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Structural and electrical properties of microwave -processed $BaTiO_3$ ceramics

O.P. Thakur, Chandra Prakash* and D.K. Agrawal[a]
Solid State Physics Laboratory, Lucknow Road, Timarpur, Delhi -110054, India
[a]Materials Research Laboratory, Pennsylvania State University, University Park, PA 16802, USA

Barium titanate ($BaTiO_3$) was synthesized and sintered by microwave processing at 2.45 GHz. Appropriate amounts of $BaCO_3$ and TiO_2 were used as starting materials for the synthesis. $BaTiO_3$ phase was obtained by heating the precursors in a multi-mode microwave cavity at 1450°C for just 25 minutes. The synthesis and sintering were carried out in air. A relative density of 97% was obtained. By contrast, it was found that to achieve the same densification, it required 4 hours of soaking at 1450°C in a conventional sintering process. The dielectric properties show the abrupt discontinuities in dielectric constant vs. temperature plots; typical properties of first order transitions. Above the Curie temperature the dielectric constant follows Curie-Weiss law with Curie constant $C=1.3\text{-}1.4\times10^5$ °C.

Key words: Microwave synthesis, Sintering, $BaTiO_3$, Ferroelectrics, Electronic ceramics.

Introduction

Barium titanate (BT) is a dielectric material, with a perovskite (ABO_3) structure that finds many applications in electronic devices [1, 2]. When pure, this material is highly resistive at room temperature but its electrical resistivity can be dramatically lowered by some dopants. There are several reports available on the structure and electrical behavior study of these ceramics synthesized by conventional and other chemical processes. However, very limited literature is available on the microwave sintering of BT ceramics. Most of the studies on microwave processed materials has been done for their structural, mechanical and positive temperature-coefficient of resistivity (PTCR) characteristics only [3-8]. The barium titanate-based normal ferroelectrics are strong candidates for field-induced piezoelectric transducers due to their large polarizations, large permittivities and the large induced strains achievable in these materials. Conventional methods for the synthesis of ferroic phases require temperatures in the range 900~1450°C and several hours soaking time. With the advent of microwave processing, using pre-reduced oxide (TiO_2, Ta_2O_5), it is possible to sinter the ferroic materials at astonishingly low temperatures, between 300°C and 700°C in 5-12 minutes [9].

Synthesis of ferroelectric titanates based on conventional ceramic methods involve long reaction times due to slow diffusion rates in the solid state and often necessitate intermittent grinding [10]. In the microwave process, the heat is generated internally within the material instead of originating from external sources, and hence there is an inverse heating profile. The heating is very rapid as the material is heated by energy conversion rather than by energy transfer, which occurs in conventional techniques *via* thermal conduction mechanism. Microwave sintering has many advantages over conventional methods [11-12]. Some of these advantages include, time and energy saving, very rapid heating rates (> 400 K/minute) without damage due to thermal shock, considerably reduced processing time and temperature, fine microstructures and hence improved mechanical properties. This process is environmentally friendly also. Here, we report the synthesis and electrical properties of barium titanate synthesized by a microwave processing method and compare the properties with conventional processed ceramics. In this study, single phase BT was synthesized by microwave heating in a much shorter time compared with conventional heating methods.

Experimental Procedure

The starting powder was prepared by mixing stoichiometric amounts of AR grade, $BaCO_3$ and TiO_2. The powder mixture was ball milled in distilled water using zirconia balls. The dried powder was calcined at 1050 °C for 4 hours. The reacted powder was ball milled again and recalcined at 1100°C for 4 hours to obtain a more homogeneous mixture. The powders were isostatically pressed in a rod form at a pressure of 200 MPa using a cold isostatic press (M/s Autoclave Engineers). The cold isostatic process gives a homogeneous and better compaction of green rods. For conventional sintering (CS), one set of these rods was sintered

*Corresponding author:
Tel : +91-11-3921692
Fax: +91-11-3913609
E-mail: c_prakash@vsnl.net

at 1450°C for 4 hours in an air atmosphere and the total cycle time was 700 minutes.

Another set of compacted rods (MS) was sintered using a microwave oven (3 kW, 2.45 GHz multi mode microwave applicator) at 1450°C for 25 minutes and the total cycle time was only 90 minutes. The temperature-time profile for CS and MS is shown in Fig. 1. The heating rate was kept at 100 K/minute (by controlling the input power to the microwave oven) for all the microwave experiments. Density and microstructural information was obtained on microwave processed and conventionally processed samples by the Archimedes principle and SEM respectively. The phase purity of the compounds was confirmed by an X-ray diffraction technique. XRD patterns were recorded using a Philips powder diffractometer with Cu-Kα radiation in a wide range of 2θ ($20^o \leq 2\theta \leq 70^o$) at a scanning rate of 2°/minute.

For the electrical properties measurements, sintered rods were ground and sliced to make specimens of 0.5 mm thickness and 10 mm diameter. Both the faces of the sliced samples were platinum sputtered. Measurements of capacitance (C) and dissipation factor (tanδ) were carried out by an HP 4284A LCR meter interfaced with a PC, both as a function of frequency (100 Hz-1 MHz) and temperature (25°~200°C). The heating rate was maintained at 1 K/minute and the data were recorded automatically.

Polarization switching was observed using an automatic PE loop tracer based on a modified Sawyer-Tower circuit. Samples were immersed in a silicone oil bath to prevent electrical breakdown of the specimen.

Results and Discussion

Figure 1 compares the time-temperature profiles between the microwave and the conventional synthesis of BT and the values of sintering temperature and time are listed in Table 1. It is evident that the microwave method takes only a fraction of the time required in the conventional processing to achieve single-phase dense material. Samples prepared by conventional sintering (CS) and microwave sintering (MS) were subjected to XRD analysis in order to determine the structure and lattice parameters. From the lattice parameters, X-ray density, d_x, was calculated. Experimental density, d_{exp}, was determined by a water immersion method. These parameters are summarized in Table 1. Experimental density (d_x) of about 97% theoretical was achieved with the microwave process while for the conventional process it is 94%. The XRD patterns for the conventionally and microwave synthesized BT powders are shown in Fig. 2. All the specimens reveal a single-phase formation with a tetragonal structure. The lattice

Table 1. Comparison of conventional and microwave processes for sintering, structural & electrical properties of BT samples

		Conventional	Microwave
Sintering Temperature		1450°C for 4 hours	1450°C for 25 minutes
Total cycle time (minute)		700	90
Lattice parameters	c (Å)	4.0207	4.0297
	a (Å)	3.9832	3.9895
	c/a	1.0094	1.0101
	Volume $(Å)^3$	63.79	64.14
X-ray Density (d_x)		6.07	6.038
Expt. Density ($d_{exp.}$)		5.72	5.78
Average grain size (μm)		10	7
Dielectric const. (ε')		1485	1555
Dissipation factor (tanδ)		0.0143	0.0145
Activation energy (eV) in paraelectric region		0.622	1.125
Curie Temp. (°C)		122	125
Curie Const. (10^5 °C)		1.30	1.34

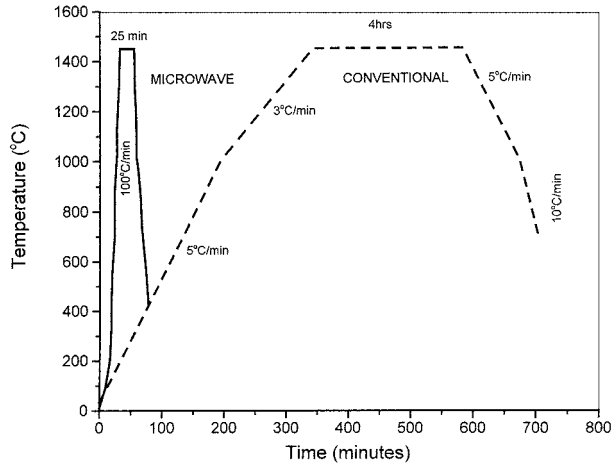

Fig. 1. Comparison of the time-temperature profiles for BT synthesis in microwave and conventional processes.

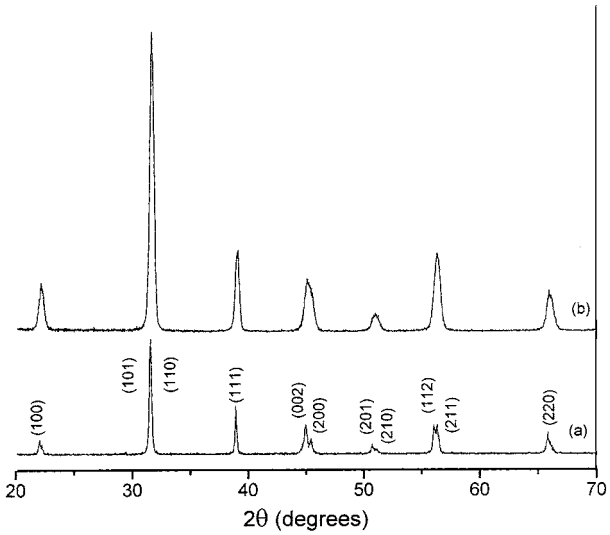

Fig. 2. XRD patterns for (a) conventional (CS) and (b) microwave sintered (MS) BT samples.

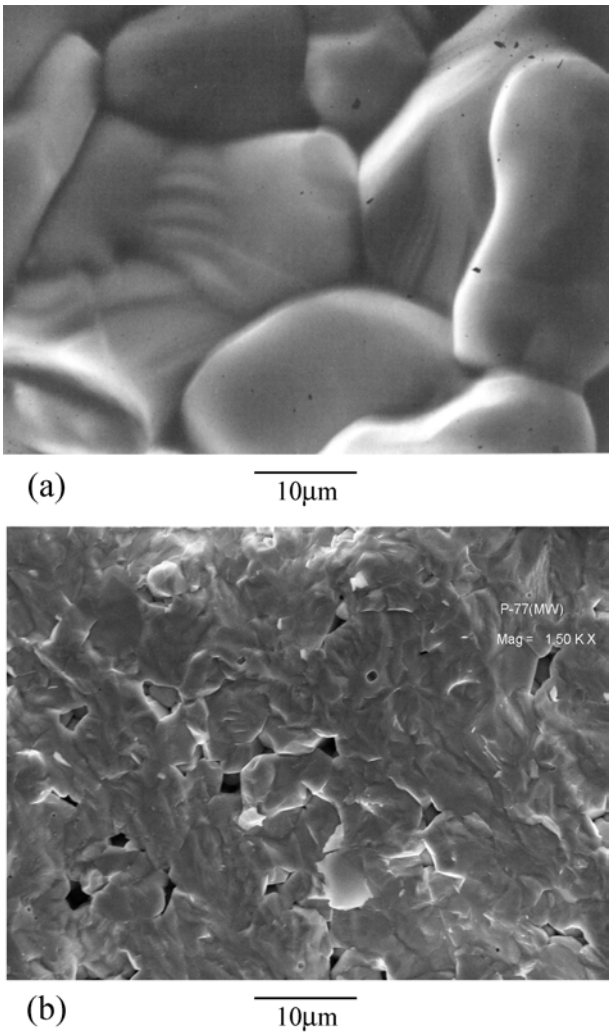

Fig. 3. Scanning electron micrographs for (a) conventional (CS) and (b) microwave sintered (MS) BT samples.

parameters and c/a ratio (listed in Table 1) are found to be slightly higher for the MS sample because the microwave sintering process results in enhanced sintering and better uniformity [13]. The unit cell volume was found to increase from 63.79 to 64.14 $Å^3$ for MS samples. MS samples show a higher density.

The microstructures of the fractured surfaces of CS and MS specimens are shown in Fig. 3. Trans-granular fracture was observed for the microwave processed BT specimen (Fig. 3b), indicating that the grain boundaries are narrow and/or do not contain sufficient defects such as porosity to produce inter-granular fracture. The grain size is fairly uniform for all the samples. The average grain size ranges between 6~12 μm and is significantly smaller in the case of the MS processed specimen. The MS processed sample is less porous than the conventional one. The rapidity of the microwave method also avoids undesirable grain growth and provides a finer and more uniform microstructure (Fig. 3), which is an attractive feature for the processing of electroceramics [14].

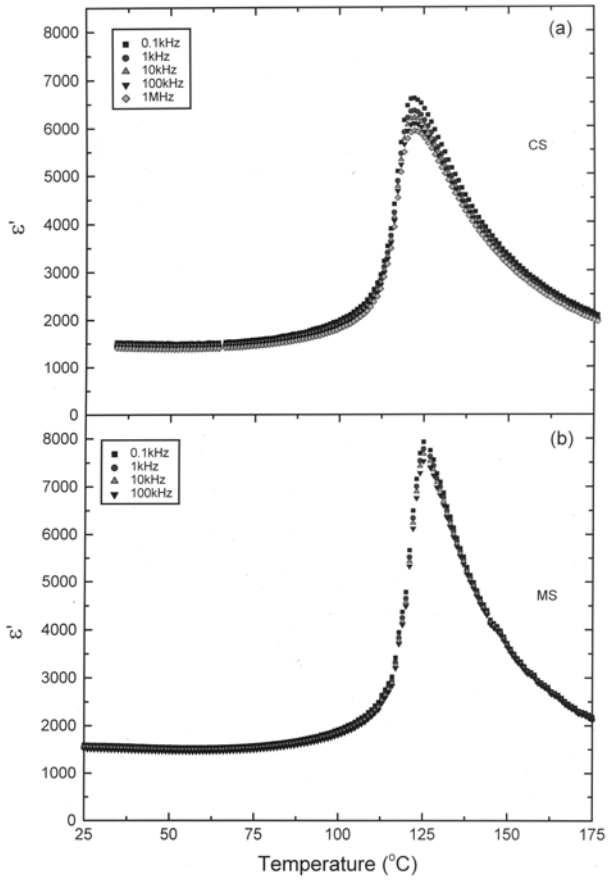

Fig. 4. Temperature dependence of dielectric constant (ε') for (a) conventional and (b) microwave processed BT samples.

The composition investigated here displayed sharp peaks in the dielectric constant *vs*. temperature plots, which is a characteristics of normal ferroelectrics. The plot of dielectric constant vs. temperature at different frequencies for CS and MS samples are shown in Fig. 4. No shift in the dielectric maxima has been observed with the increment in frequency. However, it is observed that as compared to the CS method, the frequency dispersion is very much less for the MS processed sample, which may be attributed to the uniform and finer grain size. For better comarison, the plots of temperature variation of dielectric constant (ε') and dissipation factor (tanδ) at 1 kHz for BT sintered by different routes are shown in Fig. 5. It is observed that in the case of the MS sample, the value of ε' is higher as compared to the sample obtained by the conventional method. The peak width also decreased considerably for MS samples.

In the vicinity of the paraelectric region, the dielectric constant (ε') follows the well-known Curie-Weiss law:

$$\varepsilon' = C/(T-T_o)$$

Where C is the Curie-Weiss constant and T_o is the Curie-Weiss temperature [15]. Figure 6 shows the vari-

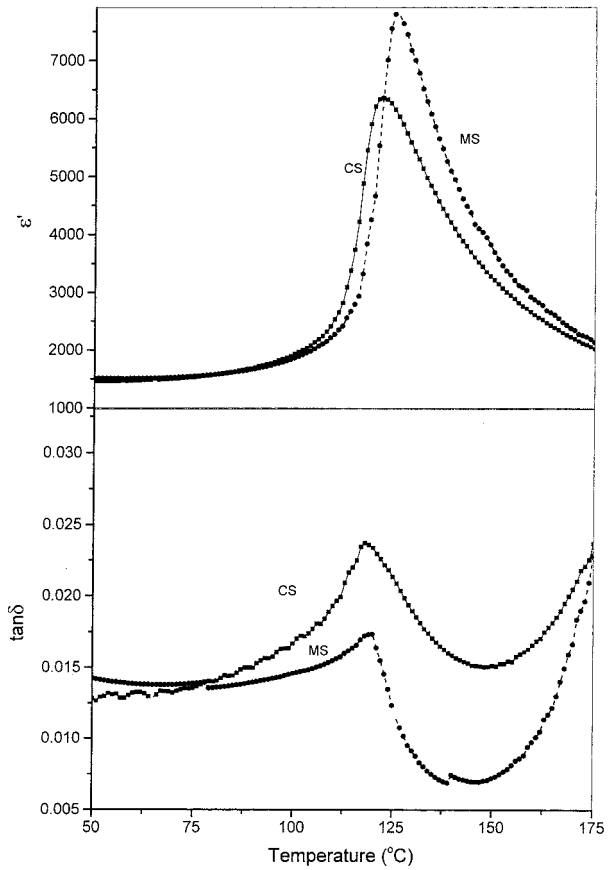

Fig. 5. Temperature dependence of dielectric constant (ε') and loss tangent (tand) for conventional (CS) and microwave sintered (MS) BT samples at 1 kHz.

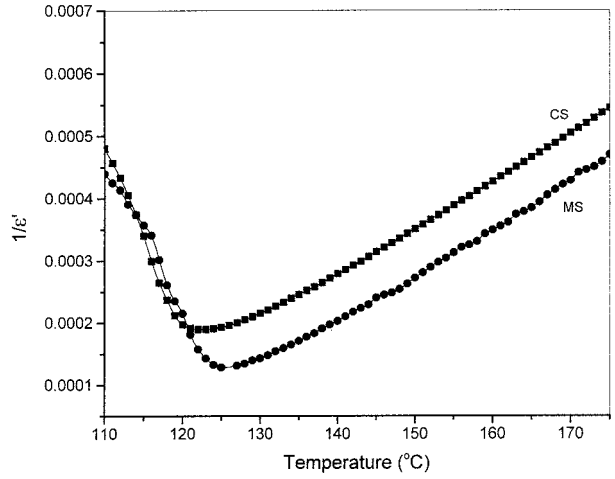

Fig. 6. Temperature dependence of inverse of dielectric constant (1/ε') in the vicinity of transition temperature for CS and MS processed samples.

ation of the inverse dielectric constant with temperature in the vicinity of the transition temperature for both the samples. The dielectric data in the paraelectric region show excellent Curie-Weiss behavior (Fig. 6). The Curie constant (C) obtained for these samples (listed in Table 1) fall in the range $1.3\text{-}1.4\times10^5$ °C, which is in

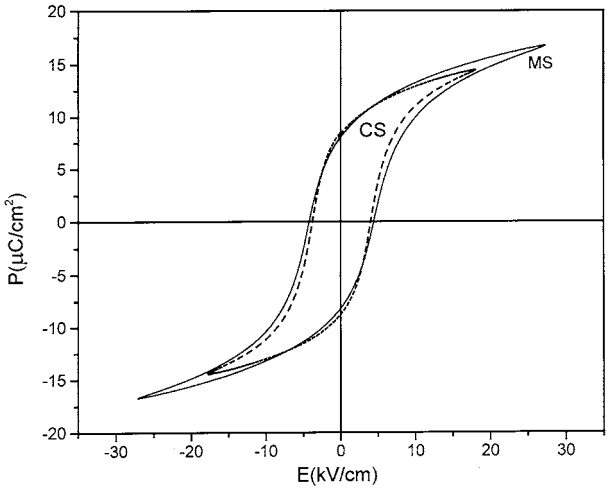

Fig. 7. The typical hysteresis loops (P *vs* E) for conventionally sintered (CS) and microwave sintered (MS) BT samples.

good agreement with the reported value for BT [16]. In the case of the CS sample, the phase transition is observed at 122°C with $\varepsilon'_{peak} \approx 6300$; however, the transition is sharper for the MS sample with a higher ε'_{peak} values of 7800 and a phase transition at 125°C. The value of the lattice parameters, which are a little higher for the MS samples result in a higher value of the Curie temperature (Tc) as compared to the conventional one. The activation energy determined from AC conductivity plots (at 1 kHz) in the paraelectric region for both the samples is included in Table 1. It is found that the activation energy is higher for the MS sample, which shows more insulating nature of the MS processed sample.

The polarization versus electric field (P *vs.* E) behavior was recarded using an AC field of 25-30 kV/cm at 50 Hz. Characteristic P-E loops for BT synthesized by the CS and MS methods are shown in Fig. 7. The coercive field (Ec) and remanant polarization (Pr) were also determined and it is observed that the magnitude of Ec is slightly higher in case of the MS sample.

Conclusions

The microwave method is found to be simple, fast and energy efficient compared with conventional method. It has been shown that microwave processing can sinter BT ceramics with better properties, in about one-tenth the cycle time required by conventional means. The transition temperature (Tc) is found to increase in case of the MS sample, as the lattice parameters are a little higher for the microwave-sintered samples. The dielectric constant is a little higher for the MS sample and the loss tangent is low. The phase transition observed for the MS sample is quite sharp and almost no frequency dispersion at and beyond the Curie temperature is found which shows fine grain sizes and pore free microstructures. Both the samples processed

by CS and MS methods depict first order phase transition to ordered systems.

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