



Electrospinning Preparation of LaFeO_3 Nanofibers

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This work was financially supported by the Science and Technology Development Planning Project of Jilin Province (Grant Nos. 20040125, 20060504, 20070402), Key Research Project of Science and Technology of Ministry of Education of China (Grant No. 207026), the Science and Technology Planning Project of Changchun City (Grant No. 2007045), the Scientific Research Planning Project of the Education Department of Jilin Province (Under grant Nos. 200224, 2005109, 2007-45) and the Scientific Research Project of Environment Protection Bureau of Jilin Province (No. 2006-24)

Abstract

Polyvinyl alcohol (PVA)/ $[\text{La}(\text{NO}_3)_3 + \text{Fe}(\text{NO}_3)_3]$ composite nanofibers were fabricated by electrospinning, and polycrystalline LaFeO_3 nanofibers were prepared by calcination of the PVA/ $[\text{La}(\text{NO}_3)_3 + \text{Fe}(\text{NO}_3)_3]$ composite nanofibers at 600°C for 10h. The samples were characterized by using X-ray diffraction spectrometry (XRD), scanning electron microscopy (SEM), thermogravimetric-differential thermal analysis (TG-DTA), and Fourier transform infrared spectrometry (FTIR). The results show that PVA/ $[\text{La}(\text{NO}_3)_3 + \text{Fe}(\text{NO}_3)_3]$ composite nanofibers are amorphous in structure, and pure phase LaFeO_3 nanofibers are orthorhombic with space group Pn^*a . The surface of as-prepared composite nanofibers is smooth, and the diameter is ca. 180nm. The diameter of LaFeO_3 nanofibers is smaller than that of the relevant composite fibers. The surface of the LaFeO_3 nanofibers becomes coarse with the increase of calcination temperatures. The diameter of LaFeO_3 nanofibers is about 80nm, and the length is greater than $100\mu\text{m}$. The mass of the sample remains constant when the temperature is above 500°C , and the total mass loss percentage is 90%. Possible formation mechanism of LaFeO_3 nanofibers is preliminarily advanced.

Keywords: La, Fe, LaFeO_3 , Nanofibers, Electrospinning

1. Introduction

The science and technology of nanostructured materials is advancing at a rapid pace (Yang, 2009, Gao, 2009, Mohapatra, 2008 & Zhang, 2007). Over the past decade, the preparation and functionalization of one-dimensional nanostructured materials has become one of the most highly energized research fields (Hu, 2008 & Kar, 2006). One-dimensional nanostructured materials, such as nanowires, nanorods, nanowhiskers and nanofibers, have stimulated great interest due to their importance in basic scientific research and potential technological applications (Huynh, 2002 & Duan, 2003). They are expected to play an important role as both interconnects and functional components in the fabrication of nanoscale electronic and optoelectronic devices. In order to obtain these materials, various preparation methods have been developed including arc discharge, laser ablation, template, precursor thermal decomposition, and other methods (Iijima, 1991, Morales, 1998, Shi, 2001 & Pan, 2001). Electrospinning technique is widely applied to prepare polymers nanofibers (Li, 2004, 1151-1170). Recently, some inorganic compounds nanofibers have been prepared by electrospinning technique using electrospun fibers of polymer/inorganic composite as the precursor (Li, 2004, Zhang, 2008 & Shao, 2004). This processing involved the following three steps: (1) Preparation of a sol with suitable inorganic precursor and proper polymer, and achieving the right rheology for electrospinning process; (2) Electrospinning of the sol to obtain fibers of polymer/inorganic precursors composite; (3) Calcinations of the composite fibers to obtain final oxide fibers. It is important; however, to control all of the above three steps in order to obtain high quality fibers with the desired final properties. LaFeO_3 has attracted much interest recently due to their specific electrical, and catalytic properties (Dong, 1994 & Yang, 2003). A few methods on the preparation of LaFeO_3

nanocrystalline materials were reported (Wang, 2006, Yang, 2005, Wang, 2006, Qi, 2003 & Yang, 2006). In this paper, LaFeO_3 nanofibers were fabricated by calcination of the electrospun fibers of $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite, and some new results were obtained.

2. Experimental

2.1 Chemicals

Polyvinyl alcohol(PVA)($M_r=80000$) was bought from the Third Chemical Reagents Factory of Tianjin, and iron nitrate enneahydrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ were purchased from Tianjin Kermel Chemical Reagents Development Center. Lanthanum nitrate hexahydrate $[\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ was obtained from Tianjin Guangfu Institute of Fine Chemicals. All chemicals were analytically pure and directly used as received without further purification. Distilled water was used as solvent.

2.2 Preparation of $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite sol

$\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite solution was prepared by dissolving an amount of PVA powders, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water, and stirring for 5h, then remaining motionlessly for 2h. Thus, a viscous sol of $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite containing 9%(wt%) PVA, 3% (wt%) metallic salts, 88%(wt%) H_2O , and the molar ratio 1:1 of La^{3+} to Fe^{3+} was obtained for electrospinning processing.

2.3 Fabrication of $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers and LaFeO_3 nanofibers

The setup used for electrospinning was indicated in Figure 1. The above composite sol of PVA, $\text{La}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$ and H_2O mixture was contained in a plastic syringe with a stainless steel needle on its top, and the diameter of the needle was 1mm. A copper wire connected to a DC high-voltage power supply was placed in the sol, and the sol was kept in the syringe by adjusting the angle between syringe and horizon, and the angle was kept at 15° . A grounded aluminum foil served as counter electrode and collector plate. The distance between the needle tip and the collector was fixed to 15cm. Electrospinning experiments were performed when ambient temperature was greater than 18°C and relative air humidity was 50%-60%. A voltage of 20kV was applied to the composite sol and a sprayed dense web of fibers was collected on the aluminum foil. The collected fibers were $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers. The prepared composite nanofibers were dried initially at 70°C for 12h under vacuum, and then calcined at a heating rate of $2^\circ\text{C}/\text{min}$ and remained for 10h at 300°C , 600°C and 900°C , respectively. Thus, LaFeO_3 nanofibers were obtained when calcination temperature was 600°C .

2.4 Characterization methods

XRD analysis was performed with a Y-2000 X-ray diffractometer made by Dandong Aolong Radiative Instrument Co. Ltd using Cu K α radiation and Ni filter, the working current and voltage were 20mA and 40kV, respectively. Scans were made from 20° to 100° at the speed of $3^\circ/\text{min}$, and step was 0.02° . The morphology and size of the fibers were observed with a S-4200 scanning electron microscope made by Japanese Hitachi company. TG-DTA analysis was carried out with a SDT-2960 thermal analyzer made by American TA instrument company at a temperature-rising rate of $10^\circ\text{C}/\text{min}$ under stable air conditions. FTIR spectra of the samples were recorded on BRUKER Vertex 70 Fourier transform infrared spectrophotometer made by Germany Bruker company, and the specimen for the measurement was prepared by mixing the sample with KBr powders and then the mixture was pressed into pellets, the spectrum was acquired in a wave number range from 4000cm^{-1} to 400cm^{-1} with a resolution of 4cm^{-1} .

3. Results and discussion

3.1 XRD results

In order to investigate the lowest crystallizing temperature and the variety of phases, the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite fibers and samples obtained by calcining the composite fibers at different temperatures for 10h were characterized by XRD, as indicated in Figure 2. The results showed that the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite fibers were amorphous in structure, only a broad peak was located around 22° , it was the typical peak of the amorphous polymer, indicating that the composite fibers were amorphous in structure. The sample was also amorphous at 300°C . The polycrystalline LaFeO_3 nanofibers with single phase were synthesized when calcination temperature was in the range of 600 - 900°C , the d (spacing between crystallographic plane) values and relative intensities of LaFeO_3 were consistent with those of JCPDS standard card(37-1493), and the crystal structure of the prepared LaFeO_3 was orthorhombic system with space group Pn^*a .

3.2 SEM images

In order to study the morphology and size of the as-synthesized fibers, the prepared fibers were investigated by SEM, as shown in Figure 3. As seen from Figure 3, the morphology and size of the fibers varied strongly with the increase of calcination temperatures. The surface of the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers was very smooth, and the diameter of the composite fibers was about 180nm. The diameter of the fibers was ca. 120nm at 300°C . The surface

morphology of LaFeO_3 nanofibers became coarse with the increase of calcination temperatures. The diameter of the synthesized LaFeO_3 nanofibers was ca. 80nm at 600°C, and their lengths were greater than 100µm. The diameters of LaFeO_3 nanofibers were smaller than those of the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers owing to the decomposition and evaporation of PVA and NO_3^- . Figure 4 was the distribution histograms of the diameters of samples. It was found that the diameters of the samples were in narrow size. The peak values of diameters of the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers and LaFeO_3 nanofibers were 180nm and 80nm, respectively. It was also found from Figure 3 that the fibers were broken at 900°C. Therefore, LaFeO_3 nanofibers with good morphology should be prepared at low calcination temperature.

3.3 TG-DTA analysis

TG and DTA curves of the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite fibers were indicated in Figure 5. It was noted that there were mainly three stages of weight loss. The first weight loss step (6%) was in the range of 40°C to 102°C accompanied by a small endothermic peak near 75.62°C in the DTA curve caused by the loss of the surface absorbed water or the residual water molecules in the composite fibers. The second weight loss step (51.6%) was noticed between 102°C and 253°C accompanied by an exothermic peak near 234.68°C in the DTA curve due to the decomposition of the nitrate and side-chain of PVA. The last weight loss was 32.4% from 253°C to 500°C. In the DTA curve, a big and a small exothermic peak were located at 296.03°C and 409.65°C. These were likely to be the oxidation combustion of the PVA main chain and further decomposition of the nitrate. And above 500°C, the TG and DTA curves were all stable, indicating that water, organic compounds, and nitrate in the composite fibers were completely volatilized and pure LaFeO_3 nanofibers could be obtained above 500°C. The total weight loss rate was 90%. This result tallied with the XRD analysis.

3.3 FTIR spectra analysis

Pure PVA, $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers and LaFeO_3 nanofibers (obtained by calcination of the relevant composite nanofibers at 600°C for 10h) were analyzed by FTIR, as shown in Figure 6. As seen from Figure 6, PVA (Figure 6a) and $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers (Figure 6b) had the identical spectra, but absorption peaks intensity of spectrum for $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers was lower than those of spectrum for pure PVA. This resulted from the lower content of PVA in the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers. All absorption peaks were attributed to PVA at 3334 cm^{-1} , 2945 cm^{-1} , 1704 cm^{-1} , 1488 cm^{-1} , 1305 cm^{-1} , 1091 cm^{-1} , 815 cm^{-1} corresponding to the stretching vibrations of hydroxyl group ($\nu_{\text{O-H}}$), C-H bond ($\nu_{\text{C-H}}$), carbonyl group ($\nu_{\text{C=O}}$), C-H bond ($\nu_{\text{C-H}}$), C-C bond ($\nu_{\text{C-C}}$), C-O bond ($\nu_{\text{C-O}}$), and O-H bond ($\nu_{\text{O-H}}$), respectively. It was seen from Figure 6c that all peaks of PVA disappeared, and at low wave number range, a new absorption peak at 567 cm^{-1} appeared. The new absorption peak was ascribed to the vibration of metal-oxygen bond, indicating that LaFeO_3 was formed. The results of FTIR analysis were in good agreement with XRD results.

3.4 Possible formation mechanism of LaFeO_3 nanofibers

Possible formation mechanism of LaFeO_3 nanofibers was indicated in Figure 7. $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and PVA were mixed with distilled water to form sol with certain viscosity. PVA acted as template during the formation processing of LaFeO_3 nanofibers. La^{3+} , Fe^{3+} and NO_3^- were mixed with or absorbed onto PVA molecules to fabricate $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite fibers under electrospinning. During calcination treatment of the composite fibers, solvent water would remove to the surface of the $\text{PVP}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite fibers and eventually evaporated from the composite fibers. With the increasing in calcination temperature, PVA molecular chains were broken, PVA and NO_3^- would oxidize and volatilize gradually, La^{3+} and Fe^{3+} were oxidized into LaFeO_3 crystallites in air, and many crystallites were sintered to form small LaFeO_3 nanoparticles, these small nanoparticles were combined into big particles, and these particles were mutually connected to generate LaFeO_3 nanofibers.

4. Conclusions

4.1 $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite nanofibers were fabricated by electrospinning. Polycrystalline LaFeO_3 nanofibers were synthesized by calcining the relevant composite fibers at 600°C.

4.2 TG-DTA analysis showed that the mass of the $\text{PVA}/[\text{La}(\text{NO}_3)_3+\text{Fe}(\text{NO}_3)_3]$ composite fibers remained constant when the temperature was above 500°C, and the total mass loss percentage was 90%.

4.3 XRD analysis revealed that the composite fibers were amorphous in structure. The crystal structure of LaFeO_3 nanofibers was orthorhombic system with space group Pn^*a .

4.4 SEM images indicated that the surface of the prepared composite fibres was smooth, and the diameter of the composite nanofibers was about 180nm. The diameters of LaFeO_3 nanofibers were smaller than those of the composite nanofibers. The surface of the LaFeO_3 nanofibers became coarse with the increase of calcination temperatures. The diameter of LaFeO_3 nanofibers was ca. 80nm, and their lengths were greater than 100µm.

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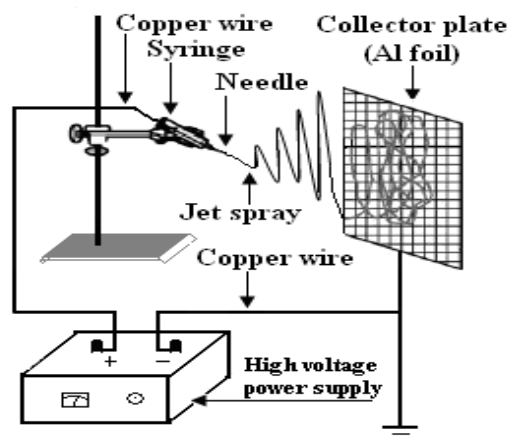


Figure 1. Schematic diagram of electrospinning setup

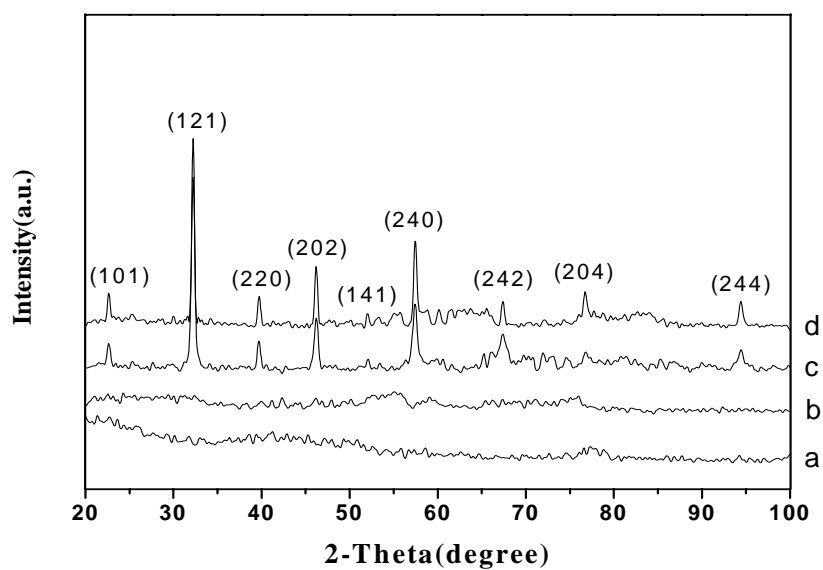
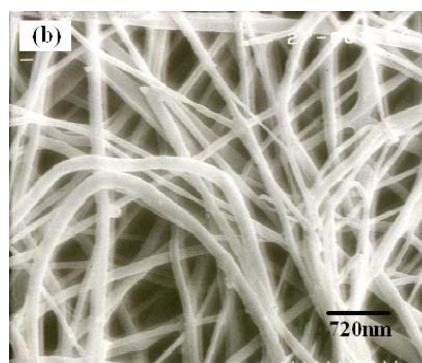
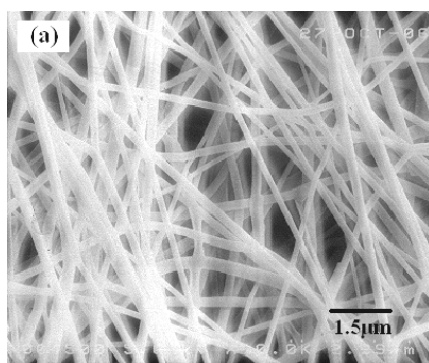


Figure 2. XRD patterns of samples

a. PVA/[La(NO₃)₃+Fe(NO₃)₃] composite fibers b. 300°C c. 600°C d. 900°C



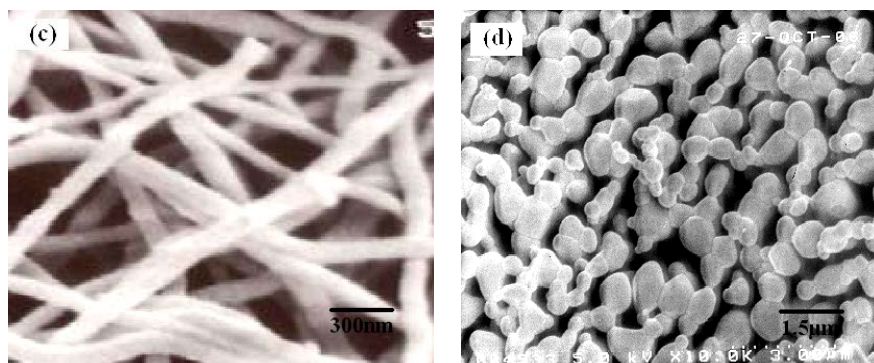


Figure 3. SEM images of the fibers obtained at different temperatures
(a) PVA/[La(NO₃)₃+Fe(NO₃)₃] composite fibers (b) 300°C (c) 600°C (d) 900°C

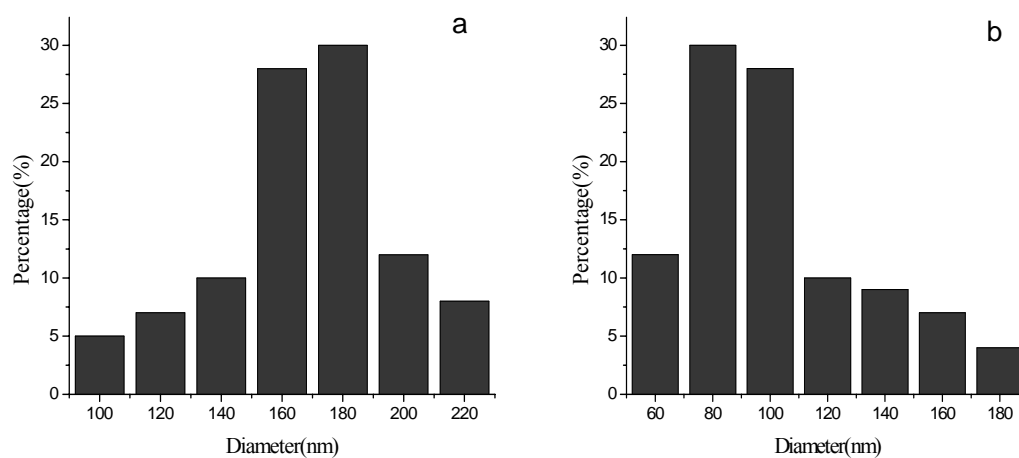


Figure 4. Distribution histograms of the diameters of samples
a. PVA/[La(NO₃)₃+Fe(NO₃)₃] composite fibers b. 600°C

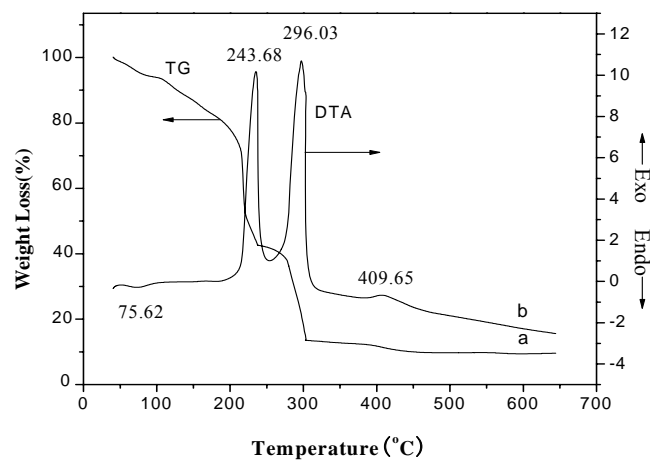


Figure 5. TG-DTA curves of PVA/[La(NO₃)₃+Fe(NO₃)₃] composite fibers

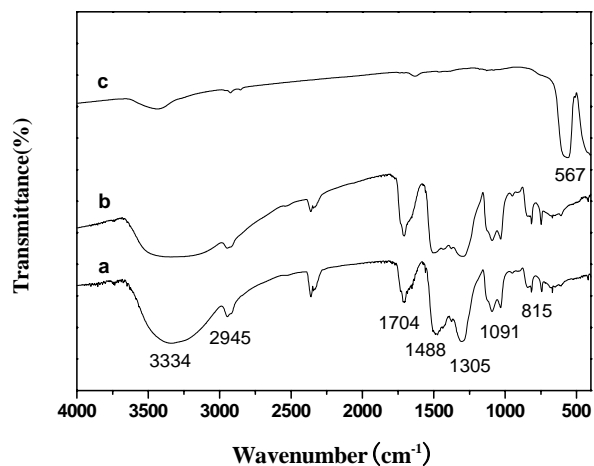
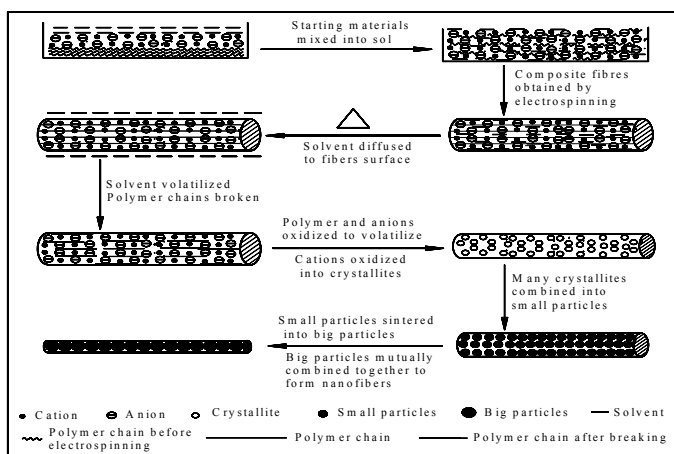


Figure 6. FTIR spectra of the samples

a. Pure PVA b. PVA/[La(NO₃)₃+Fe(NO₃)₃] composite fibers c. LaFeO₃ nanofibers

Figure 7. Illustrative diagram of possible formation mechanism of LaFeO₃ nanofibers