Preparation and Particle Size Study of Cobalt Substituted Strontium Doped Lanthanum Manganate Films by Sol-gel and Heat Treatment Method

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Abstract: In order to study the effect of B-position element substitution on strontium doped lanthanum manganate microstructure and resistivity temperature property, the cobalt substituted strontium doped lanthanum manganate ceramic powders with La$_{0.6}$Sr$_{0.4}$Co$_x$Mn$_{1-x}$O$_3$ as the main component was prepared by sol gel method combined with heat treatment process at first, then the cobalt substituted strontium doped lanthanum manganate films was prepared by silk-screen printing on the Alumina ceramic substrate. The results showed that when the x value sequentially varied from 0 to 0.2, 0.4, 0.6, 0.8, the particle size property of films would be changed by the change of the crystal structure, which was produced by the B-position cobalt substitution. It could be seen from the results that the average radius of the five powders were concentrated in the range of 16.4-19.6nm.

1.Introduction

Strontium lanthanum manganate La$_x$Sr$_{1-x}$MnO$_3$ (LSMO) film was a kind of conductive ceramic material with special perovskite structure. Because of its high geometric and chemical matching of structure, strong electrical property adjustability, good thermal stability and colossal magnetoresistance, LSMO had been widely used in electrode materials and thermal sensitive materials, Superconducting materials, catalytic materials, solar materials and other fields and had become a new functional material with broad development prospects.

As a kind of perovskite type material, LSMO especially had a unique ABO$_3$ lattice structure included LaO$_{12}$ dodecahedron composed of lanthanum ions and O ions at the A-site and MnO$_6$ octahedron composed of manganese ions and O ions at the B-site. Both A-site and B-site ions could be replaced by other element ions, which would result in microscopic changes of the lattice structure. The close relationship between lattice structure of LSMO and the conductive mechanism and conductivity of LSMO materials had been confirmed, which meant the macro electrical properties, especially thermal resistance properties, could be easily controlled by element substitution.

For the preparation of the LSMO, diversified experimental method such as hydrothermal method [13], micro emulsion method, sol-gel method, solid phase reaction method had been used by researchers. The experimental results have been achieved, among which A bit element substitution has been studied more frequently, while B bit element substitution was relatively less. In particular, the deep-seated mechanism of the effect of B-site element substitution on lattice structure and thermal resistance is lack. Therefore, in combination with previous research work, based on La$_{0.6}$Sr$_{0.4}$MnO$_3$ and La$_{0.6}$Sr$_{0.4}$Co$_{0.6}$Mn$_{1.4}$O$_3$ as the target product, the substitution of cobalt ions for B site manganese ions
by sol-gel method was carried out in this paper. The difference of temperature resistance characteristics of LSMO after element substitution was studied, which lay a foundation for further studying the relationship between B site element substitution and temperature resistance characteristics.

2. Test materials and methods

2.1 Test materials

The main raw materials of this test included: lanthanum nitrate (including crystal water), strontium nitrate, manganese nitrate (using 50wt% manganese nitrate solution), cobalt nitrate (including crystal water), citric acid, ethylene glycol, ammonia solution, deionized water, terpineol, ethyl cellulose, etc. The basic parameters were shown in table 1.

2.2 Experimental method

Comparing the previous experimental results and literature, this experiment target product was based on La0.6Sr0.4MnO3, and the cobalt nitrate was used to replace the B-site cobalt of LSMO materials to obtain La0.6Sr0.4CoxMn1-xO3 (x = 0, 0.2, 0.4, 0.6, 0.8). According to the molar ratio of elements in the target product, weigh each chemical raw material with an electronic balance, dissolve it in deionized water at 80 °C, continuously heat and stir it on a magnetic stirrer, weigh citric acid according to 1.2 times the number of moles of metal ions, and fully dissolve it. Add ethylene glycol according to 4 times the molar number of citric acid to improve its solution activity, and adjust the pH value of the above solution to 8 ~ 9 with ammonia to obtain a light red solution. Continue heating and stirring, get the yellow brown sol, stop stirring, continue heating, and finally get milky white xerogel. After sufficient cooling, take it out to obtain a black fluffy block, and then put it into an agate mortar for full grinding to obtain LSMO powder. LSMO powder and organic carrier composed of terpineol (97wt%) and ethyl cellulose (3wt%) were fully ground and stirred in a mortar according to the mass ratio of 7:3 to obtain LSMO slurry. LSMO film effectively combined with Al2O3 ceramic substrate was obtained by screen printing process.

| Material          | Purity          | Particle size/μm | Remarks        |
|-------------------|-----------------|------------------|----------------|
| La(NO3)3·6H2O     | Analytical purity | ≤30              |                |
| Sr(NO3)2          | Analytical purity | ≤20              |                |
| Co(NO3)2·H2O      | Analytical purity | ≤35              |                |
| Mn(NO3)2          | Analytical purity | -                | 50wt%          |
| Citric acid       | Analytical purity | ≤20              |                |
| Glycol            | Analytical purity | -                |                |
| Ammonia           | Analytical purity | -                | 20wt%          |
| Terpineol         | Analytical purity | -                |                |
| Ethyl cellulose   | Analytical purity | ≤5               |                |
| Deionized water   | Analytical purity | -                |                |
| Aluminum oxide    | Analytical purity | -                | α-Al2O3≥96%    |

2.3 Analysis and characterization methods

(1) The morphology of LSMO powder and LSMO film were observed by KYKY em6200 scanning...
electron microscope (SEM).

(2) The phase of LSMO powder was analyzed by Bruker D2 phase X-ray, and the ray wavelength was λ = 0.154056 nm, scanning step 0.05 °, scanning angle 10-90 °.

(3) The square resistance of LSMO film at room temperature was measured by st2258c four probe tester.

(4) Fix the ceramic substrate printed with LSMO film with self-made fixture and put it into srjx-3-9 box resistance furnace together. Connect the copper wire with ceramic protective tube with vc9804a + multimeter outside the furnace to test its temperature resistance characteristics. The resistance furnace increases from room temperature to 1300 °C at the speed of 10 °C / min and records the resistance value every 5 minutes.

3. Results and analysis

3.1 The SEM characterization of LSMO film

The SEM characterization of LSMO film powder could be seen from the Fig. 1, which displayed the particle agglomeration of LSMO film powder meant it was difficult to estimate the particle size of LSMO film powder. With the help of further analysis, the LSMO film coating prepared from the picture was relatively dense and flat, and basically no cracks could be seen, which demonstrated that the prepared powder can be evenly printed on the ceramic substrate by screen printing process.

![Fig.1 The SEM photograph of the prepared LSMO powders and thin film](image_url)

3.2 The XRD analysis of LSMO powders

In order to determine the composition of the prepared LSMO powder, XRD analysis was carried out. Fig.2 shows the XRD analysis results of five kinds of powder. It could be seen from the figure that the X-ray diffraction peaks of the prepared cobalt substituted LSMO powders with different proportions were highly similar, the diffraction peaks are sharp, and the positions are almost the same. After comparison with the standard card, it could be determined that the prepared five powders are typical perovskite structures, which showed that the ABO₃ lattice structure remains relatively stable after cobalt ions replace manganese ions at position B.
Fig. 2 The XRD analysis result of LSMO Powders

It could also be found in the figure that the diffraction peak intensity will decrease slightly with the increase of the substitution ratio $x$ value from 0.2 to 0.8 for the reason of increase of element substitution of the phase superposition of multiple crystal planes. According to shear formula, the average particle size of five LSMO powders could also be calculated. Table 2 shows the calculation results of the average particle size. It could be seen from the table that the average radius of the five powders were concentrated in the range of 16.4-19.6nm. With the increase of $x$ value, the average radius tends to increase, because the radii of Mn$^{3+}$ and Mn$^{4+}$ in manganese ions are 0.066nm and 0.052nm respectively, while the radii of cobalt ion Co$^{2+}$ and Co$^{3+}$ were 0.082nm and 0.065nm, which were larger than those of manganese ions. With the increase of the proportion of cobalt ions replacing manganese ions, The lattice structure would expand in varying degrees, resulting in the increase of the average radius of the powder.

### Table 2 The Average granule diameter of LSMO powders

| $x$  | 16.4 | 17.2 | 18.1 | 18.8 | 19.6 |
|------|------|------|------|------|------|
| $x=0$ |      |      |      |      |      |
| $x=0.2$ |      |      |      |      |      |
| $x=0.4$ |      |      |      |      |      |
| $x=0.6$ |      |      |      |      |      |
| $x=0.8$ |      |      |      |      |      |

4. Conclusion

In this paper, La$_{0.6}$Sr$_{0.4}$Co$_x$Mn$_{1-x}$O$_3$ ($x=0, 0.2, 0.4, 0.6, 0.8$) was prepared by the Sol-gel and Heat Treatment Method as the target product. Cobalt substituted LSMO films were prepared on the alumina ceramic board by screen printing method, and the temperature resistance characteristics of LSMO thin films were analyzed. The main conclusions were summarized:

1. The Cobalt with different proportion of LSMO powder could be prepared by sol-gel combined with heat treatment process.
2. The average radius of the five powders was concentrated in the range of 16.4-19.6nm. With the increase of $x$ value, the average radius increased. And it could be seen from the SEM pictures that the powders showed the property of agglomeration, and the prepared films were relatively flat.
3. When the B site manganese ions were replaced by cobalt ions by sol-gel method, and the difference of temperature resistance characteristics of LSMO after element substitution could be studied, which would lay a foundation for further studying the relationship between B site element substitution and temperature resistance characteristics.

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