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Nd_{0.67}M_{0.33}MnO₃ (M=Mg, Ca, Sr, Ba) 的制备、结构与电性李亚栋^{1,2} 章建辉¹ 段镶峰¹ 朱长飞² 刘卫² 钱逸泰^{1,3}⁽¹⁾ 中国科学技术大学应用化学系, 合肥 230026)⁽²⁾ 中国科学技术大学内耗与固缺陷体开放实验室, 合肥 230026)⁽³⁾ 中国科学技术大学结构成分开放实验室, 合肥 230026)

本文通过共沉淀工艺合成了系列陶瓷化合物 Nd_{0.67}M_{0.33}MnO₃ (M=Mg, Ca, Sr, Ba)。与传统的陶瓷法相比, 其成相温度降低了 400℃。经 X 射线衍射分析表明, 所得化合物为立方钙钛矿结构, 各化合物的成相温度范围受碱土二价金属离子 (M²⁺) 的影响。样品的四极法电阻率测试结果表明, M²⁺ 的离子半径对样品的导电性起决定作用, 并提出了反铁磁性 (AF) 与铁磁性 (AF) 等磁性结构假设, 解释了该系列化合物的导电性。

陶瓷化合物

关键词: 共沉淀工艺 钙钛矿结构 导电性

PREPARATION, STRUCTURE AND ELECTRICAL PROPERTIES OF**Nd_{0.67}M_{0.33}MnO₃ (M=Mg, Ca, Sr, Ba)**Li Yadong Zhang Jianhui¹ Duan Xiangfeng Zhu Changfei² Liu Wei² Qian Yitai¹⁽¹⁾ Department of Chemistry, University of Science and Technology of China, Hefei 230026)⁽²⁾ Laboratory of Internal Friction and Defects in Solid Academia Sinica, Hefei 230026)⁽³⁾ Structure Research Laboratory, Academia Sinica, Hefei 230026)

The bulk ceramic compounds Nd_{0.67}M_{0.33}MnO₃ (M=Mg, Ca, Sr, Ba) were prepared by the coprecipitation route. Compared with the conventional ceramic technique, the temperature at which the compounds were synthesized has been reduced by 400℃. The results of X-ray diffraction show all the samples are cubic and the phase formed temperature range is affected by the divalent alkali-earth ion (M²⁺). The electrical measurements by standard four-probe method indicate the radius of M is crucial to the electrical conduction of sample.

Keywords: coprecipitation method perovskite-type phase electrical properties

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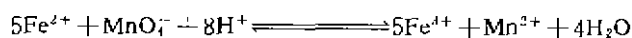
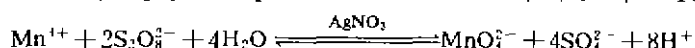
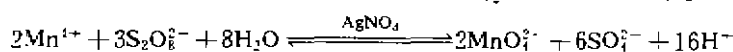
0 Introduction

The striking correlation between magnetic order and conductivity in $\text{La}_{1-x}\text{M}_x\text{MnO}_3$ (M represents divalent metal ion) was first revealed by Jonker and Santen^[1]. The alkaline earth substituted lanthanide elements manganites are technically important due to their interesting electrical, magnetic and catalytic properties, especially the phenomenon of giant magnetoresistance in $\text{Ln}_{1-x}\text{M}_x\text{MnO}_3$ (Ln=lanthanide element, M=divalent element) has attracted considerable attention in recent years^[2-5]. Some studies reported very recently^[6-8] indicate that I-M transition temperature (T_p) of $\text{Ln}_{1-x}\text{M}_x\text{MnO}_3$ varies systematically with the ionic radius of A-site cation. T_p and the peak resistivity (ρ_p) are relevant to the giant magnetoresistance phenomenon. In order to understand the effect of the ionic radius of the A-site cation on the electrical conduction in $\text{Ln}_{1-x}\text{M}_x\text{MnO}_3$, we have successfully synthesized $\text{Nd}_{0.97}\text{M}_{0.03}\text{MnO}_3$ (M=Mg, Ca, Sr, Ba) by coprecipitation technique and the influence of the radius of M^{2+} has been discussed.

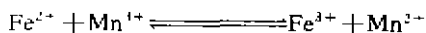
1 Experiment

Analytical pure reagent Nd_2O_3 , MCO_3 (M=Mg, Ca, Sr, Ba), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were used as starting materials. First, the stoichiometric Nd_2O_3 and MCO_3 was dissolved in hot dilute nitric acid (equivalent weight). Then the stoichiometric $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was dissolved in the solution. The enough saturation solution of $(\text{NH}_4)_2\text{CO}_3$ (99.0%) was slowly added to the aforementioned solution which is being stirred to coprecipitate. The coprecipitation solution was filtered, and the coprecipitate was washed with distilled water for several times, baked at 150 °C for 6 hours and then heated at 900 °C for 15 hours. A black powder was obtained. The powder was pressed under 10 Mpa and calcined at 950 °C, 1000 °C, and 1100 °C for 24 hours respectively. The bulk ceramic $\text{Nd}_{0.97}\text{M}_{0.03}\text{MnO}_3$ was prepared.

X-ray diffraction (XRD) was carried on a rigaku MAX-RD X-ray diffractometer ($\text{CuK}\alpha$ $\lambda = 1.5418\text{\AA}$). The resistivities were measured by a standard four-probe method. The content of Mn^{4+} was determined by capacity volume titrations. The quantitative sample was dissolved in hot phosphoric acid, first, the amount of Mn was obtained by the reactions below.



Second, the content of Mn^{4+} was obtained by the reactions below.



2 Results and Discussion

The diagrams of XRD for all samples are showed in Fig. 1. All samples calcined at 950 °C are sin-

gle phase (cubic). Compared with the conventional ceramic technique^[2,3], the temperature at which the compounds were synthesized has been reduced by 400 °C. The unit cell parameter of all samples are listed in table 1. Obviously, the unit parameter varies with the radius of M regularly. With calcining temperature increasing to 1000 °C, 1100 °C, $\text{Nd}_{0.57}\text{Ca}_{0.35}\text{MnO}_3$ (NCM) and $\text{Nd}_{0.57}\text{Ba}_{0.11}\text{MnO}_3$ (NBM) are still single phase and their diffraction peaks become sharp. In diagrams of $\text{Nd}_{0.47}\text{Mg}_{0.33}\text{MnO}_3$ (NMM) and $\text{Nd}_{0.47}\text{Sr}_{0.32}\text{MnO}_3$ (NSM), there exists some little impure diffraction peaks. The impurities in NMM are $\text{Mg}(\text{O}_2)_2$, MnO , Mn_2O_3 , Mn_3O_4 and in NSM are Mn_2O_3 , Mn_3O_4 , MnO_2 , as indicated in the Fig. 1.

In Fig. 2 the unit cell of a perovskite cubic ABO_3 is given. Here A denotes a large ion like Nd^{3+} , M^{2+} (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}), while B stands for a small ion like Mn^{3+} , Mn^{4+} . Goldschmidt^[3] pointed out that the perovskite structure is stable only if the tolerance factor t , defined by $t = (r_A + r_O) / (r_B + r_O) \sqrt{2}$, (r_A , r_B , r_O denote respectively the radius of ions A, B, O) approximately equals unity. The t of all samples are listed in table 1. In NMM, the presence of impurity may be attributed to the reason that the tolerance factor t is too little to bear the pyroprocessing. However, it is puzzling that NCM is still single phase at 1100 °C while there are impure phases in NSM despite that the t of NSM is larger than that of NCM.

In Fig. 3, the resistivity dependencies of temperature for all samples are showed. NMM and NCM are semiconductor-like, the resistivity transition peak develops at 200K, 90.2K for NSM, NBM respectively. It should be noted that at 57 K there is a little resistivity peak in NBM. In order to get better insight into the electrical conduction mechanism, the $\ln\rho$ vs $1/T$ relation is showed in

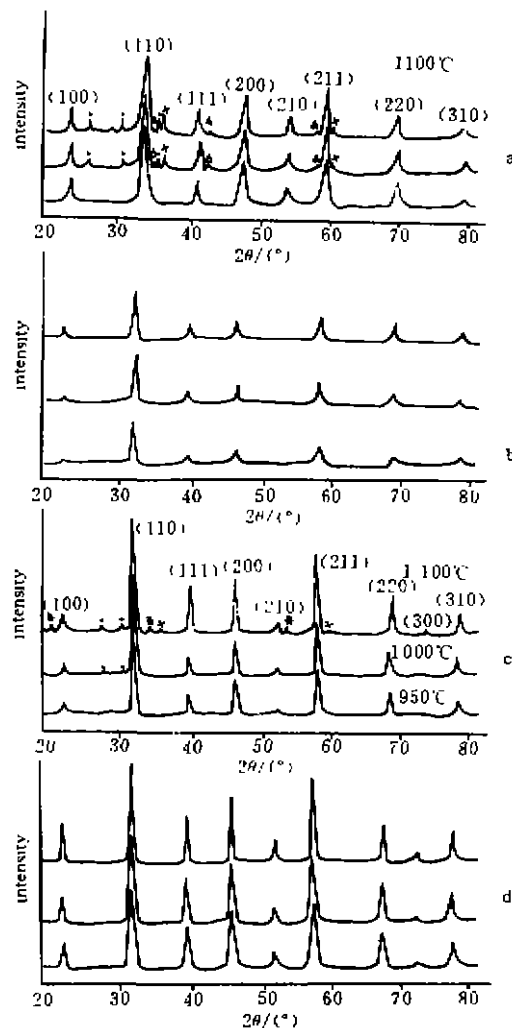


Fig. 1 X-ray diffraction patterns of the samples at 950 °C, 1000 °C, 1100 °C
a = $\text{Nd}_{0.47}\text{Mg}_{0.33}\text{MnO}_3$, b = $\text{Nd}_{0.57}\text{Ca}_{0.32}\text{MnO}_3$
c = $\text{Nd}_{0.47}\text{Sr}_{0.32}\text{MnO}_3$, d = $\text{Nd}_{0.57}\text{Ba}_{0.13}\text{MnO}_3$
* MnO_2 , □ Mn_2O_3 , ● $\text{Mg}(\text{O}_2)_2$,
× Mn_3O_4 , ▽ MnO

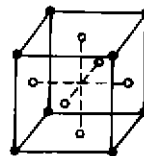


Fig. 2 Unit cell of perovskite (ABO_3)

Fig. 4. The linear relation between $\ln \rho$ and $1/T$ indicates all the samples are semiconductor-like in high temperature region, according to the formula $\rho = \rho_0 e^{E/kT}$ of the electric conduction of semiconductor, the estimated values of the thermal activation energy of NMM, NCM, NSM, NBM are 180.2 meV, 171.8 meV, 142.6 meV, 149.3 meV respectively. But in low temperature region, NMM and NCM is insulator while the electrical conduction of NSM and NBM change from semiconductor-like to metal-like (S-M transition).

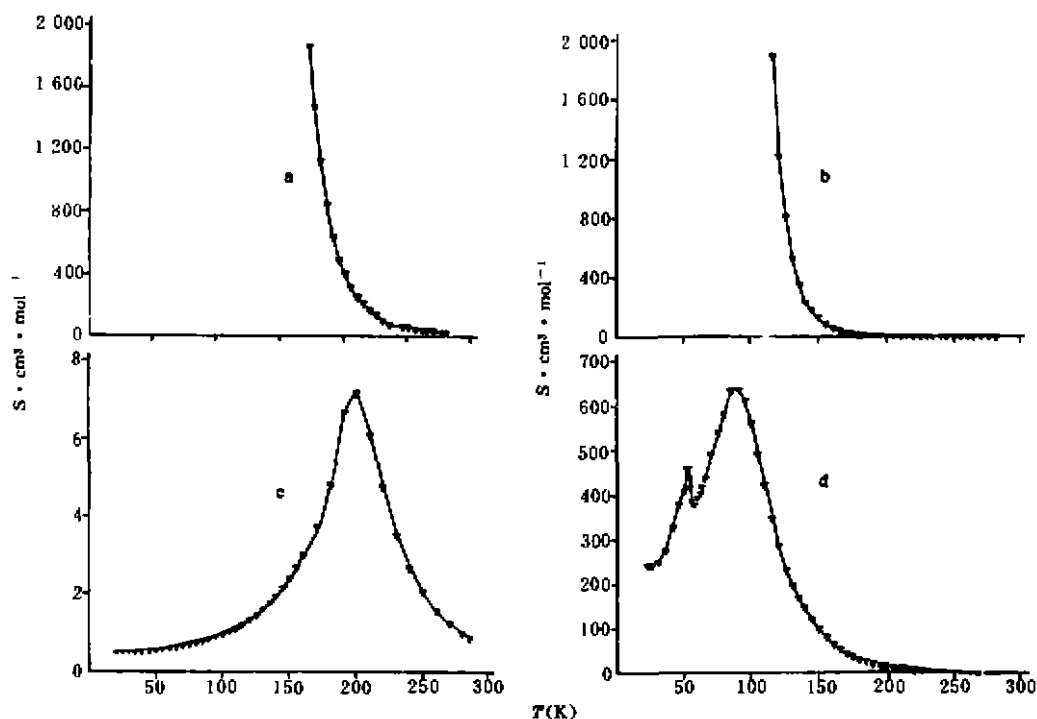


Fig. 3 Temperature dependence of the resistance of the samples

a = Nd_{0.47}Mg_{0.53}MnO₃, b = Nd_{0.47}Ca_{0.53}MnO₃, c = Nd_{0.47}Sr_{0.53}MnO₃,
d = Nd_{0.47}Ba_{0.53}MnO₃

Due to the hund rule, the Mn³⁺ in NdMnO₃ have three electrons in the t_{2g} orbit and a single electrons in the e_g orbit. There is Hund coupling between t_{2g} spin and e_g electrons within which there exists on-site coulomb repulsion, NdMnO₃ is antiferromagnetic (AF) insulator^[7-9]. The substitution of Nd atoms by divalent ions (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺) causes equal number of Mn⁴⁺ ions to appear, namely, it leads to a depletion (or vacancy) of the e_g orbit which now become available for electrons of the surrounding Mn³⁺ ions to jump into the empty states. Because the hybridization of Mn³⁺-O 2p is strong and there is no direct coupling between Mn ions, The e_g electron of Mn³⁺ transfer to Mn⁴⁺ vacancy of e_g via O anion in Mn³⁺-O²⁻-Mn⁴⁺ bond. So the deviation of the angle of Mn³⁺-O²⁻-Mn⁴⁺ bond from 180° will affect the hopping of e_g electron. In order to study the influence of alkali-earth ions' radius, The nominal stoichiometry of M (M=Mg, Ca, Sr, Ba) in every sample are designed to

be same. In fact, the content of Mn^{4+} (listed in table 1) are proved to be approximately equal in all samples by titration analysis. It can be concluded that the number of carries in every sample should be equivalent roughly. In order to explain the electric conduction of the samples, the lengthy of ideal $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bond is hypothesized to be $d_{\text{ib}} = r_{\text{Mn}(3+)} + 2r_{\text{O}(2-)} + r_{\text{Mn}(4+)} = 3.86$ ($r_{\text{Mn}(3+)} = 0.70$, $r_{\text{O}(2-)} = 1.32$, $r_{\text{Mn}(4+)} = 0.52$). From table 1, the relations between a and d_{ib} in NMM, NCM, NSM and NBM are $a = 3.8034 < d_{\text{ib}}$, $a = 3.8125 < d_{\text{ib}}$, $a = 3.8565 \approx d_{\text{ib}}$ and $a = 3.8838 > d_{\text{ib}}$ respectively. Obviously, the degree of mismatch which cause the deviation of the angle of

$\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bond from 180° between a and d_{ib} varies with the radius of M^{2+} ($r_{\text{Mg}(2+)} = 0.78\text{\AA}$, $r_{\text{Ca}(2+)} = 1.06\text{\AA}$, $r_{\text{Sr}(2+)} = 1.27\text{\AA}$, $r_{\text{Ba}(2+)} = 1.42\text{\AA}$).

Goodenough^[10] gave a qualitative theory on the magnetic interaction in the manganites, which is based on a special type of covalent bond between Mn- and O-ions, the semicovalent bond. For this bond the distance between the ions is very important. Small lattice constants lead to antiparallel, larger ones to parallel coupling of the magnetic moments of ions sharing one O-ion. In low temperature region, the moment of t_{2g} in Mn ion begin to order. Due to the quite large deviation of the angle of $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bond and the short distance caused by $a < d_{\text{ib}}$ between Mn^{3+} and Mn^{4+} , according to the Goodenough's theory, the align between Mn^{3+} moment and Mn^{4+} moment may be antiparallel (AF) which is more stable than the align between Mn^{3+} moment and Mn^{4+} moment is parallel (FM) in NMM and NCM. Sequentially, the hopping of e_g electron in $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bond is very difficult and they become insulator. Since a is close to d_{ib} in NSM and larger than d_{ib} in NBM, the distance between Mn^{3+} and Mn^{4+} is almost equal to and larger than that of the ideal $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bond in NSM and NBM respectively. So in both of them, the deviation of the angle of $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bond is little, the align between Mn^{3+} moment and Mn^{4+} moment may be parallel which is more stable than AF in them. Due to the double exchange coupling^[6], the transfer of e_g electron in $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bond becomes very easy, and the electrical conduction changes from semiconductor into metal in NSM and NBM (the little resistivity transition peak at 57K in NBM should be further researched).

Table 1 Crystal Unit Parameter, Tolerance Factor (t) and Percentage of Mn^{4+} for Samples

samples	$\text{Nd}_{0.97}\text{Mg}_{0.03}\text{MnO}_3$	$\text{Nd}_{0.97}\text{Ca}_{0.03}\text{MnO}_3$	$\text{Nd}_{0.97}\text{Sr}_{0.03}\text{MnO}_3$	$\text{Nd}_{0.97}\text{Ba}_{0.03}\text{MnO}_3$
unit cell parameter	3.8034	3.8125	3.8565	3.8838
t	0.8468	0.8801	0.9051	0.9242
%mol Mn^{4+}	32	31	31	30

In high temperature region, the Mn moment is disorder. There is no AF or FM coupling, the elec-

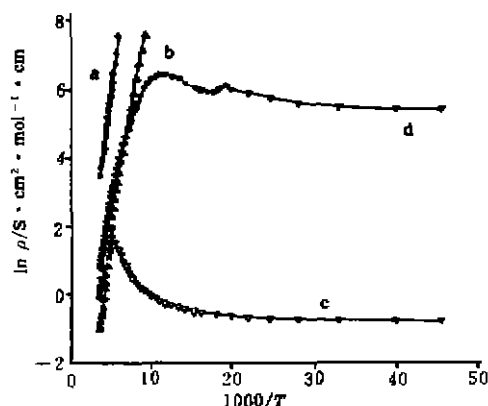


Fig. 4 $\ln \rho$ vs $1000/T$ relation curve of the samples
a = $\text{Nd}_{0.97}\text{Mg}_{0.03}\text{MnO}_3$, b = $\text{Nd}_{0.97}\text{Ca}_{0.03}\text{MnO}_3$,
c = $\text{Nd}_{0.97}\text{Sr}_{0.03}\text{MnO}_3$, d = $\text{Nd}_{0.97}\text{Ba}_{0.03}\text{MnO}_3$

trical conduction of all sample is semiconductor-like. According to the scenario hypothesis, the order of the values of D ($D = |a - d_{10}|$) should correspond to that of the degree of the deviation of the angle of $\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ bond. Since the order of the values of D is $D_{\text{NSM}} = 0.0035 < D_{\text{NBM}} = 0.238 < D_{\text{NCM}} = 0.475 < D_{\text{NMM}} = 0.566$, the active energies order should be $E_{\text{NSM}} < E_{\text{NBM}} < E_{\text{NCM}} < E_{\text{NMM}}$, which is well consistent with experimental data.

In summary, Nd_{0.87}M_{0.33}MnO₃ (M=Mg, Ca, Sr, Ba) were prepared by coprecipitation route. The temperature at which the compounds were synthesized has been reduced by 400°C. The influence of the radius of M on structure, The temperature at which the compounds were synthesized and electric conduction was studied. The hypothesis of AF and FM magnetic structure was proposed to explain the electrical conduction of Nd_{0.87}M_{0.33}MnO₃ (M=Mg, Ca, Sr, Ba).

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