

MATERIALS AND INTERFACES

Nonhydrolytic Sol–Gel Synthesis of $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ NanopowderXianghua Xie,[†] Yaming Dong,^{*,†,‡} Chaojie Chen,[†] and Lin Lin[†]*East China University of Science and Technology, Shanghai, People's Republic of China 200237, and Shanghai Normal University, Shanghai, People's Republic of China 200234*

A novel process for making nanopowders has been investigated by using the nonhydrolytic sol–gel synthesis (NHS GS) method, with which around 70% organic solvent can be recycled. $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) nanopowders, for example, were synthesized with the parent precursors $\text{Sr}(\text{CH}_3\text{COO})_2$, $\text{Ba}(\text{CH}_3\text{COO})_2$, $\text{Ti}(n\text{-C}_4\text{H}_9\text{O})_4$, and glacial acetic acid. The properties of BST powders were characterized by atomic force microscopy (AFM), transmission electron microscopy (TEM), laser scattering, and an Autosorb surface area analyzer. The mean size of primary BST particles is around 30 nm, and the diameters of 50% BST agglomerates are less than 344 nm. With the NHS GS process the period of synthesis was greatly shortened and cost and pollution were largely minimized as well. Furthermore, the NHS GS method can also be applied to the preparation of $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ and $\text{PbZr}_{0.75}\text{Ti}_{0.25}\text{O}_3$ nanopowders.

Introduction

Sol–gel is a widely used method for synthesizing powders of micrometer, sub-micrometer, and nanometer size with high purity and homogeneity. Many different methods have been conducted to produce fine powders by means of hydrolyzing, changing the temperature, mixing the electrolyte, and increasing the sol concentration. Of these methods, hydrolyzing is the one most frequently used.^{1–3} Conventionally, there are four steps in the sol–gel process: sol preparation–dissolution, gel preparation–hydrolyzing, gel drying, and gel calcining. For drying under ambient condition, it normally takes days or weeks to obtain the xerogel while large quantities of waste organic solvent may pollute the atmosphere. Furthermore, the quality of the final product is affected by several factors, such as precursor, solvent, pH, catalyst, water amount, sol temperature, stirring time, and additive.⁴ All of the above aspects retard the progress of applications of sol–gel methods. Thus, it is necessary and important to improve the conventional sol–gel methods. In recent years, a nonhydrolytic sol–gel synthesis method was developed for making nanoparticles. On the basis of this method, different kinds of nanoparticles were prepared by using the multi-stepped combination of hydrolyzing and nonhydrolyzing processes.^{5–7} In this paper, a nonhydrolytic sol–gel synthesis (NHS GS) method for synthesizing BST nanopowders is introduced, with most of the organic solvent being recycled. The reaction mechanism, particle morphology, and dispersion of the nanopowders are also discussed.

$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) ceramic, one of the most interesting materials due to its pyroelectric, ferroelectric and

piezoelectric characteristics,^{8,9} has been widely used in infrared imaging systems. The composition, temperature, and thermo-/ferroelectric properties have been extensively studied experimentally.¹⁰ At the interface, BST ceramics have shown high electromechanical coupling and low coercive fields. Due to studies of the tremendous applications of this material, a better understanding of the structure at the nanoscale level has become more important. Recently Sharma et al. reported their work on porous BST using the traditional sol–gel method in the presence of water.¹¹ In this work, however, a novel NHS GS preparation method for BST ceramic nanopowders is presented.

Experimental Section

Barium(II) acetate, $\text{Ba}(\text{CH}_3\text{COO})_2$ (AR grade, >99%), strontium(II) acetate, $\text{Sr}(\text{CH}_3\text{COO})_2$ (AR grade, >99%), titanium(IV) *n*-butyloxide, $\text{Ti}(n\text{-OC}_4\text{H}_9)_4$ (CP grade, >98%), and glacial acetic acid (AR grade, >99%) were used as precursors and solvent, respectively. Acetates were dried under vacuum prior to use. Residual water of glacial acetic acid was removed by distillation below 100 °C. A reflux distillation set was employed with a flask connected to an isobaric funnel, a condensation return pipe, and a drying tube. When distillation was being carried out, the stopcock of the isobaric funnel was closed.

The synthesis was carried out in four steps: preparation of sol, gel, condensed gel (or xerogel), and powder. At first, titanium *n*-butyloxide (102.1 g, 0.300 mol) was poured into the isobaric funnel and barium acetate (49.8 g, 0.195 mol) and strontium acetate (21.6 g, 0.105 mol) were added to 280 mL of glacial acetic acid in the flask. The Ba–Sr mixture was stirred at 80 °C until the acetates dissolved completely. $\text{Ti}(n\text{-OBu})_4$ was added to the mixture drop by drop over ~15 min, and a pale yellow Ba–Sr–Ti (molar ratio Ba: Sr: Ti = 0.65:0.35:1) sol formed. Next, Ba–Sr–Ti sol was heated to 118 °C

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and refluxed for ~30 min. After this, the refluxing process was switched to a distillation process. When ~5 mL of solvent was collected, the reaction sol lost its fluidity, yielding Ba–Sr–Ti gel as a homogeneous white starchy substance.

The third gel-drying step could be achieved in two different ways. One way was slow drying,^{1–3,11} in which the gel was kept in air at room temperature for weeks or in an oven at 90 °C for 6–7 days, and the xerogel was obtained. The other way was a fast-drying distillation technique, which can be done in the reflux distillation or in a normal distillation set. After 2.0 h of distillation, the gel was concentrated into a pale yellow condensed gel (236.8 g). Then 200 mL of distillate was collected (bp 90–110 °C). In the final step, the condensed BST gel (or xerogel) was kept in a stove at 400 °C for 0.5 h and crushed into a powder (76.2 g) with a mortar and pestle. Then the crushed powder was subsequently calcined at 930 °C for 2.0 h, yielding BST as a fine white powder (62.5 g, 0.290 mol, η = 96.6%).

The components of the solvent were examined by a gas chromatograph (GC) (GC-9A, Shimadzu). FTIR (Nicolet Magna-IR550) and SDTA/TGA (Mettler-Toledo GmbH) were used to study the components and decomposition of the gel. An X-ray diffractometer (Japan Rigaku D/max-2400), AFM (AJ-III) and TEM (JEOL JEM-200CX), a laser scattering meter (LS230), and an Autosorb surface area analyzer (ASAP2010, N₂) were also applied to study the crystal phase, morphology, agglomerate size distribution, and specific surface area of the BST powder, respectively.

Results and Discussion

Modification of the Sol–Gel Process. Of the four steps introduced above, gel synthesis and gel drying are the two most important steps and gel synthesis is the most important, since the homogeneity and purity of the gel will directly effect the quality of the final powder. In a comparison of NHSGS with the hydrolyzing method, the former benefited the purity, homogeneity of gel, operation routes, and recycling of the solvent.¹² In NHSGS, a reflux distillation method was introduced in the gel formation. As described in the Experimental Section, the first reflux process for 30 min guaranteed the homogeneity of the sol and the following reflux distillation gradually concentrated the sol to induce the polymerization. The absence of the water addition process avoided the precipitation of oxides in the sol.¹¹ IR spectra of the gel synthesized by the reflux distillation method show that the strong absorption peak of water (~3400 cm⁻¹) disappears, in comparison with the literature data for a BST sol in the presence of water.¹⁰ The characteristic peaks of acetates (1568.0, 1433.0 cm⁻¹) and M–O (659.2 cm⁻¹; M = metal)¹³ indicate that metal atoms exist as M–OAc and M–O groups. The glacial acetic acid solvent (1695.8, 1381.9, 1297.9, cm⁻¹) and the acetic acid ester product (2956.5 w, 2913.0 w, 1695.8, 1327.1 cm⁻¹) remained in the gel. IR (cm⁻¹): 3413.0 w, 2956.5 w, 2913.0 w, 2521.7 w, 1947.6 w, 1878.3 w, 1695.8 m, 1568.0 s, 1433.0 s, 1381.9 s, 1327.1 m, 1297.9 m, 1046.1 w, 1020.5 w, 932.9 w, 849.0 w, 786.9 w, 732.2 w, 659.2 m, 619.0 w, 531.4 w, 498.6 w, 465.7 m, 414.6 w.

The mechanism of reflux distillation in synthesizing the gel is complicated. An increase of the temperature during sol refluxing increased the collision probabilities between molecules, which provided much more chances

Table 1. Different Products under Different Operations

	operation	temp	concn	product
1	reflux distillation	increased	increased gradually	gel
2	distillation	increased	increased	deposition
3	refluxing for hours	increased	unchanged	sol
4	aging for weeks	unchanged	unchanged	sol

Table 2. Dependence of Products on Ingredients

	parent precursors	sol-vent	product	W _{Ti} (mol ratio)
1	Ba(CH ₃ COO) ₂ /Sr(CH ₃ COO) ₂	<i>a</i>		0
2	Ba(CH ₃ COO) ₂ /Sr(CH ₃ COO) ₂ /Ti(<i>n</i> -OBu) ₄	<i>a</i>	BST	0.5
3	Pb(CHCOO) ₃ /Zr(NO ₃) ₅ /Ti(<i>n</i> -OBu) ₄	<i>b</i>	PZT95	0.025
4	Pb(CHCOO) ₃ /Zr(NO ₃) ₅ /Ti(<i>n</i> -OBu) ₄	<i>b</i>	PZT75	0.125

^a Glacial acetic acid. ^b Glycol methanol ether.

for the formation of gel. On the other hand, increasing the temperature might result in a higher solubility of particles, which does not benefit the gel formation. How the problem could be solved with two contradictory aspects brought by increased temperature? The answer is to gradually increase the sol concentration by reflux distillation. The quantity of distillate was 5 mL, described in the Experimental Section, but it was varied on the basis of the solvent dosage of the sol. The distillate was a mixture of acetic acid and acetic acid ester, examined by GC and FTIR.^{1,12} When the sol concentration reached a critical value, a polymerization reaction took place to produce the gel. Thus, it is necessary to meet the conditions of both temperature and concentration.

For example, if the sol was concentrated quickly by means of distillation, only deposition would occur, which might result from the fast increment of the concentration of particles. The failure to form a gel by refluxing the sol for hours was due to the unchanged concentration. Furthermore, when the conditions mentioned above were not met, BST sol remained unchanged while aging for weeks, indicating that the sol was very stable.¹ Table 1 shows the products obtained under different conditions.

In addition to the appropriate temperature and concentration, the sol should have at least one kind of metal-organic compound. This is the same condition required by the hydrolyzing method.¹¹ In this experiment, Ti(*n*-OBu)₄ was used. The difference consisted of the ratio of metal-organic precursors (W_{Ti}). For the hydrolyzing method, W_{Ti} was around 0.5.^{2–4} In the case of the NHSGS method, a very low ratio of 0.025 could be used, as shown in Table 2.

Table 2 also shows that the reflux distillation method could be applied to synthesize other materials such as PbZr_{0.75}Ti_{0.25}O₃ (PZT75) and PbZr_{0.95}Ti_{0.05}O₃ (PZT95). It should be noted that PZT95 gel could not be synthesized by direct addition of water because of the low proportion of Ti(*n*-BuO)₄. Using the NHSGS method, however, a homogeneous gel was formed and the final PZT95 nanopowder was synthesized successfully.^{14,15} As shown in Table 2, different kinds of solvents were employed, because glacial acetic acid was the necessary solvent for Ba(CH₃COO)₂ while glycol methanol ether was an excellent dispersant for Zr(NO₃)₅.

Both slow and fast processes were employed in gel drying, as described in the Experimental Section. Fine calcined powders with an excellent dispersed state were obtained by both drying methods. However, there were

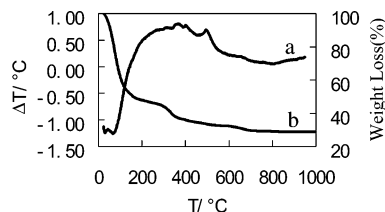


Figure 1. DTA (a) and TG curves (b) of the condensed gel.

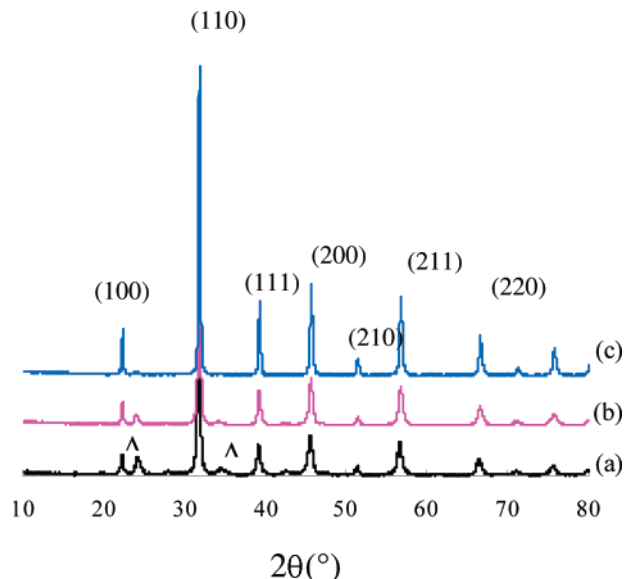


Figure 2. Powder X-ray diffraction patterns of calcined powders: (a) 700 °C; (b) 800 °C; (c) 930 °C.

more advantages to the latter. The drying time was reduced from 6 to 7 days to 2.0 h. The pollution and cost could be largely minimized, for most of the solvent was recycled. For example, 200 mL of solvent was

recycled from the total dosage of 280 mL and its ratio reached 71%. GC and FTIR data indicate that glacial acetic acid is the main component of the recycled solvent. Compounds such as acetic acid ester (not butyl ester) and an unknown kind of ether exist, too. Although it was a mixture, the recycling solvent could be reused for the preparation of Ba–Sr–Ti sol and we have succeeded in obtaining BST gel.

Two stages of heating processes were applied during gel drying on the basis of the thermal decomposition of condensed gel shown in Figure 1. Two weight losses were observed in the temperature range 20–150 °C and 150–400 °C of the TG curve. The losses were due to the solvent evaporation and oxidation of organic compounds referenced to the DTA curve. Since some amount of solvent remained, decomposition of the gel was carried out at a lower temperature, below 400 °C. This prevented the organic compounds from combusting and the resultant powder from particle gathering. Then the powder was calcined above 700 °C, on the basis of a small exothermic peak of perovskite-like crystallization at around 700 °C in the DTA curve. Different temperatures were used in order to obtain the lowest calcined temperature for pure perovskite-like phase crystal formation.

Analysis and Measurement. Figure 2 shows the XRD patterns of BST powders calcined at different temperatures, and the cube perovskite-like phases are labeled on the curves. The XRD data indicated that at 700 °C the perovskite-like phase crystallization occurred. Inside the crystals, however, there was still an impurity of barium carbonate (BaCO_3), whose peaks were marked by “ Δ ”. The impurity resulted from the reaction of acetate and atmospheric carbon dioxide during the conversion process.^{11,16} At higher temperature, the carbonate reacted with the remaining TiO_2 and formed BaTiO_3 . The carbonate impurity was also re-

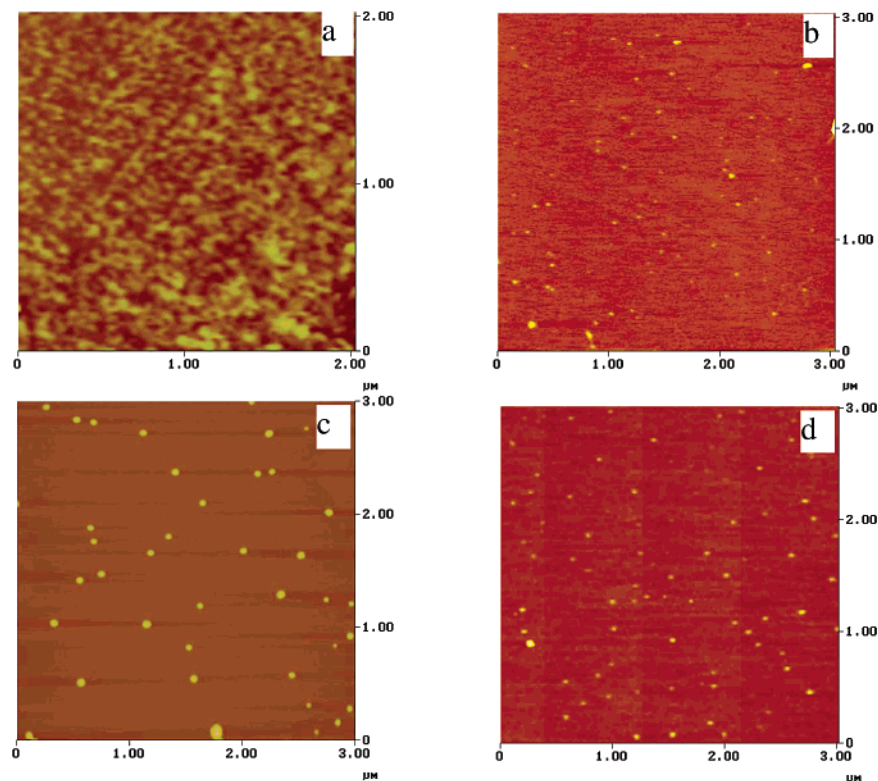


Figure 3. AFM images of BST powders calcined at 930 °C on micas: (a) high concentration; (b) low concentration; (c) ethanol suspension; (d) xerogel dried in air.

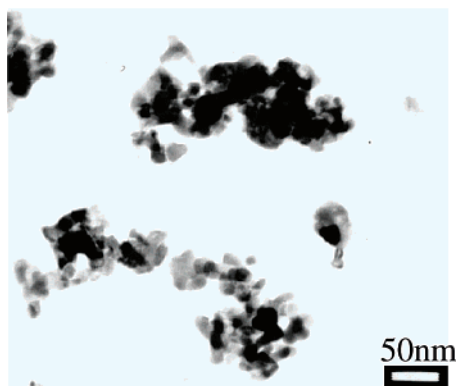


Figure 4. TEM image of BST powder calcined at 930 °C (ethanol as the dispersant).

ported in Zeng and Sharma's work, in which the hydrolysis process was involved.^{10,11} Pure perovskite-like phase BST powder was obtained at 930 °C, indicated by the disappearance of carbonate peaks in the XRD curve.

AFM is a newly developed analytical tool with many outstanding advantages. Since the first AFM was invented in 1986, thousands of scientists have committed themselves to research on AFM and have made great progress in its stability, new capabilities of exploitation, and applications.^{17,18} The morphology of BST powders was observed using AFM with an Ultrasharp NSC11 cantilever (MikroMasch Corp.) in the tapping mode. BST calcined powders were dispersed in double-distilled water by the ultrasonic method and spread on freshly cleaved mica substrates. When the concentration was very high (~3 g/L), as shown in Figure 3a, many particles gathered together to form large clusters; however, a few particles were unattached. When the suspension was diluted by 30 times, the BST particles showed an excellent dispersed state, as shown in Figure 3b. Nanosize spherical-shaped crystals are widely spread over the field of vision, and the mean grain size is about 30 nm. In comparison with water, an image of particles with proportional space was also obtained using ethanol as the dispersant (Figure 3c). The experiments above indicate that clusters like those shown in Figure 2a are just a simple accumulation of particles that could be easily dispersed. They also indicate that the sample preparation is very important to the powder analysis. Figure 3d is the AFM image of a calcined powder from xerogel dried in air, which shows an excellent dispersed state within the visible area as well. Similar mean diameters are displayed in Figure 3b–d.

Figure 4 illustrates the TEM image of a BST powder calcined at 930 °C. As shown, the primary particle exhibits a uniform spherical-shaped morphology. The mean grain size is estimated to be around 30 nm, which matches the result of AFM. Although some large clusters could be seen in the TEM image, detailed information shows that these clusters are composed of many nanoparticles. From the BET analysis, the BST powder has a surface area of 13.6 m²/g. The agglomerate size distribution of the calcined BST powder shows that the diameter of 50% agglomerates is smaller than 340 nm and the maximum size is 3.204 μm (Figure 5). The difference between the particle size and the agglomerate size was also reported in the literature.^{3,19} The proper-

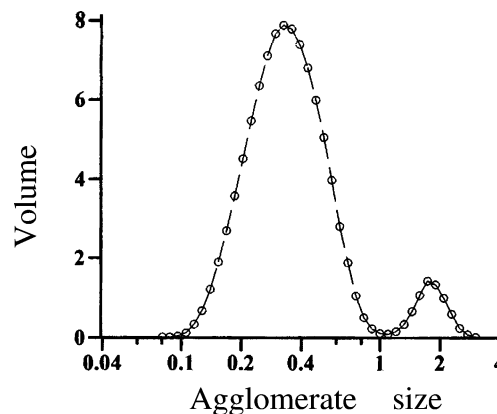


Figure 5. Agglomerate size distribution of the powder calcined at 930 °C (water as dispersant).

ties of BST synthesized by NHSGS are equal to and even better than those of BST reported in the literature.^{3,10,11}

Conclusions

A novel nonhydrolytic sol–gel synthesis (NHSGS) process was designed, and BST nanopowder has been successfully synthesized. In comparison with the hydrolytic sol–gel method, reflux distillation used in the NHSGS process could meet the conditions of temperature and concentration while BST gel was prepared. Since no water involved was in the experiments, the process is favorable for solvent recycling. In the fast-drying process, the period of synthesis was greatly shortened while the cost and pollution were largely minimized. Furthermore, the NHSGS method can also be applied to preparation of other nanopowders such as PbZr_{0.95}Ti_{0.05}O₃ and PbZr_{0.0.70}Ti_{0.30}O₃. The calcined powders show a spherical-shaped morphology with a mean grain size of around 30 nm, estimated by both AFM and TEM images. Agglomerate size distribution indicates that 50% of the agglomerates are smaller than 344 nm. These results indicate that NHSGS is a very effective and efficient method for the synthesis of nanopowders of high quality. Studies on the mechanism of the process and electrical measurements of the synthesized BST powder will be done in the future.

Acknowledgment

We are grateful for financial support from the Shanghai Nanotechnology, Optical Scientific Program (Grant Nos. 0214nm098, 035907022, and 015261048) and the Education Committee of Shanghai City, China.

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Received for review June 14, 2004

Revised manuscript received November 24, 2004

Accepted December 1, 2004

IE0494824