Lanthanum doped multiferroic DyFeO3: Structural and magnetic properties

Yi Du  
*University of Wollongong, ydu@uow.edu.au*  

Zhenxiang Cheng  
*University of Wollongong, cheng@uow.edu.au*  

Xiaolin Wang  
*University of Wollongong, xiaolin@uow.edu.au*  

S X. Dou  
*University of Wollongong, shi@uow.edu.au*  

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Keywords
Lanthanum, doped, multiferroic, DyFeO$_3$, Structural, magnetic, properties

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Lanthanum doped multiferroic DyFeO$_3$: Structural and magnetic properties

Y. Du, Z. X. Cheng,$^{a)}$ X. L. Wang, and S. X. Dou

Institute for Superconducting and Electronic Materials, University of Wollongong, Wollongong, New South Wales 2522, Australia

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Lanthanum doped multiferroic DyFeO$_3$ was synthesized by solid state reaction. X-ray diffraction and refinement show that the lattice parameters of Dy$_{1-x}$La$_x$FeO$_3$ increase linearly with the La content. Raman spectroscopy reveals that the short-range force constant in Dy$_{1-x}$La$_x$FeO$_3$ is decreased by La$^{3+}$ ion substitution. The spin reorientation phase transition temperature (TSRPT) is observed to decrease along with the doping level. The antiferromagnetic ordering temperature $T_N$ of Fe$^{3+}$ ions is depressed with increasing doping level. Both decreasing TSRPT and decreasing $T_N$ indicate that Fe–Dy and Fe–Fe interactions are weakened by La substitution. It is found that the electron configuration of Fe$^{3+}$ is high spin state and not affected by the La doping in all the samples above $T_N$. © 2010 American Institute of Physics. [doi:10.1063/1.3360354]

Compounds which display coexistence of magnetic and ferroelectric (FE) orders are known as multiferroic materials. Among these materials, FE (anti-)ferromagnets have been extensively studied due to their possible applications in many fields, such as nonvolatile memory devices, sensors, and actuators. However, only a few single-phase multiferroic materials which exhibit both large electric polarization ($P$) and strong magnetoelectric (ME) coupling have been studied so far. Recently, a magnetic-field-induced FE state has been observed in DyFeO$_3$ single crystal. A large linear ME tensor component $-2.4 \times 10^2$ was found below $\sim 4$ K. It was reported that the exchange interaction working between antiferromagnetically ordered Fe$^{3+}$ and Dy$^{3+}$ layer structures is the possible origin for the multiferroic behavior. Thus, study of the interaction between the two types of magnetic atoms (Dy and Fe) in DyFeO$_3$ is quite important to reveal the microscopic mechanism behind multiferroic behavior. As one of typical perovskite ReTmO$_3$ (Re: rare-earth; Tm: transition metal) compounds, DyFeO$_3$ crystallizes in the orthorhombic structure with space group $Pnma$. The Dy$^{3+}$ ions are located in the space between the FeO$_6$ octahedra in the crystal structure. The magnetic interactions in DyFeO$_3$ should follow the hierarchy of Fe–Fe, Fe–Dy, and Dy–Dy in descending order. In previous works, the magnetic structure, as well as the Fe–Dy and Dy–Dy antiferromagnetic (AFM) interactions were studied by Mössbauer spectrometry and neutron diffraction. Generally, substitution into Re or Tm sites in ReTmO$_3$ compounds will result in modifications of the crystal structure, causing changes in the physical properties. In the case of DyFeO$_3$, doping with La$^{3+}$ ions, which have a larger ionic radius than Dy$^{3+}$ ions, would lead to structural distortion, which possibly alters the electronic structure and magnetic properties. In addition, the doped nonmagnetic La$^{3+}$ ions are expected to dilute the concentration of Dy$^{3+}$ ions, which would depress the AFM Dy–Dy and Fe–Dy interactions.

In the present work, the crystal structure, magnetic properties, and electron configuration of Dy$_{1-x}$La$_x$FeO$_3$ ($x=0.0$, $0.1$, $0.2$, $0.3$, and $0.4$) are investigated. The goal of this work is to provide useful information on the chemical pressure effects resulting from Re-site doping on the crystal structure and magnetic properties. Dy$_{1-x}$La$_x$FeO$_3$ ($x=0.0$, $0.1$, $0.2$, $0.3$, and $0.4$) powder samples were prepared by solid state reaction of the ternary oxides Dy$_2$O$_3$, La$_2$O$_3$, and Fe$_2$O$_3$. The purity of all the chemicals, obtained from Sigma-Aldrich, is $99.9\%$. The mixtures were pressed into pellets and sintered at $1200$ °C for 12 h. Then, the products were crushed, ground, pressed into pellets, and sintered again at $1300$ °C for 24 h.

The crystal structures of samples were examined by x-ray diffraction (XRD); GBC Mini-Materials Analyzer, using Cu $K\alpha$ radiation at $\lambda = 1.540 56$ Å. XRD refinement calculations were conducted via the RIETICA software package (version 1.7.7). Raman scattering measurements, with a shift ranging from 100 to 2000 cm$^{-1}$, were performed with a laser Raman spectrometer (HORIBA Jobin Yvon HR320) at room temperature. An Ar$^+$ laser with wavelength of 632.8 nm was used for excitation of the Raman signals. The magnetic measurements were carried out using a 14 T physical properties measurement system (PPMS; Quantum Design) equipped with a vibrating sample magnetometer over a wide temperature range from 2 to 700 K.

The phase and crystallinity of the as-prepared Dy$_{1-x}$La$_x$FeO$_3$ ($x=0.0$, $0.1$, $0.2$, and $0.3$) samples were examined with XRD, as shown in Fig. 1. All the samples are phase-pure without any observable impurities. The diffraction patterns could be indexed with an orthorhombic perovskite structure (space group $Pnma$) according to Joint Committee on Powder Diffraction Standards Card No. 47–0069. The Rietveld XRD refinement was carried out to calculate the lattice parameters, bond lengths, and bond angles. The lattice parameters $a$, $b$, and $c$ are increased along with the La doping level. Overall, the lattice expands as a result of La substitution. In addition, the distortion of Fe–O octahedra in Dy$_{1-x}$La$_x$FeO$_3$ samples is reduced with doping. The in-plane

$^{a)}$Author to whom correspondence should be addressed: Electronic mail: cheng@uow.edu.au
Fe–O bond lengths decrease, and the out-of-plane bond lengths increase along with the doping level. Distances of the nearest $\text{Re}^{3+}$ ions in $\text{Dy}_{1-x}\text{La}_x\text{FeO}_3$ were calculated to increase along with the $x$ value as well. The modified crystal structure can be attributed to the different radii of the La$^{3+}$ and Dy$^{3+}$ ions.

Due to the relatively weak contribution to the structural factors by O$^{2-}$ ions in the XRD analysis, some disorder effects in the anion sublattice cannot be distinguished. Therefore, Raman spectroscopy analysis of $\text{Dy}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0.0, 0.1, 0.2, 0.3,$ and 0.4) has been performed with special attention to the vibration bands that are most affected by crystal structure disorder. Figure 2 shows Raman spectroscopy results for the $\text{Dy}_{1-x}\text{La}_x\text{FeO}_3$ ($x = 0.0, 0.1, 0.2, 0.3,$ and 0.4) samples at room temperature. The irreducible representation for Dy$\text{FeO}_3$ at the center of the Brillouin zone is given by

$$\Gamma = 7\Lambda_1 + 8\Lambda_2 + 7B_1 + 8B_2 + 5B_3 + 10B_4 + 5B_5 + 10B_6,$$

in which there are 24 Raman-active modes, 28 infrared modes, and 8 inactive modes. In order to identify the Raman shift peaks for different samples, the $\text{Dy}_{1-x}\text{La}_x\text{FeO}_3$ Raman spectra were fitted in the range of 100–550 cm$^{-1}$ by the Gaussian fitting method, as is shown in Fig. 2(b). There are ten vibration modes that have been identified. This agrees with results from a previous study on Dy$\text{FeO}_3$ ceramics.

Based on a Raman study of Sm$\text{FeO}_3$, the effective mass ($m_{\text{eff}}$) is introduced for the discussion of the doping effect on the Raman shift in $\text{Dy}_{1-x}\text{La}_x\text{FeO}_3$. Most of the Raman modes above 100 cm$^{-1}$ show a frequency decrease with the effective mass of $\text{Re}^{3+}$ ions in $\text{Dy}_{1-x}\text{La}_x\text{FeO}_3$. Due to the systematic increase in the cell size with the decreased $m_{\text{eff}}$ of the $\text{Re}^{3+}$ ions, the $\text{Re}–\text{O}$ and Fe–O force constants will be slightly decreased, which results in decreased frequency of the vibration modes. Unlike the sharp vibration peaks observed in pure Dy$\text{FeO}_3$, the Raman spectra of La doped samples exhibit significantly broadened peaks. This effect is related to the disordered crystal structure induced by the La$^{3+}$ ion substitution in Dy$\text{FeO}_3$. The presence of La$^{3+}$ in Dy$^{3+}$ sites causes less distortion of the FeO$_6$ octahedra than in pure $\text{DyFeO}_3$, which has been confirmed by the XRD refinement calculations. The high frequencies ($>100$ cm$^{-1}$) of these vibration modes and the broadening of the peaks should be attributed to the disordered O$^{2-}$ ions, as well as the different masses of La$^{3+}$ and Dy$^{3+}$ ions.

The field cooled magnetic susceptibility ($\chi$) as a function of temperature $T$ from 10 to 700 K in magnetic field of $H = 1000$ Oe is plotted in Fig. 3. The data were collected by a
field cooling measurement on the Dy$_{1-x}$La$_x$FeO$_3$ samples. A spin reorientation phase transition (SRPT) of Fe$^{3+}$ ions was observed at $T_{\text{SRPT}}=60.1$ K. It was found that $T_{\text{SRPT}}$ decreases linearly with increasing La doping level, as shown in inset of Fig. 3(a). There are three possible Fe$^{3+}$ spin configurations, labeled $\Gamma_4$, $\Gamma_5$, and $\Gamma_6$, which are compatible with the canting of the iron spins, the magnetic symmetry group ($m'm'n'$) of these crystals, and the strong AFM coupling between nearest-neighbor Fe$^{3+}$ sites.\textsuperscript{14} According to a previous study,\textsuperscript{15} DyFeO$_3$ undergoes a $\Gamma_4$-$\Gamma_5$ SRPT at $T_{\text{SRPT}}$. It has been proven that this temperature-induced SRPT is determined by the exchange interactions between Fe$^{3+}$ and Re$^{3+}$ ions in ReFeO$_3$ compounds.\textsuperscript{9} Because the total angular momentum is $J=0$ for La$^{3+}$ ions, this results in a zero magnetic moment for the La$^{3+}$ ion. The La$^{3+}$ substitution will contribute to the total effective magnetic moment in Dy$_{1-x}$La$_x$FeO$_3$ samples. Thus, the exchange interaction of Fe–Dy is weaker in doped samples, which results in decreasing $T_{\text{SRPT}}$ with increasing content of La$^{3+}$ ions in Dy$_{1-x}$La$_x$FeO$_3$. In addition, the magnetic moments of Dy$_{1-x}$La$_x$FeO$_3$ at $T_{\text{SRPT}}$ decreased along with the increasing value of x, which should be ascribed to the increasing concentration of nonmagnetic La$^{3+}$ ions. An antiferromagnetic transition temperature ($T_N$) was observed for Dy$_{1-x}$La$_x$FeO$_3$ above 300 K. It indicates that $T_N$ decreases with increasing doping level. Broadening of the AFM peaks was observed due to the weaker AFM ordering in doped samples. The Dy$_{1-x}$La$_x$FeO$_3$ samples with $x \geq 0.1$ show weak ferromagnetic behavior [inset of Fig. 3(b)] in the high temperature $M$-$T$ curve due to a possible canting angle arising from the increased Fe$^{3+}$ magnetic ordering [similar to the spiral magnetic structure in BiFeO$_3$ (Ref. 16)]. However, further neutron diffraction study of this material is necessary to determine its detailed magnetic structure.

Figure 4 shows the Curie–Weiss law fitting of $1/\chi$–$T$ from 600 to 700 K for all the samples. The total effective magnetic moments in Dy$_{1-x}$La$_x$FeO$_3$ were calculated to be 5.872 $\mu_B$, 5.791 $\mu_B$, 5.895 $\mu_B$, 5.906 $\mu_B$, and 5.210 $\mu_B$ for samples with $x=0.0$, 0.1, 0.2, 0.3, and 0.4, respectively, where $\mu_B$ is the Bohr magneton. Because only Fe$^{3+}$ ions contribute to the total effective magnetic moment in Dy$_{1-x}$La$_x$FeO$_3$ above $T_N$, the spin state $S$ of Fe$^{3+}$ can be used to calculate $\mu_{\text{eff}}$ via the formula $\mu_{\text{eff}}=2(S^2+S+1)^{1/2}$. The Fe$^{3+}$ ions in Dy$_{1-x}$La$_x$FeO$_3$ have five electrons in the $3d$ shell, which leads to a total possible spin quantum number $S$ with values 1/2, 3/2, and 5/2. Therefore, the possible $\mu_{\text{eff}}$ are 5.916 $\mu_B$/Fe$^{3+}$ for the high spin state (HS), 3.873 $\mu_B$/Fe$^{3+}$ for the intermediate spin state, and 1.732 $\mu_B$/Fe$^{3+}$ for the low spin state, respectively. Compared with the results from linear fitting of the $1/\chi$–$T$ curves, the spin state was found to be HS for all the samples.

In summary, the effects of La doping on the structure and magnetic properties of DyFeO$_3$ have been studied. XRD refinement and Raman spectroscopy revealed that the crystal structure of Dy$_{1-x}$La$_x$FeO$_3$ ($x=0.0$, 0.1, 0.2, 0.3, and 0.4) is modified sequentially by the increasing La content. The vibration modes in the Raman spectra show a frequency decrease with increasing doping level in Dy$_{1-x}$La$_x$FeO$_3$, which is attributed to decreasing Re–O and Fe–O force constants. The doped nonmagnetic La$^{3+}$ ions weaken the Fe–Dy interaction in Dy$_{1-x}$La$_x$FeO$_3$, which results in a decreased $T_{\text{SRPT}}$ and moment. The AFM temperature $T_N$ decreases due to distorted Fe–O bond lengths, which leads to weak ordering of Fe–Fe. The electron configuration of Fe$^{3+}$ ions is found to be HS for all the samples above $T_N$.

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