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Short communication

Microwave-hydrothermal synthesis of barium titanate under stirring condition

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Abstract

The role of in situ stirring under microwave-hydrothermal (M-H) conditions on the synthesis of barium titanate was investigated for the first time by powder X-ray diffraction and scanning and transmission electron microscopy. Stirring under M-H conditions in the temperature range of 150–200 °C led to enhanced crystallization of Ba titanate as revealed by yields compared to the static condition. In addition, stirring led to smaller and more uniform crystals under M-H conditions compared to those crystallized without stirring. Powder X-ray diffraction revealed the formation of only cubic polymorph of Ba titanate at or below 200 °C in 4 h with or without in situ stirring under M-H conditions. These results show that stirring is an important parameter during M-H synthesis of nanophase Ba titanate.

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Keywords: Barium titanate; Cubic phase; Ferroelectric; Microwave-hydrothermal synthesis; Stirring

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1. Introduction

Barium titanate is by far the largest amount of dielectric material used in the ceramic capacitor industry. It is also a ferroelectric material with piezoelectric properties although lead zirconate titanate (PZT) replaced Ba titanate because PZT has better piezoelectric properties. Ba titanate material is widely used in multi-layer ceramic capacitors (MLCCs), piezoelectric and ferroelectric devices, positive temperature coefficient (PTC) thermistors, field-effect transistors, etc. Ba titanate has been prepared by the traditional solid-state process, sol–gel process and many other techniques including the hydrothermal process [1–3]. An excellent review of the various BT synthesis techniques was previously published [1]. Among these, the hydrothermal process is ideally suited for preparing nanopowders of Ba titanate (BT) and in fact, hydrothermally produced BT has been commercially sold [4] for several years. Nanophase Ba titanate is a necessity for making compact MLCCs. The main advantages of the hydrothermal process are (a) it is a low temperature process, (b) it is an environmentally benign process as the processing is done under closed system conditions and (c) it is easy to control the size and shape of the particles. The conventional-hydrothermal process has been extensively used in single crystal as well as powder preparation for over a century because of the above advantages [5,6]. Over the years, there are a few modifications to the conventional-hydrothermal (C-H)

Table 1
Microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) syntheses of $BaTiO_3$.[a]

Reaction	Yield[b] (%) of $BaTiO_3$	
	No stirring	Stirring at 157 rpm
M-H 150 °C—10 min	90.7	96.4
M-H 150 °C—60 min	91.3	97.7
M-H 180 °C—10 min	86.7	91.9
M-H 180 °C—30 min	89.5	94.5
M-H 180 °C—120 min	95.9	96.4
M-H 200 °C—15 min	93.1	97.2
M-H 200 °C—2 h	–	97.4
M-H 200 °C—4 h	–	97.9
C-H 200 °C—24 h	96.6	–
C-H 200 °C—48 h	97.2	–

[a] Only cubic phase formed in all cases.
[b] Yield (%) is calculated as the weight ratio of product obtained to that expected upon complete crystallization.

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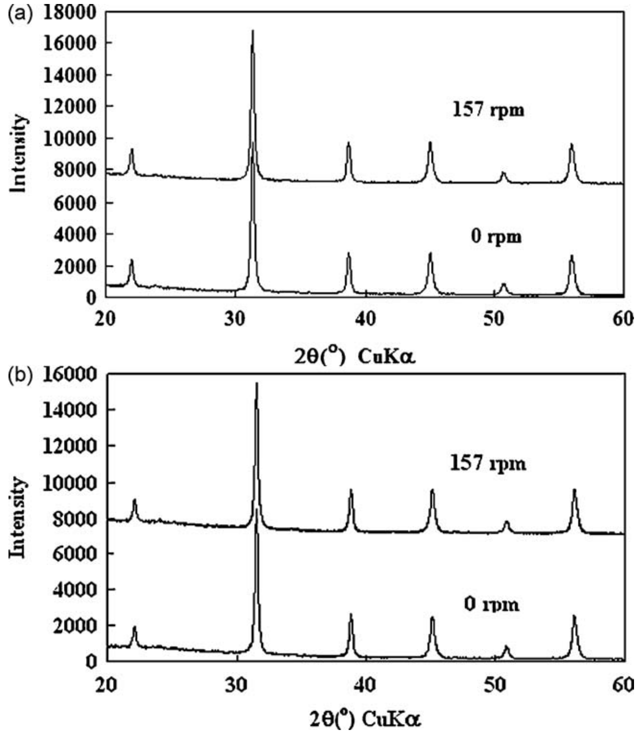

Fig. 1. XRD patterns of $BaTiO_3$ powder prepared at 150 °C (a) and 200 °C (b) for 4 h with and without stirring using microwave-hydrothermal process.

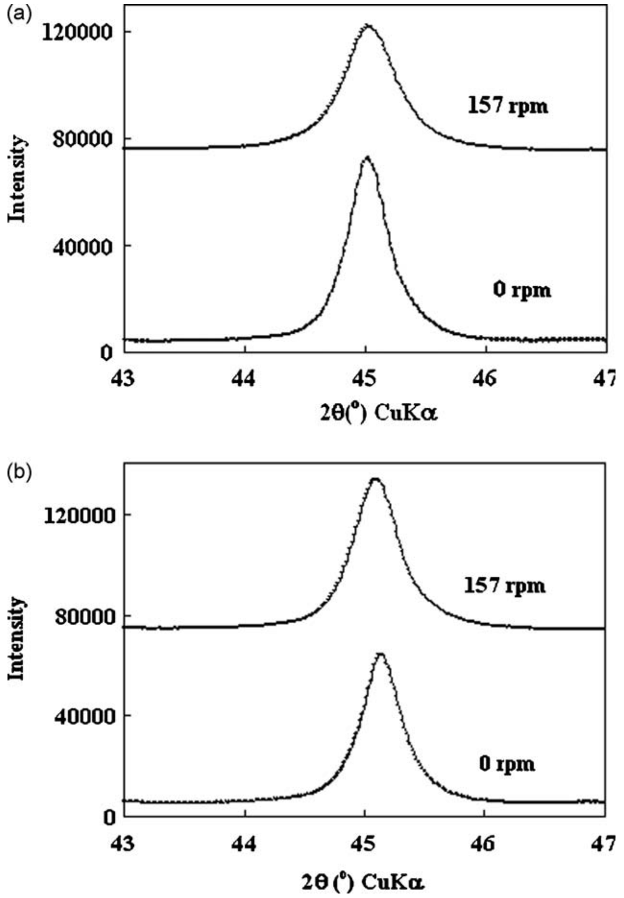

Fig. 2. (0 0 2) XRD pattern of cubic $BaTiO_3$ prepared at 150 °C (a) and 200 °C (b) for 4 h with and without stirring treatment under microwave-hydrothermal conditions.

process involving the addition of microwave [7], electric [8], and ultrasonic [9] fields to the hydrothermal vessels to enhance the reaction rates. Among these, the addition of microwaves to the hydrothermal system became popular starting in the eighties and the term ''microwave-hydrothermal'' (M-H) process was coined by us and documented in a publication in 1992 [7]. Although C-H process was used for the synthesis of Ba titanate as early as in 1970 [10–13], the M-H process was used by us for the first time in 1992 [7], which led to the synthesis of 100–200 nm Ba titanate particles. Subsequent studies by us and others [14–18] optimized the M-H process for Ba titanate synthesis. One of the disadvantages of the M-H process is the aggregation of particles because of extremely rapid crystallization [7,19,20] if no stirring or mixing was applied during synthesis. All the Ba titanate syntheses to date by the M-H process were done without stirring during the reaction [13–18] because stirred M-H reactors were not available until recently. With the advent of stirred M-H reactors, it would be useful to see the role of stirring on the M-H synthesis of Ba titanate because one recent study [21] showed that nanophase $BaTiO_3$ powders with narrow size distribution and high tetragonality could be synthesized by the rotary-hydrothermal process where the contents were mixed during C-H reaction. Thus the objective of this study was to investigate the

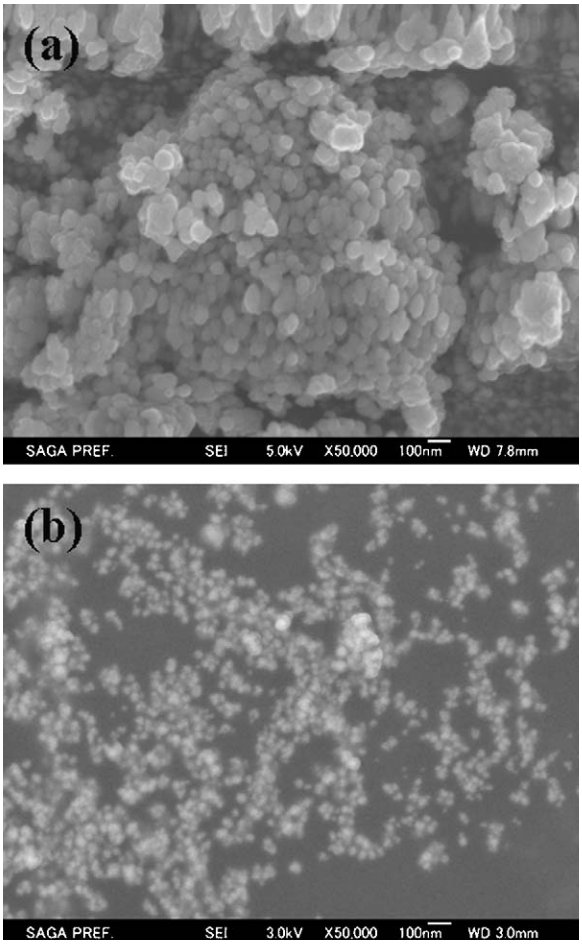

Fig. 3. Scanning electron micrographs showing the effect of stirring on the morphology of $BaTiO_3$ particles prepared at 180 °C for 4 h: (a) without stirring and (b) with stirring of 157 rpm.

role of stirring on synthesis of Ba titanate particles during M-H process.

2. Experimental

A microwave digestion system (model MARS 5, CEM Corp., Matthews, NC) was used to conduct the M-H reactions. $BaTiO_3$ powders were prepared from 0.6361 g (7.9×10^{-3} mol) of TiO_2 (Anatase type, ST01, Ishihara Sangyo Ltd., Japan) and 1.3695 g (7.99×10^{-3} mol) of $Ba(OH)_2$ (Special grade, Wako Pure Chemical Ltd., Japan) and 15 ml of pure water. Molar ratio of Ba/Ti was 1. The mixture was treated at 150, 180 and 200 °C for 10 min to 4 h in a vessel lined with Teflon^{TM} (Dupont, Wilmintong, DE). The

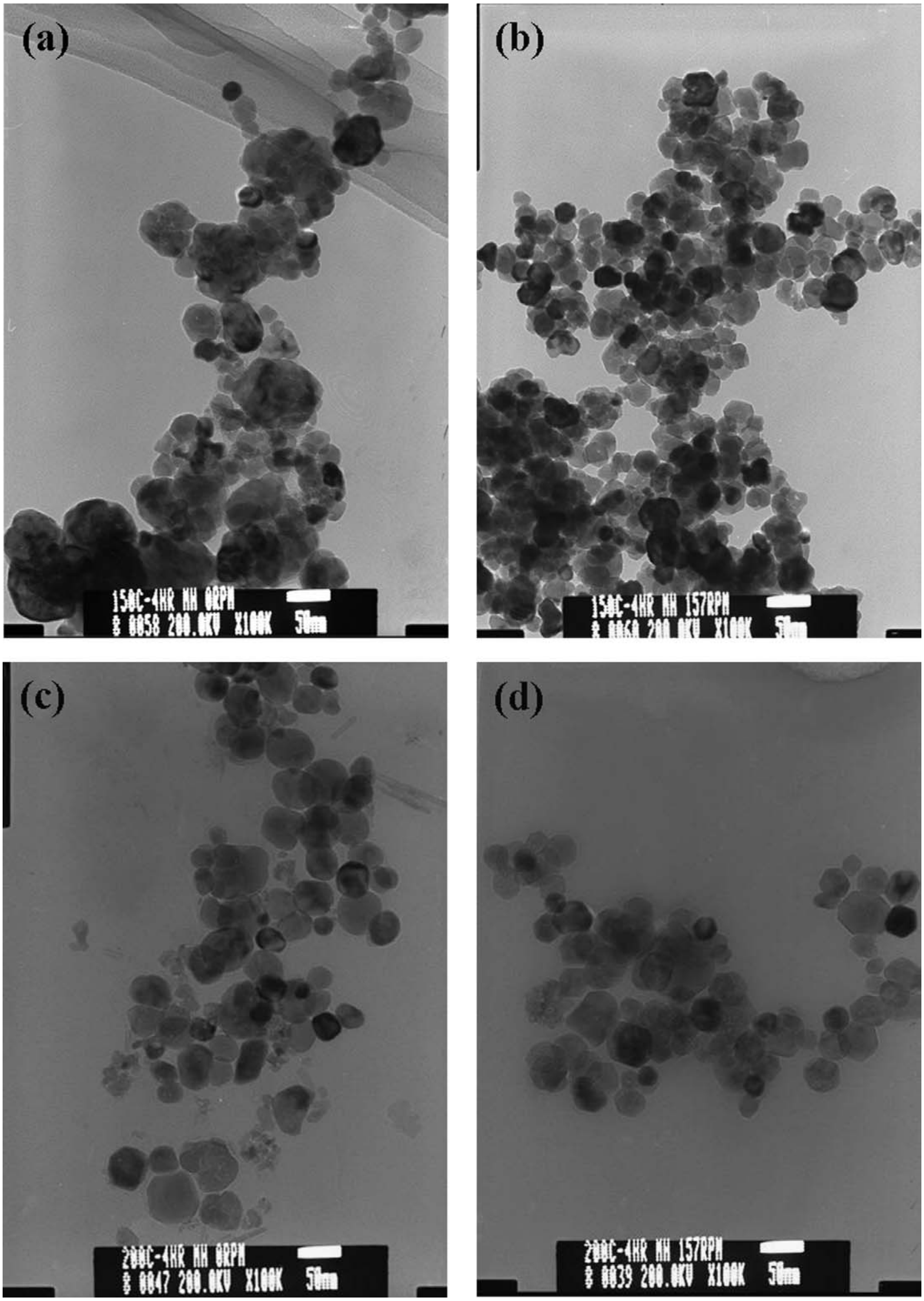

Fig. 4. Transmission electron micrographs showing the effect of stirring on the morphology of $BaTiO_3$ particles prepared at 150 and 200 °C for 4 h: (a) 150 °C without stirring, (b) 150 °C with 157 rpm, (c) 200 °C without stirring, and (d) 200 °C with 157 rpm.

system operated at a frequency of 2.45 GHz and could operate at 0–100% full power with 600 W. The temperature of the system was controlled using an in-vessel temperature sensor (Model EST-300, CEM Corp., Matthews, NC). The effect of the agitation of the reactant mixture on the formation of $BaTiO_3$ powder was also investigated using a small stirrer with 157 rpm in the vessel. The mixture powder of TiO_2 (0.6361 g) and $Ba(OH)_2$ (1.3695 g) was placed inside a Teflon vessel with a small stirrer and mixed with 15 ml of water before M-H reaction. The vessel was set up in the microwave digestion system and the stirring with 157 rpm was carried out during microwave irradiation. The C-H reactions were carried out in Teflon^{TM}-lined steel vessels of 50 ml capacity at 180 and 200 °C for 30 min to 48 h without stirring. The vessel was introduced into a drying oven that was preheated at 180 and 200 °C.

After the hydrothermal reactions, the samples were thoroughly washed with pure water, and then dried at 70 °C. The percent $BaTiO_3$ powder was calculated from the expected amount of $BaTiO_3$ from the complete reaction of TiO_2 and $Ba(OH)_2$. The crystalline phases were analyzed by powder X-ray diffraction (XRD) with a model X'Pert-MRD (PANalytical Co., Japan) using Cu Kα radiation. The morphology and particle size were determined by a field emission scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan) on samples coated with very thin carbon and transmission electron microscope (TEM; Model 2010, JEOL, Tokyo, Japan).

3. Results and discussion

Table 1 presents all the Ba titanate synthesis results under microwave-hydrothermal (M-H) and conventional-hydrothermal (C-H) conditions with and without stirring at different temperatures. Powder XRD results (Table 1 and Fig. 1) at all temperatures with and without microwaves and with and without stirring showed the crystallization of cubic Ba titanate with trace amount of Ba carbonate, the latter as expected, especially at lower temperatures and durations of treatment because of incomplete reaction. No tetragonal phase of Ba titanate could be detected in any of the samples treated under all conditions including C-H conditions of 200 °C for 24–48 h (Table 1). Stirring of contents under M-H conditions led to two main advantages compared to samples prepared without stirring: (a) the yields of Ba titanate are higher at all temperatures with stirring compared to without stirring and (b) the peaks of Ba titanate showed broadening with stirring compared to without stirring (Fig. 2). Stirring led to higher yields (Table 1) under M-H conditions because of more complete reaction of the components, as expected. Stirring resulted in broader XRD peaks (Fig. 2) because of smaller but uniform crystal size as has been observed by Kubo et al. [21] under C-H conditions. The broadening of peaks occurred even at low theta angles but could not be seen in Fig. 1 because of compression of the XRD patterns but can be clearly seen in Fig. 2 which shows XRD peaks at higher angles on an expanded scale. X-ray diffraction patterns in the 2θ range of 44–46° of $BaTiO_3$ powders (Fig. 2) did not show any splitting of (0 0 2) and (2 0 0) peaks, which suggests that the Ba titanate phase is cubic, not tetragonal [21]. However, it is anticipated that tetragonal phase would form either at higher temperatures or much longer durations under stirring [21] than were used in this study. Our M-H system, unfortunately, did not permit us to use either higher temperatures or much longer durations.

Morphology and crystal size of differently treated samples were observed by SEM (Fig. 3) and TEM (Fig. 4). Scanning electron micrographs of Ba titanate samples synthesized at 180 °C clearly showed that stirring led to well-dispersed and smaller crystals on the order of about 30 nm (Fig. 3b) while static condition, i.e., without stirring yielded aggregated and larger crystals of 60–100 nm. Transmission electron micrographs of Ba titanate samples synthesized at 150 °C clearly showed that stirring led to better dispersed crystals (Fig. 4b) compared to static M-H condition (Fig. 4a). Similarly, Ba titanate samples crystallized at 200 °C showed that stirring had led to better dispersed crystals (Fig. 4d) compared to static (no stirring) M-H condition (Fig. 4c). The crystal size was smaller and more uniform with stirring at 150 °C compared to samples prepared with no stirring (Fig. 4a and b). At 200 °C under stirring, the crystals were not only more uniform but well-faceted (Fig. 4d) compared to the crystals prepared under M-H conditions without stirring (Fig. 4c). Thus stirring under M-H conditions clearly affected the yields, size of particles and their uniformity.

4. Conclusions

Stirring under microwave-hydrothermal (M-H) conditions led to smaller and more uniform Ba titanate crystals compared to those prepared under static (no stirring) conditions under otherwise similar conditions. Stirring under M-H conditions also led to better yields of Ba titanate compared to those prepared under no stirring conditions.

References

[1] P.P. Pule, S.H. Risbud, J. Mater. Sci. 25 (1990) 1169–1183.
[2] J.O. Eckert Jr., C.C. Hung-Houston, B.L. Gersten, M.M. Lencka, R.E. Riman, J. Am. Ceram. Soc. 90 (1996) 311–314.
[3] B. Li, X. Wang, L. Li, Mater. Chem. Phys. 78 (2002) 292–298.
[4] J.A. Kenchner (Cabot Corp.), U.S. Patent 6,129,930 (2000).
[5] S. Komarneni, E. Fregeau, E. Breval, R. Roy, J. Am. Ceram. Soc. Commun. 71 (1988), C-26–C-28.
[6] S. Komarneni, Curr. Sci. 85 (2003) 1730–1734.
[7] S. Komarneni, R. Roy, Q.H. Li, Mat. Res. Bull. 27 (1992) 1393–1405.
[8] R. Bacsa, P. Ravindranathan, J.P. Dougherty, J. Mater. Res. 7 (1992) 423–428.
[9] P.E. Meskin, A.Ye. Barantchikov, V.K. Ivanov, E.V. Kisterev, A.A. Burukhin, B.R. Churagulov, N.N. Oleynikov, S. Komarneni, Yu.D. Tretyakov, Doclady Chem. 389 (2003) 207–210.
[10] A.N. Christensen, Acta Chem. Scand. 24 (1970) 2447–2452.
[11] T.R. Kutty, R. Vivekanandan, P. Murugaraj, Mater. Chem. Phys. 19 (1988) 533–546.
[12] S. Venigalla, D.J. Clancy, D.V. Miller, J.A. Kerchner, S.A. Costantine, Am. Ceram. Soc. Bull. 78 (1999) 51–54.
[13] P.K. Dutta, J.R. Gregg, Chem. Mater. 4 (1992) 843–846.

[14] S. Komarneni, Q. Li, K.M. Stefansson, R. Roy, J. Mater. Res. 8 (1993) 3176–3183.
[15] S.-F. Liu, I.R. Abothu, S. Komarneni, Mater. Lett. 38 (1999) 344–350.
[16] B. Newalkar, S. Komarneni, H. Katsuki, Mater. Res. Bull. 36 (2001) 2347–2355.
[17] Y. Ma, E. Vileno, S.L. Suib, P.K. Dutta, Chem. Mater. 9 (1997) 3023–3031.
[18] E.K. Nyutu, C.-H. Chen, P.K. Dutta, S.L. Suib, J. Phys. Chem. C 112 (2008) 9659–9667.
[19] S. Komarneni, Q.H. Li, R. Roy, J. Mater. Chem. 4 (1994) 1903–1906.
[20] S. Komarneni, V.C. Menon, Q.H. Li, R. Roy, F.W. Ainger, J. Am. Ceram. Soc. 79 (1996) 1409–1412.
[21] T. Kubo, M. Hogiri, H. Kagata, A. Nakahira, J. Am. Ceram. Soc. 91 (2008) 1–5.