Synthesis of Perovskite-type Oxides $LaMnO_3$ Nanofibers via Electrospinning

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Keywords: electrospinning, $LaMnO_3$, nanofibers, synthesis

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 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). 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.

1. Introduction

People use a variety of methods to prepare $LaMnO_3$ Nanophase Materials and these methods are mainly used for the preparation of nanopowders and nano-films,[1,2] 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.[3] So far more than 20 inorganic materials microfibers have been prepared by people.[4-6] In this paper, electrospinning together with Sol-Gel processing is used to prepare $LaMnO_3$ nanofibers.

2. Experiments

2.1 Reagent and Instruments

Lanthanum Acetate(La(CH3COO)3·1.5H2O, analytical reagent, Mw=343.05, Alfa, Aesar Co.), Manganese Acetate (Mn(CH3COO)2·4H2O, analytical reagent, Mw=245.09, Bei-jing Chemistry Preparation Co., China), Polyvinylpyrrolidone（PVP, Mw=1300000, Aldrich）, Anhydrous Alcohol (C2H5OH, 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).

2.2 Preparation of Precusor Sol

According to LaMnO3 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 / LaMnO3 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 LaMnO3 Nanofibers

The prepared PVP / LaMnO3 composite fiber was put into a muffle furnace, temperature was rised in the fixed rate(1℃ / min). And then at different temperatures (300 ℃, 500 ℃, 700 ℃, 900 ℃) heat for 2h and then cool down to room temperature to obtain different structures of nanofiber.

3. Results and Discussions

3.1 Morphology of the Fibers

3.1.1 SEM Analysis

Fig.1 shows SEM images of PVP /LaMnO3 composite fibers at different calcination temperature. From the figure it can be observed at low temperature calcination at 300℃ that the surface of the fiber is relatively smooth and the fiber diameter is thick and uneven; calcination at 500℃, due to the PVP and acetic acid and other organic ingredients gradually decompose with increasing temperature, fibers becomes thinner; when calcined to 700℃, the fiber diameter get further thinner into a diameter around 250nm, the fiber surface becomes rough and then emerge a local minor fragmentations phenomenon, which is mainly due to LaMnO3 fibers shrinkage when LaMnO3 fibers form; at 900 ℃, there was a significant fragmentations phenomenon, the fiber surface is more rough, but the thickness of diameter did not change significantly.

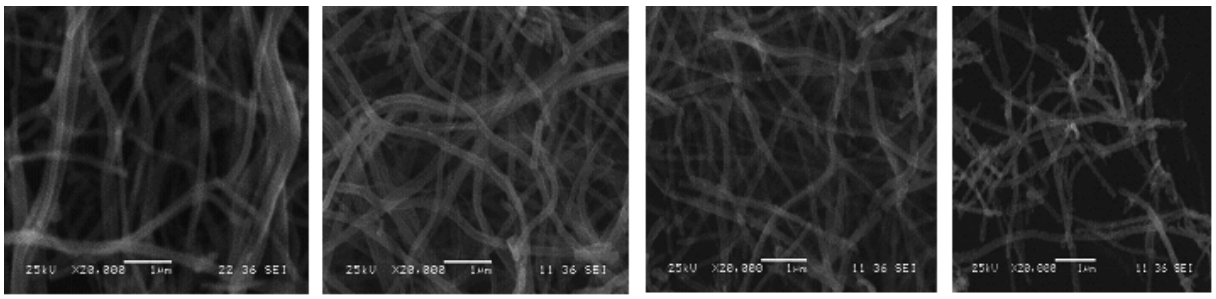

Fig.1 SEM images of various fiber samples.

(a) calcined at 300℃;(b) calcined at 500℃; (c) calcined at 700℃; (d) calcined at 900℃

3.1.2 TEM Analysis

Fig.2 shows TEM and ED images of the finer fiber samples calcined at 900℃. From the figure it can be observed that there is a diameter of about 50nm, the surface of the fiber is extremely rough, ED electron diffraction results show that the sample at 900℃ chain-like structure has been formed of single-crystalline grain, the grain size of about 20nm.

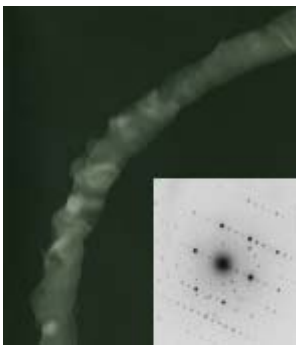

Fig.2 TEM images with corresponding ED of the fibers calcinated at 900℃.

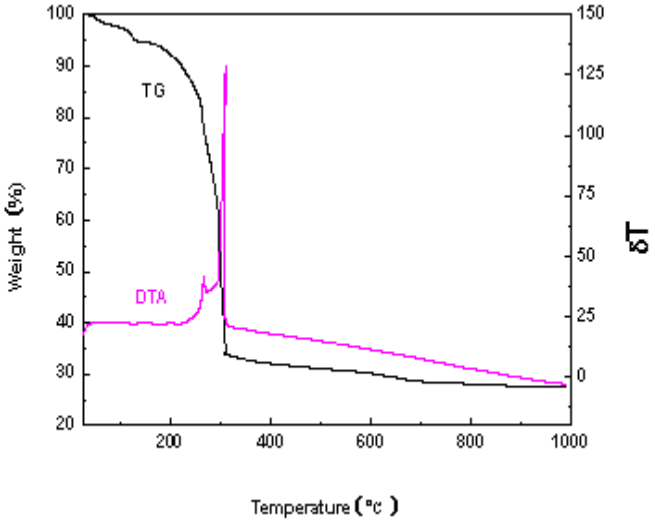

Fig.3 TG-DTA curves of hybrid fibers of PVP/ $LaMnO_3$

3.2 Thermoanalysis of PVP/ LaMnO3 Composite Fibers

Fig.3 shows TG-DTA curves of hybrid fibers of electrospinning PVP/LaMnO3 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;[7] from 295 ℃ to 312 ℃ weightlessness is about 27%, there is a strong exothermic peak at 309℃, mainly acetate and PVP decomposition, combustion caused;[8,9] from 312 ℃ to 730 ℃ weightlessness is about 5%, mainly is about decomposition of lanthanum acetate and the structural formation of LaMnO3.

3.3 Structure Analysis of Fiber

Fig.4 shows about XRD patterns of electrospinning PVP / LaMnO3 composite fibers at different calcination temperature. These pattern shows that there is no appearance characteristic peaks of La2O3 and LaMnO3 calcined at 300 ℃. At 500 ℃ a hexagonal structure characteristic peak of La2O3 appear, and when calcined to 700 ℃, relatively clear and complete cubic perovskite structure LaMnO3 characteristic peaks appeared, but the presence of undesired peak of La2O3. When the calcination temperature reaches 900℃, La2O3 yet fully transformed into a cubic structure of LaMnO3 and the analysis may be due to the La slight excess of the ratio of the precursor solution.

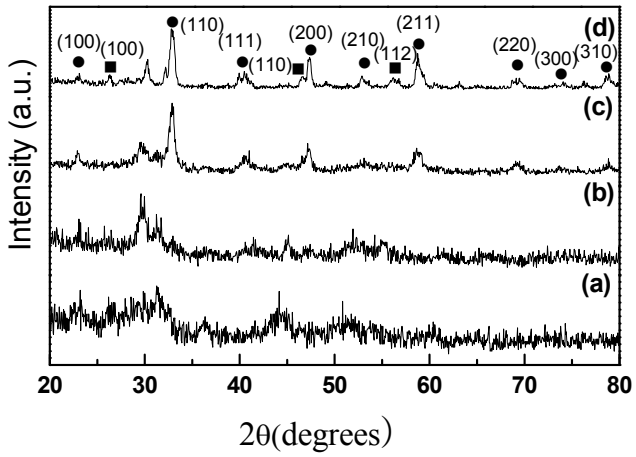

Fig.4 XRD patterns of the fibers.(a) calcinated at 300℃; (b) calcinated at 500℃; (c) calcinated at 700℃;(d) calcinated at 900℃.(●$LaMnO_3$;■La_2O_3)

4. Conclusion

Perovskite-type cube structure LaMnO3 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. This research will contribute to the development of catalytic and electrolyte materials.

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