Magnetic properties of $DyMn_{0.9}Ni_{0.1}O_3$ compound

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Mn-site doped $DyMn_{0.9}Ni_{0.1}O_3$ compound by magnetic element Ni was successfully prepared by a solid-state reaction method. The sample shows an orthorhombic structure (space group Pnma) at room temperature. Magnetic properties, including field cooled, zero-field-cooled and field dependence of magnetization, were systematically studied. The plot of reciprocal susceptibility can be fitted to a Curie-Weiss Law in paramagnetic region, giving a paramagnetic temperature Θ_{weiss}=-18.71 K, suggesting the presence of weak antiferromagnetic interactions. It is also observed the narrow hysteresis loops in field dependence of magnetization at T=28 K and 35 K, giving the presence of weak ferromagnetic interactions. The hysteresis loops disappeared at lower temperature of 20 K, indicating the existing of the competition between ferromagnetism and antiferromagnetism.

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1. Introduction

Multiferroic manganite $DyMnO_3$ with orthorhombic structure has been intensively investigated since the discovery of gigantic magnetocapacitance effect in it [1-3]. The structure and magnetic properties play an important role in magnetoelectric effects of multiferroic manganite. So the structure and magnetic properties have been widely investigated in recent years, and as a result, many interesting phenomena have been reported. As some studies have been reported, $DyMnO_3$ has an orthorhombic perovskite structure with $GdFeO_3$ type at room temperature and hexagonal at above 1600°C [4]. In $DyMnO_3$, the Dy magnetic moments order in a commensurate structure below 6.5 K, while the Mn moments order below 39 K [5]. At the temperature of 18 K, the change of the magnetic structure connected with the Mn sublattice is observed. Below 18 K this order is collinear while above 18 K it is sine modulated [5, 6].

In recent years, a lot of research works have been done on doping effects of $DyMnO_3$, such as $Dy_{1-x}Ca_xMnO_3$ [7], $DyMn_{1-x}Al_xO_3$ [8], and so on. It is found that the physical properties of $DyMnO_3$ are sensitive to the B-site nonmagnetic doping [8]. We think that the physical properties of $DyMnO_3$ may be affected by B-site magnetic doping too. In order to explore such possibilities, we have undertaken studies of Mn-site doping experiments. The research focuses specifically on magnetic properties. It is expected that this research would bring more understanding the magnetic properties of Mn-site doping $DyMnO_3$.

2. Experimental

Mn-site doped $DyMn_{0.9}Ni_{0.1}O_3$ compound was synthesized by a standard solid-state reaction method, with MnO_2 (purity>99%), Dy_2O_3 (purity>99.99%) and NiO(purity>99.99%) as starting materials. Polycrystalline samples of orthomanganites $DyMn_{0.9}Ni_{0.1}O_3$ were obtained from a mixture of simple oxides taken in the stoichiometric ratio. All the starting materials were milled in anhydrous ethanol for 12h, and then calcined in air at 1050°C for 12h, then ground it and pressed into pellets. The pellets were sintered at 1250°C for 12h. The sintered material was crushed and ground into powders. The powders were again pressed into pellets, and then sintered at 1350°C for 24h. The samples were characterized by using X-ray diffractometer (XRD, Rigaku 18 kW D/max-2500 diffractometer). The magnetic properties of $DyMn_{0.9}Ni_{0.1}O_3$ compound were characterized with vibrating sample magnetometer (VSM option on PPMS-9T).

3. Results and discussion

The powder X-ray diffraction patterns for $DyMnO_3$ and $DyMn_{0.9}Ni_{0.1}O_3$ are shown in Fig.1, and the lattice parameters have been optimized by the least-squares refinement. Two compounds have orthorhombic structures with space group Pbnm and with unit-cell parameters as follows: a=5.27748Å, b=5.82333Å, c=7.37975Å for $DyMnO_3$ and a=5.27039Å, b=5.75410Å, c=7.41779Å for $DyMn_{0.9}Ni_{0.1}O_3$, respectively. Any hexagonal phase, which is competitive strongly with the orthorhombic phase in solid-state method, does not appear in the systems. Perovskite-based structures occasionally show lattice distortion as modifications from the cubic structure [9]. But for Mn-site doping, the lattice distortion may be due to two other main reasons. One is the deformation of MnO_6 octahedron arising from

the Jahn–Teller effect that is inherent to the high-spin (S=2) Mn^{3+} with double degeneracy of the e_g orbital [9]. The other is the connection pattern of MnO_6 octahedra in the perovskite structures, forming the orthorhombic lattices [9, 10].

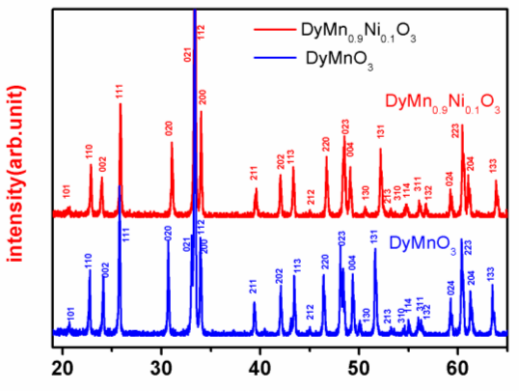

Fig. 1. XRD pattern of $DyMn_{0.9}Ni_{0.1}O_3$, indexed in an orthorhombic unit cell with parameters a=5.27039Å, b= 5.75410Å and c= 7.41779 Å.

Magnetization profiles in the field cooled (FC) and zero-field-cooled (ZFC) cycles measured for orthorhombic $DyMn_{0.9}Ni_{0.1}O_3$ are presented in Fig. 2. These curves were recorded by heating the samples from 4 K up to 305 K under the applied field of 50 Oe. From the ZFC cycles, we can find that the magnetization undergo an abrupt increase below 100 K with decrease of temperature, reaching a maximum value at the temperature of 4 K. It is observed that the magnetization curves of orthorhombic $DyMn_{0.9}Ni_{0.1}O_3$ at a higher temperature resemble each other. However, at very low temperature (about 27 K), splitting of the FC and ZFC is observed. The magnetization of $DyMn_{0.9}Ni_{0.1}O_3$ smoothly increases on cooling without showing any significant anomaly, which suggests the absence of a strong long-range magnetic ordering effect [11].

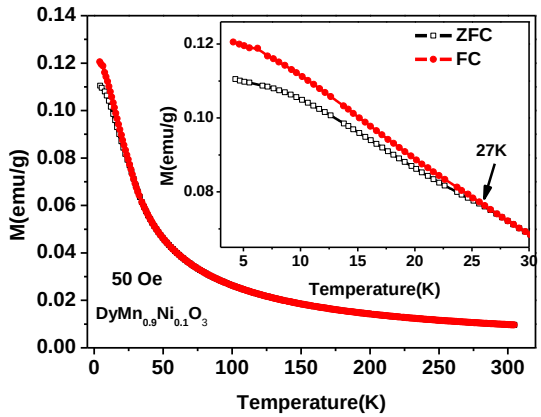

Fig. 2. DC magnetization of orthorhombic $DyMn_{0.9}Ni_{0.1}O_3$ at applied field of 50 Oe. Inset shows clear bifurcation in FC and ZFC cycles at low temperature.

Fig. 3 shows the plot of reciprocal susceptibility (χ^{-1}) against temperature for $DyMn_{0.9}Ni_{0.1}O_3$. The χ^{-1} can be fitted to a Curie-Weiss Law in paramagnetic region (goodness of the fit R=0.99987), giving a paramagnetic temperature Θ_{weiss}=-18.71 K, suggesting the presence of weak antiferromagnetic interactions [11]. As shown in Fig. 2, the splitting of the FC and ZFC show that there has mictomagnetic state in $DyMn_{0.9}Ni_{0.1}O_3$ at low temperature. With the decrease of temperature, the reciprocal susceptibility data show upwarping phenomenon at ~20K as shown in Fig.3, which also could indicate the presence of weak antiferromagnetic interactions. The effective paramagnetic moment can be calculated from the fit using the expression as follow:

$$\mu_{eff} = \frac{3\kappa_B}{\sqrt{N_0\mu_B^2}} \cdot \sqrt{\chi_{mol} \cdot T} \approx 2.828\sqrt{\chi_{mol} \cdot T} = 2.828\sqrt{\frac{1}{0.05778}} \approx 11.8\mu_B$$

The theoretical effective magnetic moment for the $DyMn_{0.9}Ni_{0.1}O_3$ can be calculated using the equation [12]:

$$\mu_{total} = [\mu_{eff}(Dy^{3+})^2 + 0.9\mu_{eff}(Mn^{3+})^2 + 0.1\mu_{eff}(Ni^{3+})^2]^{1/2} \approx 11.6\mu_B$$

The effective magnetic moments for spin-only Dy^{3+}, Mn^{3+} and Ni^{3+} are 10.6, 4.9 and 3.0μ_B [13], respectively. The theoretical effective magnetic moment value is in excellent agreement with the experimental value.

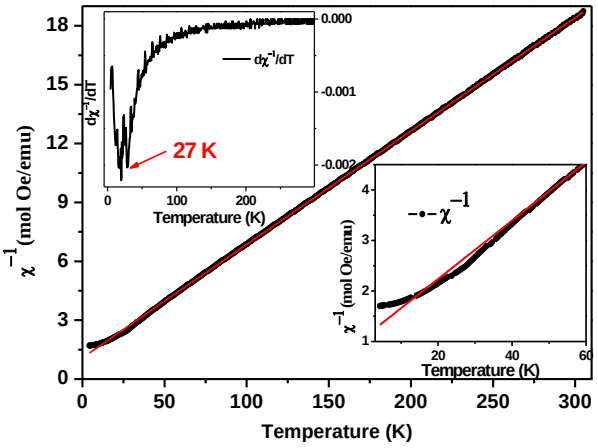

Fig. 3. Plot of reciprocal susceptibility (χ^{-1}) against temperature for $DyMn_{0.9}Ni_{0.1}O_3$ obtained by hydrothermal synthesis with the applied field of 50 Oe (ZFC data). Upper inset: $d\chi^{-1}/dT$ versus temperature for the samples. Lower inset: χ^{-1} at low temperature.

In the isothermal magnetization curves displayed in Fig. 4, all the magnetization curves almost present a linear behavior, corresponding to a paramagnetic state. Narrow hysteresis loops (coercive field about 29.56 Oe) are observed at T=28 K and 35 K as shown in the insert of Fig. 4. This indicates the presence of a weak ferromagnetism effect. But the hysteresis loop is not occurred at T=20K. As some studies have been previously reported, $DyMnO_3$ is antiferromagnet less

than 40K and does not exhibit the hysteresis [5, 9]. It is assumed that spontaneous magnetization in the $DyMn_{0.9}Ni_{0.1}O_3$ at low temperature of 28K and 35K is associated with the formation of ferromagnetic clusters in the antiferromagnetic matrix due to the presence of Mn and Ni ions [14]. This indicated that there exists mictomagnetism in $DyMn_{0.9}Ni_{0.1}O_3$. At lower temperature, there exists competition between ferromagnetism and antiferromagnetism. The weak ferromagnetism disappeared at 20K maybe due to the increase of antiferromagnetism. We can conclude that this is associated with a change in the magnetic order of rare-earth sublattice at lower temperature [14].

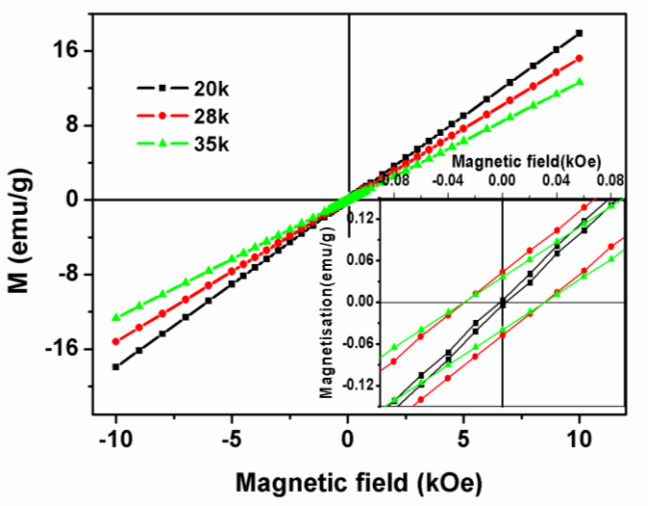

Fig. 4. Magnetization VS magnetic field isotherms at T=20, 28, and 35K. Inset: Magnetization VS magnetic field at low field from -100 Oe to 100 Oe.

4. Conclusion

In this paper, we have synthesized $DyMn_{0.9}Ni_{0.1}O_3$ with orthorhombic perovskite structures. The magnetic properties have been investigated and show that it is a mictomagnetic phase exhibiting different magnetic behaviors in the FC process and ZFC process. The χ^{-1} can be fitted to a Curie-Weiss Law in the high temperature paramagnetic region. At lower temperature, the competition between ferromagnetism and antiferromagnetism is observed.

Acknowledgments

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