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Synthesis and characterization of $Ba_{1-x}Sr_xTiO_3$ nanopowders by citric acid gel method

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Abstract

Stoichiometric and monophasic $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) nanopowders were successfully prepared by the citric acid gel method using barium nitrate, strontium nitrate and tetra-*n*-butyl titanate as Ba, Sr, Ti sources and citric acid as complexing reagent. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), infrared (IR) spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the thermal decomposition behavior, the crystallization process and the particle size and morphology of the calcined powders. The results indicated that single-phase and well-crystallized $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) nanopowders with particle size around 80 nm could be obtained after calcining the dried gel at 950 °C for 2 h.

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Keywords: $Ba_{1-x}Sr_xTiO_3$; Sol–gel synthesis; Nanopowders

1. Introduction

$Ba_{1-x}Sr_xTiO_3$ (BST) ceramics, one of the most interesting materials due to its pyroelectric, ferroelectric and piezoelectric characteristics, has been widely used in the preparation of high dielectric capacitors, PTC resistors, transducers and ferroelectric memories [1–4]. BST powders are usually prepared by solid-state reaction [5,6] with calcination temperatures in the range of 1300–1450 °C. Other preparation routes, including the hydrothermal method [7], the precipitation method [8], the metalorganic solution deposition (MOSD) technique [9] and the sol–gel method [10,11], have been reported. It is widely recognized that chemical synthesis methods are able to provide high chemical purity, precise composition, uniform microstructure and a lower formation temperature of the perovskite phase based on molecular scale mixing in the preparation of the precursor [12]. The sol–gel route is proved to be a very commonly applied chemical method for fabricating uniform large area thin films and synthesizing powders of micrometer, sub-micrometer, or nanometer size with high purity and homogeneity [13]. However, the sol–gel process based on hydrolysis of metal alkoxides needs long refluxing time. Furthermore, the expensive and unstable metal alkoxides or mixtures of metal salts and metal alkoxides must be dissolved in large quantities of organic solvents, implying a high cost. As an alternative to methods reported previously, Liu and coworkers [14] synthesized BST powder using a citrate gel method firstly. The process has the advantages of simplicity and no use of any contaminative and expensive reagents. Furthermore, the morphology of the particles could be easily controlled by changing the synthesis parameters.

In this paper, we focus on a novel sol–gel synthesis method of BST nanopowders involving a new stable aqueous precursor based on a metal–citrate complex system reported recently. Our method herein offers an easy route to shorten the procedures, save energy, easily control the final stoichiometry of BST composition and lead to uniform, fine powders.

2. Experimental details

$Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) powders were synthesized by a complex precursor route as summarized in Fig. 1. Citric acid (99.5+%), tetra-*n*-butyl titanate, $Ti(n\text{-}OC_4H_9)_4$ (98+%), H_2O_2

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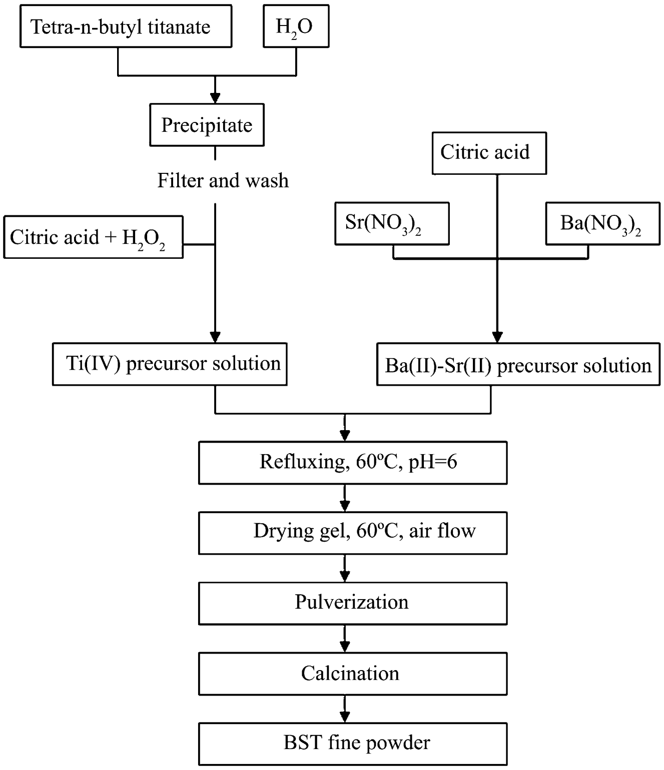

Fig. 1. Flowchart for the preparation of BST powders.

(30 wt.% in H_2O), $Ba(NO_3)_2$ (99.5+%), $Sr(NO_3)_2$ (99.5+%) and ammonia solution (25–28 wt.% in H_2O) were employed as the starting ingredients.

$Ti(n\text{-}OC_4H_9)_4$ was added to stirred deionized water, the precipitation and turbidity were observed gradually, then the precipitate was filtered and washed for several times with deionized water. Citric acid and H_2O_2, both in a 2:1 molar ratio against $Ti(n\text{-}OC_4H_9)_4$, were added. With the addition of these ingredients, the solution became orange in color and viscous. The pH value of the solution was adjusted to 6 using ammonia solution. A water-soluble crimson precursor for Ti(IV) was prepared with continuous stirring and refluxing at 60 °C. After stoichiometric amounts of $Ba(NO_3)_2$ and $Sr(NO_3)_2$ were dissolved in citric acid solution (5 M) of pH 6 adjusted by ammonia solution with molar ratio of CA:M=2:1 (CA, citric acid, M, Ba, Sr), Ba(II) and Sr(II) precursors were mixed with Ti(IV) precursor. During the process, the cations molar ratio of Ba:Sr:Ti was 0.7:0.3:1. The whole mixture was refluxed at 60 °C for 1–2 h with continuous stirring and then a porous yellow resin was formed after drying in a furnace at 60 °C overnight under flowing air. This solid resin precursor was pulverized and then calcined at various temperatures for 2 h to obtain the BST powders.

The FT-IR spectrum was recorded with an EQUINOX55 (BRUKER) spectrometer by using KBr pellet. The XRD patterns of the powders were recorded on a Model χ'Pert PRO of PANalytical B.V. diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) in the range from 10° to 80° (2θ) to examine the crystallization and structural development of BST powders. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TG/DSC apparatus (Model NETZSCH STA 409 PC) with a heating rate of 10 °C/min under flowing dry air. The particle size and morphology of the samples were determined with a scanning electron microscope (SEM, Model FEI Sirion 200).

3. Results and discussion

The synthesis method is an easy way of obtaining an aqueous water-soluble precursor without large quantities of organic solvents used in the synthesis process. In general, the process consists of three major steps [15]: (1) the metal cations react with carboxylate ligands to form metal carboxylate complexes; (2) the formation of metal carboxylate gel by cross-linking metal carboxylate complexes into a three-dimensional structure; (3) the decomposition of the precursor gel at moderate temperature. Note that the compositional homogeneity of the final BST powders is no longer ensured at molecular level mixing once insoluble precipitates have formed during the precursors preparation. Therefore, a key to success in the preparation is to find out an experimental condition, wherein the formation of insoluble precipitates does not occur throughout sol and gel preparation, so that powders with high chemical purity and precise composition can be synthesized. The flowchart presented in Fig. 1 is based on the synthesis of Ba(II) precursor and Sr(II) precursor reported by Liu and co-workers [14], however, the preparation of Ti(IV) precursor is modified: an easy way to synthesize clear Ti(IV) precursor by the addition of H_2O_2 and ammonia, which can effectively avoid the separation of an oil-like two-layer liquid to get Ti(IV)–citrate complex in the works of Xu et al. [16] and Shen et al. [17]. Moreover, the formation of a porous drying gel at lower temperature in furnace does not need higher temperature (120 °C in vacuum [17]), which is significant in potential industrial application. During the synthesis process, when the molar ratio of citric acid to the Ba^{2+}, Sr^{2+} metal cations was less than 1.5, white precipitates were observed in the sol due to relatively low solubility of barium nitrate and strontium nitrate without insufficient complexation with citric acid. Furthermore, the pH value of the precursor solution is also important to obtain a clear gel without precipitation. Considering the stability constants for BaH_2Cit^+ ($\log_{10}K_{(BaH2Cit^+)}/(\mathrm{mol^{-1}\,dm^3}) = 0.6$) and $BaCit^-$ ($\log_{10}K_{(BaCit^-)}/(\mathrm{mol^{-1}\,dm^3}) = 2.95$) [14], it was appropriate that the optimum pH value range was 6.0–7.0.

Fig. 2 shows the TGA and DSC curves of the $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) precursor. The TG curve shows a drastic weight loss at 162–219 °C, followed by two small weight loss at 219–305 °C and 305–462 °C; there is a big weight loss in the temperature range 462–491 °C and no further weight loss beyond 619 °C. The endothermic peak at 187.4 °C is due to the evaporation of volatile components, corresponding to a weight loss of 27.6%. Two successive faint exothermic peaks at 252.9 and 292.2 °C are caused by the burnout of organic species, corresponding to a total weight loss of 16.2%. Most of organic components are removed below 488 °C. Exothermic peaks at 479.1 °C, accompanied by a weight loss of 15.7%, might be due to the thermal decomposition of citrate complex [16].

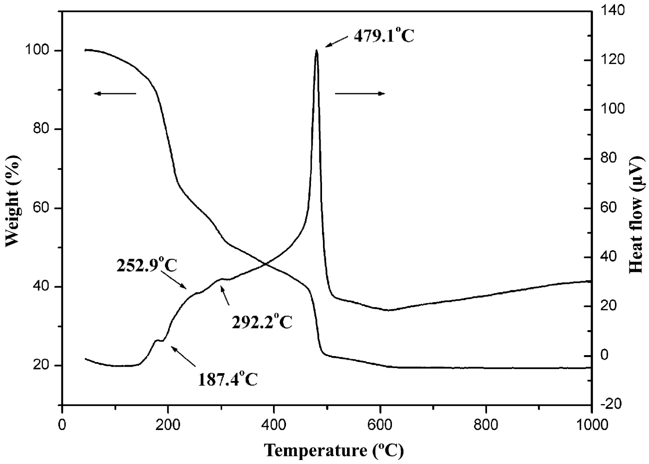

Fig. 2. Combined TG-DSC curves of uncalcined BST precursor with $x = 0.3$.

Fig. 3 shows the FT-IR spectra of the $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) precursor. For the precursor with CA/M = 1.0 and pH 6.0, two bands, possibly the asymmetric and symmetric stretching vibrations of carboxylate [18], are observed at 1581 and 1398 cm^{-1}. For the precursor with CA/M = 2.0 and pH 6.0, there are two strong absorption peaks at 1574 and 1400 cm^{-1}, corresponding to the asymmetric stretching mode and the symmetric stretching mode of COO^- for a bridging complex, respectively [19]. The band at 1078 cm^{-1} is observed, which is attributed to the organic network or the COH groups [20]. The broad absorption band around 3400 cm^{-1} is due to the O–H stretching modes for the intermolecular hydrogen bond or molecular water. The FT-IR spectrum of $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) precursor with CA/M = 1.5 and pH 6.0 is similar to that of the precursor with CA/M = 2.0 and pH 6.0. The characteristic intensity increased for the metal carboxylate complexes (Fig. 3c) can be ascribed to the enhanced interaction between metal cations and carboxylate ligands. Fig. 4 is the FT-IR spectra of $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) gel powders heat-treated at various temperatures, showing the evolution of the materials with the increase in calcinations temperature. For the spectrum of gel powders, the strong and sharp absorption bands at 1399 and 1572 cm^{-1} may be ascribed to the $\nu_{sym}(COO^-)$ and $\nu_{asym}(COO^-)$ of acetyl groups, respectively. Broadened absorption band at 3440 cm^{-1} associates with O–H stretch of intermolecular hydrogen bonds or molecular water. The HOH bending mode characteristic of water appears at 1630 cm^{-1}. After firing more than 800 °C, the band intensity of the carbonate group at 1443 cm^{-1} was reduced significantly, but a large broad band appeared at 555 cm^{-1}. Music et al. [21] have assigned that this band is caused by the metal-oxygen stretching vibration of Ti–O bond. It revealed that the formation of a large amount of BST.

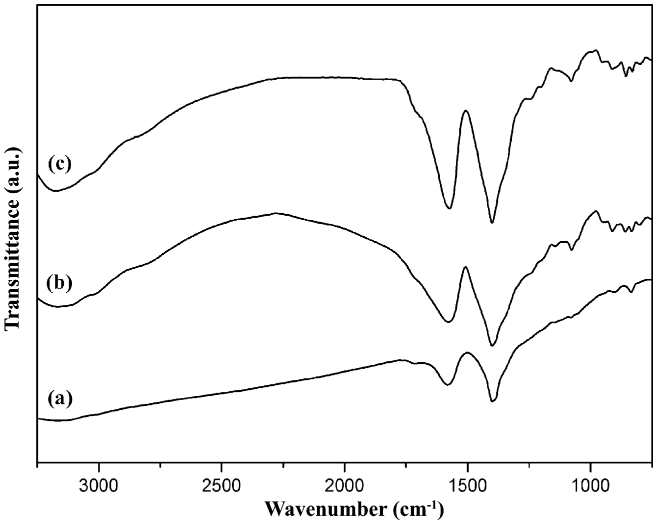

Fig. 3. FT-IR spectra of (a) CA/M = 1; (b) CA/M = 1.5; (c) CA/M = 2.0 in the condition of pH 6.0.

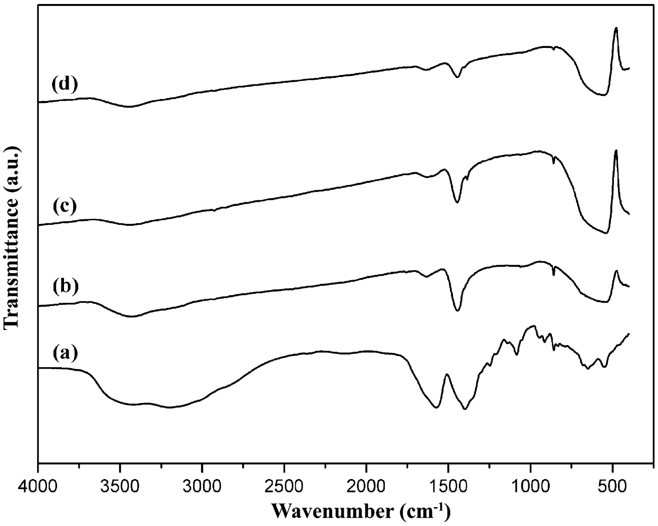

Fig. 4. FT-IR spectra of the gel (a) and the powders calcined at (b) 600 °C; (c) 800 °C and (d) 950 °C.

The phase formation starting from the BST precursor was studied by means of XRD. Fig. 5 shows the XRD patterns of the $Ba_{1-x}Sr_xTiO_3$ precursor with $x = 0.3$ and powders calcined at various temperatures. Fig. 5a shows the precursor to be amorphous. Some small diffraction peaks appeared for the powders calcined at 500 °C, indicating that incipient crystallization starts from around 500 °C. The perovskite-like phase crystallization occurred at 600 °C. However, there was still an impurity phase of barium carbonate (JCPDS 01-0506) with the diffraction peaks at 24.0° and 34.2° (2θ °). The intensity of the diffraction peaks of $BaCO_3$ decreased with the increase in calcination temperature, which agreed with FT-IR results (Fig. 4). At 950 °C, the carbonate impurity phase disappeared and the tetragonal perovskite monophase of $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) was obtained (JCPDS 89-0274). Obviously, this temperature was much lower than for the solid-state reaction method [22]. The crystallite size of the particles calcined at various temperatures could be calculated by the Scherrer's equation: $D = k\lambda/\beta\cos\theta$, where D is the crystallite size, k is a constant (0.9, spheres), λ is the wavelength of the X-ray radiation, β is the line width obtained after correction for the instrumental broadening and θ is the angle of diffraction. The crystallite size obtained from XRD data (950 °C) is 86 nm.

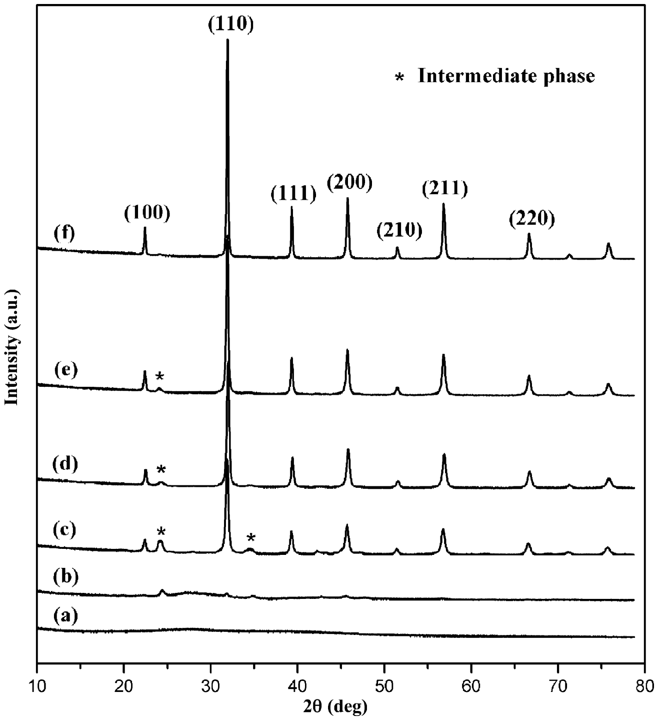

Fig. 5. Powder X-ray diffraction patterns of $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) precursor (a) and powders calcined at (b) 500 °C; (c) 600 °C; (d) 800 °C; (e) 900 °C and (f) 950 °C.

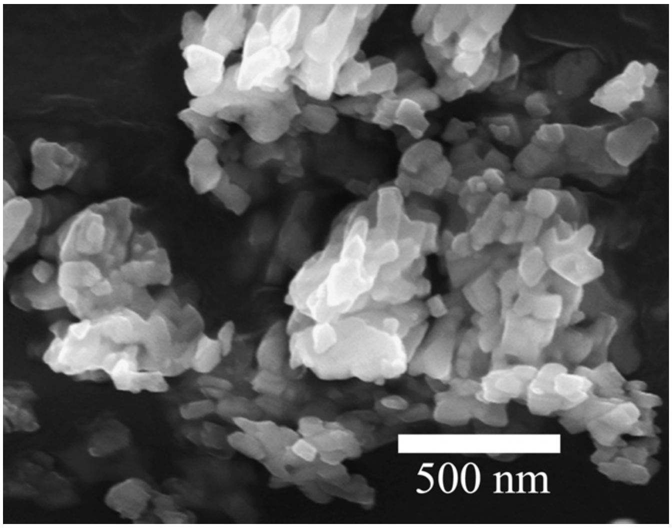

Fig. 6. SEM micrograph of BST powders calcined at 950 °C for 2 h.

From the SEM image (Fig. 6) of the $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) sample calcined at 950 °C, the particle size was estimated to be around 80 nm, a value consistent with the one calculated by the XRD data.

4. Conclusions

A novel synthesis process was designed and stoichiometric and monophasic $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) nanopowders were successfully prepared by the citric acid gel method. The process is an easy way for obtaining an aqueous water-soluble precursor. Single-phase and well-crystallized $Ba_{1-x}Sr_xTiO_3$ ($x = 0.3$) nanopowders could be synthesized at 950 °C with particle size of around 80 nm.

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