Dy doping effect on the magnetic behavior and magnetization processes of polycrystalline $La_{0.7}Pb_{0.3}MnO_3$ perovskites

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Abstract

Herein the magnetic behavior and magnetization processes for the polycrystalline $(La_{0.7-x}Dy_x)Pb_{0.3}MnO_3$ perovskites have been systematically synthesized. Low field magnetic behavior observed in FC and ZFC curves shows a long-range spin order for La-rich compounds and a short-range state for Dy-rich ones. Ferromagnetism is suppressed with the increase of Dy content. The hysteresis behavior can be modelled by the formula $M=M_S(1-a/H^n)$ for ferromagnetic materials. The term a/H^n expresses the deviation of magnetization from saturation. The larger factor *n* and smaller factor *a* for La-rich samples result in sharper square curves which should be associated with the long-range spin order of magnetic moment.

Keywords: Perovskite; Spin order; Hysteresis; Ferromagnetism; Magnetization.

1. Introduction

Recently, there have been renewed interest in physical properties of manganese oxides, $La_{1-x}A_xMnO_3$ (Ln = La, Nd, Pr, Y etc., and A = Ca, Sr, Ba, Pb etc.), with ABO_3 perovskite structure, for the discovery of colossal magnetoresistance (CMR) effects accompanied with rich variety of magnetic and transport properties [1-3]. A few possible mechanisms have been proposed for the magnetic phenomenon and magnetortransport properties [4,5]. Zener proposed double exchange (DE) interaction [6,7] based on the magnetic coupling between neighboring Mn^{+3} and Mn^{+4} ions that result from the motion of an e_g electron between two partially filled d shells with strong on-site Hund's coupling [8]. There appears to be a direct relationship between the complex lattice effects and the physical properties in these perovskite compounds [9]. The introduction of Ln ion which is smaller than La into the perovskite is expected to produce a deformation of the MnO_6 octahedra that results in a modified Mn-O-Mn bond angle and in a consequent reduction of the DE interaction between Mn^{3+} and Mn^{4+}. To evaluate the effect of rare-earth element substitution on magnetic properties, we have studied a series of samples in which La^{3+} is partially replaced by smaller Dy^{3+} , and the mean radius of the A-site ions is systematically decreased in the $La_{0.7-x}Dy_xPb_{0.3}MnO_3$ compounds.

2. Experimental Procedure

Polycrystalline bulk samples of the compounds, $La_{0.7-x}Dy_xPb_{0.3}MnO_3$ ($0 \leqq x \leqq 0.2$), were prepared by conventional ceramic fabrication technique of solid-state reaction. Various La_2O_3, Dy_2O_3, $PbCO_3$,

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and $MnCO_3$ oxides were mixed in a stoichiometric ratio, calcined in air at 800°C for 24 hours, and sintered in air at 1250°C for 72 h. For the structure determinations, x-ray diffraction patterns were recorded with a powder diffractometer. Magnetization measurements were performed in a quantum designed superconducting quantum interference device (SQUID) magnetometer. Zero field cooling (ZFC) and field cooling (FC) curves were taken under an applied field of 100 Oe. Temperature dependence magnetization curves at an applied field of 5 teslas and hysteresis loops at 5 K and up to 5 teslas were also recorded.

3. Results and Discussion

The structure and phase purity of the samples $La_{0.7-x}Dy_xPb_{0.3}MnO_3$ ($0 \leqq x \leqq 0.2$) were examined by the powder x-ray diffraction, which shows no secondary phase as shown in Fig. 1. x-ray diffraction spectra for the compounds indicates that the structures are diminutively tuned from rhombohedral phase with space group R-3c (No.167) for x = 0.0 to orthorhombic symmetry with space group Pbnm (No.62) for $x \geqq 0.05$ due to the replacement of smaller rare earth Dy^{3+} ion (1.083 angstrom, ionic radius) on La^{3+} (1.36 angstrom) sites. The size mismatch effect occurs when the Ln-site ions are smaller to fill the space in the MnO_6 octahedra, consequently, resulting in a more distorted structure and Mn-O-Mn bond bending [10].

For the observation of the spin order and magnetic behavior, the zero field cooling-field cooling (ZFC-FC) magnetization curves in the field of 100 Oe were measured as shown in Fig. 2. The method of low field ZFC-FC measurement is one of the types generally used to characterize spin order behavior of magnetic materials. The ZFC-FC curve with x = 0.0 shows that the FC curves coincide with

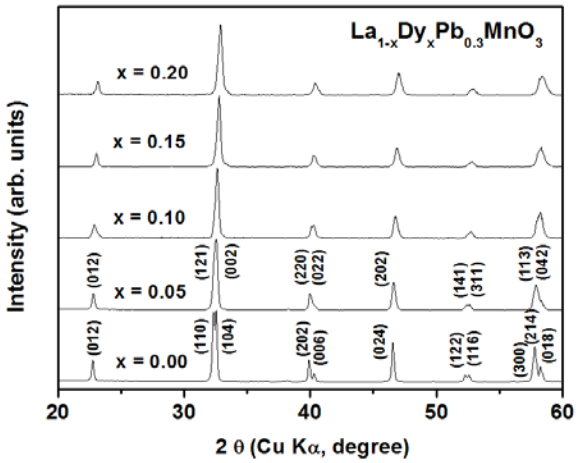

Figure 1： X-ray diffraction spectra for all polycrystalline $La_{0.7-x}Dy_xPb_{0.3}MnO_3$ perovskites.

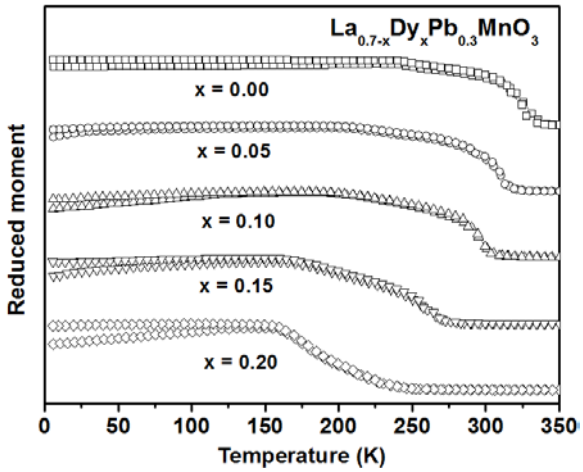

Figure 2：Temperature dependence magnetization measured at a low field of 100 Oe for all polycrystalline $La_{0.7-x}Dy_xPb_{0.3}MnO_3$ perovskites.

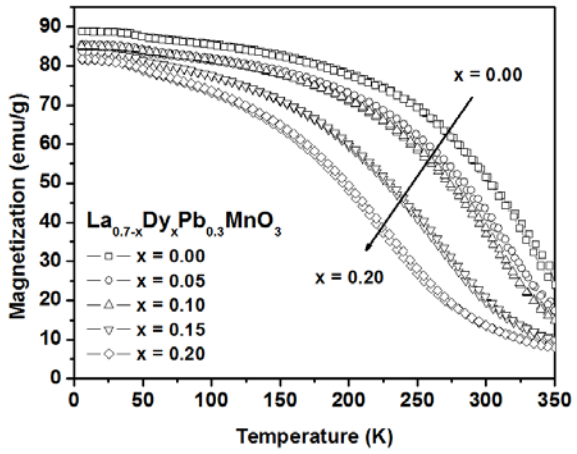

Figure 3: Temperature dependence magnetization measured at an applied field of 5 teslas for all polycrystalline $La_{0.7-x}Dy_xPb_{0.3}MnO_3$ perovskites.

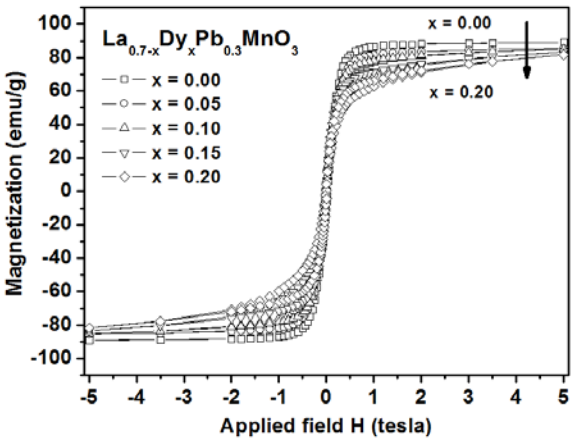

Figure 4: Magnetic hysteresis curves for all polycrystalline $La_{0.7-x}Dy_xPb_{0.3}MnO_3$ perovskites.

the ZFC curves at high temperature, but it deviates the ZFC traces and becomes almost flat just below transition temperature. The saturation moment of Mn spins clearly suggests a ferromagnetic long-range spin order. Conversely, the ZFC-FC curves displayλ-shape traces with the increase of Dy content, suggesting the possibility of a short-range spin order nature. Analogous spin order behaviors are also reported when La is partially substituted by other trivalent rare earth ions [11]. The substitution of La by Dy results in a considerable decrease of T_C (defined as the temperature where the slope reaches a maximum value) from 323K for x=0.0 to 233K for x=0.2 as listed in Table I, where the values vary considerably due to the effect of lattice distortion and Mn-O-Mn bonds bending induced by substituting smaller Dy^{3+} for La^{3+}.

Figure 3 shows the temperature dependence magnetization measured at 5 K in an applied field of 5 teslas for all compounds. The samples undergo a paramagnetic (PM) to ferromagnetic (FM) transition as temperature decreases. For the Dy-doped compounds, the saturation magnetization (defined as the magnetization at 5 K and an applied field of 5 teslas) decreases with the increase of Dy content as listed in Table I. It can be inferred that the substitution of smaller nonmagnetic Y^{3+} for La^{3+} can distort the perovskite structure and give rise to a larger bending angle of the Mn-O-Mn, which consequently weakens the ferromagnetic double exchange interaction between Mn^{3+} and Mn^{4+}.

The Magnetic hysteresis loops at 5K with -5T to 5T applied field taken from all samples are shown in Fig 4. As you shall observe, the curves raise slowly as the content of Dy increases. The magnetization is easily saturated by an external applied magnetic field

Table 1: Values of the T_C, M_S, high-field slope, factor *a* and factor *n* for all polycrystalline $La_{0.7-x}Dy_xPb_{0.3}MnO_3$ perovskites.

sample	T_C (K)	M_S (emu/g)	Slope (μ_B/T)	*a*	*n*
x=0.00	323	81.6	0.0139	3.9	0.98
x=0.05	310	83.8	0.0316	15.7	0.92
x=0.10	296	84.9	0.0628	242.0	0.82
x=0.15	255	85.7	0.1223	557.0	0.44
x=0.20	233	89.1	0.1667	2250.0	0.23

in the rich La compounds with shaper square curves. The curve of x = 0 compound shows essentially lowest high-field sloped dM/dH of 0.0139 μ_B/T indicating a collinear ferromagnetic state. Conversely, curves of the others remain unsaturated in the highest fields, showing slopes of 0.3166 μ_B/T, 0.0628 μ_B/T, 0.1223 μ_B/T and 0.1667 μ_B/T for x = 0.05, 0.10, 0.15, and 0.20, respectively. It is reasonable to conclude that the observed behavior corresponds to the spin order in which short-range spin order is harder to be magnetized than the long-range one. The hysteresis behavior can be modelled by the law of approach to saturation in the form,

$$M = M_s(1-a/H^n)^n, \quad (1)$$

Where $0 \leqq n \leqq 1$. The term of a/H^n expresses the deviation of magnetization from saturation and the factor *n* changes with respect to the origin of deviation. The factor *a* is correlated with the ferromagnetic correlation length. The values of *a* and *n* are both listed in Table I. Obviously, *a* increases and *n* decreases as the Dy substitution concentration increases. Therefore, the values of factor *a* depends on the concentration of substitution and are associated with the stability of the magnetic phase. The smaller factor *a* and larger factor *n* for the rich La samples resulting in sharper square curves should be associated with the long-range spin order of magnetic moment.

4. Conclusions

We have presented the study of the magnetic and magnetotransport behavior in $La_{0.7-x}Dy_xPb_{0.3}MnO_3$. The ZFC-FC magnetization and hysteresis curves were obtained. The results have shown that substitution of Dy for La in $La_{0.7}Pb_{0.3}MnO_3$ induces the structural distortion, leading the oxides to a short-range ferromagnetic state. The appropriate fitting of hysteresis curves of $(La_{0.7-x}Nd_x)Pb_{0.3}MnO_3$ compounds to the law $M=M_s(1-a/H^n)$ suggests ferromagnetically aligned spins which result in the short-range spin order as Dy content increases.

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