LETTER

Magnetization of $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ System

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Magnetization of $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ (x=0.3, 0.5, 0.6 and 0.7) is reported. An abnormal negative magnetization appears in the temperature-dependent magnetization curves, and the temperature-dependent coercive field shows a maximum in the vicinity of the compensation temperature where the total magnetization is zero. These results suggest that in the ferrimagnetic-like $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ system the Gd and Fe magnetic sublattices are coupled antiferromagnetically.

Key words: Multiferroic materials, Negative magnetization, Ferrimagnetic

Multiferroic materials in which ferroelectric and magnetic orderings coexist have attracted much attention in recent years [1]. This is due to not only the fact that such multiferroics are promising materials for the design of multifunctional devices, such as spintronic devices and sensors, but also the interesting physics found inside.

$BiFeO_3$ has long been known to be an antiferromagnetic, ferroelectric multiferroic, with antiferromagnetic Néel temperature T_N=673 K, and ferroelectric Curie temperature T_C=1103 K [2]. In the bulk, it possesses a rhombohedrally distorted perovskite structure with space group $R3c$ [3]. $BiFeO_3$ has a spiral spin structure and its magnetization vectors of antiferromagnetic sublattices vary from point to point with a period of 620 Å [4]. This spiral spin structure leads to the cancellation of macroscopic magnetization and inhibits the observation of the linear magneto-electric effect [5]. Previous studies suggest that the inhomogeneous magnetic spin structure can be effectively suppressed by La doping [6]. Ederer *et al.* have shown that if this spiral spin structure is suppressed, the system shows weak ferromagnetism with the magnetic moments oriented perpendicular to the rhombohedral axis and a slight canting of these magnetic moments resulting in a small macroscopic magnetization [7]. However, magnetic and ferroelectric measurements in the bulk have been hampered by the high leakage problems, likely due to defects and nonstoichiometry. Palkar *et al.* have recently found ferro- or ferrimagnetism in the $Bi_{0.825}Tb_{0.075}La_{0.1}FeO_3$ sample which is attributed to the larger magnetic moments introduced by partial substitution of Bi with Tb [8]. However, it is suggested that bulk $BiFeO_3$, especially synthesized through solid state reaction method exhibits weak ferromagnetism, which is believed to arise from the impurity phase related to the coexistence of Fe^{3+} and Fe^{2+} [9]. The origin of ferromagnetism in $Bi_{0.9-x}R_xLa_{0.1}FeO_3$ (R=rare earth element with large magnetic moments) system is not clear. In order to investigate the magnetism inside, single phase $Bi_{0.9-x}R_xLa_{0.1}FeO_3$ samples should be synthesized. The sol-gel technology can lower the synthesis temperature and accurately control the chemical composition at molecular level [10].

In this work, we doped magnetic Gd^{3+} with a magnetic moment μ_{eff}=7.96 μ_B into $BiFeO_3$ (a small amount of La is added to stabilize the perovskite phase of $BiFeO_3$) to investigate the coupling of A-site ions and Fe ions. The synthesis, characterization of the crystal structure and magnetic properties of $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ system for x=0.3, 0.5, 0.6 and 0.7 are reported.

Polycrystalline samples of $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ (x=0.3, 0.5, 0.6 and 0.7) were obtained by the sol-gel method. Stoichiometric amounts of Bi_2O_3, Gd_2O_3, La_2O_3 and iron nitrate nonahydrate $Fe(NO_3)_3{\cdot}9H_2O$ were used as starting materials; the oxides were converted into metal nitrates by adding nitric acid. After achieving completed dissolution, $Fe(NO_3)_3{\cdot}9H_2O$ was added. Citric acid was added with constant magnetic stirring, and the ratio of metal cations to citric acid was 1:2. Appropriate amount of ethylene glycol was also added to the solution. The resultant solution was heated at 140 °C and stirred to evaporate excess ethylene glycol in order to form a homogeneous mixture. Then, the solution was heated at 180 °C until it transforms into a dry gel. The dried gel was preheated at 400 °C for 5 h to evacuate hydrocarbon and NO_x impurities contained in the gel, and then annealed at 700-750 °C for 1 h.

Powder X-ray diffraction measurements were made on the MXP18AHF powder X-ray diffractometer (MAC Science Co. Ltd., Japan) using a high-intensity Cu Kα (λ=1.54056 Å) radiation to check the structure of the system. The magnetic measurements were carried out using a superconducting quantum-interference device (SQUID) magnetometer (MPMS 5, Quantum De-

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sign) in the temperature (T) range of 10-400 K in a zero-field-cooled (ZFC) mode. The magnetization (M) of $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ samples is at least 2 orders larger than that from a background noise of the sample holder which mainly arises from the capsule, i.e. about -1×10^{-7} emu at 500 Oe.

Figure 1 shows the X-ray diffraction (XRD) patterns of $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ (x=0.3, 0.5, 0.6 and 0.7) samples at room temperature. The crystal structure of $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ system at room temperature was analyzed using Rietveld method. All the observed peaks for each sample could be indexed to an orthorhombic phase with space group *Pnma*, which reveals that all the samples are single phase.

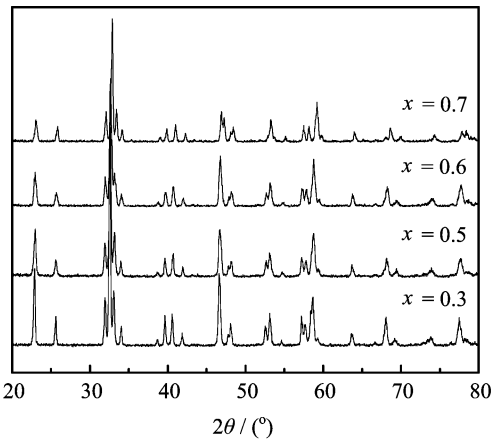

FIG. 1 X-ray diffraction patterns of $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$.

Figure 2 shows the temperature dependence of magnetization for $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ (x=0.3, 0.5, 0.6 and 0.7) samples measured under magnetic field H=10 Oe in ZFC mode. A significant increase in M-T curves occurs at temperature below 20 K, which might be attributed to the paramagnetic contribution of partial Gd^{3+} [11]. As temperature increases, an inflexion appears in each M-T curve at a certain temperature,

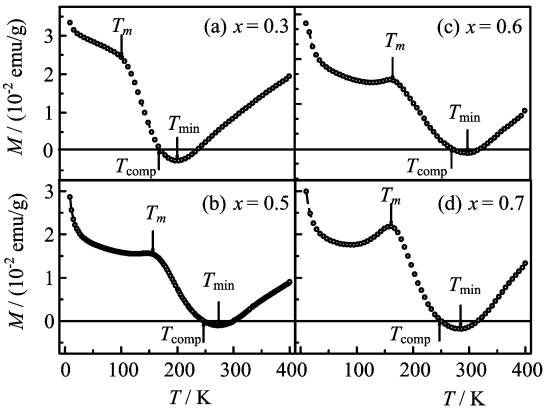

FIG. 2 Temperature dependence of magnetization in H=10 Oe for $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ in ZFC mode.

marked as T_m. At temperature above T_m, the magnetization decreases rapidly with increasing temperature, even becomes negative and reaches a minimum at $T_{\min}$. The abnormal negative magnetization in the M-T curves is observed for all samples. It should be noted that $T_{\min}$ increases and the diamagnetism decreases monotonously with x for $x\leq0.6$, whereas the $Bi_{0.2}Gd_{0.7}La_{0.1}FeO_3$ (x=0.7) sample deviates from the monotonous relation. This may be due to over-doped Gd ions, and the the phenomena is still under further investigation. With further increasing temperature, the magnetization increases and becomes positive again. The rapid decrease of magnetization with temperature increasing slightly above T_m suggests there is a weakly ferromagnetic coupling among the left partial of Gd^{3+}. Similarly, the ferromagnetic coupling between Dy^{3+} (which is a rare earth element carrying large magnetic moments too, $\mu_{\rm eff}$=10.83 $\mu_{\rm B}$) in Dy doped manganese oxides has been reported [12].

The temperature-dependent magnetization behavior above $T_{\min}$ can be understood in the framework of antiferromagnetic correlation [9]. The possible explanation for those abnormal magnetization is that there is ferrimagnetic-like state in the system which results in the distinctive temperature-dependent magnetization behavior in the temperature range of $T_m<T<T_{\min}$. $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ (x=0.3, 0.5, 0.6 and 0.7) samples display the magnetic properties much like that in the ferrimagnetic $Dy_3Fe_5O_{12}$ garnet, in which a specific temperature dependence of coercive field ($H_{\rm C}$) was found [13]. The temperature of maximum $H_{\rm C}$ on the $H_{\rm C}$-T curve corresponds to the compensation temperature ($T_{\rm comp}$) where the total magnetization is zero in ferrimagnet. In Fig.3(a), we show a hysteresis loop, M-H at 10 K, which can be clearly observed in the left inset. The coercive field $H_{\rm C}$ is defined as the minimum value of the external field needed for the total magnetization to go to zero. The right inset in Fig.3(a) shows the temperature dependence of coercive field for $Bi_{0.6}Gd_{0.3}Fe_{0.1}O_3$ which exhibits two interesting features: (i) $H_{\rm C}$ increases rapidly until it reaches its maximum at 180 K ($T_{\rm comp}$), and then decreases with increasing temperature. (ii) The asymmetric behavior of the coercive field is around the compensation temperature. To our knowledge, these behaviors of $H_{\rm C}$ have only been found in ferrimagnets [14]. In general, $H_{\rm C}$ should decrease monotonously with increasing temperature if the system is ferromagnetic, so there is ferrimagnetic-like state in current system.

Recently, it was reported that some Gd-based perovskites show specific magnetic features, in particular a reversal of the magnetization connected to the interplay of two interacting magnetic networks [15,16]. Such anomalies were interpreted as a ferrimagnetic ground state formed by an induced antiferromagnetic coupling of the Mn(Cr) spins with the Gd spins [17]. In the current system, the canted Fe lattice orders antiferromagnetically showing weak ferromagnetism as the spi-

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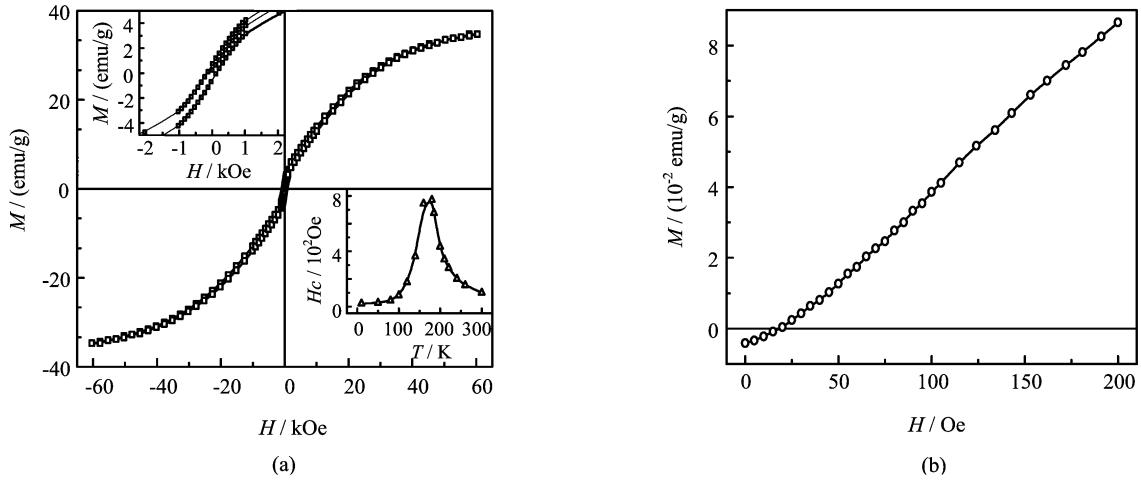

FIG. 3 (a) M-H curves at 10 K for $Bi_{0.6}Gd_{0.3}La_{0.1}FeO_3$; The left inset shows the enlargement of the low field data; The right inset shows the temperature dependence of coercive field for $Bi_{0.6}Gd_{0.3}La_{0.1}FeO_3$; (b) The field dependence of magnetization for $Bi_{0.6}Gd_{0.3}La_{0.1}FeO_3$ measured at 200 K.

ral spin structure is suppressed by the doped La ions [7]. We suppose that there exists an antiferrromagnetic coupling between the Gd and Fe magnetic sublattices, i.e. the moment of the Gd sublattice is antiparallel to the net magnetic moment of the Fe sublattice. Thus the total magnetic moment $M_{\rm tot}$ can be written as

$$M_{\rm tot} = M_{\rm Fe} - M_{\rm Gd} \qquad (1)$$

where $M_{\rm Fe}$ and $M_{\rm Gd}$ are the magnetic moments of the Fe sublattice and Gd sublattice in which Gd^{3+} ordered ferromagnetically, respectively.

At low temperature region, the magnetic moment of Gd magnetic sublattice is larger than that of Fe magnetic sublattice and the magnetic moment in Gd sublattice turns to be parallel to the orientation of applied magnetic field. But the magnetic moment orientation in Fe sublattice is antiparallel to the magnetic field because the antiferromagnetic coupling between the two sublattices is so strong that the magnetic field can not rotate the magnetic moments in Fe sublattice. With temperature increasing, the magnetic order in Gd sublattice changes from ordered state of ferromagnetism to disordered state of paramagnetism at a certain temperature. Above T_m, the Gd sublattices should enter into the paramagnetic state gradually and the Fe sublattice is still antiparallel to the magnetic field because the applied magnetic field is too small to rotate the magnetic moments in Fe sublattice. The $M_{\rm tot}$ decreases with increasing temperature. At $T_{\rm comp}$, both contributions become of the same amplitude but with opposite sign ($M_{\rm tot}\sim0$). Whereafter, the $M_{\rm tot}$ reaches the negative value. With further increasing temperature, the thermal fluctuations speed up, and the magnetic moments in Fe sublattice easily turn parallel to the applied magnetic field and then the $M_{\rm tot}$ increases, crosses zero, and becomes positive again. This is why there is abnormal negative magnetization in M-T curves shown in Fig.2.

In order to confirm the negative magnetization observed in the M-T curves and the orientation of magnetic moment in Fe sublattice, the field dependence of magnetization was performed on $Bi_{0.6}Gd_{0.3}La_{0.1}FeO_3$ at 200 K after the sample was cooled from room temperature down to 10 K in zero field and then warmed up to 200 K in an applied field of 10 Oe. Figure 3(b) shows the M-T curve at 200 K for $Bi_{0.6}Gd_{0.3}La_{0.1}FeO_3$ sample. The magnetization displays negative value in low field, H<20 Oe, which indicates that the magnetic moment is antiparallel to the orientation of the applied magnetic field. In addition, the magnetic contribution from paramagnetic Gd ions and/or Gd sublattice can be neglected at 200 K. Hence it can be concluded that the negative magnetization only originates from Fe sublattice, which means that the magnetic moment orientation in Fe sublattice is antiparallel to the magnetic field below 20 Oe.

The influence of Gd doping at A site on the magnetism in $Bi_{0.9-x}Gd_xLa_{0.1}FeO_3$ (x=0.3, 0.5, 0.6 and 0.7) system is studied. The abnormal negative magnetization phenomena are observed in the M-T curves. The coercive field reaches its maximum in the vicinity of the compensation temperature. These results can be interpreted in terms of two interacting antiferromagnetically magnetic networks: a Fe-based canted antiferromagnetic sublattice and a negatively-aligned Gd-based sublattice.

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