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Structure and Magnetic Properties of $REMnO_3$ System

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Abstract: In this study, the perovskite manganites $REMnO_3$ (with RE = La, Nd, Pr) were prepared by a solid-state reaction. The structure and magnetic properties of these samples are reported. The crystal structure of the samples is cubic with $LaMnO_3$ and is orthorhombic with $NdMnO_3$ and $PrMnO_3$ samples. The surface of $LaMnO_3$ sample is dense and quite tight, while the surface of two samples $PrMnO_3$ and $NdMnO_3$ are more porous than $LaMnO_3$ sample surface. The temperature and magnetic field dependent of the magnetizations for all the samples were measured. All the samples are paramagnetic. The maximum value of magnetizations at magnetic field H = 12 kOe for the samples $LaMnO_3$, $PrMnO_3$ and $NdMnO_3$ are 2.32 (emu/g), 1.11 (emu/g) and 0.97 (emu/g), respectively. It shows that the M_{max} of $LaMnO_3$ is greater than the M_{max} for $PrMnO_3$ and $NdMnO_3$ samples. The results showed the existence of both ferromagnetic and antiferromagnetic phase in all the samples. The Curie temperature, Weiss temperature and Curie constant are ditermined. A comparision of the magnetic property in our samples with the other one is discussed in this paper.

Keywords: Magnetic material, $REMnO_3$, perovskite.

1. Introduction

Perovskite structural was discovered by Gustav Rose in $CaTiO_3$ material. Today, this term "perovskite" is used for materials with a general chemical formula ABO_3, where A is the cation 1, 2 or 3 valence such as Na^{1+}, K^{1+}, Sr^{2+}, Ba^{2+}..., B is the cation 4 or 5 valence such as Nb^{5+}, Ti^{4+}, Eu^{3+}... [1].

Most of the perovskite structure materials with no doped expressed antiferromagnetic. When doped, depending on the type of ion and the concentration of doping, the crystal structure will be changed, no longer ideal structure. Because of the crystal lattice distortion and appearing mixed valence state or many other effects, electrical and magnetic properties of the material have a major change, leading to the emergence of many interesting physical effects.

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Usually, the perovskite is antiferromagnetic, but this property can be converted into ferromagnetic by doping different elements. Doping elements lead to the creation of different valence ions in position B. From there, forming mechanism of indirect exchange interaction and generate ferromagnetism. Especially, the magnetic properties can be changed in many different states in the same material.

Until the present time, there are a lot of researches being done on the system $REMnO_3$ (RE is a rare earth elements) because these ions have the same outer shell ($6s^2$), so the chemical properties of rare earth elements are similar. The results of $REMnO_3$ system (RE = La, Pr, Nd) are given in the references [2 - 11].

The crystall structural and magnetic properties depended very much on the sintered temperature. For $LaMnO_3$, when the sintered temperature $T > 750$ K, the crystal structure of $LaMnO_3$ is cubic, but when $T < 750$K, it has the orthorhombic structure with Pbnm space group. The difference about structures of these samples can be explained by Jahn-Teller effect [5, 10]. For $PrMnO_3$ and $NdMnO_3$ samples, at different condition methods, they had orthorhombic crystal structure with Pmna space group [11] but they had orthorhombic crystal structure and Pbnm space group in the results of J. Hemberger [2]. The magnetization depent on the magnetic field M(H) of the $LaMnO_3$, $PrMnO_3$ and $NdMnO_3$ is nealy and they are paramagnetic. The maximum magnetization (M_m) of the $LaMnO_3$ sample at 10 kOe (~ 8 emu/g) is greater than M_m for $PrMnO_3$ and $NdMnO_3$ samples (< 1 emu/g) [6].

In this work, we report our study on structural and magnetic properties of $REMnO_3$ system, with RE = La, Nd, Pr, in order to see clearly different properties of manganite perovskite when doped with various rare earth ions.

2. Experimental

$REMnO_3$ (with RE = La, Pr, Nd) samples were prepared by using a conventional solid-state reaction method from high purity oxides La_2O_3, Pr_2O_3, Nd_2O_3, MnO_2 up to 99.9%. The samples were presintered at 1000°C for 10 h. The heated samples were cooled to room temperature, reground to fine particles, pressed into pallets and sintered at 1250°C for 10 h.

The structure of the samples was examined in a Brucker D5005 X-ray diffractometer (Germany). The microstructure and chemical composition were studied on scanning electron microscope (SEM) equipment–450–FEI. Magnetic measuments including Hysteresis loops and isothermal magnetization curves of the samples were performed in a vibrating sample magnetometer (VSM) DSM-880 in a magnetic fileds up to 13.5 kOe. The temperature dependences of magnetization M(T) curves were measured on a SQUIDS device at temperature range from 5 K to 350 K.

3. Resuts and discussion

Fig.1 presents the X-ray diffraction patterns of the $REMnO_3$ system (with RE = La, Nd, Pr). We can see that all the samples are of single phase.

From Fig. 1, we can see the diffraction peaks are quite sharp, the position of the diffraction peaks of the samples coincide with the positions of the peaks in the previously published [3, 5, 13]. $LaMnO_3$ sample has cubic crystal structure (cubic), Nd MnO_3 and $PrMnO_3$ samples have orthorhombic crystal structure (orthorhombic), belong to Pbnm space group. The parameters of the lattice constants and unit cell volume are calculated by Checkcell software and are given in Table 1.

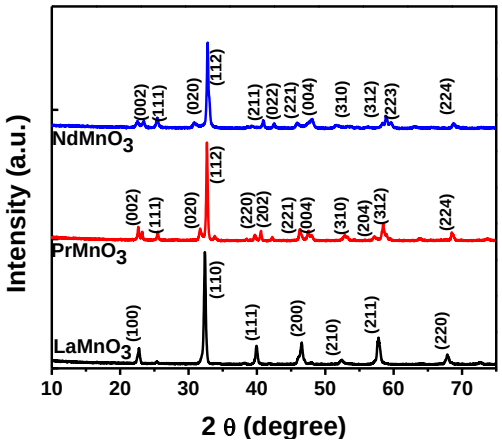

Fig.1. X-ray diffraction patterns for $REMnO_3$ system.

The lattice constant of $LaMnO_3$ sample is calculated by formula for cubic crystal system. The two samples $PrMnO_3$ and $NdMnO_3$ with orthorhombic crystal structure (orthorhombic), the lattice constant is calculated using the formula for orthorhombic crystal system.

Tab.1. Lattice parameters of the samples

Samples	Structure	a (Å)	b (Å)	c (Å)	V(Å^3)
$LaMnO_3$	Cubic	3.92	3.92	3.92	60.24
$PrMnO_3$	Orthorhombic	5.54	5.78	7.58	242.72
$NdMnO_3$	Orthorhombic	5.40	5.75	7.56	235.19

The result of this calculation is fairly consistent with the results of research on the $LaMnO_3$ sample [4], on the $NdMnO_3$ and $PrMnO_3$ samples [4, 12]. From X-ray data, we also calculate the particle size based on the Debye – Scherrer formula. The average particle size of $REMnO_3$ system is 87 nm (for $LaMnO_3$), 65 nm (for $NdMnO_3$) and 93 nm (for $PrMnO_3$).

The SEM images of surface of $REMnO_3$ system (with RE = La, Pr and Nd) showed that the samples are homogeneous. From the SEM images, we can observe the size of particles cloud, particle size of the cloud nearly equal. The surface of $LaMnO_3$ sample is dense and quite tight, while the surface of two samples $PrMnO_3$ and $NdMnO_3$ are more porous than $LaMnO_3$ sample surface.

In order to investigate the magnetic properties of the $REMnO_3$ sample system, we measured hysteresis loops depends on the magnetic field M(H) at room temperature and magnetization depends on the temperature M(T) at H = 500 Oe.

Fig.2 presents the hysteresis loops of $REMnO_3$ system (with RE = La, Nd, Pr).

From Fig.2, we see that the magnetization depend on magnetic field M(H) at room temperature of all the samples $REMnO_3$ have a liner format, so all samples $LaMnO_3$, $NdMnO_3$ and $PrMnO_3$ are paramagnetic. This result is completely consistent with the results of Tokeer Ahmad [11].

The maximum magnetization values M_{max} of the samples $LaMnO_3$, $PrMnO_3$ and $NdMnO_3$ at magnetic field H = 12 kOe are 2.32 (emu/g), 1.11 (emu/g) and 0.97 (emu/g), respectively. It was found that $LaMnO_3$ sample has a larger maximum magnetization value than the two samples $PrMnO_3$ and $NdMnO_3$, nearly as twice. This may be beacause of spins in Mn lattice are closely associated with

spins in A lattice. When placed samples in an external magnetic field, the spins in A lattice are not affected directly by this external magnetic field, leading to a total magnetization values decrease. Meanwhile, La^{3+} ion is a non-magnetic ion. That explains why the magnetization value of $LaMnO_3$ sample valued higher than $PrMnO_3$ and $NdMnO_3$ samples [6].

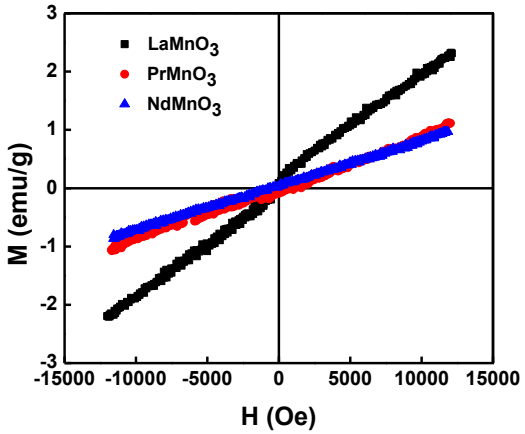

Fig.2. Hysteresis loops of $REMnO_3$ system at room temperature.

Fig.3 shows the thermomagnetic curve M(T) for $REMnO_3$ system, was measured at magnetic field H = 500 Oe.

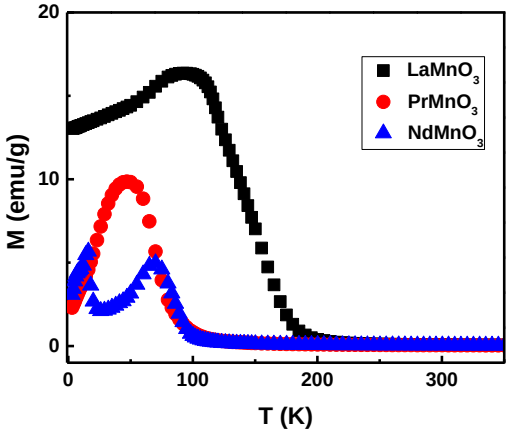

Fig.3. Temperature dependences of magnetization for $REMnO_3$ samples at magnetic field H = 500 Oe.

Typically, no doped manganite materials such as $LaMnO_3$ is antiferromagnetic, because La is a nonmagnetic material and Mn^{3+} ions have antiferromagnetic properties. But from the Fig.3, we see that the dependence of magnetizations on temperature M(T) (or the thermomagnetic curves M(T)) exist both ferromagnetic phase and antiferromagnetic phase. In theory, Mn^{4+} ions decide ferromagnetism properties and Mn^{3+} ions decide antiferromagnetic properties. This demonstrates the existence of both Mn^{4+} and Mn^{3+} ions in crystal lattice.

$PrMnO_3$ sample also shows the existence of both ferromagnetic and antiferromagnetic phases as $LaMnO_3$ sample. Because Pr^{3+} is a magnetic rare earth ion, the ferromagnetic phase of $PrMnO_3$ sample expresses clearly.

$NdMnO_3$ sample also shows the existence of both the ferromagnetic phase and antiferromagnetic phase. While observing the M(T) curve, we see that it has two peaks which appeared at T = 15 K and T = 75 K. This is explained by the influence of the far ordering of Nd^{3+} ions at T = 15 K. When the temperature increases, the magnetic moment decreases suddenly because the far ordering of Nd^{3+} ions is nolonger available. At T = 75 K, the M(T) curve of $NdMnO_3$ appears the second peak. This is explained because of the influence of magnetic ordering by Mn^{3+} ions. In theory, when spin is in the high-spin state, it will produce an effective magnetic moment, approximately equals to 6.09 μ_B. When spin is in the low-spin state, the effective magnetic moment approximately equals to 4.59 μ_B. Meanwhile, in experimental, the effective magnetic moment calculated 6.1 μ_B empirically. This shows that the calculation results of the effective magnetic moment in experimental approximately equals to case of spin in the high-spin state. When Mn^{3+} ions are in high-state, it will determine the antiferromagnetic properties in crystal lattice.

From data of M(T) curves in Fig.3, we can determine the magnetic susceptibility χ, χ^{-1} and $d\chi/dT$ depedent on the temperature. Figure 4 shows the temperature dependencies of magnetic susceptibility χ and $d\chi/dT$ for $REMnO_3$ samples (RE = La, Nd, Pr).

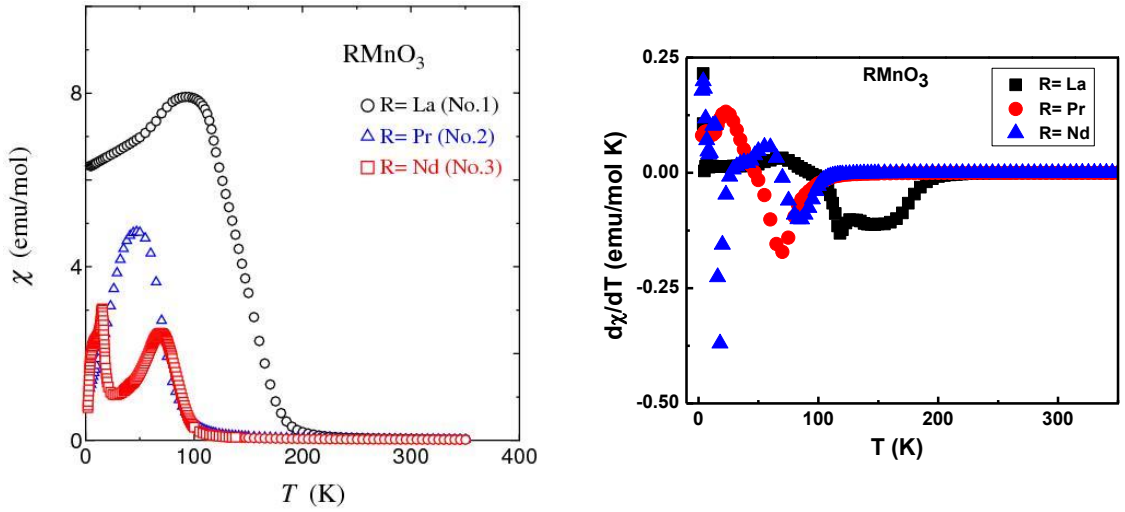

Fig. 4. Temperature dependencies of (a) the magnetic susceptibility χ(T) and b) $d\chi/dT$ for $REMnO_3$ samples (RE = La, Nd, Pr).

The χ-1(T) is a linear line indicates the sample is paramagnetic at temperatures above the Curie temperature. This result is consistent with the law of Curie - Weiss paramagnetic region: $\chi = C/(T-\theta)$, with χ is the magnetic susceptibility, C is the Curie constant, θ is the Weiss temperature. By fit linear paramagnetic region, we can calculate the value of the Weiss temperature θ.

The Curie temperature T_C, the Weiss temperature θ, the Curie constants C and the effective permeability μ_{eff} of all samples $LaMnO_3$, $PrMnO_3$ and $NdMnO_3$ are given in Table 2.

Tab.2. Curie temperature (T_C), Weiss temperature (θ), Curie constant (C) and effective permeability (μ_{eff}) of the $REMnO_3$ system.

Sample	T_C (K)	θ (K)	C (emu-K)	μ_{eff}
$LaMnO_3$	147	162	4.95	6.29 μ_B
$PrMnO_3$	69	89.8	5.11	6.39 μ_B
$NdMnO_3$	84	58.3	4.66	6.10 μ_B

According to Tokeed Ahmad [11], the μ_{eff} values of $LaMnO_3$ samples were prepeared at 773 K and 1173 K by chemical method are 4.60 μ_B and 4.05 μ_B, respectively. Meanwhile, the effective permeability μ_{eff} of our $LaMnO_3$ sample is 6.29 μ_B. This can be explained that the μ_{eff} values decrease with increasing the ratio of Mn^{4+}/Mn^{3+}. So the $LaMnO_3$ is paramagnetic.

4. Conclusions

The $REMnO_3$ (RE = La, Nd, Pr) manganite perovskite samples were prepared with single phase. The crystal structure of the samples is cubic with $LaMnO_3$, the orthorhombic structure with $NdMnO_3$ and $PrMnO_3$ samples. All the samples are paramagnetic at the room temperature. The Curie temperature increases from 69 K ($PrMnO_3$) to 84 K ($NdMnO_3$) and 147 K ($LaMnO_3$).

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