J Electroceram (2009) 22:125–130
DOI 10.1007/s10832-008-9441-2

Microwave processing of electroceramic materials and devices

Chris Y. Fang · Clive A. Randal · Michael T. Lanagan · Dinesh K. Agrawal

Received: 15 March 2007 / Accepted: 6 February 2008 / Published online: 19 March 2008

Abstract Microwave synthesis of nano-sized $BaTiO_3$ and decrystallized titania, and microwave sintering of electroceramics including $BaTiO_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT), lead zirconate–titanate (i.e. $Pb(Zr_xTi_{1-x})O_3$, or PZT), etc., as well as multilayer ceramic capacitors based on X7R, C0G, and ferrite multilayer chip inductors are presented. The results indicate that microwave processing significantly accelerated synthesis and sintering kinetics. As a result, processing time can be saved up to 90%, with the product properties comparable to or better than that of the conventional products.

Keywords Microwave processing · Nano material · Barium titanate · Electroceramics · Multilayer capacitor · Inductor · X7R · C0G

1 Introduction

Microwave processing is a unique technique alternative to the conventional thermal process for material synthesis, sintering, and processing. The main characteristics of microwave processing are due to the internal heating by the heat generated within the workload through microwave–material interaction. Due to the penetrating feature of microwaves in microwave absorbing materials, microwave heating is volumetric and material dependent. For the materials that are fairly susceptive to microwaves, the kinetics of microwave synthesis and sintering can be much faster than in the conventional process. In addition, microwave processing could bring about quality improvement of the products. Detail information about microwave processing of ceramic materials can be found in review articles by Sutton [1] and Katz [2]. Early microwave assisted synthesis of inorganic and organic materials was reported over 20 years ago [3, 4] and has become more and more popular. This paper presents microwave processing of the electroceramic materials and devices to illustrate a promising future of microwave processing for various electroceramic materials and devices.

C. Y. Fang (✉) · C. A. Randal · M. T. Lanagan · D. K. Agrawal
Materials Research Institute, Pennsylvania State University, University Park, PA 16802, USA
e-mail: yxf101@psu.edu

2 Experimental

The materials studied in this work include barium titanate, titania, $Ba(Zn_{1/3}Ta_{1/3})O_3$, $Pb(Zr_xTi_{1-x})O_3$ (or BZT, PZT, respectively), multilayer capacitors (MLC) based on X7R and C0G dielectrics, and ferrite multilayer chip inductors (MLCI). All the experiments but the decrystallization of titania were carried out in a multimode microwave furnace. The decrystallization work was conducted in a single-mode TE_{103} applicator in which the sample could be treated either in the essentially pure magnetic (H) field, or pure electric (E) field, or the mixed electromagnetic field [5]. The frequency of both the multimode and single-mode microwave applicators is 2.45 GHz. For the runs in the multimode microwave furnace, the sample was loaded in a microwave transparent and thermally insulating package, made of Fiber-Frax™ porous mullite fibers, to prevent heat loss. The insulating package was placed on a turntable. Within the insulating package, appropriate amount of silicon carbide was used as microwave susceptor around the sample to preheat the sample and compensate the heat loss from the sample. This configuration makes the microwave heating more uniform. The temperature of the sample was monitored with either

optical or IR pyrometer, or thermocouple specially shielded with platinum foil and grounded properly to avoid microwave interference to the electromotive force (EMF) of the thermocouple. All the experiments were carried out under ambient pressure. The microwave processed samples were properly characterized and compared with the conventionally prepared samples.

3 Results and discussion

3.1 Microwave synthesis of barium titanate

Barium titanyl oxalate (BTO), $BaTiO(C_2O_4)_2 4H_2O$, was heated in a microwave furnace at 20 °C per minute up to various temperatures from 600 °C to 750 °C, and cooled down without any holding at the peak temperature. It was found that barium titanate formation started below 600 °C, and the reaction was completed once been microwave heated up to 680 °C. As a result, XRD indicated that pure nano-sized cubic barium titanate was obtained. The average particle size of the resultant barium titanate was found to be 70 nm, as determined by both BET surface area (14.2± 0.5 m^2/g) and SEM (Fig. 1). Parallel study by conventional heating using a regular resistance furnace and identical heating schedule did not result in complete decomposition of BTO to form pure barium titanate even up to 720 °C. This indicates that conversion of barium titanate from BTO was significantly accelerated by microwave processing. Figure 2 shows the XRD patterns of the barium titanate powders synthesized from BTO at 680 °C without holding.

3.2 Microwave decrystalliztion of titania

Titania (TiO_2) was partially reduced to TiO_{2-x} by treating the powder in a tube furnace at 1000 °C for 4 h in a flowing forming gas containing 10% H_2. The reduced sample was compacted into 2 mm thick circular pellets of 6 mm diameter. One pellet sample was loaded in a quartz tube with flowing forming gas (95% N_2–5% H_2) and treated at the essentially pure microwave magnetic (H) field in a TE_{103} single mode microwave applicator [5, 6]. Due to the excellent microwave absorption of the reduced titania, the sample was instantly heated up to around 1000 °C in seconds. As a result, decrystallized titania was obtained within 30 s (Fig. 3), as evidenced by SEM, TEM, XRD, and Raman spectroscopy. Obviously, the regular crystal lattice structure of the titania has been destructed by the microwave H-field.

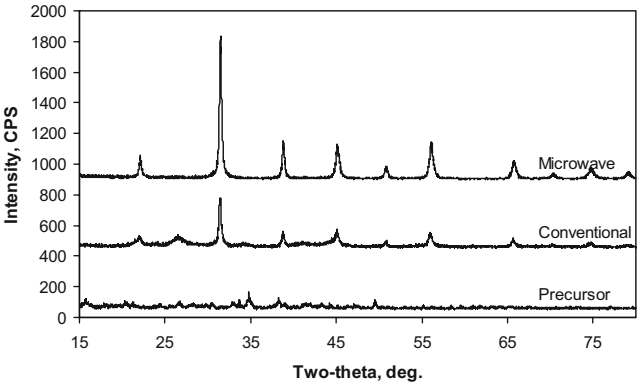

Fig. 2 XRD patterns showing formation of pure cubic barium titanate from precursor (BTO) by microwave processing up to 680 °C, compared with the sample conventionally heated to the same temperature. The conversion in the conventional processing was incomplete

3.3 Microwave sintering of BZT ceramics

Uniaxially pressed circular BZT [$Ba(Zn_{1/3}Ta_{1/3})O_3$] pellets, 25 g each, 25.4 mm in diameter, were conventionally presintered in air at 1300 °C to 60% relative density. The presintered samples were sintered in a microwave furnace at various temperatures from 1200 °C to 1500 °C. It was found that there was obvious densification in the microwave field even only at 1200 °C: the density increased to 71% in 30 min. At 1300 °C, the sample was microwave sintered to 91% in 10 min. Full density (100%) was

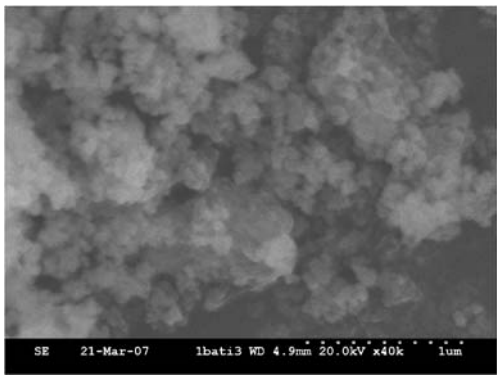

Fig. 1 SEM image showing the microstructure of the microwave synthesized nano-size $BaTiO_3$ powder

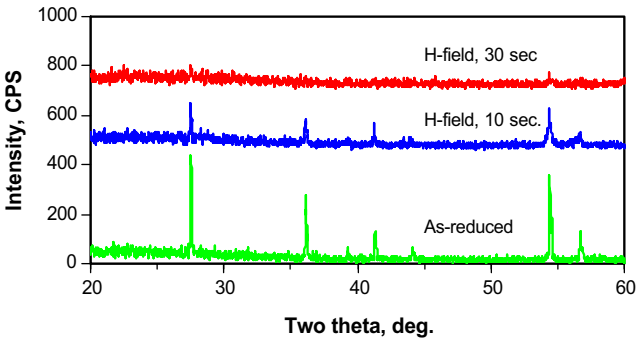

Fig. 3 XRD patterns showing decrystallization of titania in microwave H-field

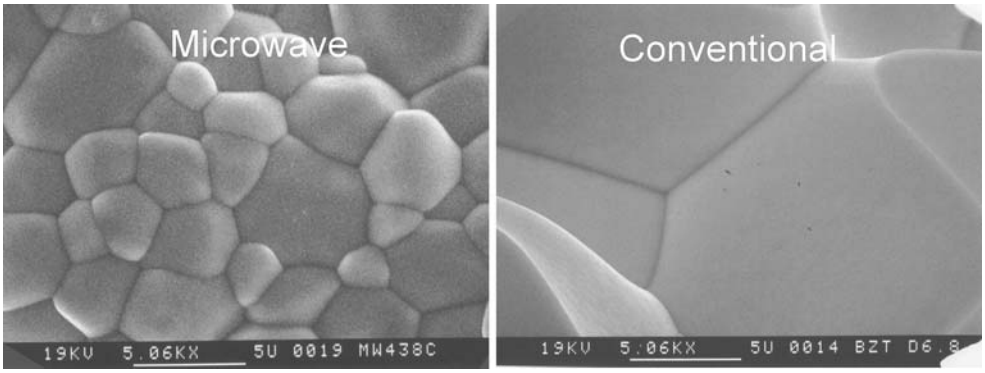

Fig. 4 SEM images showing grain size of BZT sintered by microwave and conventional processing, respectively

achieved at 1400 °C by microwave processing within 10 min. By contrast, conventional sintering kinetics of BZT was extremely slow: Little densification was obtained below 1600 °C. For example, 12 h sintering at 1500 °C only led to 63.4% relative density. To reach full density conventionally, the sample had to be sintered at 1600 °C for 24 h. In this case, microwave sintering lowered the sintering temperature of BZT by 300–400 °C, and sintering time by over 95%. Due to the substantial difference in processing time, the average grain size of the microwave sintered sample was much finer than the conventionally sintered sample (Fig. 4). The substantially enhanced densification kinetics in the microwave sintering is attributed to the fairly high dielectric loss of the BZT material.

3.4 Microwave sintering of PZT ceramics

Using acrylic binder, fine grain PZT [$Pb(Zr_xTi_{1-x})O_3$] powder fluxed by V_2O_5 was pressed into circular pellets of 12.7 mm diameter and 5 mm thickness. The green density of the sample was 4.4 g/cm^3. After binder burnout, the samples were buried with lead source powder in an alumina crucible and sintered in air by microwave processing ramping at 20 °C/min. Temperature of the sample was monitored with a type-S (Pt10Rh) thermocouple shielded with platinum foil and grounded to the inner metallic wall of the microwave furnace. The samples were sintered at various temperatures from 500 °C to 900 °C, holding 20 min at the peak temperature. Comparative conventional sintering was carried out in a regular resistance furnace at the same heating rate but holding for 120 min. The densification effect of microwave sintering vs. conventional sintering is shown in Fig. 5(a) and the microstructure of the microwave sintered PZT is shown in Fig. 5(b). It was found that in the microwave processing, densification of the PZT sample started at about 500 °C. The densification rate from 500 °C to 600 °C was linear, 0.0448 g/cm^3 per °C. While in the conventional sintering, there was no significant densification below 700 °C. The densification rate in the temperature range from 750 °C to 950 °C was linear, 0.0158 g/cm^3 per °C. Taking the holding time into consideration (20 vs. 120 min), the densification rate of microwave was 17 times that of the conventional. Yet, in the beginning of the sintering process around 4.5 g/cm^3, microwave processing temperature was 200 °C lower than the conventional sintering. This span increased to 300 °C at 7 g/cm^3. The maximum density in both microwave and conventional sintering was 7.7 g/cm^3. This clearly indicates

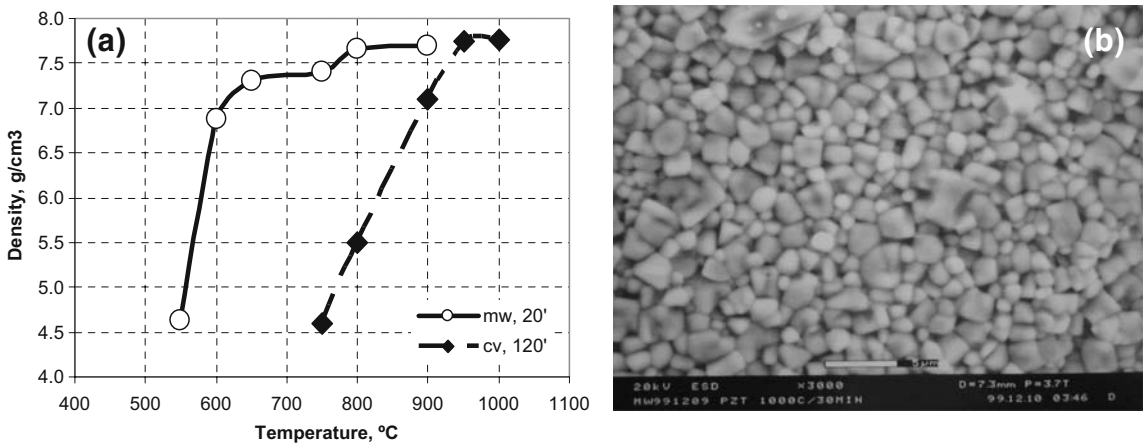

Fig. 5 (**a**) Densification effect of PZT sintered by microwave processing holding for 20 min and conventional processing holding for 120 min (**a**), respectively; (**b**) Microstructure of the as-sintered surface of a microwave-sintered PZT sample

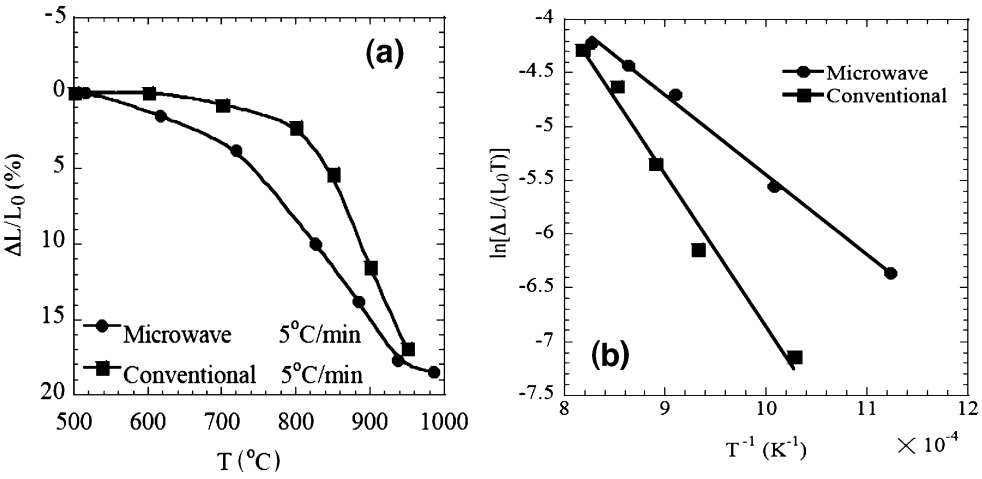

Fig. 6 Kinetics of microwave and conventional sintering of ferrite ceramics: (**a**) temperature dependence of linear shrinkage of ferrite during sintering, $(\Delta L/L_0)\%$; (**b**), $\ln[\Delta L/L_0 T]$ as a function of T^{-1} in which the slope of each line represents the activation energy of diffusion in the corresponding sintering process

that microwave sintering substantially enhanced the densification of PZT.

3.5 Microwave sintering of multilayer structure devices

3.5.1 Ferrite and multilayer chip inductors (MLCI)

NiCuZn ferrite ceramics and MLCI were effectively sintered by microwave processing. The chemical composition of the ferrite in this study was FeO_3/NiO/CuO/ZnO= 48:23:15:14 (mol%), with a 7.48 m^2/g BET surface area. For sintering kinetic study of the ferrite, circular pellets of 12.7 mm diameter and 2 mm thick were uniaxially pressed with a binder. After binder burnout, the samples were sintered by both microwave and conventional sintering in air at temperatures up to 1000 °C, ramping at 5 °C/min. Temperature of the sample was measured by an S-type (Pt10Rh) thermocouple shielded with platinum foil. The peak temperature of the sample was carefully calibrated [7]. The densification effect was evaluated by linear shrinkage $(\Delta L/L_0)$ of the samples (Fig. 6). The results show that the microwave sintering enhanced sintering of the samples. It was found that the microwave enhancement in densification of ferrite was temperature-dependant. It increased with temperature, reached maximum at 800–850 °C, decreased afterwards and finally diminished. The microwave processing at 660 °C reached the same densification as conventional processing at 800 °C, lowered by 140 °C. No significant microwave enhancement in densification was observed below 500 °C or above 950 °C. This is understandable because microwave heating depends on dielectric and magnetic losses whereas these losses increase with temperature. Above 800–850 °C, the ferrite had been significantly densified and further shrinkage became a very slow process, thus microwave enhancement eventually diminished. At 850 °C, the shrinkage in the microwave processing was 11.3%, 105% higher than in the conventional process (5.5%). The maximum microwave enhanced densification was found in the range of 800–850 °C. From the linear shrinkage data, the effective activation energy of diffusion of ferrite at a constant heating rate was found [8] from the slope of the $\ln[\Delta L/L_0 T]$ vs. T^{-1} curves [Fig. 6(b)] to be 61 kJ/mol and 118 kJ/mol for microwave and conventional sintering, respectively. This indicates a significantly accelerated sintering kinetics by microwaves.

Microwave sintering of inductors was conducted with bulk toroidal inductor and MLCI samples, respectively, at about 900 °C. The sintered samples of both types were dense and uniform. No delamination or other defects were found in the sintered MLCI samples. The properties of the microwave samples were comparable with the conventional samples.

3.5.2 Ag–Pd electrode multilayer ceramic capacitors

In the attempt of microwave sintering of MLC, commercial green chips of Ag–Pd internal electrodes MLC size 0805 of X7R dielectric were used. The chips were mixed with the

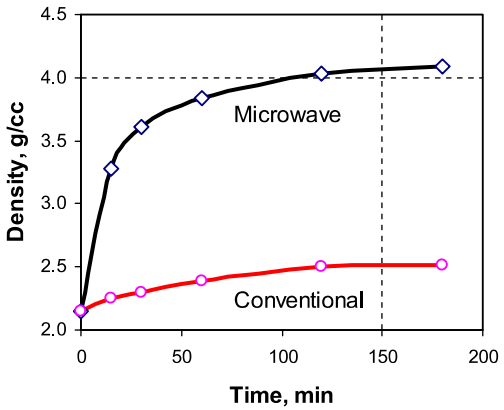

Fig. 7 Density of the C0G MLC chips sintered by microwave and conventional processing, respectively

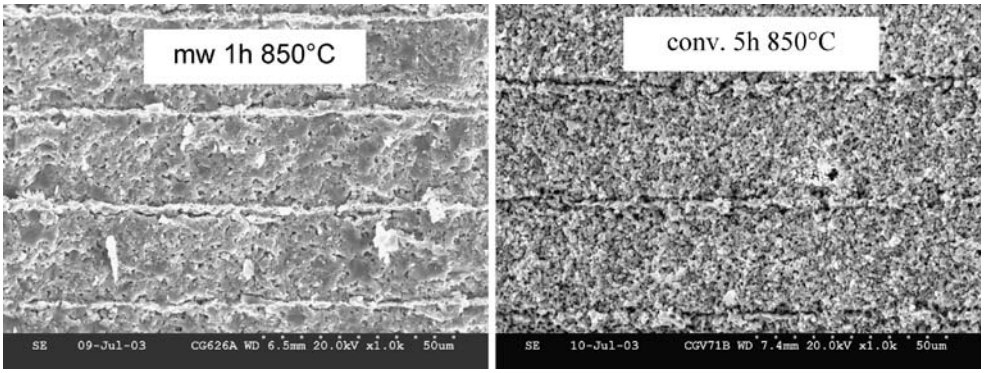

Fig. 8 SEM images showing the fracture surface of C0G MLC sintered at 850 °C by microwave processing for 1 h, and by conventional sintering for 5 h, respectively

bedding powder of the same composition as the dielectric and sintered by microwave processing. The chips were heated in the microwave furnace at 20–25 °C/min up to a desired temperature, with or without holding at the peak temperature. It was found that the sintering process was very quick. The chips could be heated stably to the desire temperature and sintered with holding for only a few minutes or even without holding. The distribution of the capacitance of the microwave sintered MLC was normal.

C0G MLC chips, size 0805, of $MgZnTiO_3$ (MZT) dielectrics with 90Ag10Pd internal electrodes were sintered in air between 850 °C to 950 °C by microwave processing ramping at 20 °C/min. Comparative conventional sintering experiments were also carried out under the identical temperature profile. The results show that the microwave processing substantially enhanced densification kinetics of C0G MLC (Fig. 7). In the microwave processing, the sample was sintered to fairly high density in 1 h at 850 °C, whereas conventional processing under the same condition led to little densification. Even after 5 h, the conventionally sintered sample was still much more porous than the one microwave sintered for 1 h (Fig. 8). As a result, the C0G MLC sintered by microwave showed significantly better properties than the conventional sample. The enhanced densification kinetics is clearly seen in the sintering of C0G MLC. In this case, microwave processing lowered the densification temperature by at least 100 °C and accelerated the sintering kinetics substantially.

3.5.3 Base-metal electrode multilayer ceramic capacitors

Commercial green chips of X7R MLC 0603 with Ni electrodes were sintered by microwave processing at 1250 °C/20 min in dry nitrogen containing 0.4% hydrogen. The nickel electrodes remained metallic when sintered. X-ray diffraction on the sintered samples did not find any nickel oxide, which was confirmed by the ceramic-electrode interfacial study by TEM [9]. Conventional sintering of the same MLC was carried out under the required condition at 1320 °C for 2 h in wet nitrogen containing 0.4% hydrogen. The microwave sample achieved the same density (5.75 g/cm^3) as the conventional sample. Both the microwave sintered and the conventionally sintered MLC samples passed highly accelerated life test (HALT) at 125 °C, 50 V, for 92 h. The capacitance of the microwave sintered samples was up to 8% higher than the nominal value for the standard (100 nF). The capacitance of the microwave sample was 5–8 nf higher (in the range from room temperature to 140 °C), and the dielectric loss (D) of the microwave sample was 0.01 lower

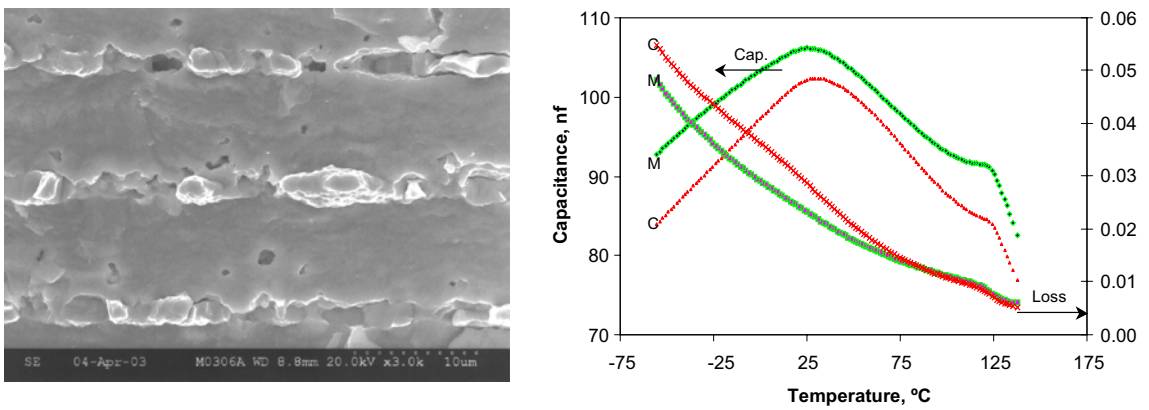

Fig. 9 SEM image showing the fracture surface of Ni-electrode MLC microwave sintered at 1250 °C for 20 min, as well as the capacitance and dielectric loss of the microwave sintered sample (*M*) compared with the conventional (*C*) sample sintered at 1320 °C for 2 h

than the conventional sample from room temperature to 75 °C, and identical to that of the conventional sample from 75 °C to 140 °C, as shown in Fig. 9. By comparison, the microwave process saved processing time by 90% and achieved the similar product at temperature 100 °C lower than the conventional process.

4 Conclusions

Pure cubic barium titanate with 70 nm particle size was synthesized from BTO precursor by microwave heating to 680 °C without holding. Amorphous titania was obtained by treating the partially reduced titania in microwave magnetic field within a minute. Microwave sintering of BZT, PZT, MLC, and MLCI was carried out. The results indicate that microwave processing substantially enhanced the kinetics in both synthesis and sintering in the study. The enhancement depends on the microwave absorption related to the dielectric and magnetic losses of the materials. For the system with fair loss, such as BZT and PZT, the kinetics was accelerated by one order of magnitude. As a result, the processing time was saved by up to 90%, and the processing temperature was lowered by 100–400 °C.

References

1. W.H. Sutton, Am. Ceram. Soc. Bull. **68**(2), 376 (1989)
2. J. Katz, Microwave sintering of ceramics Annu. Rev. Mater. Sci. **22**, 153–170 (1992)
3. R. Roy, S. Komarneni, L.J. Yang, J. Am. Ceraam. Soc. **68**(7), 392–95 (1985)
4. R. Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge, J. Rousell, Tetrahedron Lett. **27**, 279 (1986)
5. J. Cheng, R. Roy, D. Agrawal, J. Mat. Sci. Lett. **20**, 1561–1563 (2001)
6. R. Roy, Y. Fang, J. Cheng, D. Agrawal, J. Am. Ceram. Soc. **88**(6), 1640–1642 (2005)
7. H. Saita, Y. Fang, A. Nakano, D. Agrawal, M.T. Lanagan, T.R. Shrout, C. Randall, Jpn. J. Appl. Phys. **41**, 86–92 (2002)
8. W.S. Young, I.B. Cutler, J. Am. Ceram. Soc. **53**, 659 (1970)
9. Y. Fang, D.K. Agrawal, G.Y. Yang, M.T. Lanagan, C.A. Randall, T.R. Shrout, A. Henderson, M. Randall, A. Tajuddin, J. Electroceramics. **15**, 13–19 (2005)