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Ceramics International 38 (2012) 1585–1589

CERAMICS INTERNATIONAL

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Low temperature synthesis and dielectric, ferroelectric and piezoelectric study of microwave sintered $BaTiO_3$ ceramics

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Received 10 August 2011; received in revised form 22 September 2011; accepted 23 September 2011
Available online 17 October 2011

Abstract

Barium titanate ($BaTiO_3$/BT) ferroelectric system was synthesized in single perovskite phase at low temperature by using powders derived from modified solid state reaction (MSSR) and sintered by microwave (MW) processing routes. Conventional calcination temperature was optimized at 900 °C for 4 h. MW sintering of BT samples was carried out at 1100 °C for 30 min to get dense (98% density) ceramics. Room temperature (RT) dielectric constant (ε_r) and dielectric loss (tan δ) at 1 kHz frequency of MW sintered BT samples was found to be ~2500 and 0.03, respectively. Saturated polarization vs. electric field (*P*–*E*) loops with remnant polarization (P_r) ~6 μC/cm^2 and coercive field (E_c) ~1.45 kV/cm confirmed the ferroelectric nature of MW sintered BT samples. Piezoelectric coefficient from strain vs. electric field (*S*–*E*) loops study was found to be 335 pm/V.

Keywords: C. Dielectric properties; $BaTiO_3$; Solid state reaction; Microwave; Ferroelectric; *S*–*E* loop

1. Introduction

Barium titanate ($BaTiO_3$/BT) is one of the most extensively investigated ferroelectric system because of its promising electrical, chemical and mechanical properties [1–3]. Also, the BT based normal ferroelectrics are strong candidates for field-induced piezoelectric transducers due to their large polarizations, large permittivity and the large induced strains achievable in these materials. Being a lead free ferroelectric ceramic, BT is an environmentally friendly material, thus making it a good candidate for various applications such as capacitors, positive temperature coefficient resistors, high-density optical data storage, ultrasonic transducer, piezoelectric devices and semiconductors [4]. Traditionally BT is prepared by solid state reaction (SSR) route at relatively high processing temperatures using oxide/carbonate powder precursors. However, BT powders thus obtained exhibit high impurity contents caused by grinding and repetitive calcinations required to circumvent lower chemical reactivity [2]. The main application of BT based ceramics is in multilayer ceramic capacitors (MLCC) [5]. In order to use low-cost base metal electrodes, such as Ni and Cu, to replace the more expensive Ag–Pd system inner electrode in BT based MLCC's, the BT based compounds must be sintered at a temperature low enough to prevent electrode oxidation and melting [5–7]. Unfortunately, lowering the sintering temperature may result in a significant decrease in the ε_r. Many low temperature syntheses processes like wet chemical methods such as sol gel, oxalate process, hydrolysis of BT alkoxides and MW assisted hydrothermal reduction techniques have been reported in the literature [8]. But, these methods are complex and require high purity expensive precursor chemicals. Both wet chemical and solid state reaction (SSR) routes have relative advantages and disadvantages over each other. Therefore, it is imperative to devise a novel method to combine the advantages of both these routes to synthesize BT ceramic at low temperature and with relatively cheaper precursors. The performance of BT ceramics significantly depends on the microstructure of sintered material [9]. The literature data mainly reports the preparation of BT system by SSR and wet chemical routes [3,10–12]. The microwave processing of ceramics can be utilized as an alternative

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doi:10.1016/j.ceramint.2011.09.045

approach with potential advantages such as rapid heating, penetrating radiation, more uniform microstructure and hence higher density [13–19]. In conventional furnace, it requires generally rather long time for sintering of ceramics and consumes lot of energy and still high densification is difficult to achieve. These disadvantages could be avoided by using microwave processing of ceramics. An important feature of microwave sintering is the heating of the sample from inside to out, this could change the microstructure and this may improve the dielectric properties [20–22].

Therefore, in the present work, MSSR processed BT ceramics were sintered using MW heating. The synthesized powders were characterized for their morphology; and the sintered samples were characterized for their dielectric, ferroelectric and mechanical properties using standard methods.

2. Experimental procedure

Barium titanate (BT) samples were fabricated by the combination of modified solid state reaction (MSSR) and microwave (MW) heating routes. In MSSR route, barium acetate hydrate and fumed titanium oxide (all from Aldrich, USA) were used as precursors along with 2-methoxyethanol as solvent and acetic acid as catalyst. Barium acetate was dissolved and transparent solution was prepared using 2-methoxy ethanol as the solvent and acetic acid as the catalyst. Finally, the stoichiometric proportion of titanium oxide was mixed in the transparent solutions and stirred for 4 h. This solution was dried, and dry cake was crushed in a mortar with pestle. A thermo gravimetric analysis (TGA) was conducted and from this, the annealing temperature was identified as ~900 °C. Calcination of BT powder was carried out at 900 °C for 4 h and single perovskite phase formation was confirmed by X-ray diffractometry (XRD). The calcined powders were mixed thoroughly with 2 wt.% polyvinyl alcohol (PVA) and pressed into disks of diameter ~10 mm and thickness ~1.5 mm under ~60 MPa pressure. The microwave sintering of the sample was carried out at 1100 °C for 30 min with a heating rate of 25 °C/min by placing the pellets in the centre of a 4.4 kW, 2.45-GHz multi mode microwave cavity. A schematic diagram of microwave sintering system is shown in Fig. 1. The sample temperature in the microwave furnace was monitored by using a Raytek non-contact sensor (XRTG5). For phase identification of the sintered samples, XRD analysis of the pellets were performed using PW 3020 Philips diffractometer equipped with Cu K_α ($\lambda = 0.15405$ nm) radiation. The sintered microstructures were observed using JEOL T-330 scanning electron microscope (SEM). Silver paste was applied on both sides of the samples for the electrical measurements. Dielectric constant (ε_r) and dielectric loss (tan δ) were measured as a function of temperature at different frequencies using computer interfaced HIOKI 3532-50 LCR-HITESTER. A conventional computer interfaced Sawyer–Tower circuit was used to measure the polarization vs. electric field (*P*–*E*) hysteresis loops at 20 Hz frequency. The strain vs. electric field (*S*–*E*) and piezoelectric properties (namely the d_{33} coefficients) were measured using the MTI-2000 potonic sensor (Radiant Technologies).

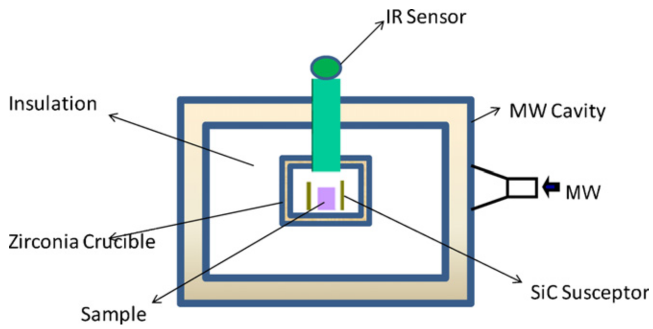

Fig. 1. Schematic diagram of microwave sintering system.

3. Results and discussions

Fig. 2 shows the TGA/DSC graphs of MSSR processed BT powder. A weight loss of ~10.23% was observed up to 200 °C, which is attributed to the evaporation of absorbed water and solvent. Further a large weigh loss of ~16% around 300 °C is due to the decomposition of acetyl and bonded alkyl groups and their combustion [23]. The weight loss at around 800 °C (5.65%) is due to the decomposition of residual $BaCO_3$. There was no weight loss over 900 °C, indicating the calcination temperature to be ~900 °C.

Fig. 3 shows the room temperature (RT) XRD patterns of MSSR processed BT powders calcined at 800 and 900 °C for 4 h, respectively. XRD peaks confirm single perovskite phase at 900 °C, which is significantly lower than the same system processed through SSR route [3,11]. Low calcination temperature in BT samples synthesized by MSSR route can be attributed to the fine particle size of the precursors. In MSSR route, the particle size of the precursors used is lower than the size of the precursors used in SSR route. Since, lower is the particle size higher is the ratio of surface area to volume. Therefore, we can summarize following reasons for the

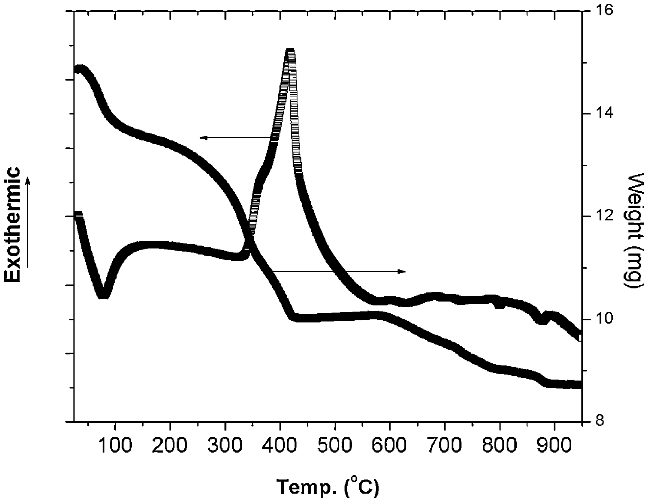

Fig. 2. TGA/DSC graph of dried BT powder obtained from MSSR route.

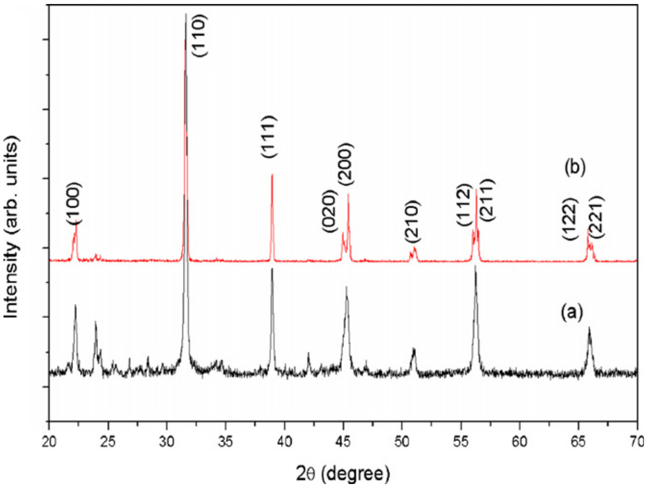

Fig. 3. XRD patterns of BT samples synthesized by MSSR route and calcined at (a) 800 and (b) 900 °C.

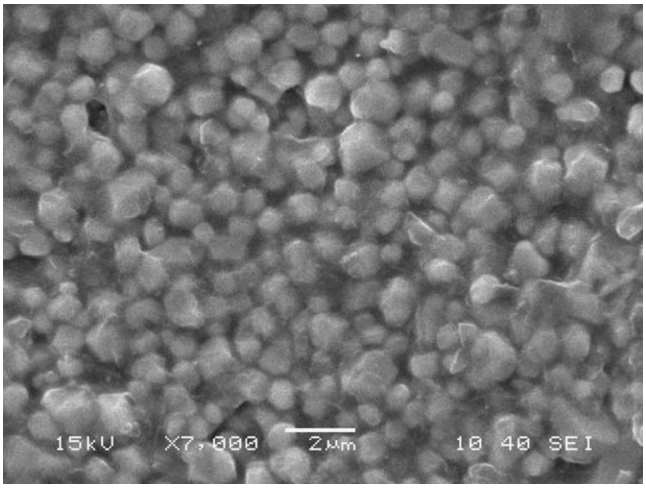

Fig. 4. SEM micrographs of MW sintered BT samples.

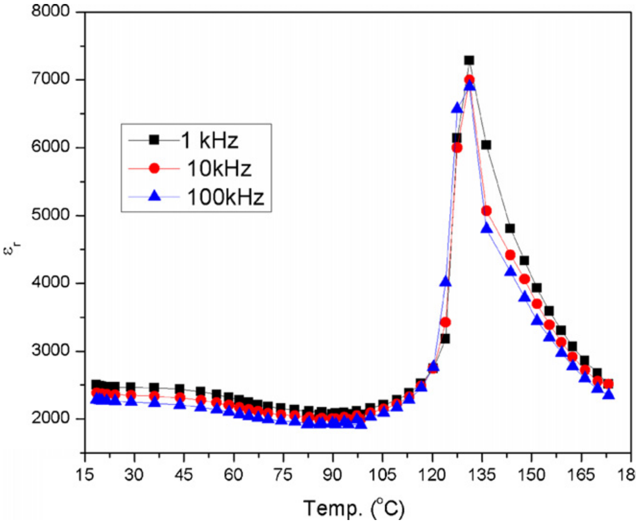

Fig. 5. Variation of ε_r at different frequencies with temperature of MW sintered BT samples.

increase in rate of reaction with the decrease in particle size: (i) increasing the surface area to volume ratio of the reactants results in a higher number of reaction sites. (ii) Increasing the number of reaction sites increases the number of total collisions. (iii) If the frequency of effective collisions increases, so does the reaction rate, which results in lowering of processing temperature. Also, surfaces are higher energy regions, and they will always act to minimize their area, and thus lower their energy whenever possible [24], which lead to lower calcinations temperature in MSSR processed BT powder. The XRD lines of MW sintered BT samples are indexed in different crystal structures using a computer program package 'Powdmult' [25]. Standard deviation (SD), $\Sigma\Delta d(=d_{\text{obs}} - d_{\text{cal}})$, where '$d$' is inter-plane spacing, is found to be minimum for tetragonal crystal structure with c/a ratio given in Table 1.

Fig. 4 depicts the surface micrographs of MW sintered BT samples. Pore free uniform microstructure with grain size ~1.45 μm, estimated by the linear intercept method, are observed. Density, measured by Archimedes method (given in Table 1) is found to be higher than the earlier reported BT samples processed through different techniques [15–17,26]. This confirms the advantage of processing BT ceramics through MSSR route and sintering by MW technique.

Fig. 5 shows the temperature variation of ε_r at different frequencies (1–100 kHz) of MW sintered BT samples. RT ε_r and dielectric loss (tan δ) at 1 kHz frequency of MW sintered BT samples are found to be ~2500 and 0.03, respectively. The value of ε_r is much higher and the value of tan δ is much lower than the same system synthesized earlier by MW process and solid state reaction route by Thakur et al. [15]. Higher value of ε_r of BT samples fabricated in our study can be attributed to uniform and dense microstructure (Fig. 4), higher density and better crystallinity than the earlier reports on BT system [1,2,15,24]. Lower value of tan δ indicates that the synthesize powder was almost defect/impurity free. Values of ε_r at different frequencies increase with the increase in temperature and transition temperature (T_c) is found to be around ~128 °C. In general, for any material ε_r at different frequencies increases with the increase in temperature and, is influenced by dipolar, electronic, ionic and interfacial polarizations [27]. Interfacial polarization increases due to the creation of crystal defects and

Table 1
Different parameters of MW sintered BT ceramics.

System	Structure	Density (g/cm^3)	Grain Size (μm)	ε_r at 1 kHz	tan δ at 1 kHz	P_r (μC/cm^2)	d_{33} (pm/V)
BT	Tetragonal $c = 4.0225$ Å $a = 3.9817$ Å $c/a = 1.0102$	6.02	1.45 μm	2500	0.03	6	335

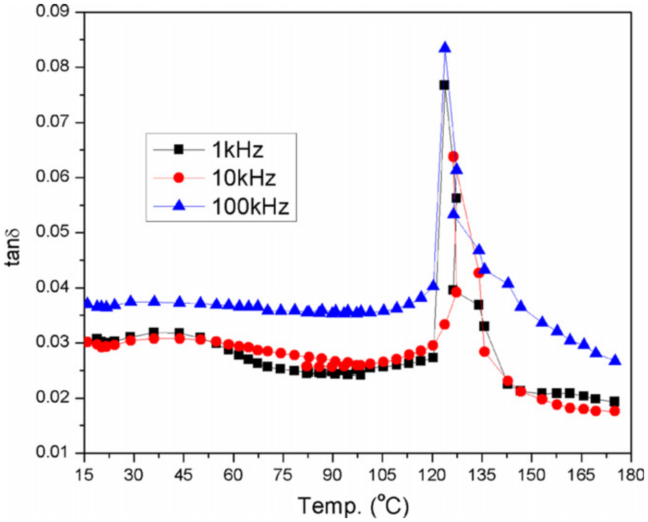

Fig. 6. Variation of tan δ at different frequencies with temperature of MW sintered BT samples.

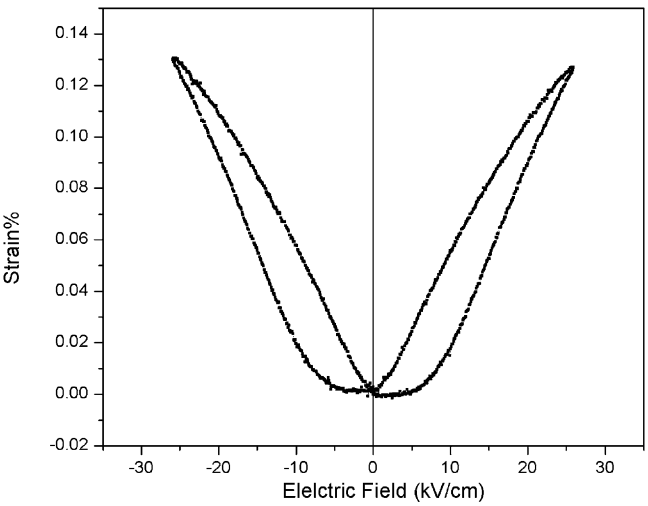

Fig. 8. Strain vs. bipolar electric field loop of BT samples.

dipolar polarization decreases due to the increase in randomness of the dipoles with temperature. However, the temperature effect on ionic and electronic polarizations is very small [28]. The increase in ε_r with temperature suggests an increase in interfacial polarization. The value of T_c is higher in our study than the earlier reports on BT system [15]. The value of c/a ratio (given in Table 1) is also little higher in our study than earlier reports [15], which also justifies the higher value of the Curie temperature (T_c) as compared to the earlier studies of conventional and MW processed BT samples. Fig. 6 shows the temperature variation of tan δ at different frequencies (1–100 kHz) of MW sintered BT samples. From RT to 120 °C the value of tan δ at different frequencies (1 kHz–100 kHz) remains lower than 0.04. This can be explained on the basis of better densification of MW sintered BT ceramic samples [29]. The temperatures of peak ε_r and tan δ do not coincide up to 100 kHz frequencies. Kramers–Kronig relation indicates that this can be the consequence of temperature dependent relaxation near Curie temperature [30].

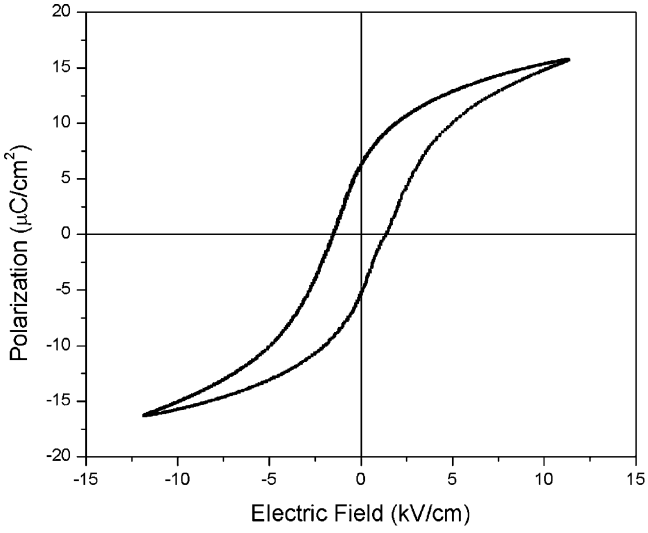

Fig. 7. *P–E* Hysteresis loops of MW sintered BT samples.

Fig. 7 shows the *P–E* hysteresis loop of MW sintered BT samples. Development of saturated *P–E* hysteresis loops confirms the ferroelectric nature of the MW sintered BT samples. The sharpness of the *P–E* hysteresis loop indicates the better homogeneity and crystallinity of the prepared system [2]. Values of remnant polarization (P_r) and coercive filed (E_c) of MW sintered BT samples are ~6 μC/cm^2 and 1.45 kV/cm. These values are in agreement with the earlier reports on BT system [15]. Decrease in E_c in MSSR and MW processed BT ceramics compared to the ceramics synthesized by other routes hints towards the low field poling process and improvement in the piezoelectric properties [15,31].

Fig. 8 shows the development of *S–E* butterfly loop with a max. strain ~0.13% at ~25 kV/cm electric field, which confirms the piezoelectric nature of the MSSR and MW processed BT samples [32]. Piezoelectric coefficient, d_{33}, has also been calculated from converse piezoelectric effect, i.e. by using the slope of the *S–E* plot in the higher field region, using the relation [33].

$$d_{33} = \frac{\Delta\text{strain}\%}{\Delta\text{electric field at higher side}}$$

The d_{33} piezoelectric coefficient calculated from the slope of *S–E* plot is found to be 335 pm/V. The very high value of d_{33} piezoelectric coefficient in MSSR and MW processed BT samples suggests the importance of this system for piezoelectric applications.

4. Conclusions

Highly dense BT ceramics with high value of dielectric constant and better piezoelectric properties were fabricated at significantly lower processing temperature and time by combining modified solid state reaction (MSSR) and MW processing techniques. MW sintering was carried out at

1100 °C for 30 min, which is significantly lower than conventional sintering process. Presence of pore free, uniform and homogeneous microstructure and higher density suggested the advantage of using MW sintering method over conventional processing. Decrease in E_c in MW sintered BT ceramics hints towards the easy poling process and improvement in the piezoelectric properties. A maximum strain ~0.13% at 25 kV/cm and appearance of butterfly shaped S–E loop confirmed the piezoelectric nature of the material. Higher density, lower processing time and temperature with good dielectric and piezoelectric properties signify the importance of MSSR and MW processed BT ceramics for MLCC and piezoelectric applications.

References

[1] B. Jaffe, W.R. Cook, Piezoelectric Ceramics, Academic Press, London, U.K., 1971.

[2] G.H. Heartling, Ferroelectric ceramics: history and technology, J. Am. Ceram. Soc. 82 (1999) 797.

[3] B.D. Stojanovic, V.R. Mastelaro, C.O. Paiva Santos, J.A. Varela, Structure study of donor doped barium titanate prepared from citrate solutions, Sci. Sintering 36 (2004) 179.

[4] D. Hennings, Barium titanate ceramic materials for dielectric use, Int. J. High Technol. Ceram. 3 (1987) 91.

[5] C.C. Lin, W.C.J. Wei, C.Y. Su, C.H. Hsueh, Oxidation of Ni electrode in $BaTiO_3$ based multilayer ceramic capacitor (MLCC), J. Alloys Compd. 485 (1–2) (2009) 653.

[6] H. Kishi, Y. Mizuno, H. Chazono, Base-metal electrode-multilayer ceramic capacitors: past present and future perspectives, Jpn. J. Appl. Phys. 42 (2003) 1.

[7] Y. Sakabe, Multilayer ceramic capacitors, Curr. Opin. Solid State Mater. Sci. 2 (5) (1997) 584.

[8] S. Ghosh, S. Dasgupta, A. Sen, H. Sekhar Maiti, Synthesis of barium titanate nanopowder by a soft chemical process, Mater. Lett. 61 (2007) 538.

[9] G.S. Pozan, İ. Boz, Crystalline $BaTiO_3$ synthesis by ultrasound and microwave-assisted sol–gel process, Can. J. Chem. Eng. 88 (1) (2010) 76.

[10] A. Beauger, J.C. Mutin, J.C. Niepce, Synthesis reaction of metatitanate $BaTiO_3$. Part 1. Effect of the gaseous atmosphere upon the thermal evolution of the system barium carbonate-titanium dioxide, J. Mater. Sci. 18 (1983) 3041.

[11] J. Bera, S.K. Rout, On the formation mechanism of $BaTiO_3$–$BaZrO_3$ solid solution through solid-oxide reaction, Mater. Lett. 59 (2005) 135.

[12] D.F.K. Hennings, B. Schreinemacher, H. Schreinemacher, High-permittivity dielectric ceramics with high endurance, J. Eur. Ceram. Soc. (1994) 81.

[13] C.T. Hu, et al., Effect of SiO_2 sintering aids on high critical temperature positive temperature coefficient of resistivity properties of $(Pb_{0.6}Sr_{0.3}Ba_{0.1})TiO_3$ materials prepared by microwave sintering technique, Jpn. J. Appl. Phys. 37 (1) (1998) 186.

[14] E.T. Thostenson, T.W. Chen, Microwave processing: fundamentals and applications, Compos. Part A 30 (1999) 1055.

[15] O.P. Thakur, C. Prakash, D. Agrawal, Structural and electrical properties of microwave-processed $BaTiO_3$ ceramic, Int. J. Ceram. Process. Res. 3 (2) (2002) 75.

[16] O.P. Thakur, C. Prakash, D. Agrawal, Dielectric behavior of $Ba_{0.95}Sr_{0.05}TiO_3$ ceramics sintered by microwave, Mater. Sci. Eng. B 96 (2002) 221.

[17] O.P. Thakur, C. Prakash, D. Agrawal, Microwave synthesis and sintering of $Ba_{0.95}Sr_{0.05}TiO_3$, Mater. Lett. 56 (2002) 970.

[18] M. Fu, D. Agrawal, Y. Fang, Microstructure and electrical properties of microwave-sintered PTC thermistors, J. Microwave Power Electromagn. Energy 40 (3) (2007) 133.

[19] C.Y. Fang, C. Wang, A.V. Polotai, D.K. Agrawal, M.T. Lanagan, Microwave synthesis of nano-sized barium titanate, Mater. Lett. 62 (2008) 2551.

[20] C. Masingboon, P. Thongbai, S. Maensiri, T. Yamwong, S. Seraphin, Synthesis and giant dielectric behavior of $CaCu_3Ti_4O_{12}$ ceramics prepared by polymerized complex method, Mater. Chem. Phys. 109 (2008) 262.

[21] W.P. Chen, W. Xiang, M.S. Guo, W.C. You, X.Z. Zhao, H.L.W. Chan, Hydrogen-induced degradation in $CaCu_3Ti_4O_{12}$ ceramics, J. Alloys Compd. 422 (2006) L9.

[22] S. Gopalan, A.V. Virkir, Interdiffusion and Kirkendall effect in doped $BaTiO_3$–$BaZrO_3$ perovskites: effect of vacancy supersaturation, J. Am. Ceram. Soc. 82 (1999) 2887.

[23] S. Tangwiwat, S.J. Milne, Barium titanate sols prepared by a diol-based sol–gel route, J. Non-Cryst. Solids 351 (2005) 976.

[24] A.J. Moulson, J.M. Herbert, Electroceramics, Chapman and Hall, London, NY, 1992.

[25] E. Wu, POWD, an interactive powder diffraction data interpretation and indexing program, Ver. 2.1, School of Physical Science, Finder's University of South Australia, Bedford Park.

[26] M.M. Vijatovic, B.D. Stojanovic, J.D. Bobic, T. Ramoska, P. Bowen, Properties of lanthanum doped $BaTiO_3$ produced from nanopowders, Ceram. Int. 36 (2010) 1817.

[27] A.K. Singh, T.C. Goel, R.G. Mendiratta, O.P. Thakur, C. Prakash, Dielectric properties of Mn-substituted Ni–Zn ferrites, J. Appl. Phys. 91 (2002) 6626.

[28] C. Kittel, Introduction to Solid State Physics, Wiley, New York, 1995.

[29] P. Pakawanit, S. Ananta, Influence of sintering temperature on densification and microstructure of $Zn_3Nb_2O_8$ ceramics derived from nanopowders, Adv. Mater. Res. 656 (2011) 194.

[30] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Clarendon Press, Oxford, 1977.

[31] D. Lin, K.W. Kwok, Structure and electrical properties of $Bi_{0.5}Na_{0.5}TiO_3$–$Y_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$ lead-free piezoelectric ceramics, J. Mater. Sci.: Mater. Electron. 21 (3) (2010) 291.

[32] P. Kumar, S. Sharma, S. Singh, O.P. Thakur, C. Prakash, T.C. Goel, Structural and electrostrictive behaviour in PMN-PT (68:32) ceramics, Ferroelectrics 326 (2005) 55.

[33] K. Uchino, Ferroelectric Devices, Marcel Dekker, New York, 2000.