Preparation of cauliflower-like shaped Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ powders by modified oxalate co-precipitation method

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The quantitative barium–strontium titanate (Ba$_{1-x}$Sr$_x$TiO$_3$, BST) ferroelectric materials have shown great promise for application as the phase shifting elements in phased array antennas and as tuning elements in devices operating at microwave frequencies [1–3] due to their chemical stability, high permittivity, high tunability and low dielectric losses, etc. In view of their merits, the investigation on BST materials is therefore significantly important [4–7]. Various innovative approaches, like sol–gel [8,9], spray pyrolysis [10,11], combustion synthesis [12], chemical co-precipitation [13,14], hydrothermal method [15], etc. have been used to synthesize BST powders. The chemical co-precipitation method has attracted special interest due to its simple procedure and low reaction temperature, etc. Barium–strontium titanyl oxalate (BSTO) [Ba$_{1-x}$Sr$_x$TiO(C$_2$O$_4$)$_2$·4H$_2$O] is one of the important molecular precursors [16,17] for the production of BST powders with satisfying physical and chemical characteristics. However, the prior methods suffer from the problem that very stringent control of pH is required during the precipitation [18]. In view of this, an attempt is made in the present work to overcome the problem. For this purpose, we developed a simple oxalate-based co-precipitation method for the synthesis of spherical BSTO powders by adding quantitative ammonia into a precursor solution containing stoichiometric quantities of Ba and Sr ions before the co-precipitation procedure. The pyrolysis of BSTO in air produced the homogeneous BST powders. Few studies have been reported on controlling morphology of BST powders. Most of the powders show equiaxed or spherical morphology from either solid-phase synthesis or wet chemical synthesis method. Khollam et al. [19] successfully prepared star-shaped barium–strontium titanate powders through oxalate co-precipitation method by using in-situ C$_2$O$_4$$^{2-}$ ions as a capping agent. In our case, when polyethylene glycol (PEG) was added during the co-precipitation procedure, the BSTO particles grew into spindle shape. All these results related to the synthesis and characterization of pure, single phase BSTO and thereby BST powders are discussed in the present paper.

1. Introduction

Recently, barium–strontium titanate (Ba$_{1-x}$Sr$_x$TiO$_3$, BST) ferroelectric materials have shown great promise for application as the phase shifting elements in phased array antennas and as tuning elements in devices operating at microwave frequencies [1–3] due to their chemical stability, high permittivity, high tunability and low dielectric losses, etc. In view of their merits, the investigation on BST materials is therefore significantly important [4–7]. Various innovative approaches, like sol–gel [8,9], spray pyrolysis [10,11], combustion synthesis [12], chemical co-precipitation [13,14], hydrothermal method [15], etc. have been used to synthesize BST powders. The chemical co-precipitation method has attracted special interest due to its simple procedure and low reaction temperature, etc. Barium–strontium titanyl oxalate (BSTO) [Ba$_{1-x}$Sr$_x$TiO(C$_2$O$_4$)$_2$·4H$_2$O] is one of the important molecular precursors [16,17] for the production of BST powders with satisfying physical and chemical characteristics. However, the prior methods suffer from the problem that very stringent control of pH is required during the precipitation [18]. In view of this, an attempt is made in the present work to overcome the problem. For this purpose, we developed a simple oxalate-based co-precipitation method for the synthesis of spherical BSTO powders by adding quantitative ammonia into a precursor solution containing stoichiometric quantities of Ba and Sr ions before the co-precipitation procedure. The pyrolysis of BSTO in air produced the homogeneous BST powders. Few studies have been reported on controlling morphology of BST powders. Most of the powders show equiaxed or spherical morphology from either solid-phase synthesis or wet chemical synthesis method. Khollam et al. [19] successfully prepared star-shaped barium–strontium titanate powders through oxalate co-precipitation method by using in-situ C$_2$O$_4$$^{2-}$ ions as a capping agent. In our case, when polyethylene glycol (PEG) was added during the co-precipitation procedure, the BSTO particles grew into spindle shape. All these results related to the synthesis and characterization of pure, single phase BSTO and thereby BST powders are discussed in the present paper.

2. Experimental procedure

The starting materials used for the present synthesis of barium–strontium titanyl oxalate [Ba$_{1-x}$Sr$_x$TiO(C$_2$O$_4$)$_2$·4H$_2$O, $x=0.4$] were barium nitrate (>99.0%), strontium nitrate (>99.0%), titanium tetrabutoxide and oxalic acid dihydrate (SD’s fine, 99.5%). The BSTO powders were synthesized by the procedure described in the flowchart as given in Fig. 1. Initially, 102 ml of titanium tetrabutoxide (0.3 M) was dissolved in 500 ml of ethanol. Then 0.6 M of oxalic acid solution was made by dissolving 75.642 g of oxalic acid in 350 ml of ethanol and 350 ml of distilled water. To this solution, titanium tetrabutoxide solution in ethanol was added with continuous stirring when a white precipitate initially obtained is redissolved, resulting in a clear solution of 0.3 M oxalotitanic acid (HTO) [H$_2$TiO(C$_2$O$_4$)$_2$]

$$\text{(CaH}_2\text{O}_4\text{Ti} + 2\text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{TiO(C}_2\text{O}_4)\text{)}_2 \quad \text{(HTO)} + 4\text{C}_4\text{H}_6\text{OH} \quad (1)$$

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Accurately weighed quantities, 47.041 g of Ba(NO₃)₂ and 25.396 g of Sr(NO₃)₂, were dissolved into 1142 ml of distilled water. Then 58 ml of ammonia (25%) and polyethylene glycol were added respectively to the above nitrate solution. The nitrate solution and the above clear HTO solution were added dropwise into ammonia nitrate solution simultaneously and were vigorously stirred. The resulting reaction-mixture was further stirred vigorously at 80 °C for another 2 h and then kept overnight for the reaction to go to its completion

\[ \text{H}_2\text{TiO(C}_2\text{O}_4\text{)}_2 \ (\text{HTO}) + 0.6\text{Ba}^{2+} + 0.45\text{Sr}^{2+} \]

\[ \rightarrow \text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3 \ (\text{BST}) + 2\text{H}^+ \]  

(2)

The precipitate of BSTO powders was filtered, washed and dried in air. The pyrolysis of BSTO at 800 °C/4 h produced the Ba_{0.6}Sr_{0.4}TiO_3 (BST) powders

\[ \text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3 \ (\text{BST}) + \text{O}_2 \]

\[ \rightarrow \text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3 \ (\text{BST}) + 4\text{CO}_2 + 4\text{H}_2\text{O} \]  

(3)

The FTIR technique (PC Shimadzu spectrophotometer, model 8201) was employed to record IR spectra. Powder X-ray diffraction (XRD) measurement was performed on an X-ray diffractometer (BDX3300, China) with a copper anticathode (wavelength Cu Kα/λ = 0.15406 nm) from 10° to 80°. Finally, scanning electron microscopy (SEM) (PHILIPS XL-30 TEP, Netherlands) was used to estimate particle size, morphology and nature of agglomerates in the as-dried BSTO powders as well as calcined BST powders.

3. Results and discussion

According to Schrey [20], the pH value appears to be the key factor on the transformation of titanium species. The titanium exists as TiO\text{C}_2\text{O}_4 form below pH 2.0. In the pH range 2.5–3.5, TiO\text{C}_2\text{O}_4\text{O}_4 accounts for the main existing form of titanium. Above pH 4.0 the titanium precipitates as TiO(OH)₂. However, the transformation of titanium has not been reported systematically. In order to prevent the formation of TiO₂ and obtain single phase BST, the very stringent control of pH of 2.5–3.5 is required during the precipitation. In the present work, the oxalate-based co-precipitation method was improved to make the operation much more controllable.

The improved simple oxalate-based co-precipitation method was designed as described in Fig. 1 by adding appropriate amounts of ammonia in advance to achieve the pH condition as clarified above. The 1200 ml of nitrate solution and 1200 ml of the above clear HTO solution were mixed by adding them dropwise into ammonium nitrate solution. The co-precipitation reaction produced the BSTO powders as described in the chemical Eq. (2). The resulting mixture-solution was always below pH 6 (pH ~ 5.0 when keeping the same flowing velocity of the HTO and the nitrate solution) during the whole mixing procedure. After stirring vigorously at 80 °C for 2 h, the pH gradually declined from ~5.0 to ~3.0 considering the cation-exchange reaction (4) finally resulting in the BSTO powders.

\[ \text{BSTO (with H}^+ \text{ adsorption)} + \text{Ba}^{2+}/\text{Sr}^{2+} \text{ (in solution)} \]

\[ \rightarrow \text{BSTO} + \text{H}^+ \text{ (in solution)} \]  

(4)

To confirm the formation of HTO and single-phase BSTO, a systematic study was undertaken by using FTIR spectroscopy [Fig. 2(a and b)]. Fig. 2(a) shows the IR spectrum of HTO and Fig. 2(b) is the IR spectrum for BSTO obtained by the present route. The broad band around 3550 cm⁻¹ may be assigned to the antisymmetric and symmetric stretching vibration of the OH group. Both curves show the absorption bands at 1640, 1420 and 1280 cm⁻¹ corresponding to the different modes of vibration of the oxalate group [21]. Further, the intensities of three oxalate bands are in decreasing order as reported in the literature [21]. The above observations show that stable clear solution of HTO and single-phase BSTO were successfully synthesized.

Fig. 3 shows the XRD pattern of BST powders obtained by the pyrolysis of BSTO at 800 °C/4 h in air. It can be seen that all the peaks corresponding to only BST are present and the peaks perfectly match with the standard pattern. Also, the XRD pattern shows that all the peaks are perfectly symmetric and no shoulders corresponding to reflections of a BaTiO₃ or SrTiO₃ phase are observed in the

![Fig. 2. Typical IR spectra of (a) HTO and (b) BSTO.](image-url)
pattern. This rules out the possibility of formation of both barium and/or strontium titanyl oxalates separately during the chemical reaction. A close look at a slow scan of (1 1 0) reflection shown as an inset indicates that there is a slight shift of this reflection to higher angles (i.e. from 31.35° to 31.88°) which is due to the incorporation of Sr2+ ions in the BaTiO3 lattice. From Fig. 3, it may be concluded that single phase Ba0.6Sr0.4TiO3 powders were successfully prepared by the present chemical co-precipitation method.

Fig. 4(a) and (b) shows the SEM photographs of BSTO and BST powders, respectively. BSTO particles are of spherical type with sizes in the range of 1–1.5 μm. The particles of BST are spherical in nature with sizes in the range of 0.8–1.2 μm and are agglomerated. Further, it can be seen that the morphology of thus obtained BSTO powders show no notable distinction from those BSTO powders obtained from traditional co-precipitation procedures considering that they are quasi spherical with rather smooth surface. However, the present BST powders from the as-dried BSTO powders exhibit a cauliflower-like morphology with rough surface which is rather 'special'. It seems that every BST particle is the conglomeration of numerous grains. But the hypothesis can be rejected easily only if we take the particle size of BSTO and BST powders into consideration. The special shape of BST comes into being during the calcining process with pyrolysis of BSTO and release of CO2 (Eq. (3)). In order to find out the formation mechanism of the special shape of BST powders, attention should be paid to the formation course of BSTO powders. In traditional co-precipitation procedures, as it is reported, the growth of BSTO grains goes through three steps [14] including (i) formation of germ nuclei, (ii) tiny particles' precipitation on germ nuclei and (iii) nucleus' growth into crystal grains. But as for the present co-precipitation route, the growth of BSTO particles goes through different stages. During
the co-precipitation process at room temperature, point-like particles precipitate on germ nuclei and numerous isolated nuclei are formed. During post-heat treatment in a thermostatic bath at 80 °C with violent stirring, the rate of the cation-exchange reaction (Eq. (4)) between mother liquid and isolated nuclei is greatly promoted and thus brings vast deficiency such as vacancy and interstitial ions on the surface of isolated nuclei. Vast deficiency on the surface increases the chemical potential energy of the isolated nuclei. Agglomeration of isolated nuclei takes place during mutual collision to reduce the surface energy and the agglomerated nuclei are thus formed. When the agglomeration has increased to a certain extent, the surface energy declines rapidly and the reunion of agglomerated nuclei no longer occurs. Then the point particles precipitated on the agglomerated nuclei and multiple deposition layers of particles cover the initial agglomerated nucleus morphology and eventually form the rather smooth shape. After BSTO powders were heat-treated at 800 °C/4 h, the morphology of these agglomerated nuclei was reconstructed by the emission of gases and the rearrangement of particles. Above all, the formation of cauliflower-like morphology may be related to the ionic exchange reaction between H⁺ and Sr²⁺/Ba²⁺. Similar observations have been reported recently by Zhang et al. [22] in the case of the synthesis of ZnO microcrystals wherein growth habit is controlled by its intrinsic structure and external conditions like temperature, pH and capping agent.

Another way was designed to confirm the hypothesis of the crystal-growth mechanism by adding some polyethylene glycol into the precursor solution. When PEG was added during the co-precipitation procedure, the BSTO precursor powders, as well as the BST powders, were not spherical but were spindle-shaped, as shown in Fig. 5(a) and (b). The results further confirmed the hypothesis about the mechanism of crystal growth. The zigzag structure of PEG molecular chain in anhydrous environment changed [23] when dissolved in water. The hydrophilic groups of PEG extended outside the molecular chain to act with H₂O and formed special structure. Then the hydrophilic groups acted with the hydrated shell of isolated germ nuclei and formed spindle-shaped composite nuclei. Then the point particles precipitated on the composite nuclei and multiple deposition layers of particles cover the initial agglomerated nuclei morphology and eventually form the spindle shape shown in Fig. 5(a). The morphology of these agglomerated nuclei was reconstructed by the emission of gases and the rearrangement of particles after BSTO powders were heat-treated, as shown in Fig. 5(b).

The BST powders obtained from the present route are expected to have good sintering activity since they show cauliflower-shaped agglomerates build up from submicron particles and possess a large surface area of 18.32 m²/g. The sintering activity of ceramic powders becomes higher as the surface area increases. In order to obtain a large surface area, often small size nano-powders are required.
But sintering nano-powders will form ceramics with low density. Interestingly, in our case the issue is successfully resolved and this has great significance to enable BST to co-fire with cheaper and better electrical performance electrodes, such as Ag. Our proceeding experiments have confirmed this hypothesis and the related results will be reported in the next papers. Further work to obtain the unagglomerated BST powders by varying the synthesis parameters of BSTO and processing the BST powders in the form of dense compacts to study its ferroelectric and dielectric properties is in progress.

4. Conclusion

Single-phase BSTO powders was obtained by a modified oxalate co-precipitation method. The pyrolysis of BSTO powders in air produced micron-sized BST powders with cauliflower-like morphology. The effect of PEG on morphology of obtained BSTO and BST powders was also studied. Without PEG, the powders showed homogeneous quasi-spherical shape. The powders grew into spindle shape with the effect of PEG.

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References