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# Hydrothermal synthesis of tetragonal Ba<sub>x</sub>Sr<sub>(1-x)</sub>TiO<sub>3</sub> powders

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Barium-strontium titanate ( $Ba_xSr_{(1,x)}TiO_3$  or BST) powders, with *x* ranging from 0 to 1, were synthesized hydrothermally at 200 °C by reacting a Ti(OH)<sub>4</sub> gel with Ba(OH)<sub>2</sub> and Sr(OH)<sub>2</sub>. The resulting BST powders were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. The mean particle sizes were found to be between 80 nm to 150 nm. The BST powders were found to be richer in Sr relative to the compositions of the corresponding hydrothermal solutions, indicating easier incorporation of Sr, compared to Ba, in the powders. All powders were found to be single-phase solid-solutions, and were determined to be cubic using XRD. However, Raman spectroscopy has revealed, for the first time, the presence of tetragonality in Ba-rich hydrothermal BST powders.

Key words: Ceramics, Powders, Hydrothermal, Raman, Barium Strontium Titanate.

## Introduction

The hydrothermal process affords the synthesis of micrometer-sized, crystalline ceramic powders at low temperatures without the need for the calcination step [1-3]. This makes it very attractive for the synthesis of powders of various ceramics, including one of the most popular perovoskite electroceramics: barium titanate or BaTiO<sub>3</sub>. There have been numerous studies on the hydrothermal synthesis of ultra-fine BaTiO<sub>3</sub> powders over the past five decades (see e.g. [4-13]). In those studies, the resulting hydrothermal BaTiO<sub>3</sub> powders were found to be cubic at room temperature, as determined by XRD [7, 9-13]. Since BaTiO<sub>3</sub> is expected to be tetragonal at room temperature, where the tetragonalto-cubic phase transformation occurs at 120 °C (Curie temperature), three primary hypotheses have been proposed to explain the XRD results. First, XRD is inadequate in resolving the subtle differences between the tetragonal and the cubic structures - the characteristic tetragonal splitting of the peaks - due to peak overlap and broadening, especially in the case of ultra-fine powders [14]. Second, the ultra-fine nature (particle size < 130-190 nm) of some of the powders results in the stabilization of the cubic phase (the so-called sizeeffect) [14-16]. Third, incorporation of hydroxyl groups in the BaTiO<sub>3</sub> lattice during the hydrothermal process results in the stabilization of the cubic phase [7].

In this context, Clarke *et al.* [10] have used both Raman spectroscopy and XRD to examine hydrothermal

BaTiO<sub>3</sub> powders, and they have concluded that Raman spectroscopy is a more sensitive tool for the phase characterization of BaTiO<sub>3</sub> powders. They observed a Raman peak characteristic of tetragonal symmetry at 305 cm<sup>-1</sup> in hydrothermal BaTiO<sub>3</sub> powders of size 20-40 nm, both before and after the elimination of hydroxyl groups from the structure, while XRD revealed only the cubic phase in those powders [10].

In order to determine the crystal phases present in barium-strontium titanate (Ba<sub>x</sub>Sr<sub>(1-x)</sub>TiO<sub>3</sub> or BST) solidsolution powders, we have synthesized such powders and characterized them using Raman spectroscopy, in conjunction with XRD, SEM and TEM. BST ceramics offer key advantages over BaTiO<sub>3</sub>, such as the ability to tailor the Curie temperature in the range 120 to -220 °C [17] and superior electrical and electro-mechanical properties [18]. However, the study of hydrothermal BST powders has been limited [19-21]. Roeder and Slamovich [21] prepared hydrothermal BST powders by reacting TiO<sub>2</sub> nanopowders with aqueous BaCl<sub>2</sub> and  $SrCl_2$  at < 100 °C (in 1 M NaOH), and they found that all the resulting powders (x=0 to 1) were cubic, as determined using XRD. In some cases they found the resulting powders to be biphasic: cubic with different compositions. Other researchers have also reported the presence of only the cubic phase in hydrothermal BST powders, as determined using XRD [19, 20].

In this study we have prepared BST powders by reacting a Ti(OH)<sub>4</sub> gel with Ba(OH)<sub>2</sub> and Sr(OH)<sub>2</sub> at 200 °C, with ((Ba+Sr)/Ti=1.1) in the solution. We find that although all the resulting powders (x=0 to 1) appear to be single-phase and cubic in XRD investigations, Raman spectroscopy is able to reveal that the Ba-rich powders (x=0.67 to 1.0) contain the tetragonal phase.

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## **Experimental Procedure**

First a Ti(OH)<sub>4</sub> gel was prepared by dissolving TiCl<sub>4</sub> (Alfa Aesar, Ward Hill, MA) in ice-cold distilled water, and reacting it with 3% NH<sub>4</sub>OH solution. The resulting gel was then filtered and washed with distilled water three times. The freshly prepared gel was suspended in solutions of Ba(OH)<sub>2</sub>·8H<sub>2</sub>O + Sr(OH)<sub>2</sub>.8H<sub>2</sub>O in CO<sub>2</sub>free water at 80 °C. Seven different solutions were prepared such that in each solution the cations molar ratio ((Ba+Sr)/Ti) was 1.1, and the total (Ba+Sr) concentration was 1 M, but the (Ba/(Ba+Sr)) molar ratio was 0, 0.25, 0.5, 0.7, 0.8, 0.9, or 1. The solutions were then poured into separate Teflon<sup>TM</sup>-lined stainless steel acid-digestion reactors or "bombs" (Model 4744, Paar Instrument Company, Moline, IL), filled to 70% of the 45 ml capacities of the vessels. The reactors were sealed and placed in a forced-air convection oven at 200 °C for 24 h in air. After cool down, the resultant powders were filtered and washed with hot (80 °C) distilled water three times. The washed powders were then dried at 60 °C for 24 h in air.

The resulting powders were characterized using XRD, Raman spectroscopy, SEM, and TEM, all at room temperature. Powder XRD was performed on a D5005 diffractometer (Bruker AXS, Madison, WI) using Cu  $K_{\alpha}$  radiation. A pure silicon standard was used as a standard to correct for any errors in the diffractometer. The 1 1 0 peak, in conjunction with the area method, was used to determine the lattice parameter, where the background and the intensity from Cu  $K_{\alpha 2}$  radiation were subtracted. A laser of 514.5 nm wavelength was used to perform Raman spectroscopy (Ramanscope 2000, Renishaw, Gloucestershire, UK) on the hydrothermal BST powders, and a reference BaTiO<sub>3</sub> powder obtained commercially (non-hydrothermal, 99.7% purity, Alfa Aesar, Ward Hill, MA). For SEM characterization, the powders were dispersed on gold-coated glass slides and observed in a SEM equipped with a field-emission source (JSM6335F, JEOL, Tokyo, Japan). For TEM characterization, the powders were dispersed on carbonsupported copper grids, and they were observed in a TEM operated at 100 keV (EM420, Philips, Eindhoven, The Netherlands).

## **Results and Discussion**

Figure 1 shows XRD patterns of powders produced from the seven different hydrothermal solutions. The lack of 1 1 0 peak-splitting indicates the presence of a single, cubic phase in all the powders. Note the systematic shift of the 1 1 0 peak to smaller angles, or increase in the lattice parameter, with increasing Ba concentration. Plotted in Fig. 2A is the lattice parameter of the powders as a function of the (Ba/(Ba+Sr)) concentration in the hydrothermal solutions. The lattice parameter values for BaTiO<sub>3</sub> (3.998 Å) and SrTiO<sub>3</sub>



**Fig. 1.** XRD patterns of the seven different hydrothermal Ba<sub>x</sub>-Sr<sub>(1-x)</sub>TiO<sub>3</sub> powders. The x value represents the composition of the powder. Note the systematic shift in the 1 1 0 peak to smaller  $2\theta$  angles with increasing *x*.



**Fig. 2.** Plots of (Ba/(Ba+Sr)) concentration in the hydrothermal solution versus: (A) lattice parameter of the corresponding BST powders (calculated from XRD patterns in Fig. 1) and (B) estimated composition of the corresponding BST powders using Vegard's law.

(3.902 Å) measured here compare favorably with those reported in the literature [22]. In hydrothermal BST powders Vegard's law has been verified, where the lattice parameter has been shown to scale linearly with the (Ba/(Ba+Sr)) concentration in the powders [21]. Accordingly, using Vegard's law the (Ba/(Ba+Sr)) concentration in the hydrothermal solutions versus that in the powders is plotted in Fig. 2B. All the data points for BST powders in Fig. 2B deviate from the 45° line, and they all lie below that line. This results indicates that there is a clear preference for Sr to be incorporated in the powder over Ba. This is consistent with thermodynamic calculations, where preferred incorporation of Sr in hydrothermal BST powders is predicted [21, 23]. In contrast, Roeder and Slamovich [21] found a closer match between the solution composition and the corresponding powder composition in hydrothermal BST powders, possibly due to incomplete reaction [21]. However, in the case of hydrothermal solutions containing an excess of (Ba+Sr) relative to Ti, i.e. ((Ba+Sr)/Ti) =5.0, Roeder and Slamovich [21] found a result similar to ours – preferred incorporation of Sr in BST powder. This could be due to two key differences in the synthesis processes. First, the more reactive Ti(OH)<sub>4</sub> gel [10, 24] used by us in the hydrothermal solution, instead of the less reactive TiO<sub>2</sub> nanopowders used by Roeder and Slamovich [21], promotes completion of the reaction, precluding the need for a large excess of reactants. Second, the higher temperature used in our work (200 °C), instead of the 80 °C used by Roeder and Slamovich [21], is also likely to promote completion of the reaction.

Figure 3 shows room-temperature Raman spectra of the various hydrothermal BST powders, including the reference BaTiO<sub>3</sub> powder obtained commercially. In the Raman spectrum of the reference BaTiO<sub>3</sub> powder (Fig. 3), the A<sub>1</sub> symmetry bands centered around 267 cm<sup>-1</sup> and 519 cm<sup>-1</sup> are assigned to transverse optical



**Fig. 3.** Raman spectra of the seven different hydrothermal  $Ba_xSr_{(1-x)}TiO_3$  powders, and a reference  $BaTiO_3$  powder obtained commercially. The characteristic peak at ~305 cm<sup>-1</sup> representing tetragonal symmetry is indicated by arrows.

modes (TO), and the band centered around 717 cm<sup>-1</sup> is assigned to longitudinal optical modes (LO) [25]. The sharp peak around 305 cm<sup>-1</sup> is assigned to the B<sub>1</sub> mode, and is characteristic of tetragonal BaTiO<sub>3</sub> [25]. The sharp peak around 305 cm<sup>-1</sup> in Fig. 3 is also observed in the hydrothermal BST powders with x=1.00 and 0.83, which provides a clear indication of the presence of the tetragonal phase in those powders. The 305 cm<sup>-1</sup> peak reduces to a shoulder for x=0.67, and it

[26, 27]) and bulk materials (see *e.g.* [28]). Figures 4A-4D show SEM micrographs of hydrothermal BST powders with compositions x=1, 0.83, 0.12, and 0. In each case the particles are observed to be uniform in size, and faceted. The average particle size for the Barich powders (x=1 and x=0.83) is ~150 nm in both

disappears for smaller x values. This is consistent with

the fact that the Curie temperature is ~20 °C (room

temperature) for a BST ceramic of composition  $x \sim 0.65$ 

[17]. Thus, we have confirmed for the first time, the

presence of the tetragonal phase in hydrothermal BST

powders. Note that Raman spectroscopy has been used

to confirm the presence of the tetragonal phase in BST

ceramics, but in non-hydrothermal thin films (see e.g.



**Fig. 4.** SEM images of  $Ba_xSr_{(1-x)}TiO_3$  powders: (A) x=1, (B) x=0.83, (C) x=0.12, and (D) x=0. All micrographs recorded at same magnification.



Fig. 5. Bright-field TEM image of Ba<sub>0.83</sub>Sr<sub>0.17</sub>TiO<sub>3</sub> powder.

cases, whereas the average particle size for the Sr-rich powders (x=0.12 and x=0) is ~80 nm in both cases. A smaller particle size in Sr-rich hydrothermal BST powders has also been reported by Roeder and Slamovich, but the reason for this effect is not clear at this time [21].

Figure 5 shows a bright-field TEM micrograph of BST powder (x=0.83), and the powder particles appear to be single-crystal. Although Raman spectroscopy confirmed this powder to be tetragonal, like XRD, electron diffraction was unable to show tetragonality in this powder. It is believed that cubic and tetragonal phases can co-exist in hydrothermal powders [11, 12, 29, 30]. However, the lack of diffraction contrast between the two phases precludes the observation of this mixture in conventional TEM.

## Summary

We have synthesized barium-strontium titanate (Ba<sub>x</sub>-Sr<sub>(1-x)</sub>TiO<sub>3</sub> or BST) powders, with x ranging from 0 to 1, by reacting a Ti(OH)<sub>4</sub> gel with Ba(OH)<sub>2</sub> and Sr(OH)<sub>2</sub> hydrothermally at 200 °C. The composition of the resulting powders, as determined by the lattice parameter (Vegard's law), was found to be richer in Sr relative to the corresponding solution composition. All powders were found to be single-phase solid-solutions, and although they were determined to be cubic using XRD, Raman spectroscopy revealed, for the first time, the presence of tetragonality in the Ba-rich hydrothermal BST powders. The mean particle sizes were found to be ~150 nm in the case of Ba-rich powders and ~80 nm in the case of Sr-rich powders.

#### References

- 1. R.A. Laudise, Chem. Eng. News 65 (1987) 30-35.
- W.J. Dawson, Am. Ceram. Soc. Bull. 67 (1988) 1673-1678.
- 3. M. Yoshimura, W.L. Suchanek, and K. Byrappa, Mater. Res. Soc. Bull. 25 (2000) 17-25.
- 4. S.S. Flaschen, J. Am. Chem. Soc. 77 (1955) 6149-6194.
- K. Kiss, J. Magder, M.S. Vukasovich, and R.J. Lockhart, J. Am. Ceram. Soc. 49 (1966) 291-299.
- K.S. Mazdiyasni, R.T. Dolloff, and J.S. Smith, J. Am. Ceram. Soc. 52 (1969) 523-529.
- 7. D. Hennings and S. Schreinmacher, J. Eur. Ceram. Soc. 9

(1992) 41-46.

- A. Chien, J.S. Speck, F.F. Lange, A. Daykin, and C.G. Levi, J. Mater. Res. 10 (1995) 1784-1789.
- P. Pinceloup, C. Courtois, A. Leriche, and B. Thierry, J. Am. Ceram. Soc. 82 (1999) 3049-3056.
- I.J. Clark, T. Takeuchi, N. Ohtori, and D.C. Sinclair, J. Mater. Chem. 9 (1999) 83-91.
- 11. S.W. Lu, B.I. Lee, Z.L. Wang, and W.D. Samuels, J. Cryst. Growth 219 (2000) 269-276.
- E. Ciftci and M.N. Rahaman, J. Mater. Sci. 36 (2001) 4875-4882.
- 13. B.W. Lee and G.S. Choi, J. Ceram. Proc. Res. 4 (2003) 151-154.
- K. Uchino, E. Sadanaga, and T. Hirose, J. Am. Ceram. Soc. 72 (1989) 1555-1558.
- B.D. Begg, E.R. Vance, and J. Nowotny, J. Am. Ceram. Soc. 77 (1994) 3186-3192.
- E.K. Akdogan and A. Safari, J. Appl. Phys. 41 (2002) 7170-7175.
- F. Jona and G. Shirane, in "Ferroelectric Crystals" (Dover Publications Inc., New York, NY, USA, 1993) p.
- T.M. Shaw, Z. Suo, M. Huang, E. Liniger, R.B. Laibowitz, and J.D. Baniecki, Appl. Phys. Lett. 75 (1999) 2129-2131.
- C.H. Lin and T.S. Yan, Mater. Res. Soc. Symp. Proc. 346 (1994) 231-236.
- S. Kormaneni, Q. Li, M. Stefansson, and R. Roy, J. Mater. Res. 8 (1993) 3176-3183.
- 21. R.K. Roeder and E.B. Slamovich, J. Am. Ceram. Soc. 82 (1999) 1665-1675.
- Powder Diffraction Files, International Centre for Diffraction Data (ICDD), Newtown Square, PA (formerly Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA), 1995.
- 23. M.M. Lencka and R.E. Riman, Ferroelect. 151 (1994) 159-164.
- 24. C.T. Xia, E.W. Shi, W.Z. Zhang, and J.K. Guo, J. Cryst. Growth 166 (1996) 961-966.
- 25. M. DiDomenico, S.H. Wemple, S.P.S. Porto, and R.P. Bauman, Phys. Rev. 174 (1968) 522-530.
- F.M. Pontes, E.R. Leite, D.S.L. Pontes, E. Longo, E.M. S. Santos, S. Mergulha, P.S. Pizani, F. Lanciotti, T.M. Boschi, and J.A. Varela, J. Appl. Phys. 91 (2002) 5972-5978.
- Y.I. Yuzyuk, R.S. Katiyar, V.A. Alyoshin, I.N. Zakharchenko, D.A. Markov, and E.V. Sviridov, Phys. Rev. B 68 (2003) 104104.
- P.S. Dobal, A. Dixit, R.S. Katiyar, D. Garcia, R. Guo, and A. S. Bhalla, Ferroelect. Lett. 29 (2002) 1-10.
- T. Takeuchi, K. Ado, T. Asai, H. Kageyama, Y. Saito, C. Masquelier, and O. Nakamura, J. Am. Ceram. Soc. 77 (1994) 1665-1668.
- 30. H. Xu and L. Gao, J. Am. Ceram. Soc. 86 (2003) 203-205.