Precursor Linear Self-Assembly Nonhydrolytic Sol-Gel Synthesis of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ Ceramic Fibers

Guo Feng (✉ fengguo@jci.edu.cn)

Jingdezhen Ceramic Institute

Li Yin

Jingdezhen Ceramic Institute

Feng Jiang

Jingdezhen Ceramic Institute

Zhijun Yan

Jingdezhen Oceano Ceramic Co., Ltd

Jinlin Xu

Jingdezhen Oceano Ceramic Co., Ltd

Wentao Fang

Jingdezhen Oceano Ceramic Co., Ltd

Tao Jiang

Jingdezhen Oceano Ceramic Co., Ltd

Qian Wu

Jingdezhen Ceramic Institute

Jianmin Liu

Jingdezhen Ceramic Institute

Weihui Jiang

Jingdezhen Ceramic Institute

Research Article

Keywords: Ceramics, Dielectrics, Ferroelectrics, Fibers, $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$

Posted Date: August 26th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-821667/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

$\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic fibers were synthesized via the precursor linear self-assembly nonhydrolytic sol-gel (NHSG) method, taking TiCl_4 as the titanium source, anhydrous barium acetate and strontium acetate as the barium source and strontium source, anhydrous ethanol and glycol as the oxygen donor and solvent, respectively. The NHSG method promotes the formation of Ba-O-Ti and Sr-O-Ti through heterogeneous condensation. The bimolecular association structure of the reaction intermediate (chlorotitanium ethoxide) between ethanol and titanium tetrachloride facilitates the self-linear assembly of precursors. It also enables linear colloidal particle formation and excellent spinnability of the sol. The novel $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic fibers would promote the flexibility of electronic products.

1. Introduction

Capacitors are important electronic components, accounting for the largest part of the total output of electronic components [1]. The global output value of capacitor components has exceeded billions of US dollars, which has a huge market value. The industrial requirements for capacitor performance are gradually improving with the rapid development of the information technology industry [2].

The capacitor components should realize miniaturization, large capacity and flexibility due to the requirements of miniaturization, multifunctionality and flexibility of electronic products [3]. $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic fibers have great application prospects in the field of high-power capacitor materials and embedded packaging because of their high dielectric constant, high flexibility and high energy storage density [4–5]. In this work, the novel precursor linear self-assembly nonhydrolytic sol-gel method was utilized to synthesize novel $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic fibers.

2. Materials And Methods

2.1. Samples preparation

TiCl_4 (AR, Shanghai), $\text{Ba}(\text{OOCCH}_3)_2$ (AR, Shanghai), $\text{Sr}(\text{OOCCH}_3)_2$ (AR, Shanghai) and $\text{CH}_2\text{OHCH}_2\text{OH}$ (AR, Shanghai) were chosen as original materials. According to the nominal composition of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$, 4.1 mL TiCl_4 was slowly added to 5.5 mL anhydrous EtOH in a conical flask (100 mL) (approximately 10 mL/min) by pipetting in a glove box with stirring for 6 h and the formation of a transparent bright yellow solution. $\text{CH}_2\text{OHCH}_2\text{OH}$ (17 mL) was added to the solution with stirring for 0.5 h. Then, 6.670 g $\text{Ba}(\text{OOCCH}_3)_2$ and 2.403 g $\text{Sr}(\text{OOCCH}_3)_2$ were added to the solution. Then, the mixture was fluxed and stirred at 80°C for 2 h and further aged at 60°C for 48 h to obtain a spinnable sol with a viscosity of approximately 50 Pa·S. Then, the sol is formed by drawing at a speed of 0.5 m/s with a glass rod. After thread throwing, $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ wet gel fibers were obtained and dried at 80°C for 4 h. The xerogel fibers were ultimately calcined at 700 °C for 0.5 h to obtain the final fibers.

2.2 Characterization

The phases of the samples were determined by XRD (X-ray diffractometer, Bruker) using CuK α radiation at 40 kV and 30 mA. The morphology of the sol was confirmed by TEM (transmission electron microscopy, JEOL). The microstructure of the fibers was observed by FE-SEM (field-emission scanning electron microscopy, JEOL). The xerogel thermal decomposition process was tested by DTA-TG (differential thermal analysis and thermogravimetric analysis, NETZSCH). Bonds of samples were tested by FT-IR (Fourier transform infrared spectroscopy, Thermo) at 400–4000 cm⁻¹.

3. Results And Discussion

Figure 1(a) presents the DTA-TG curves of xerogel. Figure 1(b) shows the XRD patterns correspondingly. The DTA curve shows an endothermic peak centered at 116°C, corresponding to a 3.35% weight loss from room temperature to 270°C in the TG curve. This is due to further desolvation and polycondensation of the xerogel. The second and third exothermic peaks are located at 351 and 502 °C, respectively, and they are due to gel decomposition and combustion. The forth exothermic peak centers at 592 °C. Combined with no corresponding obvious weight loss and the phase change of samples calcined at 500 and 600 °C, it can be confirmed that the peak at 592 °C is caused by the crystallization of amorphous BaTiO₃. The sample calcined at 700°C shows higher crystallinity. In addition, all diffraction peak peaks slightly shift to the higher angle direction relative to the standard diffraction pattern of barium titanate (JCPDS Card No. 05-0626), and each diffraction peak shows obvious branching peaks, indicating that Sr²⁺ has been doped into the barium titanate lattice.

Figure 2(a) and (b) shows the TEM graphs of sol. As shown in Fig. 2(a), all the sol particles were in a linear colloidal state in needle-like or rod-like shapes. The diameter of the linear sol particles is approximately 0.1–0.25 μ m, and their aspect ratios are greater than 10. The higher magnification image shown in Fig. 2 (b) indicates that the linear sol particles are in the solid rod state. As seen from the FE-SEM graphs of fibers shown in Fig. 2(c) and (d), a typical SEM micrograph of the fibers is shown. The average diameter of Ba_{0.7}Sr_{0.3}TiO₃ ceramic fibers was determined to be approximately 2-2.5 μ m. The aspect ratio is greater than 10. The surface of the fibers is smooth. The cross-section of the fibers is in the solid state.

To confirm the synthesis mechanism of Ba_{0.7}Sr_{0.3}TiO₃ fibers, especially the formation mechanism of linear sol particles, Fig. 3 (a) shows the FT-IR spectra of samples prepared in different stages of the sol-gel process. In the comparison of samples (I) EtOH and (II) EtOH + TiCl₄, all ν (C-O)H bonds disappeared in sample (II) EtOH + TiCl₄[6]. Instead, Ti-Cl and Ti(O-C) bonds appear[7]. These results certificate the reaction between EtOH and TiCl₄ shown in Eq. (1)[6]. The reaction intermediate chlorotitanium ethoxide (TiCl₂(OEt)₂) prefers to be in the bimolecular association structure shown in the left part of Fig. 3(b) to meet the hexa-coordination requirement of Ti. Meanwhile, due to the reaction activity differences between Cl and EtO groups, CH₃COO tends to react with EtO groups for deacetylation reactions. Therefore, chlorotitanium ethoxide, Ba(OOCCH₃)₂ and Sr(OOCCH₃)₂ finally assemble into linear colloidal particles, as shown in Fig. 2 (a) and (b). The precursor linear assembly mechanism is shown in Fig. 3 (b).

4. Conclusion

A novel linear self-assembly nonhydrolytic sol-gel method is developed for novel $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic fiber preparation. $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ fibers are approximately 2-2.5 μm in average diameter, more than 10 in aspect ratio, smooth surface and solid cross-section structures. The bimolecular association structure of chlorotitanium ethoxide, which is the reaction intermediate between ethanol and titanium tetrachloride, promotes the self-linear assembly of precursors. The precursor linear self-assembly nonhydrolytic sol-gel method is a novel promising method for ceramic fiber preparation.

Declarations

Competing interests

The authors declare no competing interests.

Data availability

Data will be made available on reasonable request.

Acknowledgments

This work was supported by the National Natural Science Foundation of China [grant numbers 52072162, 51962014]; Jiangxi Provincial Natural Science Foundation [grant numbers 20202ACBL214006, 20202ACBL214008, 20192BBEL50022, 2020ZDI03004, 20202BABL214013]; Open fund project of the Key Laboratory of Inorganic Coating Materials, Chinese Academy of Science (ICM-202001); the Projects of Jiangxi Provincial Department of Science and Technology (20202BABL214013); and the Science Foundation of Jiangxi Provincial Department of Education (GJJ201324, GJJ201345).

References

1. Fedorovskaya, E. O. *et al.* Supercapacitor performance of vertically aligned multiwall carbon nanotubes produced by aerosol-assisted CCVD method. *Electrochim. Acta*, **139**, 165–172 (2014).
2. Asrar, A., Ghuzanfar, S. & Sooman, L. Screen-printed activated carbon/silver nanocomposite electrode material for a high performance supercapacitor. *Mater. Lett*, **273**, 1–4 (2020).
3. Yuan, H. *et al.* A stretchable, asymmetric, coaxial fiber-shaped supercapacitor for wearable electronics. *Nano Res*, **13**, 1686–1692 (2020).
4. Kim, J. K., Kim, S. S. & Kim, W. J. Improved ferroelectric properties of Cr-doped $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films prepared by wet chemical deposition. *Mater. Lett*, **60**, 2322–2325 (2006).

5. Guo, H. L., Gao, W. & Yoo, J. The effect of sintering on the properties of Ba_{0.7}Sr_{0.3}TiO₃ ferroelectric films produced by electrophoretic deposition. *Mater. Lett*, **58**, 1387–1391 (2004).
6. Zhu, Y., Zhang, L., Gao, C. & Cao, L. The synthesis of nanosized TiO₂ powder using a sol-gel method with TiCl₄ as a precursor. *J. Mater. Sci*, **35**, 4049–4054 (2000).
7. Albury, A. M. M. & Jennings, M. P. TiCl₄ mediated preparation of (E)-non-conjugated homoallylic alcohols with α -substituted allylsilanes. *Tetrahedron Lett*, **54**, 4487–4490 (2013).

Figures

Figure 1

DTA-TG curves of the xerogel (a) and XRD pattern of samples prepared at different temperatures (b)

Figure 2

TEM graphs of sol (a)(b) and FE-SEM graphs of fibers (c)(d)

Figure 3

FT-IR spectra of samples (a) and linear assembly mechanism of precursors (b)