Characterization of Perovskite Oxide $LaMnO_3$ Nanofibers

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Keywords: Electrospinning; $LaMnO_3$; Nanofibers

Abstract. Perovskite-type cube structure $LaMnO_3$ nanofibers of approximately 50~100 nm in diameter were synthesized via Sol-Gel processing and electrospinning technology after calcined at 900℃ by using polyvinypyrrolidone (10 wt %PVP) as complexing agents. The nanofibers were characterized by experiment technology. The results presented that the fibers were chain-like structure and its surface were rough, and inner structure of the fibers was made up of single-crystalline grain of 20nm. The measurement results of the relation between the electrical conductivity and temperature of $LaMnO_3$ nanofibers show that the electrical conductivity of the sample of made of nanometer fiber is lower than that of the sample made of nanoparticles fiber.

1.Introduction

People use a variety of methods to prepare $LaMnO_3$ Nanophase Materials[1-3] and these methods are mainly used for the preparation of nanopowders and nano-films[4-6], while the report of the preparation of a quasi one-dimensional structure nanomaterials is very small, and this type of material has a very important significance on future catalytic, electrolyte materials. As an important and simple way to prepare Nano microfiber, electrospinning was applied to the preparation of inorganic materials nanofibers in 2002[7]. So far more than 20 inorganic materials microfibers have been prepared by people[8-13]. $LaMnO_3$ –based oxide becomes the hot topic of condensed Matter in recent decades because of its special structure and singular magnetic properties. People prepared $LaMnO_3$ nanomaterials and Nanofilms by using variety methods, however, the reports about preparation of one dimensional nanomaterials are less, in this paper, electrospinning together with Sol-Gel processing is used to prepare $LaMnO_3$ nanofibers. The nanofibers was characterized by means of scanning electron microscopy(SEM), transmission electron microscopy(TEM), X-ray diffraction(XRD) and thermogravimetric analysis-differential scanning calorimrtry(TG-DSC).

2. Experiments

2.1 Reagent and Instruments

Lanthanum Acetate ($La(CH_3COO)_3 \cdot 1.5H_2O$, analytical reagent, Mw=343.05, Alfa, Aesar Co.), Manganese Acetate ($Mn(CH_3COO)_2 \cdot 4H_2O$, analytical reagent, Mw=245.09, Bei-jing Chemistry Preparation Co., China), Polyvinylpyrrolidone(PVP, Mw=1300000, Aldrich), Anhydrous Alcohol (C_2H_5OH, analytical reagent, Bei-jing Chemistry Preparation Co., China).

Scanning electron microscope (SEM; JEOL JSM-6390), Transmission electron microscopy (TEM; JEM—2000EX), X-ray diffraction (XRD, Rigaku-D-Max rA 12kW) , Thermogravimetric analysis-differential scanning calorimrtry (TG-DSC, NETZSCH STA 449C). Digital display temperature control (MC92, 02230173).

2.2 Preparation of Precusor Sol

According to $LaMnO_3$ molecular formula the amount of lanthanum acetate and manganese acetate were dissolved in anhydrous alcohol, and stir the above solution slowly and add dropwise to 10wt% PVP (ethanol as solvent) and keep stirring for 24h at room temperature, then we can get electrospinning PVP / $LaMnO_3$ precursor solution.

2.3 Preparation of PVP / $LaMnO_3$ Composite Fiber by Electrospinning Method

Put electro-spinning precursor solution into spinning apparatus made from glass spinner (the spinning nozzle inner diameter of 0.8 mm), with an insert precursor sol copper wire as the anode, aluminum foil as the cathode. The angle between aluminum foil and a horizontal plane is 30°. The vertical distance between anode and the cathode is 14cm and increase voltage slowly, when the voltage reaches 16 kV, spinning begins to discharge, in this fixed voltage electrostatic spinning is processed, and obtain a disordered arrangement composite fiber nonwoven fabric on the aluminum foil.

2.4 Preparation of $LaMnO_3$ Nanofibers

The prepared PVP/ / $LaMnO_3$ composite fiber was put into a muffle furnace, temperature was rised in the fixed rate(1 ℃ / min). And then at different temperatures (300 ℃, 400 ℃, 500 ℃, 600 ℃, 700 ℃, 800 ℃, 900 ℃, 1000 ℃ , 1100 ℃) heat for 2h and then cool down to room temperature to obtain different structures of nanofiber.

2.5 Preparation of the Test Sample for Electrical Conductivity

Polish the calcined $LaMnO_3$ at 800℃ after 2h into fine powder, under pressure 200Mpa unidirectional pressed into wafer with a diameter of 13mm, a thickness of about 0.5mm, and then calcine at 800℃ for 2h to prepare to the testing electrical conductivity samples.

3. Results and Discussions

3.1 Morphology of the Fibers

3.1.1 SEM Analysis

Fig.1 shows SEM images of PVP /$LaMnO_3$ composite fibers at different calcination temperature. From the figure it can be observed that before calcination the surface of the fiber (Fig.1(a)) is relatively smooth and the fiber typical diameter is 300nm; at 300℃ calcination (Fig.1(b)), the fiber diameter becomes thin, its typical diameter is 200nm; From at calcination 400℃ to at calcination 600℃ (Fig.1(c)~Fig.1(e)), the fiber diameter gradually becomes thin and its surface becomes rough, which indicates that the PVP and acetic acid and other organic ingredients gradually burn and react and the sample preliminary crystalline; at 700℃ calcination (Fig.1(f)), there is the apperance of pearl chain-like structure, which indicates that organic ingredients completely volatile and the sample completely crystalline ; From calcination 700℃ to calcination 1100℃ (Fig.1(f)~ Fig.1(j)), the fiber diameter gradualy becomes thin, its surface is very rough, and there was a significant fragmentations phenomenon, the higher temperature fragmentations phenomenon is more serious, this is due to the initial fiber is made up of small grains, with the increase of temperature, the small grain size grows up to form large grains, and the big grain growth to the surrounding; When calcined to 1100℃(Fig.1(j)), the grain is grown together and the fiber structure of the sample was basically destroyed.

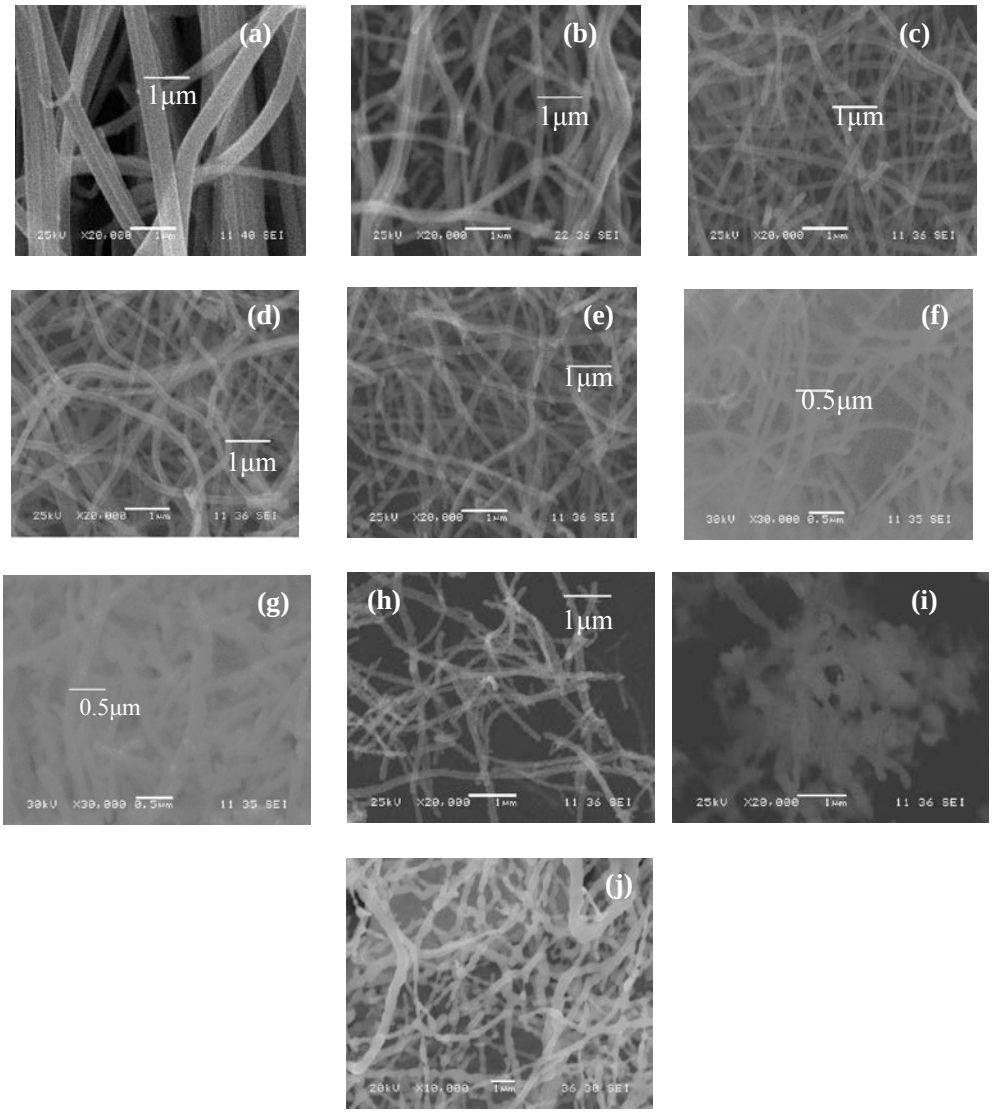
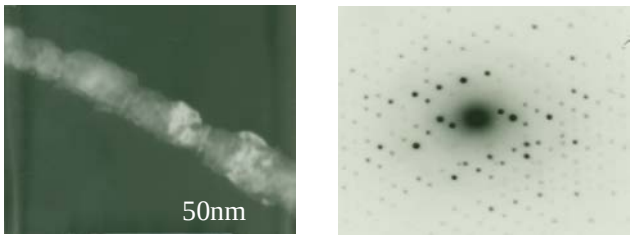


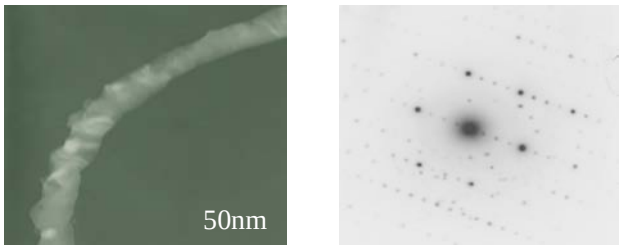
Fig.1. SEM images of various fiber samples. (a)before calcinations; (b) calcined at 300℃; (c) calcined at 400℃; (d) calcined at 500℃; (e) calcined at 600℃; (f) calcined at 700℃; (g) calcined at 800℃; (h) calcined at 900℃; (i) calcined at 1000℃; (j) calcined at 1100℃

3.1.2 TEM Analysis

Fig.2 shows TEM and ED images of the finer fiber samples calcined at 700℃ and 800℃. From the figure it can be observed that at 700℃ calcination (Fig. 2(a)), the diameter of fiber is 100nm, ED electron diffraction results indicate that the samples have been formed the structure of single crystal particles, the grain size of about15nm; at 800℃ calcination (Fig. 2(b)), fiber internal grain size becomes larger, the grain size of about 20nm, From ED figure we can see that electron diffraction spots becomes more clear, which indicates that fiber internal grain growth, the crystallization increased.



(a)



(b)

Fig.2 TEM images with corresponding ED of the fibers calcinated at 800℃ (a) and 900℃ (b)

3.2 Thermoanalysis of PVP/ LaMnO3 Composite Fibers

Fig.3 shows TG-DTA curves of hybrid fibers of electrospinning PVP/$LaMnO_3$ composite gel fibers. From the figure it can be given that thermal reaction in sintering process can be divided into four stages: starting from 120℃ to 230℃, weightlessness is about 7.4%, there is a small endothermic peak at 128℃, mainly composite gel fibers water vapor and crystal water lost; between 230℃ to 295℃, weightlessness is about 27% and there is a small exothermic peak at 265℃, mainly initial decomposition of acetate and PVP[16]; from 295℃ to 312℃ weightlessness is about 27%, there is a strong exothermic peak at 309℃, mainly acetate and PVP decomposition, combustion caused[17][18]; from 312℃ to 730℃ weightlessness is about 5%, mainly is about decomposition of lanthanum acetate and the structural formation of $LaMnO_3$.

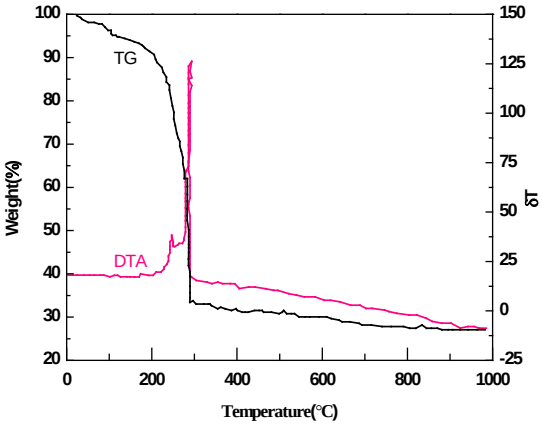


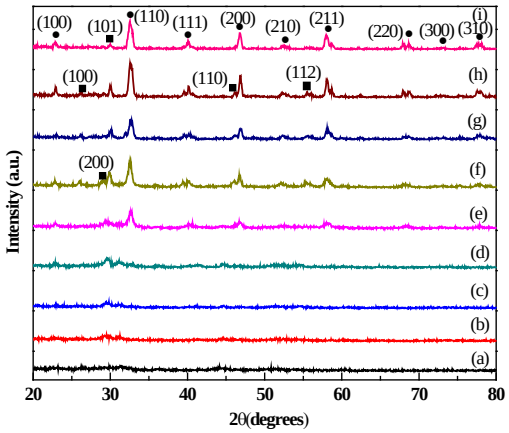
Fig.3 TG-DTA curves of hybrid fibers of PVP/ $LaMnO_3$

3.3 Structure Analysis of Fiber

Fig.4 shows about XRD patterns of electrospinning PVP / $LaMnO_3$ composite fibers at different calcination temperature. These pattern shows that there is no appearance characteristic peaks of La_2O_3 and $LaMnO_3$ calcined at 300℃. At 400℃ a hexagonal structure characteristic peak of La_2O_3 appear, and when calcined to 700℃, relatively clear and complete cubic perovskite structure $LaMnO_3$ characteristic peaks appeared, the presence of undesired peak of La_2O_3, in this condition cubic structure $LaMnO_3$ nanofibers were prepared successfully. With the increase of calcination

temperature, diffraction peaks of cubic structure of the $LaMnO_3$ enhanced, and diffraction peak of the hexagonal structure of La_2O_3 diminished. When calcined to 900℃, La_2O_3 yet fully transformed into a cubic structure of $LaMnO_3$ and the analysis may be due to the La slight excess of the ratio of the precursor solution. By the Scherrer formula, we can get that the average grain size of sample respectively is 14.6nm after 700℃ calcination and 15.2 nm after 800℃ calcination, which is in agreement with the results from the TEM diagram (Figure 2).

Fig.4 XRD patterns of the fibers. (a) calcinated at 300℃; (b) calcinated at 400℃; (c) calcinated at 500℃; (d) calcinated at 600℃; (e) calcinated at 700℃; (f) calcinated at 800℃; (g) calcinated at 900℃; (h) calcinated at 1000℃; (i) calcinated at 1100℃.(●$LaMnO_3$;■La_2O_3)



3.4 Electric Property Analysis of Fiber

Fig.5 shows temperature dependence of the electrical conductivity for $LaMnO_3$(●sythesized by electrospinning technology;■sythesized by traditional method). From this figure it can be seen that as the temperature increases, the electrical conductivity of two samples increases gradually, but changes of the electric conductivity of sample made of nanometer fiber with temperature was slower than that of sample made of nanoparticles, and at the same temperature the electrical conductivity of sample made of nanoparticles is higher than that of sample made of nanometer fiber. Furthermore, we also calculate sample density of these two kind samples, respectively, sample density that made of nanoparticles is about 3.301×10^3 kg/m^3, and sample density that made of nanometer fiber is about 2.864×10^3 kg/m^3, thus nanometer fiber sample density less than nanoparticles sample density, so it can be concluded that sample structure of nanometer fiber is loose, and that under the same temperature its electrical conductivity of the sample made of the nanoparticles is higher than that of nanometer fiber samples, this reason may be mainly due to the relatively loose sample structure of the nanometer fiber.

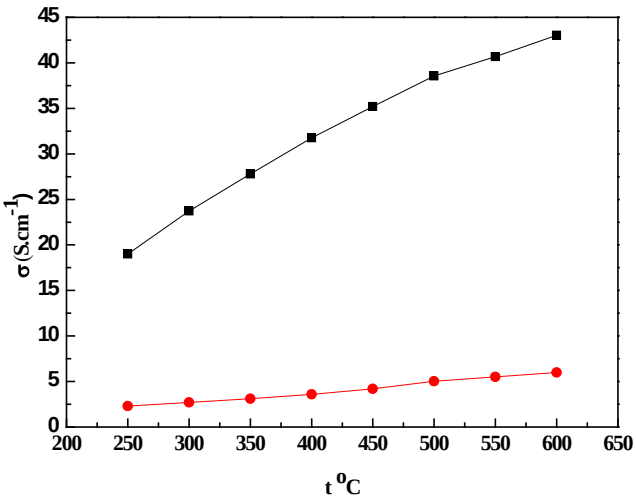


Fig.5 Temperature dependence of the electrical conductivity for $LaMnO_3$
(●sythesized by electrospinning technology;■sythesized by traditional method)

4. Conclusion

Perovskite-type cube structure $LaMnO_3$ nanofibers of approximately 50~100 nm in diameter were synthesized via Sol-Gel processing and electrospinning technology after calcined at 900℃ by using polyvinypyrrolidone (10wt%PVP) as complexing agents. The nanofibers was characterized by means of SEM, TEM, XRD and TG-DSC. The results presented that the fibers were chain-like structure and its surface were rough; inner structure of the fibers was made up of single-crystalline grain of 20nm, The measurement results of the relation between the electrical conductivity and temperature of $LaMnO_3$ nanofibers show that the electrical conductivity of the sample of made of nanometer fiber is lower than that of the sample made of nanoparticles fiber, which may be mainly due to the relatively loose sample structure of the nanometer fiber. This research will contribute to the development of catalytic and electrolyte materials.

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