

## Characterization of $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$ powder prepared from an oxalate co-precipitation and an impregnation method

Pusit Pookmanee<sup>a,\*</sup> and Sukon Phanichphant<sup>b,c</sup>

<sup>a</sup>Department of Chemistry, Faculty of Science, Maejo University, Chiang Mai, 50290, Thailand

<sup>b</sup>Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand

<sup>c</sup>NANOTEC Center Excellence at Chiang Mai University, Chiang Mai, 50200, Thailand

Barium titanate ( $\text{BaTiO}_3$ ) powder was prepared from an oxalate co-precipitation method with the starting precursors of barium chloride dihydrate and potassium titanium oxalate dihydrate with mole ratio of 1 : 1. Precipitated powder was obtained after adding oxalic acid until the pH of the final solution was 2. The precipitated powder was milled and calcined at 700 °C for 2 h. Sr-doped barium titanate ( $\text{BaSrTiO}_3$ ) powder was prepared by an impregnation method. Barium titanate calcined at 700 °C for 2 h was mixed with 2 and 4 mole % of Sr from strontium chloride hexahydrate. The mixed powder was calcined at 900 °C for 2 h. The phase of  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder was studied by X-ray diffraction (XRD) and found to have a tetragonal structure after calcination at 900 °C for 2 h. The morphology and chemical composition of  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder were investigated by a scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS). The particle size of  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder was in the range of 0.2–0.3  $\mu\text{m}$  with an irregular shape. The elemental composition of barium, strontium, titanium and oxygen showed the characteristic X-ray energy values.

**Key words:**  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$ , Oxalate co-precipitation, Impregnation.

### Introduction

Barium titanate ( $\text{BaTiO}_3$ ) has excellent dielectric properties which makes it the most important composition ceramic capacitors, especially for the manufacture of multilayer ceramic capacitors (MLCCs) [1]. In general,  $\text{BaTiO}_3$  powder is prepared using a conventional solid-state synthesis from barium carbonate and titanium dioxide, and then the mixture is calcined at a high temperature of 1200–1300 °C. It is known, however, that the solid-state reaction method causes some disadvantages, such as a large particle size, wide particle distribution, aggregation and high impurity content, which result from repetitive calcination and grinding treatments [2]. At present, the need for pure  $\text{BaTiO}_3$  powders has led to the development of many alternative low-temperature chemical synthesis methods such as a catecholate method [3], a sol-gel method [4, 5], a sonochemical method [6], a hydrothermal method [7], a microwave-hydrothermal method [8] and an oxalate co-precipitation method [9–11]. In the wet chemical processes for preparing highly quality powders, the best homogeneity, control morphology and smaller particle size are also usually obtained [12–14].

To improve the ferroelectric properties,  $\text{BaTiO}_3$  was doped with some metals such as calcium, zirconium, tin and

strontium. Barium strontium titanate ( $\text{BaSrTiO}_3$ ) powder is a high interest electronic material due to its high dielectric constant, alterable Curie temperature with composition, low dielectric loss, and high tunability of the dielectric behavior.  $\text{BaSrTiO}_3$  has been widely used in the preparation of high dielectric capacitors, PTC resistors, transducers, piezoelectric sensors, dynamic random access memories, microwave phase shifters, and uncooled infrared detectors [15].

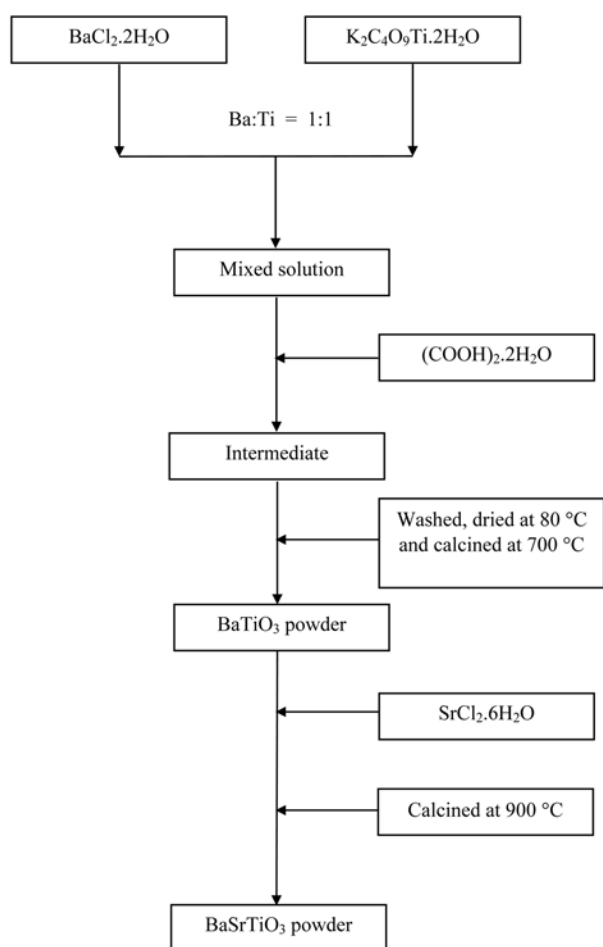
$\text{BaSrTiO}_3$  powder has been prepared by a conventional solid state reaction method [16], a sol-gel method [17], a polymeric method [18], a hydrothermal method [19], and an oxalate co-precipitation method [20]. The advantages of chemical methods over other techniques are the controlled morphology, narrow particle size distribution, high purity, high degree of crystallinity and a possible reduction in the sintering temperature. An oxalate co-precipitation method has been considered to be a promising way to prepare powders for piezoelectric materials [21]. The mentioned characteristics strongly depend on composition, raw materials, processing, microstructure, temperature, electric field, and frequency, so that, efforts on the  $\text{BaSrTiO}_3$  synthesis are still in progress in order to improve its properties [22].

In this research,  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder was prepared from an oxalate co-precipitation and an impregnation method. The phase of  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder was studied by X-ray diffraction (XRD). The morphology and chemical composition of  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder were investigated by a scanning electron microscope (SEM) and energy dispersive X-ray spectrometry (EDS).

\*Corresponding author:  
Tel : +66-53-873544-5  
Fax: +66-53-878225  
E-mail: pusit@mju.ac.th

## Experimental Procedure

Barium strontium titanate ( $\text{BaSrTiO}_3$ ) powder was prepared by an oxalate co-precipitation and an impregnation method as shown in Fig. 1. Barium chloride dihydrate [ $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ] (99.0%, Merck, Germany), potassium titanium oxalate dihydrate [ $\text{K}_2\text{C}_4\text{O}_9\text{Ti} \cdot 2\text{H}_2\text{O}$ ] (90.0%, Fluka, Switzerland) and oxalic acid dihydrate [ $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ ] (99.5%, Fluka, Switzerland) were used as the starting precursors.  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  solution was added to  $\text{K}_2\text{C}_4\text{O}_9\text{Ti} \cdot 2\text{H}_2\text{O}$  solution with a mole ratio of 1 : 1. Deionized water containing  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  was added to adjust the pH value of the solution. The white precipitated powder was obtained by adjusting the final pH of the solution to 2, then filtered, washed and dried in an oven (Gallenkamp, England) at 80 °C for 24 h. The milled precipitate was calcined in a muffle furnace (Inter Kilns, Thailand) at 700 °C for 2 h. Sr-doped barium titanate ( $\text{BaSrTiO}_3$ ) powder was prepared by an impregnation method. Barium titanate calcined at 700 °C for 2 h was mixed with 2 and 4 mole % of Sr from strontium chloride hexahydrate [ $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ] (99.0%, Merck, Germany). The ground-mixed powder was calcined in a muffle furnace at 900 °C for 2 h. The phase of  $\text{BaTiO}_3$  and  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder were studied



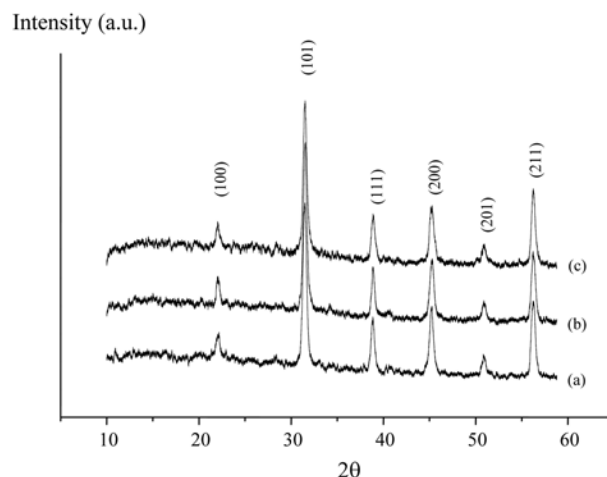
**Fig. 1.** Schematic diagram for the preparation of  $\text{BaSrTiO}_3$  powder from an oxalate co-precipitation and an impregnation method.

by an X-ray diffractometer (modified D-500, SIEMENS, Germany) using Ni-filtered monochromatic  $\text{CuK}_\alpha$  radiation. The detection range was 10–60° with a step size of 0.10° (2 $\theta$ /s/s). The structure of  $\text{BaTiO}_3$  and  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder were confirmed with the Joint Committee on Powder Diffraction Standards Card File No. 31-0174 [23] and 44-0093 [24].  $\text{BaTiO}_3$  and  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder were dispersed with an ethanol [ $\text{C}_2\text{H}_5\text{OH}$ ] (99.5%, Merck, Germany) medium in an ultrasonic bath (Model 5880, Cole-Parmer, USA) for 10 minutes, and gold sputter coated (JSC1200, JEOL, Japan) for 1 minute. The morphology of  $\text{BaTiO}_3$  and  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder were investigated by a scanning electron microscope (JSM5410-LV, JEOL, Japan) with a tungsten (W) filament K type, accelerating voltage of 25 kV, and a working distance of 18 mm. The chemical composition of  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  powder was analyzed by an energy dispersive X-ray spectrometer (ISIS300, Oxford, UK).

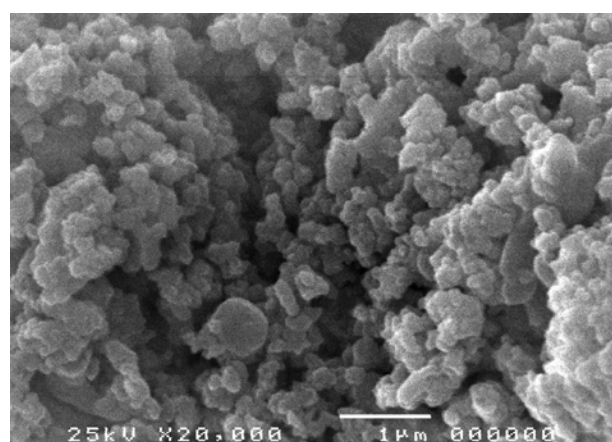
## Results and Discussion

Fig. 2 shows the XRD patterns of  $\text{BaSrTiO}_3$  powder after being calcined at 700 °C with 0 mol % Sr and 900 °C for 2 h with 2 and 4 mol % Sr. At 700 °C with 0 mol % of Sr, Fig. 2(a), a single phase of  $\text{BaTiO}_3$  with a cubic structure was obtained corresponding to the JCPDS File Card No. 31-0174 [23]. This is in good agreement with previous reports using an oxalate co-precipitation method [14, 25]. At 900 °C with 2 and 4 mol % of Sr, Fig. 2(b,c), a single phase of  $\text{Ba}_{0.77}\text{Sr}_{0.23}\text{TiO}_3$  with a tetragonal structure was obtained corresponding to the JCPDS Card File No. 44-0093 [24]. With an increase in the calcination temperature, the line width and intensity of the diffraction line decreases and increases, respectively. Obviously, this temperature was much lower than for the citric acid gel method [26].

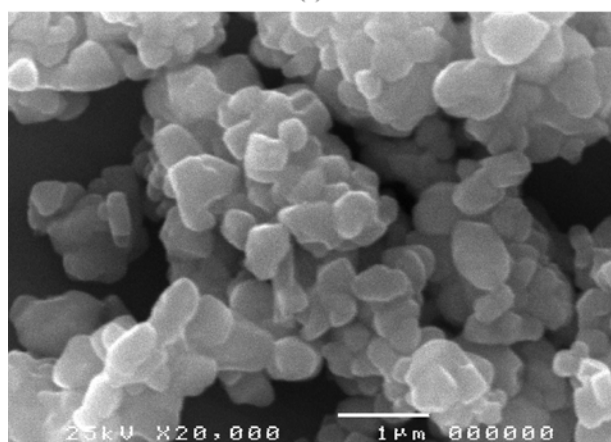
Fig. 3 shows SEM micrographs of  $\text{BaSrTiO}_3$  powder after calcination at 700 °C for 2 h with 0 mol% Sr and 900 °C for 2 h with 2 and 4 mol % Sr. The average particle



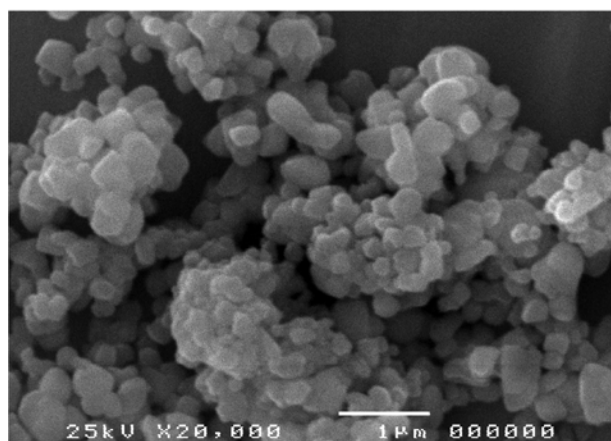
**Fig. 2.** XRD patterns of  $\text{BaSrTiO}_3$  powder with mole % of Sr as (a) 0, calcined at 700 °C and (b) 2 and (c) 4, calcined at 900 °C for 2 h.



(a)



(b)

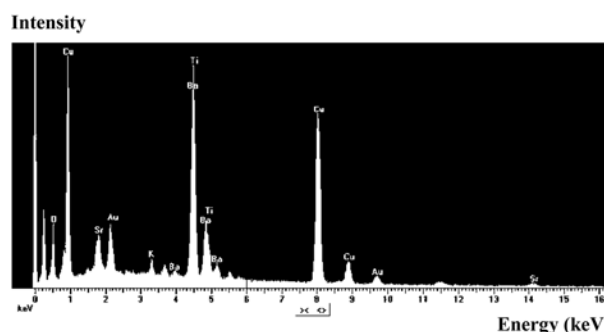


(c)

**Fig. 3.** SEM micrographs of BaSrTiO<sub>3</sub> powder with mole % of Sr as (a) 0, calcined at 700 °C and (b) 2 and (c) 4, calcined at 900 °C for 2 h.

size of BaTiO<sub>3</sub> powder was 0.1 µm, highly agglomerated and irregular in shape as shown in Fig. 3(a). The average particle size of Ba<sub>0.77</sub>Sr<sub>0.23</sub>TiO<sub>3</sub> powder with 2 and 4 mol % Sr, Fig. 3(b) and (c), were 0.3 µm and 0.2 µm, respectively, with an irregular in shape. The particle sizes were smaller than previously reported from an oxalate co-precipitation method [27-31].

Fig. 4 shows EDS spectra of BaSrTiO<sub>3</sub> powder with



**Fig. 4.** EDS spectra of BaSrTiO<sub>3</sub> powder calcined at 900 °C for 2 h with 2 mole % of Sr.

2 mol % Sr after calcination at 900 °C for 2 h. Energy dispersive X-ray spectroscopy was employed to investigate and indicate the composition of the powder calcined. The characteristic X-ray radiation of each element has different energy values; barium of L<sub>3</sub> 3.960, L<sub>2</sub> 4.470, L<sub>1</sub> 4.827 and L<sub>2</sub> 5.158 keV, strontium of L<sub>2</sub> 1.806 and K<sub>α</sub> 14.166 keV, titanium of K<sub>α</sub> 4.505 and K<sub>β</sub> 4.931 keV and oxygen of K<sub>α</sub> 0.525 keV, respectively. This is in good agreement with samples previously reported from an oxalate co-precipitation method [14, 25] and a solvothermal method [32].

## Conclusions

A single cubic structure of BaTiO<sub>3</sub> powder was prepared from an oxalate co-precipitation method after calcination at 700 °C for 2 h. A tetragonal structure of Ba<sub>0.77</sub>Sr<sub>0.23</sub>TiO<sub>3</sub> powder was obtained after calcination at 900 °C for 2 h with 2-4 mol % Sr. The average particle size of Ba<sub>0.77</sub>Sr<sub>0.23</sub>TiO<sub>3</sub> powder was 0.3 µm and 0.2 µm for 2 and 4 mol % Sr, respectively, with an irregular shape. The elemental constituents of Ba<sub>0.77</sub>Sr<sub>0.23</sub>TiO<sub>3</sub> powder were identified by X-ray energy dispersive values.

## Acknowledgements

The authors would like to thank the financial support from the Department of Chemistry, the Faculty of Science, Maejo University, Chiang Mai, Thailand. The authors would like to thank Prof. Dr. Tawee Tunkasiri and Mr. Suwich Chaisupan from the Department of Physics, Chiang Mai University, Chiang Mai, Thailand for an X-ray diffractometer (XRD) facility, Ms. Sasithorn Numthong and Ms. Passapan Sriwichai from the Department of Chemistry, the Faculty of Science and Biotechnology Center, Maejo University, Chiang Mai, Thailand for access to a scanning electron microscope and an energy dispersive X-ray spectrometer (SEM/EDS) facilities and the National Nanotechnology Center (NANOTEC), the National Science and Technology Development Agency (NSTDA), Ministry of Science and Technology, through its program of Center of Excellence Network, Thailand.

## References

1. Y. Hotta, K. Tsunekawa, C. Duran, K. Sato, T. Nagaoka and K. Watari, *Mat. Sci. Eng. A* 475 (2008) 57-61.
2. C.G. Yañez, C. Benitez and H.B. Ramirez, *Ceram. Int.* 26 (2000) 271-277.
3. W. Maison, R. Kleeberg, R.B. Heimann and S. Phanichphant, *J. Eur. Ceram. Soc.* 23 (2003) 127-132.
4. P. Yu, X. Wang and B. Cui, *Scripta Mater.* 57 (2007) 623-626.
5. P. Yu, B. Cui and Q. Shi, *Mat. Sci. Eng. A* 473 (2008) 34-41.
6. M. Xu, Y.-N. Lu, Y.-F. Liu, S.-Z. Shi, T.-S. Qian and D.-Y. Lu, *Powder Technol.* 161 (2006) 185-189.
7. S.W. Lu, B.I. Lee, Z.L. Wang and W.D. Samuels, *J. Cryst. Growth* 219 (2000) 269-276.
8. W. Sun and J. Li, *Mater. Lett.* 60 (2006) 1599-1602.
9. H.S. Potdar, S.B. Deshpande and S.K. Date, *Mater. Chem. Phys.* 58 (1999) 121-127.
10. A.V. Prasadaraio, M. Suresh and S. Komarneni, *Mater. Lett.* 39 (1999) 359-363.
11. H.S. Potdar, S.B. Deshpande, A.S. Deshpande, Y.B. Kholam, A.J. Patil, S.D. Pradhan and S.K. Date, *Int. J. Inorg. Mater.* 3 (2001) 613-623.
12. P. Pookmanee, P. Boonphayak and S. Phanichphant, *Ceram. Int.* 30 (2004) 1917-1919.
13. P. Pookmanee, *J. Ceram. Process. Res.* 9 (2008) 30-33.
14. P. Pookmanee, C. Khantha and S. Phanichphant, *Mater. Sci. Forum* 561-565 (2007) 515-518.
15. L. Wang, H. Kang, D. Xue and C. Liu, *J. Cryst. Growth* 311 (2009) 605-607.
16. L. Zhou, P.M. Vilarinho and J.L. Baptista, *J. Eur. Ceram. Soc.* 19 (1999) 2015-2020.
17. P. Vitinov, A. Harizanova, T. Ivanova, D. Velkov and Zd. Raytcheva, *Vacuum* 69 (2003) 371-377.
18. A. Ries, A.Z. Simões, M. Cilense, M.A. Zaghet and J.A. Varela, *Mater. Charact.* 50 (2003) 217-221.
19. K.A. Razak, A. Asadov, J. Yoo, E. Haemmerle and W. Gao, *J. Alloy. Compd.* 449 (2008) 19-23.
20. S. Suasmoro, S. Pratapa, D. Hartanto, D. Setyoko and U.M. Dani, *J. Eur. Ceram. Soc.* 20 (2000) 309-314.
21. Y.B. Kholam, A.S. Deshpande, H.S. Potdar, S.B. Deshpande, S.K. Date and A.J. Patil, *Mater. Lett.* 55 (2002) 175-181.
22. A. Ianculescu, D. Berger, M. Viviani, C.E. Ciomaga, L. Mitoseriu, E. Vasile, N. Drăgan and D. Crişan, *J. Eur. Ceram. Soc.* 27 (2007) 3655-3658.
23. Joint Committee on Powder Diffraction Standards, *Powder Diffraction File*, Card No. 31-0174 Swarthmore, PA.
24. Joint Committee on Powder Diffraction Standards, *Powder Diffraction File*, Card No. 44-0093 Swarthmore, PA.
25. P. Pookmanee, P. Ketwong and S. Phanichphant, *Adv. Mater. Res.* 55-57 (2008) 81-84.
26. Z. Wang, S. Jiang, G. Li, M. Xi and T. Li, *Ceram. Int.* 33 (2007) 1105-1109.
27. Y.B. Kholam, S.V. Bhoraskar, S.B. Deshpande, H.S. Potdar, N.R. Pavaskar, S.R. Sainkar and S.K. Date, *Mater. Lett.* 57 (2003) 1871-1879.
28. Y.B. Kholam, S.B. Deshpande, H.S. Potdar, S.V. Bhoraskar, S.R. Sainkar and S.K. Date, *Mater. Charact.* 54 (2005) 63-74.
29. M.-L. Li, H. Liang and M.-X. Xu, *Mater. Chem. Phys.* 112 (2008) 387-341.
30. M.-L. Li and M.-X. Xu, *J. Alloy. Compd.* 474 (2009) 311-315.
31. M.-L. Li and M.-X. Xu, *Mater. Res. Bull.* 44 (2009) 937-942.
32. X. Wei, G. Xu, Z. Ren, Y. Wang, G. Shen and G. Han, *J. Cryst. Growth* 310 (2008) 4132-4137.