reflections for tetragonal, cubic and $DyCrO_3$ phases.