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Temperature Sensitive Properties of the $La(Ti_xMn_{1-x})O_3$ System

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Abstract. The electric mechanisms of perovskite-type $LaMnO_3$ was investigated with B-site substitution in this paper. Samples of $La(Ti_xMn_{1-x})O_3$ ($0.1 \leq x \leq 0.7$) were sintered at different temperature. The voltage-temperature (V-T) curves of the samples were tested from room temperature (25°C) to 300°C, then the electric properties were measured and analyzed. The experimental results showed that the resistivity-temperature (ρ-T) curves of the samples matched NTC characteristic. The resistivity increased slightly with the increase of Ti amount as x was less than 0.5, however, it rose greatly after x exceeded 0.5; The sintering temperatures have a little influence on the resistivity, except for the sample with $x = 0.7$.

Keywords: Ti, dopant, $LaMnO_3$, negative temperature coefficient

1. Introduction

$LaMnO_3$ is p-type electric conductor that conducts electricity by transiting cations [1]. It has favorable conductivity and stability at high temperature, which makes it suitable for electrode or conjunction of solid fuel cell. Furthermore, researchers discover in recent years that $LaMnO_3$ also has giant magnetoresistance (GMR) and catalyze properties. In this experiment, we try to increase resistivity of $LaMnO_3$ to make it a type of electric ceramic with high resistivity, high B value, NTC property. Conductance values can be controlled through controlling the number of alterable ions of different valences in oxygen octahedron. According to dilution principle, the same or high valence ions can be replaced, which is equal to decreasing the number of alterable and diverse valent ions, consequently resistivity of materials increases [2].

With its cheapness, stabilization and good sensitivity at high temperature, NTC thermal sensitive resistor has been widely used [3]. The resistance of NTC thermal sensitive resistor can be expressed by this formula:

$$R = R_0 e^{(B/T)}$$

where R_0 and R are the resistance when the temperature is T_0 and T–∞ respectively. B is the material constant. To the porcelain and ceramic material, it usually changes with components, sintering temperature, sintering ambience, etc, which can be expressed as follows:

$$B_N = 2.303 \frac{\lg R_1 - \lg R_2}{\frac{1}{T_1} - \frac{1}{T_2}} \quad (1)$$

where R_1 is zero power resistance of temperature T_1 (298 K); R_2 is zero power resistance of temperature T_2 (348 K).

The main advantage of thermal sensitive resistor is high coefficient of resistance-temperature (ρ-T), high sensitivity, quick response speed, and precise temperature measuring. Its primary weakness is serious nonlinear phenomena of thermoelectricity, so linear compensate is needed [4]. The testing of linear degree is usually denoted by B-value which indicates better linear degree with its high value.

2. Experimental Details

The NTC ceramics were fabricated by the conventional solid-state reaction technique. Commercially available

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powders of La_2O_3, MnO_2 and TiO_2 acted as raw materials. which were weighed separately according to $LaMn_{1-x}Ti_xO_3$, with x from 0 to 0.7 (0–70 mol% Ti). Powders were wet-milled with agate balls in a polyethylene-lined ball mill, using distilled water for 4 h, the mixtures were granulated by addition of 5% camphor and pressed into pellets (10 mm in diameter and 2 mm thick) by hydrostatic pressing at 250 MPa. The pellets were sintered in air for 2–4 h at 1160, 1180, 1200 and 1220°C respectively and cooled naturally. Electrode paste consisting mainly of silver and zinc was printed on both sides of the samples to a thickness of 0.5 mm and calcined at 490°C for 10 min. The electrical resistivity of the sample was calculated from the voltage V (The testing voltage is 1.0 V) and the current intensity I values from 25 to 300°C. The crystal structure was analyzed using X-ray diffraction (XRD).

3. Results and Discussion

3.1. Influence of the Sintering Temperature on the Resistivity

At the beginning of our experiment, we made a pure $LaMnO_3$. Its resistivity is 2.83 ohm·cm. But it was not easy to obtain $LaMnO_3$ pellets-they always broke up during sintered. Ti-doping not only raised the resistivity of $LaMnO_3$, but also improved its sintering. When the pellets were sintered at 1160°C for 3 h and 1220°C for 2 h respectively, they were unsintered and a bit over sintered. In order for comparing, we chose 1160 for 4 h, and 1180, 1200, 1220 °C for 2 h, respectively.

Figures 1–4 are the ρ-T curves of $La(Ti_xMn_{1-x})O_3(0.1 \leq x \leq 0.7)$ samples sintered in the air at 1160°C, 1180°C, 1200°C and 1220°C, respectively. The Figs. 1–4 indicates that between 25°C (room temperature) and 300°C, the samples behave in accordance with NTC characteristic. When the temperature increases, the resistivity is invariable except for the sample $La(Ti_{0.7}Mn_{0.3})O_3$, of which the resistivity rose sharply after sintered at 1220°C. It is obvious that the sintering temperatures have a little influence on the samples' resistivity,

(In Figs.1–4, the 'unit10eN' means the value of the resistivity displayed should multiply 10^N. For example: 'unit10e2' means the value displayed should multiply 10^2.)

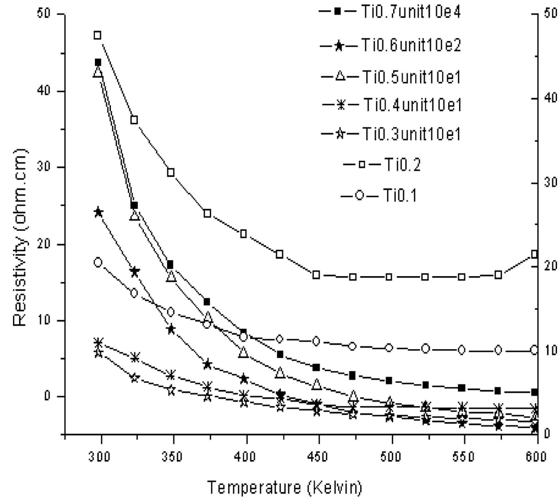

Fig. 1. 1160°C all (4 h) sample's ρ-T curves.

3.2. Influence of the Amount of Ti-doping in $LaMnO_3$ on the Resistivity

Table 1 lists B-values of the samples with different Ti-doping concentration and sintering temperatures. From Figs. 1–4 and Table 1, it can be concluded that the resistivity increases with the increase of Ti-doping concentration. B-values of samples sintered at 1180°C are better, while samples with $x = 0.5$ or 0.6 have superior B-values at every sintered temperature, and the samples with $x = 0.7$ sintered at the lower temperature have better NTC characteristic.

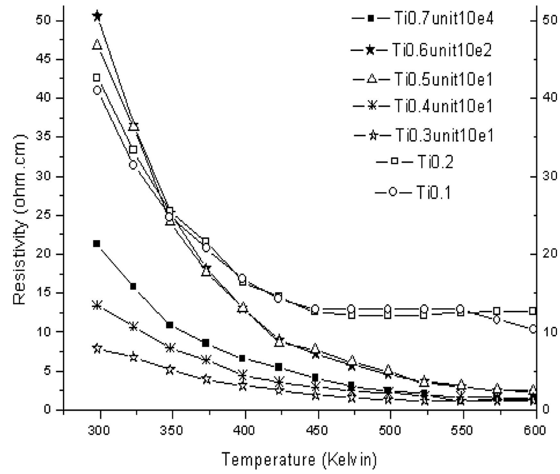

Fig. 2. 1180°C (2 h) all sample's ρ-T curves.

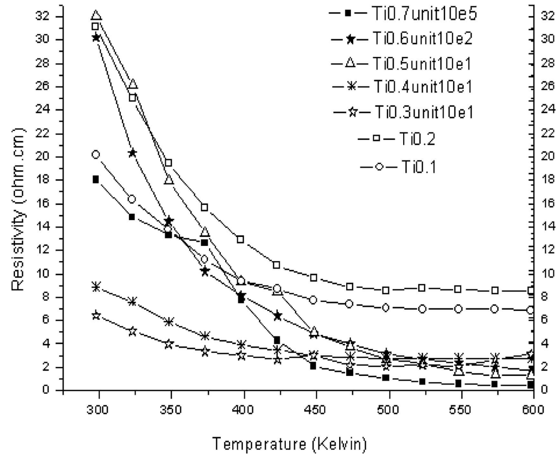

Fig. 3. 1200°C (2 h) all sample's ρ-T curves.

Table 1. B-value of all samples at different temperature (°C).

Temp	$Ti_{0.1}$	$Ti_{0.2}$	$Ti_{0.3}$	$Ti_{0.4}$	$Ti_{0.5}$	$Ti_{0.6}$	$Ti_{0.7}$
1160	707	870	1130	913	1724	1544	1931
1180	1045	1069	905	1080	1335	1436	1401
1200	788	976	1007	853	1197	1526	629
1220	606	860	1112	1015	1237	1451	251

Table 2. Room temperature resistivity of all samples sintered at different temperature (ohm.cm).

Temp.	0.1	0.2	0.3	0.4	0.5	0.6	0.7
1160	21	47	98	110	430	2651	436739
1180	41	43	79	134	468	5055	212469
1200	20	31	64	88	320	3023	1800001
1220	16	32	104	274	779	3177	10781963

Table 2 lists the resistivity values of the samples, which have different Ti-doping concentration and sintering temperatures. It indicates that resistivity values of samples increase with the increase of the Ti-doping concentration, and the trend becomes more distinct when the amount of Ti-doping becomes heavier. The resistivity increased slightly (slope is about two) with the increase of Ti amount when x was less than 0.5, and rose greatly (the maximum of the slope can reach 1,000) when x exceeded 0.5; Considering the practical requirement of proper resistivity and high B-value, such a conclusion can be presented that samples containing 0.5Ti is better than others considering both of resistivity and B-value.

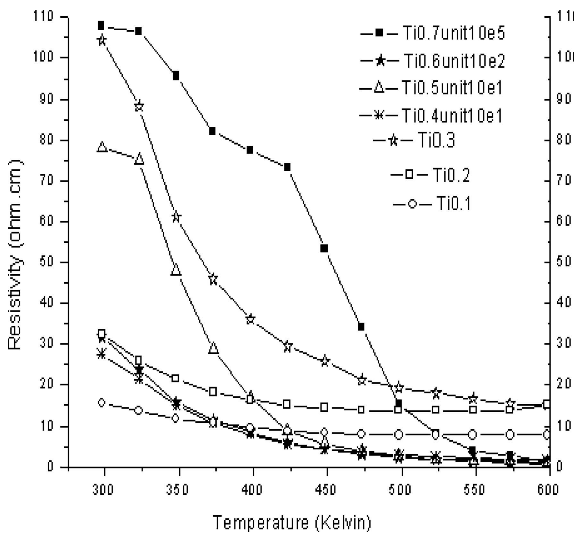

Fig. 4. 1220°C (2 h) all sample's ρ-T curves.

The NTC characteristic displayed in Figs. 1–4 can be explained as follows: $LaMnO_3$ is p-type semiconductor material, and hole is its majority carrier. TiO_2 is n-type semiconductor material, and electron is its majority carrier.

When $x \leq 0.5$, it indicates that p-type material-$LaMnO_3$ is doped with n-type material-TiO_2. When the temperature increases, both p-type and n-type semiconductors will generate more holes and electrons. Despite the recombination of electrons and holes, the quantity of holes increases, because holes are the majority carriers to the p-type material doped with n-type material. Therefore, the material's resistivity decreases with the temperature's increase. When the temperature reaches a certain degree, the concentration of the holes gets its maximum, and then the resistance ratio will nearly keep stable. When $x > 0.5$, it means that n-type material-$LaTiO_3$ ($La_2Ti_2O_7$) is doped with p-type material-MnO_2, so it can be analyzed in the same way [5].

Figures 5 and 6 is XRD patterns of La($Ti_{0.2}Mn_{0.8}$)O_3 and La($Ti_{0.7}Mn_{0.3}$)O_3 samples sintered at 1200°C. To Fig. 5, the main components are $LaMnO_3$ and $LaTiO_3$. $LaMnO_3$ is orthorhombic structure, and $LaTiO_3$ is cubic structure. To Fig. 6, the main components are $LaMnO_3$ and $La_2Ti_2O_7$, and $La_2Ti_2O_7$ is monoclinal structure. Based on the above analyse, such a conclusion can be deduced that the main component

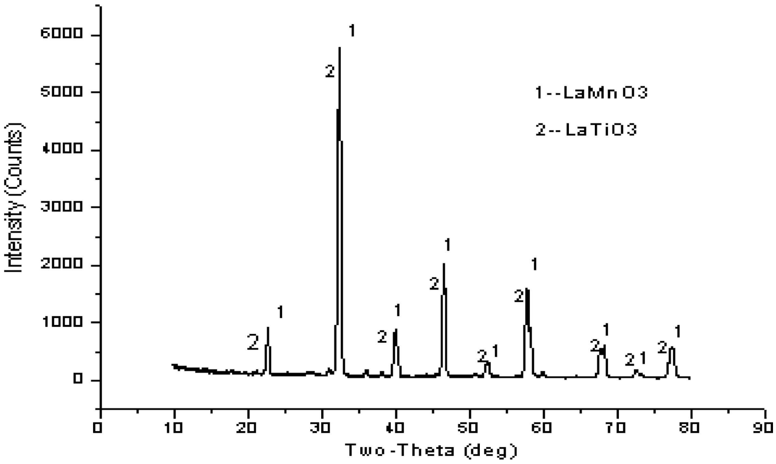

Fig. 5. XRD pattern of sample $La(Ti_{0.2}Mn_{0.8})O_3$ sintered at 1200°C.

change from $LaTiO_3$ to $La_2Ti_2O_7$ with Ti-content's increasing.

The resistivity of both $LaMnO_3$ and $LaTiO_3$ can be influenced by many factors, such as average size of ions, concentration of carriers, etc. And these factors can be changed by chemical substitution. The result of XRD (Fig. 5) displays that the sample is single-phase, so it proves that Ti has participated completely in the reaction, and joined in B-site. It doesn't change material's crystal lattice structure through doping Ti, but the constant of crystal lattice becomes a little bigger. The ion radius of Ti^{3+}(0.067 nm) is larger than that of Mn^{3+}(0.058 nm), so the Ti ion should enter the Mn ion's position and destroy the Mn-O's network structure. This action induces crystal lattice effect which resulted in the increase of the resistivity. Moreover, surface effect of crystal lattice grain also brings resistivity up: the exterior atom of crystal lattice grain becomes more out-of-order because of doping Ti, consequently the dispersion of electrons increases at interface [6]. As we have analysed above, the resistivity-increasing effect can be concluded from Table 1.

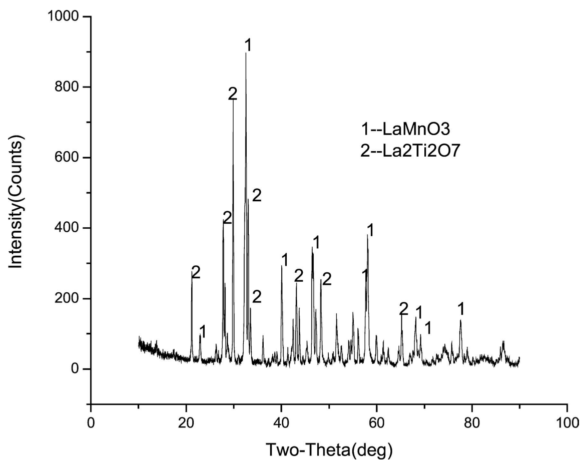

Fig. 6. XRD pattern of sample $La(Ti_{0.7}Mn_{0.2})O_3$ sintered at 1200°C.

According to Fig. 6 and Table 2, when the main components are $LaMnO_3$ and $La_2Ti_2O_7$, it means MnO_2 has been doped into $La_2Ti_2O_7$. The ion radius of Mn^{3+}(0.058 nm) is larger than that of Ti^{4+}(0.042 nm), so the Mn-doping not only changes the lattice structure, but also increases the lattice parameter. As a result, because $LaMnO_3$ is a low resistivity composite, the Mn-doping decreases the resistivity of $La_2Ti_2O_7$.

4. Conclusions

Ti was doped into the B-site of $La(Ti_xMn_{1-x})O_3(0.1 \leq x \leq 0.7)$ after it was sintered at 1160°C 1180°C, 1200°C and 1220°, respectively. Samples' resistivity-temperature (ρ-T) curves match NTC characteristic curves. When $x \leq 0.5$, resistivities of samples increased slightly with the increase of Ti amount. However, they rose greatly after x exceeded 0.5. The sintering temperatures have a little influence on the resistivity, except for the sample containing 0.7 Ti..

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