AIP | Journal of Applied Physics

Structural, magnetic, and magnetodielectric studies of metamagnetic DyFe0.5Cr0.5O3

Vidhya G. Nair, L. Pal, V. Subramanian, and P. N. Santhosh

Citation: Journal of Applied Physics **115**, 17D728 (2014); doi: 10.1063/1.4870139
View online: http://dx.doi.org/10.1063/1.4870139
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/115/17?ver=pdfcov
Published by the AIP Publishing

Structural, magnetic, and magnetodielectric studies of metamagnetic $DyFe_{0.5}Cr_{0.5}O_3$

Vidhya G. Nair,[1] L. Pal,[2] V. Subramanian,[1] and P. N. Santhosh[1,a)]
[1]*Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India*
[2]*Department of Physics, Indian Institute of Technology Bombay, Mumbai 400076, India*

(Presented 6 November 2013; received 22 September 2013; accepted 14 November 2013; published online 28 March 2014)

We present here the detailed structural, magnetic, and magnetodielectric properties of polycrystalline $DyFe_{0.5}Cr_{0.5}O_3$. Rietveld refinement reveals that $DyFe_{0.5}Cr_{0.5}O_3$ crystallizes in an orthorhombic structure, with *Pnma* space group, having a disordered arrangement of Fe and Cr ions. An anomaly observed around 250 K in the temperature dependence of magnetization indicates an onset of magnetic ordering. The field dependent magnetization of $DyFe_{0.5}Cr_{0.5}O_3$ at 13 K, 120 K, and 240 K has a small loop indicating weak ferromagnetic nature and the corresponding curve at 5 K indicates a metamagnetic behavior. The small loop and the unsaturated magnetization even for a high applied magnetic field of 7 T indicate a canted antiferromagnetic structure, the canting can be explained due to Dzyaloshinsky–Moriya antisymmetric exchange interaction. The temperature dependence of the dielectric permittivity shows a transition around 500 K. An anomaly in the temperature dependence of magnetization (supported by differential scanning calorimetry) corresponding to this dielectric transition suggests the possibility of magnetodielectric effect in $DyFe_{0.5}Cr_{0.5}O_3$. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4870139]

I. INTRODUCTION

Recently, there is a growing surge for the multiferroic materials with magnetoelectric (ME) coupling near room temperature as they find technological applications in field such as spintronics.[1–3] A large amount of work has been done to explore the applications by tuning the electric and magnetic order parameters to show large magnetoelectric coupling.[4,5] Materials possessing magnetodielectric or magnetocapacitance effect has been reported in which an anomaly is observed in the temperature dependent dielectric curve corresponding to the magnetic ordering temperature of the materials.[6] Perovskites, with general formula $AB_xB'_{1-x}O_3$ (A is rare earth ion or Yttrium and B, B′ a transition metal), are known to exhibit multiferroic property where some materials exhibit magnetic ordering temperature well below the room temperature and the ferroelectric transition temperature far above the room temperature.[7] But from the application point of view, the materials with transition temperatures near to room temperature are more suitable. $YFe_{0.5}Cr_{0.5}O_3$ is reported to have magnetic ordering temperature around 275 K and a diffused ferroelectric transition at around 507 K (at 10 kHz). Neutron diffraction studies on $YFe_{0.5}Cr_{0.5}O_3$ shows a canted G-type antiferromagnetic structure (G_zF_y) below the Neel temperature, $T_N \sim 275$ K. Near to the ferroelectric transition an anomaly is observed in the magnetization data which indicates the possibility of magnetodielectric effect.[8]

The parent material for $DyFe_{0.5}Cr_{0.5}O_3$ (DFC), $DyFeO_3$ is well known to show Morin transition, where the Fe^{3+} spins in single crystal reorient from $\Gamma_4 = G_xA_yF_z$ (canted antiferromagnet) to $\Gamma_1 = A_xG_yC_z$ (collinear antiferromagnet) around 35 K.[9] A gigantic magnetoelectric effect is reported for $DyFeO_3$ single crystal with a linear-ME tensor component as large as $\alpha_{zz} \sim 2.4 \times 10^{-2}$ esu.[10] Multiferroic $DyFeO_3$ is having *Pnma* space group with magnetic ordering temperature $T_N^{Fe} \sim 640$ K and $T_N^{Dy} \sim 4$ K.[11,12] Further, $DyCrO_3$ is reported as a distorted perovskite with *Pbnm* space group and is having a G-type antiferromagnetic structure with $T_N^{Cr} \sim 146$ K and $T_N^{Dy} \sim 2$ K.[13,14] In this paper, the structural, magnetic, and dielectric properties of $DyFe_{0.5}Cr_{0.5}O_3$ are investigated probing the possibility of magnetodielectric behavior in the material.

II. EXPERIMENTAL

Polycrystalline sample of DFC is synthesized by solid state reaction method. Stoichiometric amounts of Dy_2O_3, Cr_2O_3 and Fe_2O_3 are mixed and heated at 1423 K for 12 h in air with intermittent grinding. Further, the calcined powders are pressed into disc shaped pellets of 8 mm diameter and 1 mm thickness using polyvinyl alcohol as the binding medium by hydraulic press and are sintered at 1423 K for 6 h. Prior to the dielectric and P-E hysteresis loop measurements, the pellets are electroded with silver paint and heated at 573 K for 1 h.

X-ray diffraction (XRD) data for Rietveld refinement were recorded in the range $10° \leq 2\theta \leq 90°$ at room temperature with a step size of 0.01° using PANalytical X'Pert Pro X-ray diffractometer [Cu K_α ($\lambda = 1.5406$ Å)]. Rietveld refinement of the powder diffraction data of DFC was performed using General Structure Analysis System (GSAS).[15] The crystal structure was built using VESTA software with the refined crystal parameters.[16] Temperature dependent [zero field cooled (ZFC) and field cooled (FC)] and field

a)Author to whom correspondence should be addressed. Electronic mail: santhosh@iitm.ac.in. Fax: +91 044 2257 4852.

dependent magnetization measurements were performed using superconducting quantum interference device susceptometer (MPMS, Quantum Design) in the temperature range 5 K–320 K and fields up to ±7 T. The high temperature magnetic measurement was performed using a Vibrating Sample Magnetometer (Lakeshore VSM 7410) in the temperature range 300 K–800 K in a magnetic field of 0.2 T. The temperature dependence of dielectric permittivity and dielectric loss was measured from 305 K to 573 K in the frequency range 100 Hz–1 MHz using N4L (PSM1735) NumetriQ phase sensitive multimeter. The polarization-electric field (P-E) hysteresis loop measurement was carried out using precision premier II ferroelectric loop tracer (Radiant Technologies, USA) with a maximum field of 30 kV/cm. Differential scanning calorimetry (DSC) is done for DFC in the temperature range 300 K–700 K using DSC 200PC PHOX (NETZSCH).

III. RESULTS AND DISCUSSION

Phase purity of the sample was confirmed by X-ray diffraction technique. The room temperature Rietveld refinement plot for the X-ray diffraction pattern of DFC is shown in Figure 1. From the refinement of DFC, it is observed that the sample crystallizes in an orthorhombic structure (*Pnma*) which is same as for $DyFeO_3$. The refined lattice parameters of DFC are a = 5.5560(1) Å, b = 7.5886(1) Å, c = 5.2865(1) Å, and V = 222.896(3) $Å^3$, respectively. The low value of the R-factors, $R_{wp} = 2.30\%$, $R_p = 1.77\%$, and the goodness of fit, $\chi^2 = 1.16$ shows good agreement between the calculated and observed patterns. The crystal structure of DFC with the distorted octahedra of Fe and Cr ions at the B-site is shown in inset of Figure 1.

The temperature dependence of magnetization (ZFC and FC) for DFC carried out at applied field of 0.1 T is shown in Figure 2. Observed anomaly around 250 K in the temperature dependence of magnetization indicates an onset of magnetic ordering. The temperature dependence of inverse susceptibility which clearly shows the signature of the anomaly at around 250 K is shown in the inset of Figure 2. As the temperature decreases from room temperature, the magnetization increases and reaches a maximum at 13 K and drops sharply. The peak at around 13 K is due to the small ordered magnetic moment of Dy^{3+} as evidenced from the large magnetization observed in the M vs. H at 13 K (Figure 3).[17]

Further, a metamagnetic behavior is observed in the field dependence of magnetization (M vs. H) at 5 K as shown in Figure 3. The M vs. H shows an antiferromagnetic behavior at 13 K, 120 K, and 240 K, a small loop at these temperatures (at lower fields) depicts the weak ferromagnetic nature of the sample. The low field M vs. H at 13 K is shown in inset of Figure 3. The small loop at low fields and the unsaturated magnetization even for a high applied magnetic field of 7 T indicate a canted antiferromagnetic structure. The canting of the spins in these perovskites can be explained due to Dzyaloshinsky–Moriya antisymmetric exchange interaction.[8]

Figure 4 shows the temperature dependence of magnetization for an applied field of 0.2 T. An anomaly is observed in the magnetization curve at temperature corresponding to the relaxor like transition in the dielectric curve [will be discussed later], indicating the possibility of magnetodielectric effect in DFC. The derivative of the magnetization with respect to temperature indicating the anomalies is shown in inset (a) of Figure 4. The differential scanning calorimetry data also show a broad peak around this temperature further supporting the dielectric transition and the magnetic anomaly (inset (b) of Figure 4). There is also an anomaly corresponding to the magnetic transition temperature ($T_N \sim 640$ K) of $DyFeO_3$. This reveals that DFC retains the properties of the parent sample establishing that it contains Fe-O-Fe interactions, which can be attributed to the B-site disorder in DFC.[8,18]

The temperature dependence of the dielectric permittivity (ε_r') and dielectric loss (tan δ) of DFC at different frequencies are shown in Figure 5. The dielectric curve shows a broad peak which corresponds to relaxor like transition at around 500 K for 10 kHz which is evident from the shift of dielectric maxima to higher temperature as the frequency increases. Relaxor kind of behavior may be attributed to the randomly distributed Fe and Cr ions in the B site.[19] The dielectric permittivity at 330 K for DFC is around 15 for 1 kHz which is comparable with that of $DyFeO_3$ nanocrystals.[20] As the temperature increases, the dielectric permittivity increases and reaches maxima of around 45 for 1 kHz and then decreases. The maximum dielectric constant value

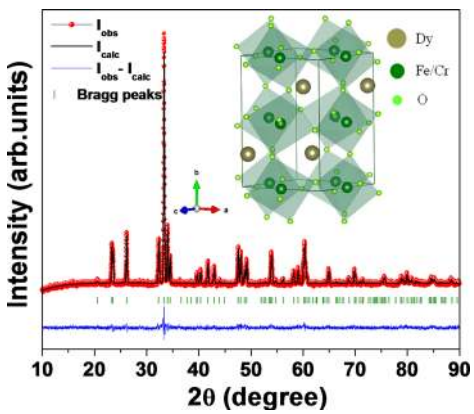

FIG. 1. Room temperature Rietveld refinement plot of $DyFe_{0.5}Cr_{0.5}O_3$ [observed (I_{obs}), calculated (I_{calc}), and difference ($I_{obs} - I_{calc}$) profiles]. Inset shows the crystal structure.

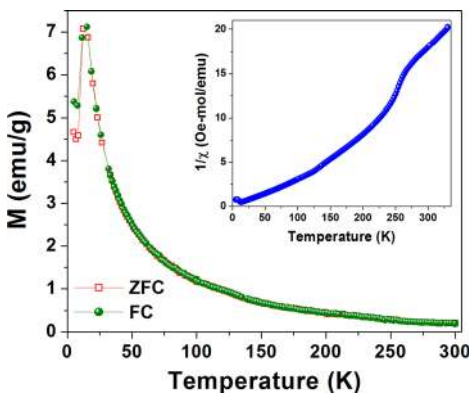

FIG. 2. Temperature dependence of magnetization (M) (at low temperatures) at 0.1 T under ZFC and FC conditions for $DyFe_{0.5}Cr_{0.5}O_3$. Inset shows the temperature dependence of inverse susceptibility which shows a clear anomaly at ~250 K.

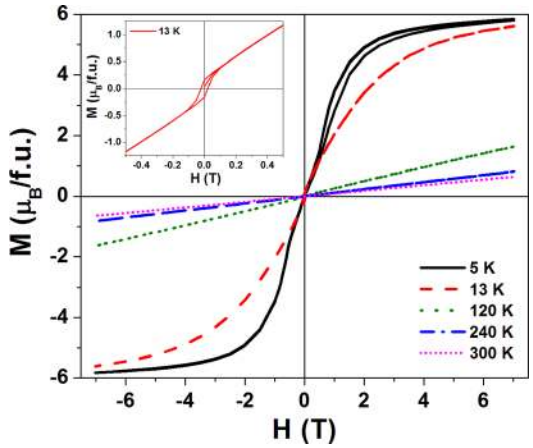

FIG. 3. Field dependence of magnetization (M) of $DyFe_{0.5}Cr_{0.5}O_3$ at different temperatures. Inset shows the small loop at lower fields indicating the weak ferromagnetic nature at 13 K.

decreases from 45 to 15 as the frequency increases from 1 kHz to 100 kHz. The increase in the dielectric loss with the increase in temperature may be due to an increase in the number of charge carriers by thermal activation. Inset of Figure 5 shows the room temperature P-E hysteresis loops of DFC at different applied electric field and it shows that DFC exhibits a weak ferroelectric behavior at room temperature.

IV. CONCLUSIONS

$DyFe_{0.5}Cr_{0.5}O_3$ crystallizes in the orthorhombic structure with *Pnma* space group. Observed anomaly around 250 K in the temperature dependence of magnetization indicates an onset of magnetic ordering which is also evident from the inverse susceptibility curve. The field dependence of magnetization of $DyFe_{0.5}Cr_{0.5}O_3$ at 5 K indicates a metamagnetic behavior. At 13 K, 120 K, and 240 K, a small loop is observed at lower fields indicating weak ferromagnetic nature. The small loop and the unsaturated magnetization even for a high applied magnetic field of 7 T indicate a canted antiferromagnetic structure for the sample. An anomaly in the temperature dependence of magnetization corresponding to the relaxor like transition at around 500 K suggests the possibility of magnetodielectric effect in $DyFe_{0.5}Cr_{0.5}O_3$. Differential scanning calorimetry curve shows a broad peak around 535 K, which supports the dielectric transition and anomaly in the magnetization curve.

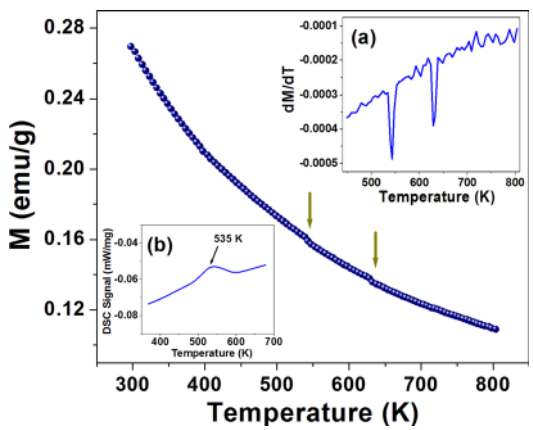

FIG. 4. Temperature dependence of magnetization (M) (at high temperatures) of $DyFe_{0.5}Cr_{0.5}O_3$ at 0.2 T. The anomalous behavior is marked by arrows hints the possibility of magnetodielectric effect in $DyFe_{0.5}Cr_{0.5}O_3$. Inset: (a) the derivative of magnetization with respect to temperature and (b) differential scanning calorimetry curve of $DyFe_{0.5}Cr_{0.5}O_3$.

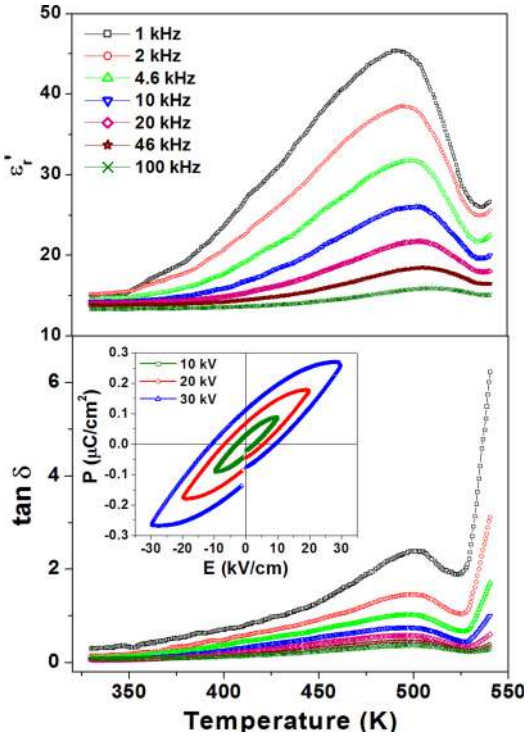

FIG. 5. Temperature dependence of dielectric permittivity (top panel) and dielectric loss (bottom panel) of $DyFe_{0.5}Cr_{0.5}O_3$ at different frequencies. P-E hysteresis loop is shown in the inset of bottom panel.

ACKNOWLEDGMENTS

P.N.S. acknowledges Department of Science and Technology, India for the financial support [Multiferroics Project (No. SR/S2/CMP-25/2005)] and for providing the facilities used in this study (Grant No. SR/FST/PSII-002/2007). The authors acknowledge SAIF, IIT Madras for magnetic measurement.

[1]G. Catalan and J. F. Scott, Adv. Mater. **21**, 2463 (2009).
[2]J. Mao *et al.*, Appl. Phys. Lett. **98**, 192510 (2011).
[3]Z. X. Cheng *et al.*, J. Appl. Phys. **107**, 09D905 (2010).
[4]V. Garcia *et al.*, Science **327**, 1106 (2010).
[5]I. Fina *et al.*, Appl. Phys. Lett. **97**, 232905 (2010).
[6]P. Mandal *et al.*, Phys. Rev. Lett. **107**, 137202 (2011).
[7]Z. J. Huang *et al.*, Phys. Rev. B **56**, 2623 (1997).
[8]V. G. Nair *et al.*, J. Appl. Phys. **113**, 213907 (2013).
[9]L. A. Prelorendjo *et al.*, J. Phys. C **13**, 2567 (1980).
[10]Y. Tokunaga *et al.*, Phys. Rev. Lett. **101**, 097205 (2008).
[11]Y. Du *et al.*, J. Appl. Phys. **107**, 09D908 (2010).
[12]A. Stroppa *et al.*, New J. Phys. **12**, 093026 (2010).
[13]K. Aoyagi *et al.*, Physica B+C **86–88**, 1207 (1977).
[14]B. Van Laar and J. B. A. A. Elemans, J. Phys. **32**, 301 (1971).
[15]A. C. Larson and R. B. Von Dreele, "General structure analysis system (GSAS)," Los Alamos National Laboratory Report LAUR 86–748 (2004).
[16]K. Momma and F. Izumi, J. Appl. Crystallogr. **44**, 1272 (2011).
[17]A. Muñoz *et al.*, Inorg. Chem. **40**, 1020 (2001).
[18]B. Rajeswaran *et al.*, Chem. Mater. **24**, 3591 (2012).
[19]A. A. Bokov and Z.-G. Ye, J. Mater. Sci. **41**, 31 (2006).
[20]A. Jaiswal *et al.*, J. Appl. Phys. **110**, 124301 (2011).