

Direct large-scale synthesis of perovskite barium strontium titanate nano-particles from solutions

Jian Quan Qi^{a,b,*}, Yu Wang^a, Wan Ping Chen^a, Long Tu Li^b, Helen Lai Wah Chan^a

^aDepartment of Applied Physics, Materials Research Center, The Hong Kong Polytechnic University, Room BC 719, Hong Kong, China

^bState Key Laboratory of Fine Ceramics and New Processing, Department of Materials Sciences & Engineering, Tsinghua University, Beijing 100084, China

Received 23 August 2004; received in revised form 5 November 2004; accepted 3 December 2004

Abstract

This paper reports a wet chemical synthesis technique for large-scale fabrication of perovskite barium strontium titanate nano-particles near room temperature and under ambient pressure. The process employs titanium alkoxide and alkali earth hydroxides as starting materials and involves very simple operation steps. Particle size and crystallinity of the particles are controllable by changing the processing parameters. Observations by X-ray diffraction, scanning electron microscopy and transmission electron microscopy TEM indicate that the particles are well-crystallized, chemically stoichiometric and ~50 nm in diameter. The nanoparticles can be sintered into ceramics at 1150 °C and show typical ferroelectric hysteresis loops.

© 2004 Elsevier Inc. All rights reserved.

Keywords: Nano-particles; Perovskite; Barium strontium titanate

1. Introduction

The properties of nanostructures differ from that of bulks due to their small sizes and large surface-to-volume ratios [1–4]. Such size effect is not only observed in metallic nanostructures but also in many complex oxides, such as the perovskite ferroelectric materials [5,6]. Aiming at a better understanding of the structure–property relationship and the development of novel electronic devices, in recent years the study of the nano-scaled ferroelectric materials has attracted immense attention. Novel synthesis techniques have been developed. Among them, wet chemical method, which is usually inexpensive, can be conducted at low temperatures and yet offers good compositional and structural control of the products, is particularly suitable for

making nano-structured ferroelectric oxides. In the past a few years, various nanostructures (nano-powders, nano-rods and nano-tubes) of typical ferroelectric families, like lead zirconate titanate (PZT) and barium titanate (BT), have been fabricated by means of wet chemical techniques in literature [7–13].

In a wet chemical processing, temperature and pressure are two factors that have critical influences on the structure and property of the products. A higher temperature and pressure may improve the crystallinity of the nano-structures but also lead to a higher level of processing inconvenience and more difficulties in the size control of the products. Continuous effort is seen in literature to develop techniques for making high-quality nano-structures at lower temperatures and under ambient pressure. Take the fabrication of barium titanate as an example. While the crystallization of BaTiO₃ via a conventional solid-state reaction requires a calcination temperature >1000 °C, the synthesis temperature for making crystallized nano-structures of BaTiO₃ via chemical method (such as hydrothermal

*Corresponding author. Department of Applied Physics, Materials Research Center, The Hong Kong Polytechnic University, Room BC 719, Hong Kong, China. Fax: +852 2333 7629.

E-mail address: apjq@polyu.edu.hk (J.Q. Qi).

method) can be low as 100~280 °C [7,9–12]. To further lower the synthesis temperature and pressure is still attracting much attention. Wada et al. have developed a method called low-temperature direct synthesis (LTDS) and has been proposed for synthesis of BaTiO₃ nanoparticles [13], but the method introduced some harmful impurities and the composite of the product, their morphology and the processing could not controlled easily.

Having noticed that titanium alkoxides are completely soluble in alcoholic solvent but get hydrolyzed in water, and with reference to literature work on titania nanocrystals [14–20], we have developed a novel process that can be conducted near room temperature and under ambient pressure and is particularly suitable for making Ti-related perovskite nano-structures. Employing titanium alkoxide and alkali earth hydroxides as start materials, this process involves mainly a water hydrolysis and an acid–base neutralizing reaction, both of which can occur at lower temperatures and under ambient pressure. A typical example to be demonstrated in this paper is the nano-particles of (Ba,Sr)TiO₃ (abbreviated as BST), which is a continuous solid solution of barium titanate (BaTiO₃) and strontium titanate (SrTiO₃). BST ceramics are widely used in capacitors and BST thin films are useful for making tunable microwave components, random access memories (RAM), and infrared detectors [21–27]. The nano-scaled BST is also a good candidate for the fundamental research of nano-ferroelectricity because of its excellent compositional and structural modifiability. As to be shown below, crystallized BST nano-particles were obtained by using our technique of which the processing temperature did not exceed 60 °C. To the best of our knowledge, this temperature is the lowest among all the wet chemical techniques for making similar ferroelectric nanostructures in literature.

2. Experimental procedure

The starting materials for the synthesis include high purity Ba(OH)₂·8H₂O, Sr(OH)₂·8H₂O, Ti(OBu)₄ and di-ionized water (DIW). The synthesis process may be divided into two steps. The first step was to separately prepare a base solution and a titanium solution. The base solution was prepared by dissolving Ba(OH)₂·8H₂O (28.392 g) and Sr(OH)₂·8H₂O (2.658 g) into DIW (500 ml). The concentration of the base solution was ~0.2 M. The solution was then heated to 60 °C in a water bath. The titanium solution was prepared by dissolving Ti(OBu)₄ (34.0 g) into absolute ethanol (250 ml). These solution concentrations are for the composition of (Ba_{0.9}Sr_{0.1})TiO₃; for other compositions, the solution concentration is changed accordingly. The second step was to allow the reaction to take place

by dripping the titanium solution into the base solution (60 °C) under vigorous stirring. An instantaneous formation of white precipitation was observed. After the reaction was completed and followed by ageing for 3 h, the white precipitation was obtained by filtration and baked at 60 °C for 24 h in an oven. The as-prepared powders were also annealed respectively at 300, 500, and 1000 °C for 2 h to check the annealing effects of the products.

The obtained white powders were characterized at room temperature by means of X-ray diffraction (XRD) on a Philips Diffractometer (Model: X'Pert-Pro MPD) using CuK α radiation (40 kV, 30 mA), a differential thermal analysis-thermogravimetric (TG-DTA) instrument (Netzsch STA 449C) with the temperature increase rate of 10 °C/min from room temperature up to 1000 °C, scanning electron microscopy (SEM) on a JEOL field-emission SEM (Model: JSM 6335F NT) and transmission electron microscopy (TEM) on a JEOL TEM (Model: JSM2010) with best point resolution 0.24 nm at 200 kV, respectively. The chemical composition of the products was determined by X-ray Fluorescence Spectrometry on XRF-1700 (Shimadzu, Australia).

Using the nano-particles, BST ceramics were prepared via a simplified ceramic processing. The synthesized BST nano-particles were dry-pressed into pellets of ~10 mm in diameter. Then the pellets were directly sintered in a box furnace at 1150 °C for 2 h. On the major surfaces of the sintered ceramic, silver electrodes were painted followed by thermal treatment at 650 °C for 10 min. Such Ag/BST/Ag samples were used in the ferroelectric tests on a Sawyer-Tower circuit (a standard technique for ferroelectric characterization).

3. Results and discussion

Elemental ICP analysis of the powders has revealed the atomic ratio Ba:Sr:Ti is in good consistence with that in the start compositions, indicating a good compositional control of our method. X-ray diffraction was performed to characterize the crystallinity and phase of the nano-particles. Fig. 1 shows the representative XRD pattern of the as-prepared powders that were synthesized and baked at 60 °C. Except for one small peak appearing at about 24°, all other peaks are identified as from perovskite BST. The peak sharpness and intensity indicate that BST is well crystallized. The particles were found to have a cubic symmetry with lattice parameter ~0.402 nm, which is different from the symmetry of bulk BST. In literature, BST ceramic of the same composition has a tetragonal phase at room temperature with lattice parameters $a = 0.399$ nm and $c = 0.401$ nm [28]. This symmetry change is a typical size effect that has been observed in other nano-scaled ferroelectric materials as well (further discussion

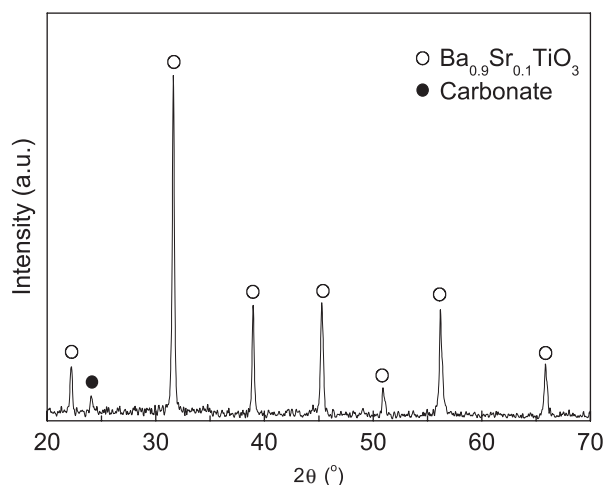


Fig. 1. X-ray diffraction pattern of $(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{TiO}_3$ nano-particles.

available later in the paper). The peak at 24° in the XRD pattern is identified as from barium carbonate. The formation of barium carbonate is believed to be a result of the reactions between carbon dioxide that dissolved into the solutions from air and reacted with the alkaline earth hydroxides during the process. The impure phase can either be avoided by undertaking the whole process in a protective atmosphere (such as argon or nitrogen) or be removed by washing the powders using dilute acids.

The post-synthesis annealing has strong influence on the lattice symmetry of the nano-particles. Fig. 2 shows the XRD patterns of the nano-particles subjected to different treatments (the scanning was conducted very slowly so as to improve the data accuracy). For the as-fabricated nano-particles and those annealed at 300 or 500 °C, one peak of a symmetric shape was observed in each case, indicating a cubic symmetry of the nano-particles. The peak corresponds to the (002) plane of the perovskite. For the samples annealed at 1000 or 1250 °C, the XRD peak is broadened and asymmetric in shape, suggesting the peak is indeed a combination of two separate peaks which correspond to the (200) and (002) planes of tetragonal BST, respectively. One of the major factors that are responsible for this symmetry change is the crystallite size of the particles. For those samples with large particles, the size was measured under SEM. For the samples with small particles (such as the as-deposited sample), the size was estimated by using Scherrer's equation

$$L = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where L is the crystallite size, λ the wavelength of the X-ray radiation (0.15418 nm for $\text{CuK}\alpha$), K usually taken as 0.89, β the line width at half-maximum height after subtraction of broadening caused by equipment, and θ

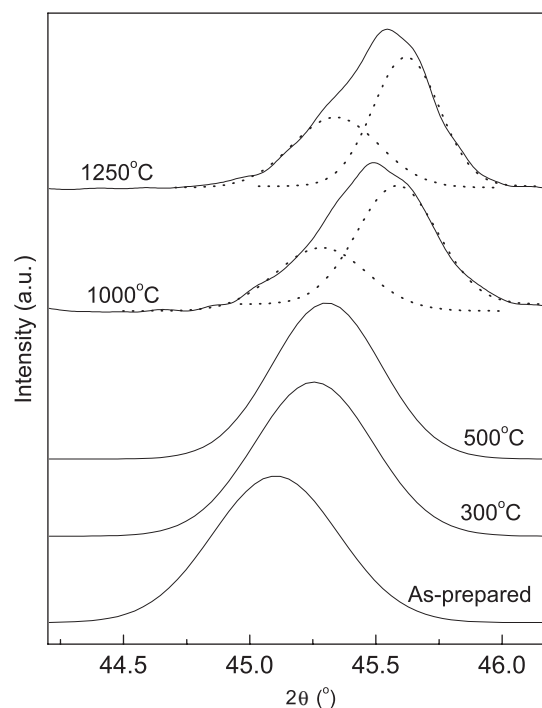


Fig. 2. XRD patterns of the nano-particles annealing at different temperatures.

the diffraction angle. A strong correlation between the crystalline size and the lattice symmetry is clearly shown in another microstructural factor that possibly affects the lattice symmetry is clearly shown in Table 1.

Another microstructural factor that possibly affects the lattice symmetry is interstitial hydrogen. Synthesized from an aqueous solution, the particles are expected to contain hydrogen that may exist in the interstitial sites of BST lattices. Despite direct observation of such interstitial hydrogen is not yet available, we have indirect evidences to support our assumption. First, our as-synthesized BST particles have a larger lattice than bulk BST. As shown in Table 1, the lattice parameters of the as-synthesized particles are $a = c = 0.4020$ nm, while the lattice parameters for bulk BST of the same composition from literature is $a = 0.3990$ nm and $c = 0.4010$ nm. We believe that the interstitial hydrogen is responsible for such slight lattice expansion in the as-synthesized BST. For the particles subjected to post-synthesis thermal treatment, the interstitial hydrogen may be partially/completely removed; hence the lattice size shows a trend of decrease as the thermal treatment temperature increases. Secondly, the chemical properties of the particles also give clue to this assumption. It is reasonable to expect that, for BST particles with interstitial hydrogen, the interstitials will introduce positive charges into the lattice and therefore, the particles have to absorb negatively charged hydroxyl groups to compensate and neutralize such positive

Table 1
Annealing temperature dependence of lattice parameters and crystallite size

Annealing temperature (°C)	As-deposited	300	500	1000	1250
Crystallite size (nm)	43	50	65	130	2000
Lattice symmetry and parameters (nm)	Cubic $a = c = 0.4020$	Cubic $a = c = 0.4008$	Cubic $a = c = 0.4003$	Tetragonal $a =$ 0.4002, $c = 0.3980$	Tetragonal $a =$ 0.4002, $c = 0.3978$

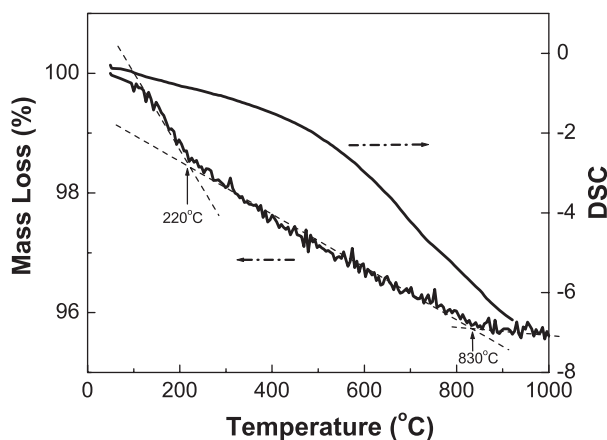


Fig. 3. DTA-TG analysis of as-prepared powders.

charges. If such particles are dispersed in water, then the solution must show an alkalescent property. On the other hand, if stoichiometric BST particles are suspended in water, the solution should keep neutral. This assumption has been proven by our experiment in which three different particles were used: (i) the as-synthesized, (ii) the 500 °C-annealed and (iii) the 1000 °C-annealed. With dispersion of the particles, the three solutions were found to have correspondingly different pH values: (i) 10, (ii) 8 and (iii) 7. While samples (i) and (ii) are obviously the cases discussed above, sample (ii) actually corresponds a case where the interstitial hydrogen has been partially removed by the thermal treatment.

The DTA-TG analysis has helped to study of the release of hydrogen from the lattices. Fig. 3 shows the weight loss and DSC of the as-synthesized powders as a function of temperature. From room temperature to about 220 °C, there is a weight loss of ~1.5%. Such weight loss is mainly due to the removal of residual alcohol and adsorbed water in the particles. From 220 to ~830 °C, another weight loss, up to ~3%, is observed. This weight loss is believed to be corresponding to the release of interstitial hydrogen and the adsorbed hydroxyl groups. At higher temperatures, the sample weight is almost a constant value, meaning that the release of the interstitial hydrogen and hydroxyl groups is completed at ~830 °C (i.e., the particles subjected to >830 °C thermal treatment are stoichiometric BST). In the DSC curve, no sharp endothermic or exothermic peak is observed. This is because the as-synthesized

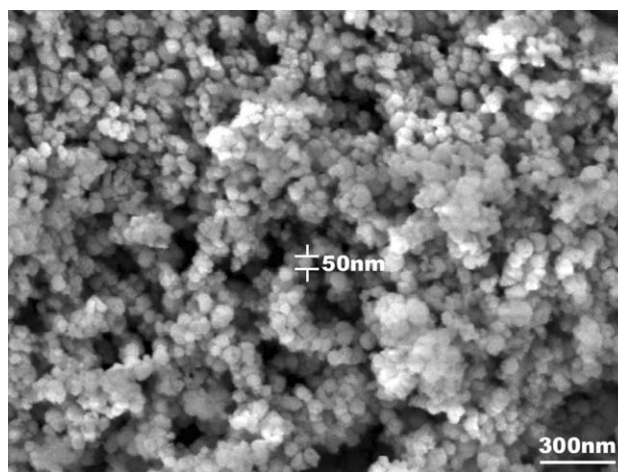


Fig. 4. BST nano-particles observed under a field-emission scanning electron microscopy (FE-SEM).

particles are already well crystallized. A rather broadened exothermic curve is observed, which is likely corresponding to the crystallite size increase at higher temperatures.

The microstructure of the as-synthesized BST particles was further characterized by means of SEM and TEM. A representative SEM image of the as-prepared BST nano-particles is shown in Fig. 4. It is observed that the particles are uniform, with ~50 nm in diameter. The result is in good agreement with the XRD estimation.

The TEM observation results are shown in Fig. 5. Fig. 6a shows the morphology of the powders. Consistent with the SEM observation, the particle size was found under TEM to be ~50 nm in diameter. A selected-area electron diffraction (SAED) pattern with indexed atom planes is shown in the inset of Fig. 5a. Fig. 5b is a high-resolution TEM image. Regularly arranged patterns can be observed in the darker region of the photo, indicating that the particles under observation are crystallized. A fast Fourier transform algorithm (FFT) has yielded structural information of the nano-particles, as shown in Figs. 5c and 5d. The lattice parameter of the material was found to be ~0.398 nm. Dislocations have also been identified in the FFT image shown in Fig. 5d. Obviously the low synthesis temperature is the main reason for the formation of the dislocations.

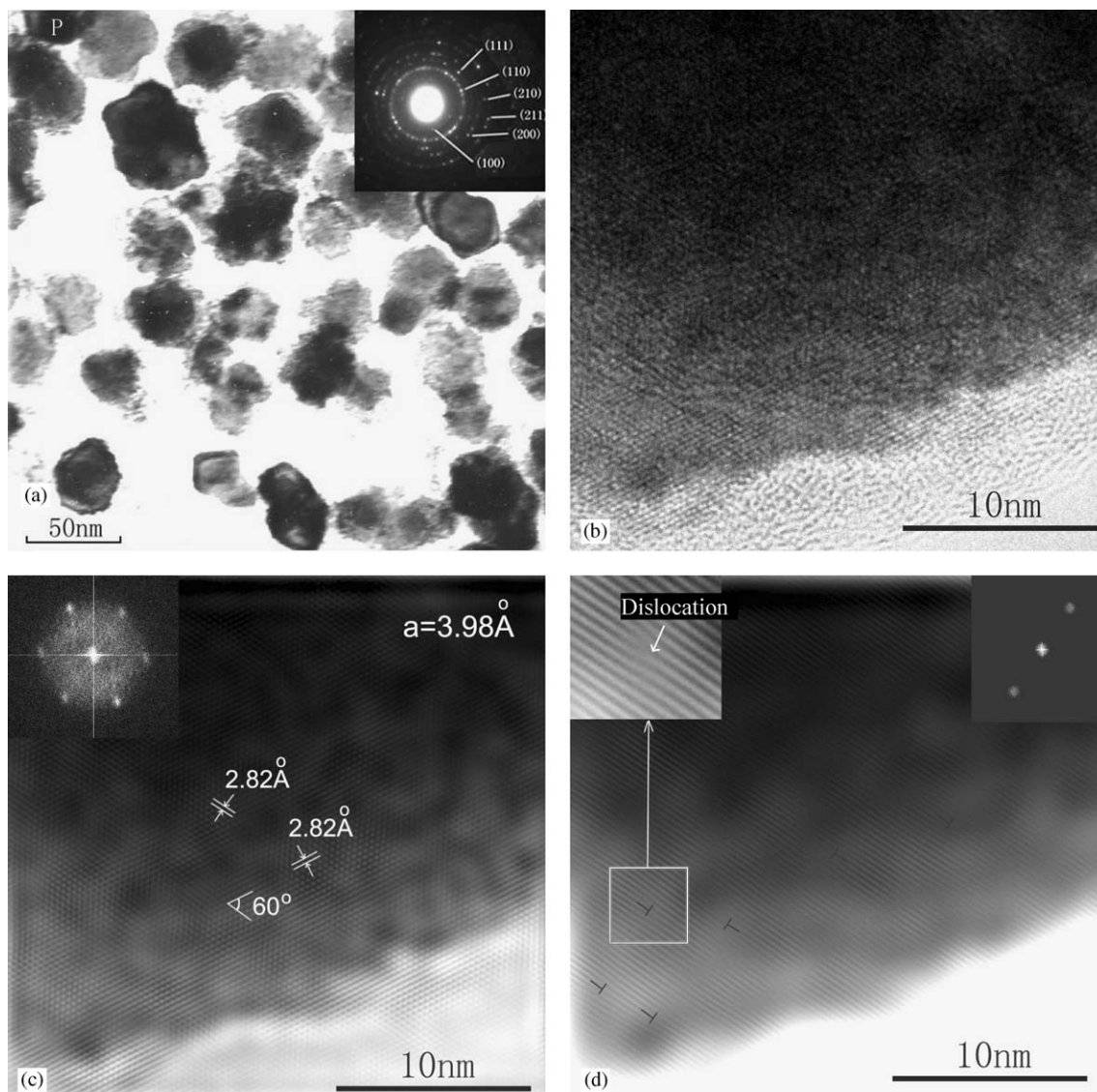


Fig. 5. TEM observation of BST nano-particles: (a) morphology, (b) high resolution image, (c) FFT image indicating relationship of atom planes and (d) FFT image revealing the dislocations in the nano-structure.

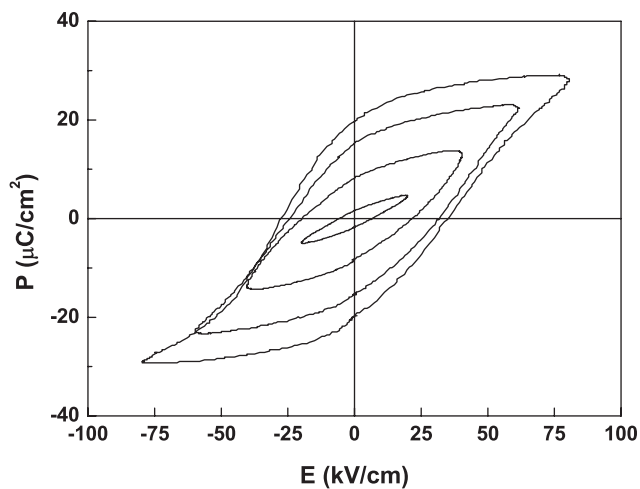


Fig. 6. Ferroelectric hysteresis loops of BST ceramics made from the nano-particles via a simplified ceramic processing.

Further experiments have indicated that the particle size can be controlled through modifying the solution concentration, the synthesis temperature, the stirring rate and/or the drying temperature. For example, finer particles can be obtained in thinner solution. Although, as a typical example, the synthesis in this paper was conducted at 60 °C, it does not mean that crystallized nano-particles could not be obtained via this technique at other temperatures. As a matter of fact, BST nano-particles with acceptable crystallinity were obtained via the same process conducted at several different temperature points (~25, 40C, 80 °C, etc.). Another point to mention is that this synthesis technique is applicable for BST with any Ba:Sr ratio, despite only the composition of Ba:Sr = 0.9:0.1 is discussed in the paper.

The BST nano-particles prepared by the above process are very useful for making high-quality ceramics

and composites. The microstructural features are very small in size (hence large specific area) and already crystallized without any high-temperature treatment mean a better sinterability of the BST nano-particles than powders prepared via regular solid-state reactions. Based on this, we have managed to prepare BST ceramics by a simplified ceramic processing in which the calcination step was omitted and the sintering temperature was lowered. The nano-particles were directly dry-pressed and then sintered at 1150 °C for 2 h. Except for a higher percentage shrinkage, the sintered ceramics from our powders showed little difference in microstructure and property from conventionally prepared ones. The ferroelectric behaviors of BST ceramics made from our nano-particles were characterized. As shown in Fig. 6, the ceramics show typical ferroelectric hysteresis loops that are analog to that of regularly prepared ceramics in terms of the values of the polarization and coercive field. BST ceramics with other compositions were also prepared by a similar processing and excellent dielectric and ferroelectric properties were obtained. The nano-particles can also be used in the fabrication of other useful structures, such as BST/MgO core-shell structures for microwave components [25]. More details will be reported in the future.

4. Conclusion

In summary, via a near room temperature and ambient pressure chemical process, we have synthesized (Ba,Sr)TiO₃ nano-particles which exhibit a well-crystallized perovskite phase and are about 50 nm in diameter. The process employs titanium alkoxide and alkali earth hydroxide as start materials and involves very simple operation steps. Particle size and crystallinity of the products are controllable by changing the processing parameters. This technique is also applicable for the synthesis of other complex oxides. The nano-particles can be used for making high quality ceramics and composites.

Acknowledgments

This work was supported by National Natural Science Foundation of China (Serial Number:

59995523) and the Center for Smart Materials of the Hong Kong Polytechnic University.

References

- [1] J. Hu, T.W. Odom, C.M. Lieber, *Acc. Chem. Res.* 32 (1999) 435.
- [2] A.P. Alivisatos, *Science* 271 (1996) 933.
- [3] L.E. Brus, J.K. Trautman, *Philos. Trans. R. Soc. London Ser. A-Math Phys. Eng. Sci.* 353 (1995) 313.
- [4] J.R. Heath, *Acc. Chem. Res.* 32 (1999) 388.
- [5] W.Y. Shih, W.H. Shih, I.A. Aksay, *Phys. Rev. B* 50 (1994) 15575.
- [6] P. Ayyub, S. Chattopadhyay, R. Pinto, M.S. Multani, *Phys. Rev. B* 57 (1998) R5559.
- [7] J.J. Urban, W.S. Yun, Q. Gu, H.K. Park, *J. Am. Chem. Soc.* 124 (2002) 1186.
- [8] F.D. Morrison, Y. Luo, I. Szafraniak, V. Nagarajan, R.B. Wehrspohn, M. Steinhart, J.H. Wendorff, N.D. Zakharov, E.D. Mishina, K.A. Vorotilov, A.S. Sigov, S. Nakabayashi, M. Alexe, R. Ramesh, J.F. Scott, *Rev. Adv. Mater. Sci.* 4 (2003) 114.
- [9] S. O'Brien, L. Brus, C.B. Murray, *J. Am. Chem. Soc.* 123 (2001) 12085.
- [10] B.A. Hernandez, K.S. Chang, E.R. Fisher, P.K. Dorhout, *Chem. Mater.* 14 (2002) 480.
- [11] L.A. Perez-Maqueda, M.J. Dianez, F.J. Gotor, M.J. Sayagues, C. Real, J.M. Criado, *J. Mater. Chem.* 13 (2003) 2234.
- [12] J.J. Urban, J.E. Spanier, L. Ouyang, W.S. Yun, H.K. Park, *Adv. Mater.* 15 (2003) 423.
- [13] S. Wada, T. Tsurumi, H. Chikamori, T. Noma, T. Suzuki, *J. Crystal Growth* 229 (2001) 433.
- [14] Y. Zhou, M. Antonietti, *J. Am. Chem. Soc.* 125 (2003) 14960.
- [15] K. Koumoto, S. Seo, T. Sugiyama, W.S. Seo, *Chem. Mater.* 11 (1999) 2305.
- [16] T. Nakashima, N. Kimizuka, *J. Am. Chem. Soc.* 125 (2003) 6386.
- [17] T.J. Trentler, T.E. Denler, J.F. Bertone, A. Agrawal, V.L. Colvin, *J. Am. Chem. Soc.* 121 (1999) 1613.
- [18] E.L. Crepaldi, G.L. Soler-Illia, D. Grosso, F. Cagnol, F. Ribot, C. Sanchez, *J. Am. Chem. Soc.* 125 (2003) 9770.
- [19] H.M. Liu, W.S. Yang, Y. Ma, Y.A. Cao, J.N. Yao, J. Zhang, T.D. Hu, *Langmuir* 19 (2003) 3001.
- [20] W.E. Stallings, H.H. Lamb, *Langmuir* 19 (2003) 2989.
- [21] W.J. Kim, W. Chang, S.B. Qadri, J.M. Pong, S.W. Kirchoefer, D.B. Chrissey, J.S. Honwitz, *Appl. Phys. Lett.* 76 (2000) 1185.
- [22] J.B.L. Rao, D.P. Patel, V. Krichevsky, *IEEE Trans Antenn. Propag.* 47 (1999) 458.
- [23] P. Padmini, T.R. Taylor, M.J. Lefevre, A.S. Nagra, R.A. York, J.S. Speck, *Appl. Phys. Lett.* 75 (1999) 3186.
- [24] Y. Gim, T. Hudson, C. Kwon, A.T. Findikoglu, B.J. Gibbons, B.H. Park, Q.X. Jia, *Appl. Phys. Lett.* 77 (2000) 1200.
- [25] A.I. Kingon, J.P. Maria, S.K. Streiffer, *Nature* 406 (2000) 1032.
- [26] E. Ngo, P.C. Joshi, M.W. Cole, C.W. Hubbard, *Appl. Phys. Lett.* 79 (2001) 248.
- [27] C.S. Hwang, *Mater. Sci. Eng. B* 56 (1998) 178.
- [28] Landolt-Bornstein Numerical Data and Functional Relationships in Science and Technology, Group III, Vol. 16, "Ferroelectrics and related substances," p. 416. Springer Verlag, Berlin-Heidelberg, Berlin, 1981.