

Preparation and characterization of dense $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ ($x = 0.0 \sim 0.2$) fibers through the sol-gel-related solvothermal process

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Dense $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ (PLT, $x = 0.0 \sim 0.2$) ceramic fibers were prepared by the sol-gel-related solvothermal method using lead acetate trihydrate, lanthanum acetate hydrate and titanium isopropoxide as the starting materials. The as-drawn fibers were pretreated in organic solvents, dimethylbenzene and triethylamine, using the solvothermal process prior to the heat treatment for crystallization so as to dehydrate the fibers *in situ*, remove the organic components and to improve the densification of the precursor fibers. The effects of the solvothermal treatment on the structure and composition of the resultant dense, crack-free transparent PLT ceramic fibers have been investigated. Furthermore, the PLT fibers have been characterized by IR, XRD, SEM, TEM and other techniques.

Introduction

Dense PbTiO_3 -based ceramics with a tetragonal polycrystal phase at room temperature show excellent piezoelectric, dielectric and ferroelectric properties; the incorporation of small amounts of La^{3+} and Ca^{2+} substituting for Pb^{2+} in the PbTiO_3 structure causes the Curie temperature to decrease.^{1,2} With the correct choice of lanthanum content, PLT ceramics can be used for various device applications, including piezoelectric sensors, dielectric and electro-optic devices and actuators.^{3,4} Fiberization of these functional ceramics will expand their utility in micro devices such as sensors, hydrophones, transducers and innovative optical modulators.⁵

Many investigations have focused on ceramic fibers, and some methods, such as the sol-gel process,^{3,5-7} VSSP (viscous solution spinning process),⁸ the template method,⁹ and electrolysis,¹⁰ have been developed for their preparation. In comparison with other techniques, the sol-gel process has some advantages, including its versatility, the homogeneity and purity of the products, and the variations in stoichiometry which can be achieved. Furthermore, it is a low temperature chemical technique for the fabrication of ceramic fibers, in which metal alkoxides are primarily used as the precursors.³ However, the low solid content in conventional gels usually leads to poor densification of the resulting ceramic fibers, although careful heat treatment can remove the organic components which might make the fibers brittle with the loss of their useful properties (dense, mechanically strong ceramic fibers are essential for the realization of compact and modulating arrays).^{3,11} The sol-gel-related solvothermal process has previously been applied to the preparation of fine oxide powders, and is an effective low temperature dehydration or organic-elimination method.¹² Here, this technique is applied to the synthesis of dense ceramic fibers and the gel fibers are solvothermally treated in a suitable system to remove most of the organic components before the calcination. This process is effective in reducing the organic content and dense ceramic fibers are readily obtained.

To the best of our knowledge, there are no reports of the preparation of the dense PLT ceramic fibers, although PbTiO_3 ,^{5,6} BaTiO_3 ,⁷ ZrO_2 ,¹⁰ etc., ceramic fibers have been

prepared. In the present study, a novel process, the sol-gel-related solvothermal method, was developed to synthesise ceramic fibers and dense PLT fibers have been prepared. In this process, the gel precursor fibers were pretreated using the solvothermal process to eliminate the organic components and improve the densification of the precursor fibers, and then heat treated to obtain the PLT ceramic fibers.

Experimental

Preparation

All reagents were of analytical grade and were not purified further.

Triethanolamine (TEA), employed as a chelating agent to suppress Ti alkoxide hydrolysis,⁶ was mixed with titanium isopropoxide in a Ti:TEA molar ratio of 3:1 and the mixture was refluxed for 2 h. After cooling to 50 °C, acetic acid was dropped in to form a transparent solution. A 5 mol% excess of lead acetate trihydrate [$\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$] was added and the reaction mixture refluxed for an additional 4 h to obtain a yellow solution. Then, the solvents and reaction by-products were removed by distillation. The PLT stock solution was made *via* a similar process. The yellow solution was aged at room temperature and its viscosity increased with increasing aging time as the solvents evaporated. Gel fibers were prepared by immersing the end of a glass rod into the sol and then pulling it up. The gel fibers were dried in air for several days to transform them into xerogel fibers. Gel-to-ceramic fiber conversion was conducted in two steps. (i) The xerogel fibers were placed in a 15.0 cm³ stainless steel autoclave with a Teflon liner and then a mixture of dimethylbenzene and triethylamine (volume ratio 1:1) was added until 70% volume of the autoclave was occupied. The solvothermal reaction was conducted at 200 °C for 12 h. After that, the autoclave was cooled to room temperature and the pretreated fibers were isolated by filtration. (ii) The pretreated fibers were then put directly into an air-atmosphere tube furnace for heat treatment at a rate of 1 °C min⁻¹ from room temperature to 700 °C. After sintering at 700 °C for 1 h, the products were cooled to room temperature in the furnace.

Characterization

The phase of the ceramic fibers was ascertained by X-ray diffraction (XRD) analysis using a Rigaku D/Max 2200PC X-ray diffractometer with a graphite monochromator and Cu-K α ($\lambda = 0.15148$ nm) radiation over the range 20–60° at room temperature while the voltage and electric current were held at 28 kV and 20 mA, respectively. A TGA-SDTA 851° METTLER thermal analyzer was used to record the weight loss of the xerogel and solvothermally pretreated fibers (initial weights 5.3879 and 6.6741 mg, respectively) from room temperature to 700 °C with a heating rate of 20 °C min⁻¹ under N₂ flow. The surface morphology and the transverse section of the fibers were investigated by scanning electron microscopy (SEM, Hitachi S-520). A JEM-100 transmission electron microscope (TEM) was applied to observe the crystal particles which compose the fibers. IR spectra were measured by the KBr method from 400–4000 cm⁻¹ using a Nicolet 5DX-FTIR spectrophotometer.

Results

IR

The IR spectra of the fibers at various stages of the process are shown in Fig. 1. The bands around 3400 cm⁻¹, and the shoulder around 1730 cm⁻¹ on the IR spectrum of the xerogel precursor fibers [Fig. 1(a)] are attributed to absorbed water.^{5,6} The peaks at 1550 and 1410 cm⁻¹ are due to asymmetric and symmetric carboxyl vibrations, respectively,^{7,13} while the absorbances at 1335 and 932 cm⁻¹ respectively result from the deformation vibration of CH₃ groups and C–C stretching vibrations.¹⁴ The weak peak around 1100 cm⁻¹ is attributed to the N–C bond of TEA. The bands in the low wavenumber region (400–650 cm⁻¹) are assigned to Ti–O bond vibrations.^{5,6} After solvothermal pretreatment in the mixture of triethylamine and dimethylbenzene, the corresponding IR absorption peaks of the water in the xerogel fibers disappear [Fig. 1(b)]. It is thought that the higher solubility of water in the organic solvents with increasing temperature and pressure results in its removal from the xerogel fibers.¹⁵ The triethylamine may also react with the acetic acid, which is suggested by its corresponding weak IR absorption. This reveals that the water, alkoxy and acetate contents are effectively reduced by the solvothermal reaction. Fig. 1(c) shows the IR spectrum of the heat treated fibers, in which the band around 600 cm⁻¹ is attributed to the characteristic vibration of Ti–O octahedra and indicates the formation of the perovskite phase.^{7,16}

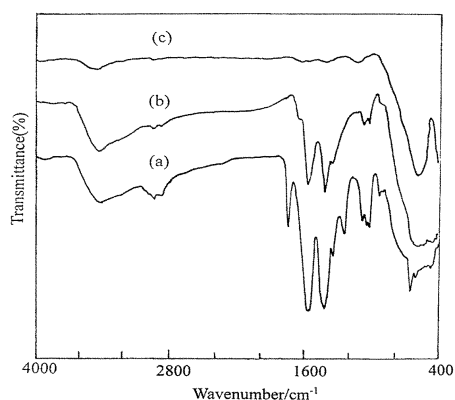


Fig. 1 IR spectra of (a) PLT xerogel fibers, (b) PLT fibers solvothermally treated at 200 °C for 12 h and (c) PLT fibers heat treated at 700 °C for 1 h.

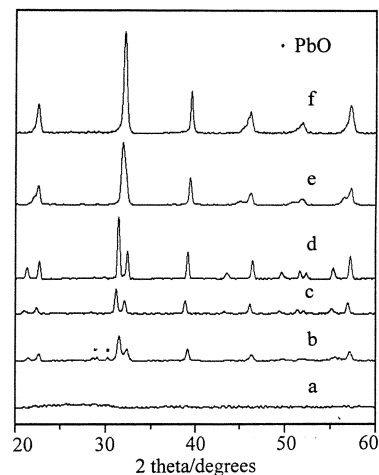


Fig. 2 XRD patterns of (a) solvothermally treated PT fibers, (b) PT fibers heat treated at 500 °C for 1 h, (c) at 600 °C for 1 h, (d) at 700 °C for 1 h, (e) PLT ($x = 0.15$) fibers heated at 700 °C for 1 h and (f) PLT ($x = 0.2$) fibers heated at 700 °C for 1 h.

XRD

The XRD patterns shown in Fig. 2 demonstrate the gel to ceramic fiber conversion. The gel fibers treated by the solvothermal process are amorphous [Fig. 2(a)]. After heat treatment at 500 °C, the fibers begin to crystallize together with a trace amount of PbO [Fig. 2(b)]. When the fibers are heat-treated at 600 °C, the PbO phase disappears [Fig. 2(c)] and only a single perovskite-structured PbTiO₃ phase exists at 700 °C [Fig. 2(d)],⁵ no undesirable pyrochlore phase was observed. The crystallinity of the PbTiO₃ increased with increasing heat temperature. With increasing lanthanum content, the (100) and (001) peaks become weak and tend to merge into a single peak [Fig. 2(e, f)], which reveals that the PT crystal structure changes from tetragonal to pseudocubic.^{2,3,17} This result agrees well with other reports which suggest a phase transformation from tetragonal to pseudocubic perovskite because of the substitution of Pb with La.

TGA

The thermal decomposition curves of the solvothermally pretreated and the xerogel fibers are shown in Fig. 3(a) and (b), respectively. There is hardly any weight loss from room temperature to 290 °C on the TGA curve of the pretreated fibers, which corresponds to the removal of water and acetic acid, while there is about a 20% weight loss in this temperature range on the TGA curve of the xerogel fibers. In the range 290 ~ 450 °C, both of the samples show a weight loss of ca. 10%, which is due to the decomposition of the organic ligands, acetate and triethanolamine. Above 450 °C, there is no significant weight loss, which demonstrates that the gel fiber is transformed into an inorganic one. It is obvious that most of

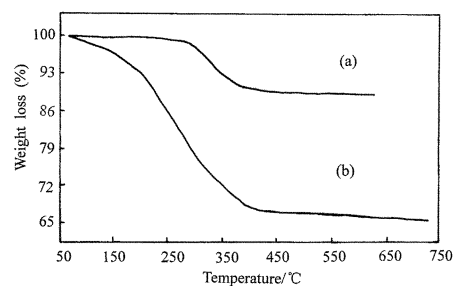


Fig. 3 TGA curve of (a) the solvothermally treated PT gel fibers and (b) the xerogel PT fibers.

the water and acetic acid in the xerogel fibers is removed by the solvothermal treatment.

SEM and TEM

Fig. 4 shows SEM photographs of the fibers at the various stages of the process. The diameter of green fibers is 10–15 μm . After solvothermal treatment, the fibers exhibit a perfect surface with a diameter of 5–10 μm . However, the corresponding ceramic fibers heat treated at 700 $^{\circ}\text{C}$ have a dense surface and round cross section and the diameter of the fibers is less than 5 μm . The TEM analysis reveals that the surfaces of PT ceramic fibers subjected to the solvothermal reaction are composed of homogeneous fine particles with a grain size of less than 100nm. No cracks or voids are observed.

Discussion

The (100) and (001) peaks of PLT fibers are observed when the La content is low [Fig. 2(d, e)]. When the La content is increased to 20 mol%, only the (100) peak is detected, as shown in Fig. 2(f), which is in agreement with the literature.⁴ The La content decreases the tetragonality of the PLT perovskite structure, which indicates that the tetragonal structure of the PLT fibers changes to the cubic structure.^{3,4,17} According to previous studies,^{1,3,5} the organic components, which cause the formation of voids and cracks in the ceramic fibers, affect the densification of the ceramic fibers. It is found that the solvothermal treatment is effective in reducing the content of organic compounds in this process. The TGA curve shows a continuous weight loss for the green PT fibers up to 450 $^{\circ}\text{C}$ [Fig. 3(b)]. The solid content in the xerogel fibers increases from *ca.* 65 to *ca.* 90%, which indicates that the amount of organic residues in these is much smaller than in the non-treated sample. The gel fibers which were not pretreated by the solvothermal reaction show an initial negligible weight loss at

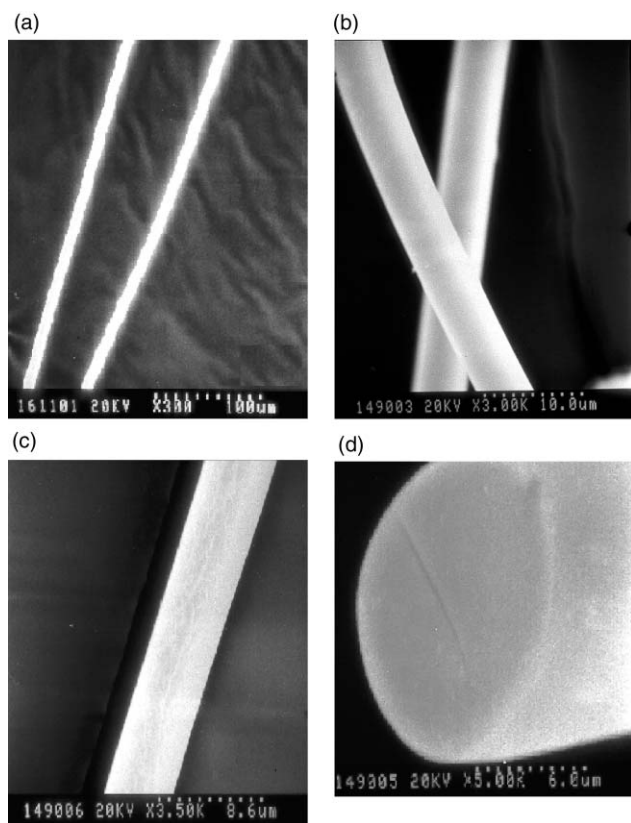


Fig. 4 SEM photographs of (a) the green PT fibers, (b) solvothermally treated PT fibers, (c) solvothermally treated PT ceramic fibers heated at 700 $^{\circ}\text{C}$ for 1 h and (d) solvothermally treated PT fiber cross section.



Fig. 5 SEM photograph of a PT fiber cross section which was not subjected to solvothermal treatment.

around 70 $^{\circ}\text{C}$ resulting from the evaporation of absorbed and chemically attached water and acetic acid. While in the case of the pretreated PT fibers, such a weight loss is not observed and there is hardly any weight loss up to 250 $^{\circ}\text{C}$ [Fig. 3(a)]. This is also clear from the IR absorption spectra, which demonstrate the reduction of the organics by the solvothermal pretreatment (Fig. 1). The lower the organic content, the less gas is produced, which contributes to the formation of dense ceramic fibers. Complete removal of organic components is an absolute requirement for preparing the dense sol-gel-derived fibers. The pretreated ceramic fibers were denser than those that were not subjected to the solvothermal treatment, which have voids in the cross section (Fig. 5). These voids are generated because of the large volume of gas lost as a result of the decomposition of the organic materials during heat treatment. Gas loss initially occurs from the fiber surface, leading to shrinkage of the surface, and subsequently propagates inside, which causes the formation of voids and cracks in the fibers.¹⁴ The removal of the organic residues prior to the gel-to-ceramic fiber transformation is a key factor in achieving dense ceramic fibers.¹⁴ Furthermore, the grain size of the fibers subjected to the solvothermal treatment is dramatically reduced. The grain size of the fibers which were not subjected to the solvothermal reaction is in the range 0.2–1.0 μm (Fig. 6). The large grain size affects the mechanical properties of the fibers.¹⁸ Thus, the fibers pretreated by the solvothermal reaction are more flexible than those which were not. As reported previously,^{14,18} another factor affecting the fiber density is the diameter of the fibers. By minimizing the thickness of the fibers, *i.e.* to less than 15 μm , the strain will be relatively small and micro cracks will not be produced. Thus, it is expected that as the fiber becomes thinner, it becomes more elastic and the removal of the acetic acid is

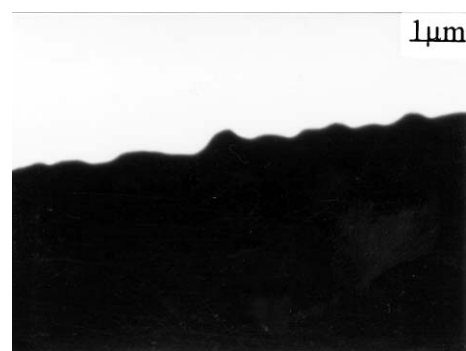


Fig. 6 TEM photograph of the surface of the non-pretreated PT ceramic fibers.

easier. So, after the autoclave pretreatment, the content of unreacted organic matter should be dramatically decreased.

Conclusions

$\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$ ($0 \leq x \leq 0.2$) dense ceramic fibers have been prepared by the sol-gel-related solvothermal method, in which the as-drawn gel fibers were pretreated by the solvothermal reaction using dimethylbenzene and triethylamine as solvents. It was found that the solvothermal treatment affected the structure and composition of the resultant ceramic fibers. After the solvothermal reaction, the content of organic residues in the precursor fibers was significantly reduced, which was revealed in the corresponding IR spectra and TGA measurements, and the surface and cross section of the ceramic fibers were free from cracks and voids. The surface area of the grains composing the fibers were dramatically reduced. The sol-gel-related solvothermal method thus led to the formation of dense, crack-free PLT fibers. The single phase PLT ceramic fibers were 5–10 μm in diameter. The phase transition took place at about 500 °C and a stable single perovskite phase was observed at 600 °C. Addition of the appropriate amount of La changed the PLT crystal structure from tetragonal to pseudocubic.

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