Magnetocapacitance in Dy-doped Ni ferrite

K. Kamala Bharathi,[1] K. Balamurugan,[2] P. N. Santhosh,[2] M. Pattabiraman,[2] and G. Markandeyulu[1,*]

[1]*Magnetism and Magnetic Materials Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai 600 036, India*

[2]*Low Temperature Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai 600 036, India*

Ferromagnetic and ferroelectric characteristics of Dy substituted nickel ferrite, $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$, were investigated. The material formed in the cubic inverse spinel phase with a small amount of $DyFeO_3$ as the additional phase. A small distortion of the cubic lattice was observed upon the substitution of Fe by Dy (in the *B* site). Substitution of Dy for Fe caused a decrease in the saturation magnetization and Curie temperature of the nickel ferrite. Magnetocapacitance of -4% was observed in $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ although the magnetostriction has not significantly changed with Dy substitution. The (high) dielectric constant with frequency is seen to reveal the dispersion in relaxation times.

Iron, cobalt, and nickel ferrites have inverse spinel structure and are some of the most versatile centrosymmetric magnetic materials.[1–5] In the inverse spinel structure, the tetrahedral (*A*) sites are occupied by the Fe^{3+} ions and the octahedral sites (*B*) are occupied by the divalent metal ions (M^{2+}) and Fe^{3+} in equal proportions. The angle *A*-O-*B* is closer to 180° than the angles *B*-O-*B* and *A*-O-*A* and, therefore, the *AB* pair (Fe-Fe) has a strong superexchange (antiferromagnetic) interaction. The net magnetic moment per molecule in the nickel ferrite is $2\mu_B$ and in the cobalt ferrite it is $3\mu_B$. Both have high Curie temperature (T_C) values and are 858 and 793 K, respectively.

All ferrites except those containing Co or Ti have small magnetostriction. The saturation magnetostriction (λ_S) at room temperature is positive for polycrystalline Fe_3O_4 (40×10^{-6}), whereas all the other ferrites have negative λ_S values.[6,7] Polycrystalline Mg ferrite and Li ferrites have very small values of λ_S (-8×10^{-6} and -5×10^{-6}, respectively) and the Co ferrite has λ_S value of -110×10^{-6}. In the cobalt ferrites the crystal field is not capable of removing the orbital degeneracy of Co^{2+} and, therefore, the orbital magnetic moment is of the same order of magnitude as the spin magnetic moment. This causes the large anisotropy and magnetostriction in these ferrites. Similarly, in the nickel ferrite, the unquenched orbital moment of Ni^{2+} leads to a large anisotropy and magnetostriction value (-26×10^{-6}).

Rare earth-iron based cubic laves phase compounds (RFe_2) are known to have very large magnetostriction[8,9] and these compounds are employed as active elements in several magnetostrictive transducers. However, the large conductivity of these compounds limits the usage of the transducers to low frequencies (a few kilohertz).[8]

Ferrites with the properties of large resistivity, low coercivity, and low eddy currents are being used for a variety of high frequency applications. Substitution of rare earth ion into the spinel structure has been reported to lead to structural distortion[10,11] and to induce strains in the material. Among the rare earth elements, Dy has large anisotropy as well as large magnetostriction[12] values. Therefore, it is of interest to investigate the effect of Dy substitution on the magnetostrictive properties of nickel ferrite and the results of our studies are presented in this Brief Report.

The $NiO \cdot Fe_{2-x}Dy_xO_3$ ($x=0, 0.075$) polycrystalline samples were prepared starting from 99.99% pure NiO and Fe_2O_3, Dy_2O_3 by the solid state reaction method. The powders of the starting materials were ground in a mortar and pestle for one hour and heat treated in air at 1200 °C for 12 h. For the electrical and magnetic measurements the powder sample was made into a pellet which was then sintered at 1250 °C in air for 12 h.

The material was characterized by taking powder x-ray diffraction (XRD) pattern employing Cu $K\alpha$ radiation. Magnetization and Curie temperature measurements were carried out employing a vibrating sample magnetometer. Magnetostriction measurements were carried out using the standard strain gauge method. Dielectric measurements were carried out at room temperature using a 4192A impedance analyzer. Ferroelectric hysteresis loop measurements were carried out at room temperature for which, the circuit suggested by Berkens and Kwaaitaal[13] (Sawyer–Tower circuit) was constructed and employed.

Figure 1 shows the XRD patterns of the $NiO \cdot Fe_{2-x}Dy_xO_3$ ($x=0, 0.075$) samples along with the calculated pattern after the Rietveld refinement was carried out using the GSAS program.[14] The weighted refined parameter and the χ^2 values of the fitting are given in Fig. 1. $NiO \cdot Fe_2O_3$ was found to form in the cubic inverse spinel phase with out any impurity phase and the value of the lattice constant was found to be $a=8.335$ Å and is seen to agree well with that reported in Ref. 15. $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ was found to form in the cubic inverse spinel phase and, in addition, a small amount of $DyFeO_3$ phase was identified. The weight fractions of the inverse spinel phase and $DyFeO_3$ are found to be 0.895 and 0.105, respectively. An increment in the lattice constant from the value $a=8.335$ Å to $a=8.3491$ Å and a small distortion in the lattice are observed upon the substitution of Fe by Dy in the *B* site. Corso *et al.*[16] reported that NiO formed as an impurity when $NiO \cdot Fe_2O_3$ was prepared by the sol-gel method. Slow scan was carried out on selected XRD peaks with the scanning step of 0.016° (Fig. 2) and no peak corresponding to the NiO phase is seen.

Magnetization measurements on the powders were carried out at room temperature as well as at 80 K for $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ and the magnetization curves are
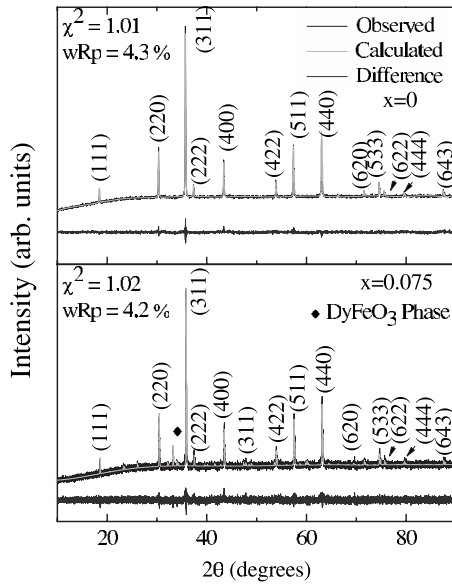
FIG. 1. XRD pattern of $NiO \cdot Fe_{2-x}Dy_xO_3$ ($x = 0, 0.075$).

FIG. 3. Magnetization curve of $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ at room temperature and at 80 K (the inset shows the magnetization curve of $NiO \cdot Fe_2O_3$ at 300 K).

shown in Fig. 3. The saturation magnetization (M_s) value of the sample at room temperature is $2.040\mu_B$ (47 emu/g) and $2.257\mu_B$ (52 emu/g) at 80 K. The inset of the Fig. 3 shows the magnetization cure of the $NiO \cdot Fe_2O_3$ sample and the M_s value is found to be $2.090\mu_B$ (49.8 emu/g), which is in good agreement with that ($2.098\mu_B$) reported in Ref. 6. Substitution of Fe^{3+} magnetic ion by Dy^{3+} ion in B site reduces the net magnetic moment. Since there is no itinerant exchange interaction in inverse spinel structure, the saturation magnetization value for $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ was calculated by using Hund's rule with the assumption that Dy magnetic moments are antiparallel to the Fe moments in the B site. The calculated value of M_s is found to be $2.250\mu_B$ (51.8 emu/g) and is in agreement with the observed value at 80 K.

The Curie temperature of $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ is found to be 775 K which is shown in Fig. 4 whereas the pure Ni ferrite has a T_C of 853 K.[6] This may be caused by the weaker

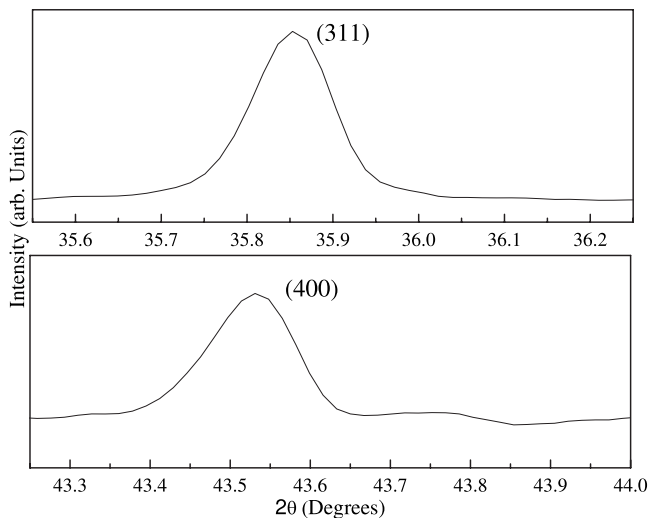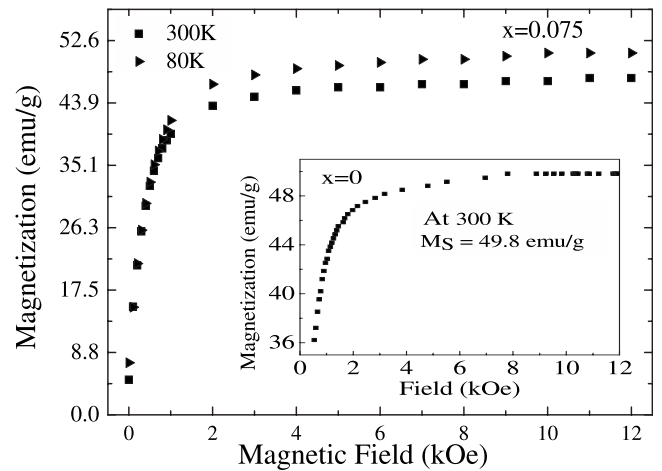Fe-Dy exchange interaction than the Fe-Fe interaction when Fe^{3+} is substituted by Dy^{3+}.

The $DyFeO_3$ phase is a canted antiferromagnetic with a Néel temperature of 645 K and has a feeble saturation magnetic moment of $0.05\mu_B/f.u.$[7] Therefore, there is no considerable contribution from the $DyFeO_3$ phase to the magnetic properties.

The ferroelectricity in the $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ compound was confirmed from the ferroelectric hysterisis loop measurements. A Sawyer–Tower circuit[17] was employed for the ferroelectric hysterisis loop measurement. The signal applied to the material was displayed as the X signal in an X-Y tracer oscilloscope. For an ordinary linear dielectric, one would expect a linear response (a straight line on the x-y display). In practice, there is an opening of the loop, which is due to dielectric loss.[18] In order to check the instrument, the measurements were carried out on $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$, an overhead projector (OHP) sheet, and the centrosymmetric Ni ferrite. For both OHP sheet and the Ni ferrite, small openings in the respective loops were observed. For
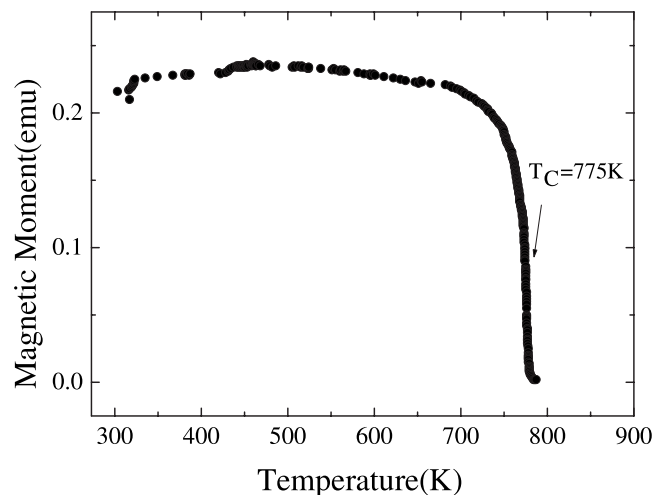

FIG. 2. Slow scan XRD pattern on selected peaks of $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$.

FIG. 4. Curie temperature curve of $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$.
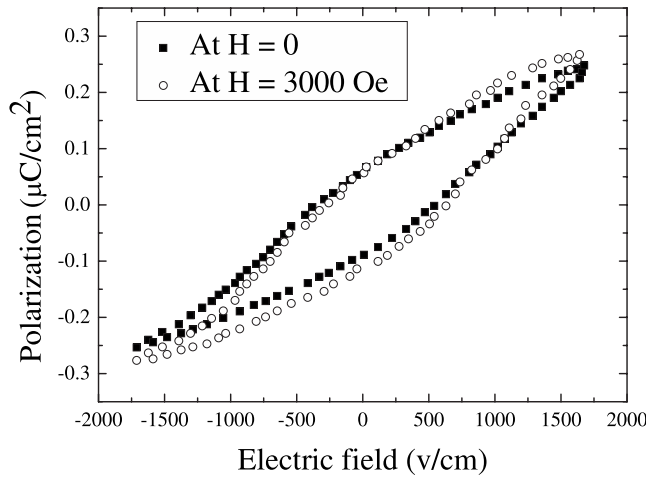
FIG. 5. *PE* loop in the absence of magnet field (open circle) and with magnetic field (dark circles) of $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$.

$NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ a clear and nearly saturated hysterisis loop was observed. Figure 5 shows the ferroelectric loops both without magnetic field and in the presence of a magnetic field of 3000 Oe for $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$. A small change in the polarization is seen in the presence of the magnetic field.

Magnetocapacitance measurements on $NiO \cdot Fe_{2-x}Dy_xO_3$ ($x=0, 0.075$) were carried out by measuring the change in the capacitance of a parallel plate capacitor, with the $NiO \cdot Fe_{2-x}Dy_xO_3$ ($x=0, 0.075$) pellet filling the space between the plates. The magnetic field was applied along the axis of the pellet. The relative change in the capacitance is $\Delta C/C = \Delta \varepsilon / \varepsilon - \Delta d/d$, where ε is the dielectric constant of the material and d is the thickness of the sample and, thus, $\Delta d/d$ is the magnetostriction of the material. The value of $\Delta C/C$ for a field of 2000 Oe was observed to be -4% for $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$, as shown in Fig. 6, and this could have arisen from either $\Delta \varepsilon / \varepsilon$ or both $\Delta \varepsilon / \varepsilon$ and $\Delta d/d$. The saturation magnetostriction of the polycrystalline $NiO \cdot Fe_2O_3$ is -25×10^{-6} (Fig. 6). The magnetostriction of $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ was determined by the strain gauge method and the saturation magnetostriction is found to be -28×10^{-6} (Fig. 6), a value which is nearly the same as in the case of pure Ni ferrite. Thus, a large value of magnetocapacitance ($\Delta C/C$) seems to have arisen nearly completely from $\Delta \varepsilon / \varepsilon$. No magnetocapacitance was observed in the $NiO \cdot Fe_2O_3$ sample.

In $RMnO_3$ ($R=Dy, Tb, Gd$) systems the spiral arrangement of the Mn magnetic moment about c axis at low temperatures leads to the breaking of centrosymmetric structure leading to ferroelectricity and magnetoelectric coupling.[19] There is no report on the existence of ferroelectricity and magnetocapacitance in $RFeO_3$ ($R=Dy, Tb, Gd$) systems. Therefore, part or all of the observed ferroelectricity and magnetocapacitance in $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ are not attributed to the $DyFeO_3$ phase.

The dielectric constant was determined in the frequency range of 100 Hz–3 MHz. The frequency (logarithmic scale) variation of the real part of the dielectric constant is shown in Fig. 7. The data were fit to the modified Debye's function
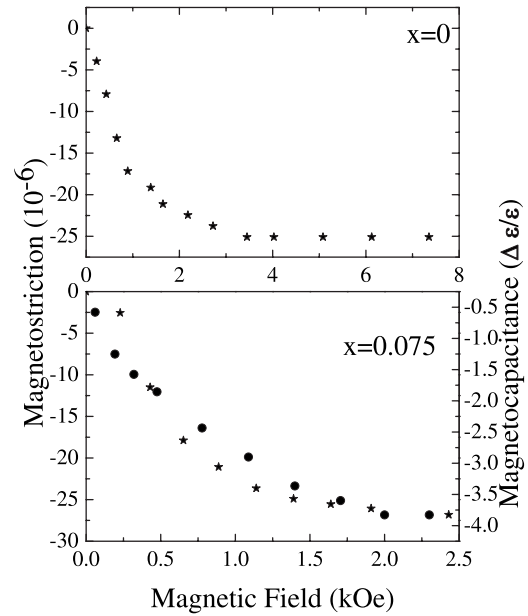

FIG. 6. Magnetostriction (stars) and magnetocapacitance (circles) plots of $NiO \cdot Fe_{2-x}Dy_xO_3$ ($x=0, 0.075$).

that considers the possibility of more than one ion contributing to the relaxation. The observed data could be fit to the equation $\in' - \in_\infty = (\in_0 - \in_\infty)/[1+(\omega\tau)^{2(1-\alpha)}]$,[20] where $\in'$ is the real part of the dielectric constant, $\tau=0.218$ and 0.302 s are the mean relaxation times, and $\alpha=0.86$ and 0.98 are the spreading factors of the actual relaxation times about the mean value for the $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ and $NiO \cdot Fe_2O_3$ systems, respectively. The measured value of $\in'=73796$ (at
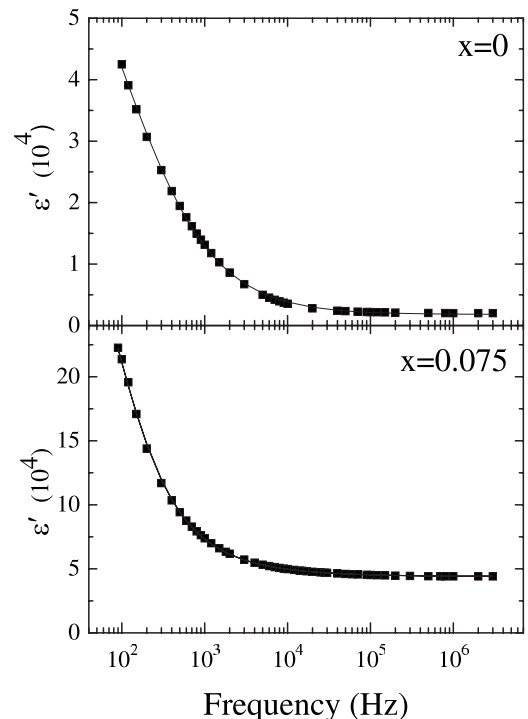

FIG. 7. Frequency (logarithmic scale) variation of dielectric constant of $NiO \cdot Fe_{2-x}Dy_xO_3$ ($x=0, 0.075$).

1 kHz) for $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$ is higher than the value of $\in' = 12927$ (at 1 kHz) for pure nickel ferrite.

In summary, substitution of a small amount of Dy for Fe is seen to improve both the dielectric constant and magnetocapacitance of the Ni ferrite. Because of the larger ionic size of Dy^{3+} in comparison to that of Fe^{3+}, the centrosymmetric fcc structure might have been distorted by a small amount and that could have led to the net electrical polarization. The decrease in the net magnetic moment in B site causes a decrease in the saturation magnetization and Curie temperature.

Since the Fe-Fe exchange interaction is stronger than Fe-Dy interaction, a decrease in the Curie temperature values was obtained. Substitution of Dy has not resulted in realizing large magnetostriction values. On the other hand, the observation of the polarization loop indicates the presence of ferroelectricity and the observation of magnetocapacitance shows a large magnetoelectric coupling in $NiO \cdot Fe_{1.925}Dy_{0.075}O_3$.

*Corresponding author; mark@physics.iitm.ac.in

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