



# Enhanced dielectric and piezoelectric properties in microwave sintered $(\text{Ba}_{0.997}\text{Nd}_{0.003})\text{TiO}_3$ ceramic when compared to conventional sintered ceramics

S MAHBOOB<sup>1,\*</sup>, RIZWANA<sup>2</sup>, G PRASAD<sup>1</sup> and G S KUMAR<sup>1</sup>

<sup>1</sup>Materials Research Laboratory, Department of Physics, Osmania University, Hyderabad 500007, India

<sup>2</sup>Institute of Aeronautical Engineering, Dundigal, Hyderabad 500043, India

\*Author for correspondence (mahboob1978@yahoo.com)

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**Abstract.** Dielectric, conductivity and piezoelectric properties have been studied on  $(\text{Ba}_{0.997}\text{Nd}_{0.003})\text{TiO}_3$  ceramic samples prepared through microwave sintered (MWS) and conventional sintered (CS) routes and the results are presented in this paper. The room temperature dielectric constant at 10 kHz for CS and MWS samples are 1245 and 5250 respectively. Room temperature dielectric constant in MWS sample was almost four times higher than that of the CS sample. The value of  $K_t$  is found to be 0.998 and 0.997; whereas the value of  $d_{33}$  is  $7.72 \text{ nm V}^{-1}$  (573 K) and  $444.66 \text{ nm V}^{-1}$  (573 K) for CS and MWS samples, respectively. In the present study almost 57 times enhancement in piezoelectric charge constant ( $d_{33}$ ) is observed for the MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramic when compared to the CS ceramic.

**Keywords.**  $(\text{Ba}_{0.997}\text{Nd}_{0.003})\text{TiO}_3$  ceramic; microwave sintering; dielectric; conductivity; impedance; piezoelectric.

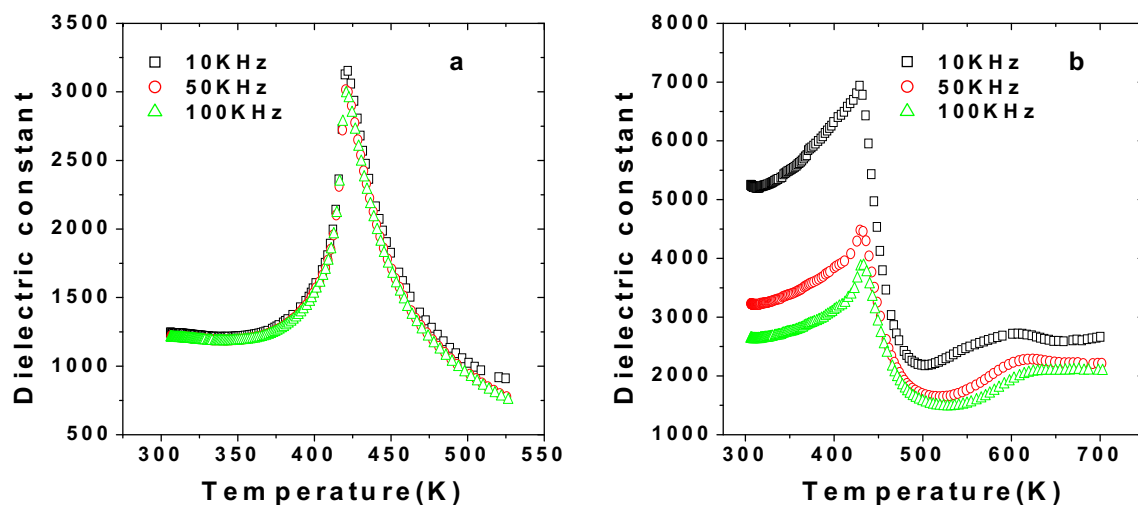
## 1. Introduction

Materials prepared through a microwave sintering (MWS) route show enhanced dielectric, ferroelectric, piezoelectric, magneto-electric and energy storage properties when compared to the conventional sintering (CS) route because of different reaction kinetics and diffusion mechanism [1–13]. Raghavendra Reddy *et al* reported structural, dielectric and ferroelectric properties of  $\text{BaTiO}_3$  ceramics prepared with hybrid sintering i.e., microwave-assisted radiant heating. They reported an enhancement of 58% in  $\epsilon$  and 17% in  $Q_{\text{sw}}$  (FE charge density) for microwave-assisted radiant heating when compared to conventional radiant heating [5]. Bafandeh *et al* studied the dielectric and piezoelectric properties of  $(1-x)\text{K}_{0.48}\text{Na}_{0.48}\text{Li}_{0.04}\text{Nb}_{0.96}\text{Ta}_{0.04}\text{O}_3-x\text{SrTiO}_3$  ceramics sintered in conventional and microwave furnace. They reported that the piezoelectric constant of microwave furnace sintered samples was more than 50% higher than conventional furnace sintered ones [6]. Praveen Kumar *et al* reported that the MWS technique rendered great improvement in dielectric and piezoelectric properties when compared to the CS technique for  $\text{Ba}_{0.80}\text{Pb}_{0.20}\text{TiO}_3$  ceramic [7]. The room temperature dielectric constant is higher for the MWS sample ( $\epsilon'_{\text{RT}} = 850$ ) when compared to the CS sample ( $\epsilon'_{\text{RT}} = 260$ ). The piezoelectric charge coefficient ' $d_{33}$ ' for the MWS sample was reported to be  $157 \text{ pC N}^{-1}$  when compared to  $130 \text{ pC N}^{-1}$  in the case of conventionally sintered sample. They ascribed the enhanced dielectric and piezoelectric properties to the MWS. This prompted the author to investigate the comparison

studies of dielectric, piezoelectric and electrical properties for the sample prepared through both MWS and CS techniques. Hence, in the present study neodymium-doped barium titanate i.e.,  $(\text{Ba}_{0.997}\text{Nd}_{0.003})\text{TiO}_3$  was chosen for investigation. Dielectric, conductivity and piezoelectric properties of the ceramic samples prepared through both the routes have been studied and the results are compared and discussed in this paper. In the present study 57 times enhancement in piezoelectric charge constant ( $d_{33}$ ) is observed for the MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramic when compared to the CS ceramic.

## 2. Experimental

$(\text{Ba}_{0.997}\text{Nd}_{0.003})\text{TiO}_3$  powder was prepared from the stoichiometric mixtures of the weighed carbonates and oxides ( $\text{BaCO}_3$ , 99.9%, E. Merck), ( $\text{Nd}_2\text{O}_3$ , 99.9%, Indian Rare-earths) and ( $\text{TiO}_2$ , 99.99%, Sigma Aldrich). Agate mortar was used to thoroughly mix and ground the stoichiometric mixture. The powder of the compounds was conventionally calcined in an electrical furnace at a temperature of  $1100^\circ\text{C}$  for 2 h. After ascertaining the formation of a single phase compound, the calcined powder was once again ground and homogenized in the agate mortar. Cylindrical pellets of 10 mm diameter and 1–2 mm thickness were compacted using a hydraulic press using polyvinyl alcohol as a binder. The pellets were then sintered in air using a household microwave



**Figure 1.** Dielectric constant vs. temperature plots for (a) CS and (b) MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramics.

**Table 1.** Parameter values obtained from dielectric data.

Parameter	Composition $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$	
	CS sample	MWS sample
Dielectric constant (10 kHz)	1245	5250
Dielectric loss (10 kHz)	0.02	0.36
$T_c$ (K)	421.82	428.71

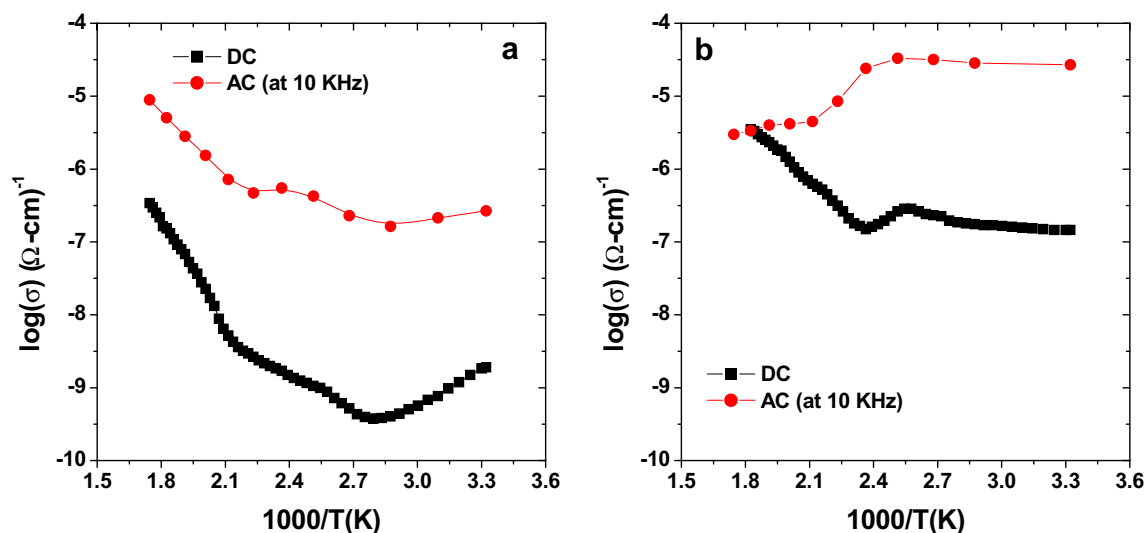
oven connected to a temperature controller and in an electrical furnace at  $1400^\circ\text{C}$  for 0.5 h and  $1500^\circ\text{C}$  for 2 h respectively.

Dielectric measurements were made over a wide range of temperature (300–700 K) at 10, 50 and 100 kHz frequencies using a HP4192A impedance analyzer. Impedance was measured as a function of frequency from 100 Hz to

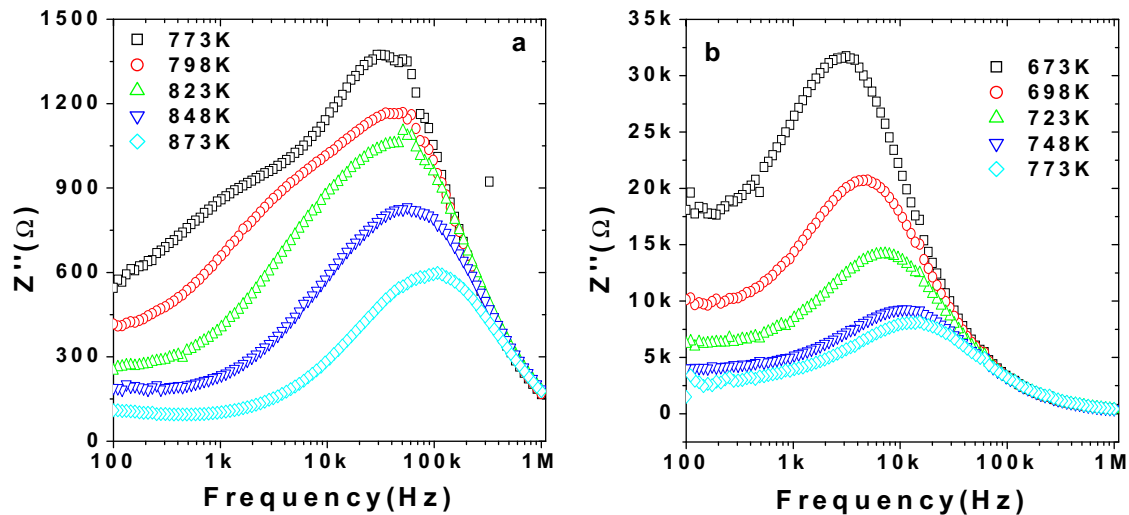
1 MHz using an AUTOLAB (PGSTAT 30) Low Frequency Impedance Analyzer. These frequency scans were carried out at different constant temperatures from 300 to 873 K in steps of 25 K. From the admittance data, AC conductivity data were obtained. DC conductivity data were obtained using a Keithley 610C electrometer.

### 3. Results and discussion

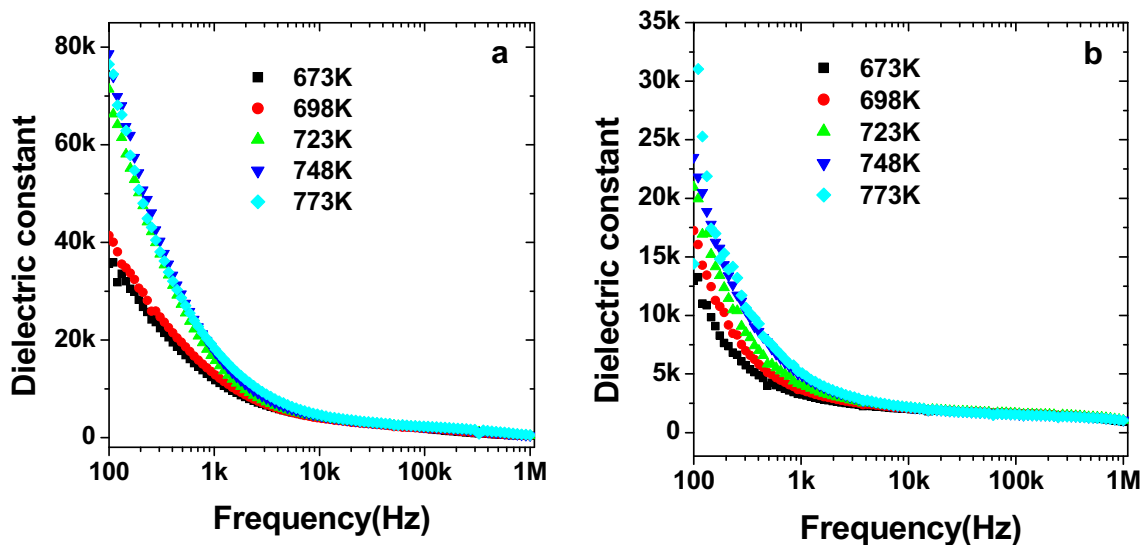
Figure 1a and b shows the dielectric constant as a function of temperature at different constant frequencies for CS and MWS ceramic samples. In the case of the CS sample, the dielectric constant is independent of frequency whereas there is dispersion of dielectric constant with frequency in the



**Figure 2.**  $\log(\sigma)$  vs.  $1000/T$  for (a) CS and (b) MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramics.



**Figure 3.**  $Z''$  vs. frequency plots for (a) CS and (b) MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramics.

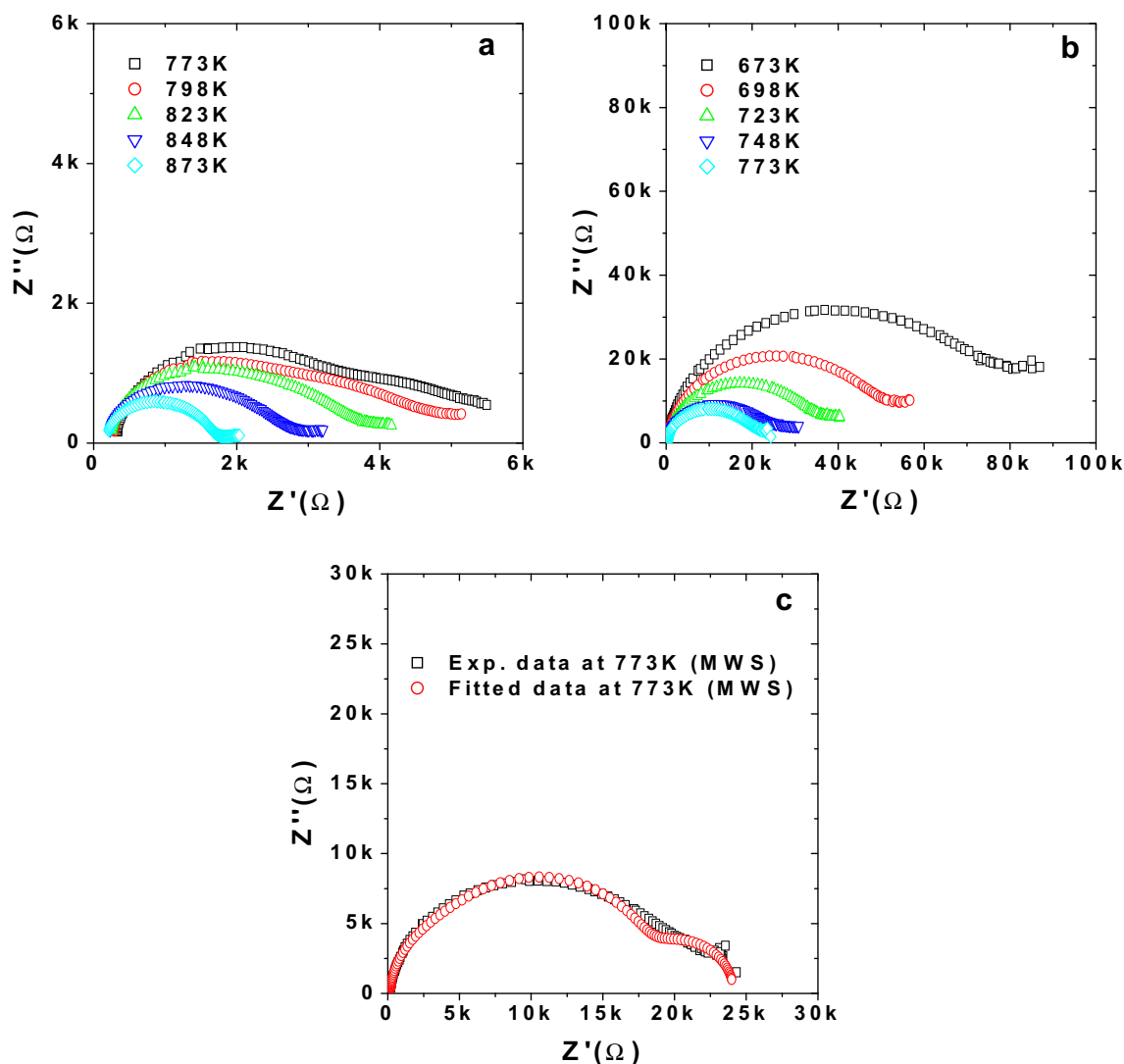


**Figure 4.** Dielectric constant vs. frequency plots at different temperatures for (a) CS and (b) MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramics.

case of the MWS sample. The room temperature dielectric constant at 10 kHz for CS and MWS samples are 1245 and 5250 respectively (table 1). Four times enhancement in the room temperature dielectric constant in the MWS sample is observed when compared to the CS sample. The transition temperatures at 10 kHz for CS and MWS samples are 421.82 and 428.71 K, respectively. In the case of the MWS sample there is a shift of transition temperature towards a higher temperature side with the increase of frequency indicating some sort of relaxor behaviour. The dielectric relaxor behaviour in the present MWS sample may be attributed to relaxation of oxygen vacancies. The oxygen vacancies arise due to the oxygen loss at higher sintering temperatures and also due to the less available time for re-oxidation to take place in the

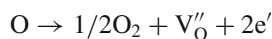
MWS sample when compared to the CS sample. Because of slower cooling rates in the CS sample there will be more ample time for re-oxidation to take place leading to fewer or no oxygen vacancies. The higher value of dielectric constant in MWS sample may be due to segregation of these oxygen vacancies across the grain boundary region and also at the sample–electrode interface region leading to highly capacitive nature than the CS sample.

Figure 2a and b shows the DC and AC (at 10 kHz) conductivity plots as a function of  $1000/T$  for CS and MWS ceramics. The MWS ceramic sample shows higher values of DC and AC conductivity when compared to the CS sample. In the case of the CS sample, the AC conductivity is one to three orders higher than the DC conductivity in the measured



**Figure 5.**  $Z''$  vs.  $Z'$  for (a) CS and (b) MWS samples and (c) experimental and fitted  $Z''$  vs.  $Z'$  curve at 773 K (MWS) for  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramics.

temperature range, whereas AC conductivity is two orders higher than the DC conductivity in the case of the MWS sample. In the case of MWS sample the DC and AC conductivity at higher temperatures is almost the same indicating intrinsic conductivity. In general, a slight amount of oxygen loss occurs in perovskite materials during their preparation at high temperatures ( $>1400^\circ\text{C}$ ) and this results in liberation of electrons, which are retained in the crystal structure [14,15]:

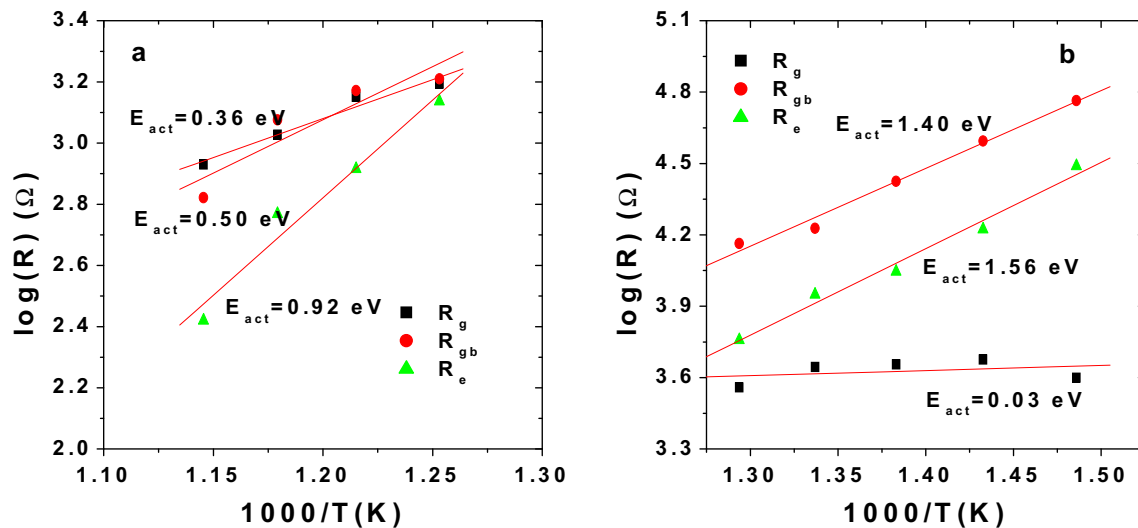


where  $\text{V}_\text{O}''$  represents double-ionized oxygen vacancy and  $e'$  represents electrons.

The observed higher value of DC and AC conductivity in the MWS sample when compared to the CS sample may be related to the response of these electrons. As explained in previous paragraphs MWS sample shows the formation of

more oxygen vacancies than the CS sample and this has resulted in more number of electrons retained in the crystal lattice of the MWS sample. Larger the concentration of electrons higher is the DC and AC conductivity, which is in good agreement with the present experimental results. The DC conductivity in both CS and MWS samples is lower when compared to AC conductivity and this may be due to the most difficult transition/transport of charge carriers at the lattice sites and also across the lattice defects. The change in slopes in different temperature regions may be attributed to the different charge carrier transport phenomena occurring in the ceramic sample and also to the transition from the ferroelectric state to the paraelectric state. The different type of charge transport phenomenon can be ascribed to free charge carriers, polaronic conduction at lattice defects etc.

Figure 3a and b shows the variation of  $Z''$  with frequency for CS and MWS samples respectively. Broad  $Z''$  peaks were



**Figure 6.**  $\log(R)$  vs.  $1000/T$  for (a) CS and (b) MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramics.

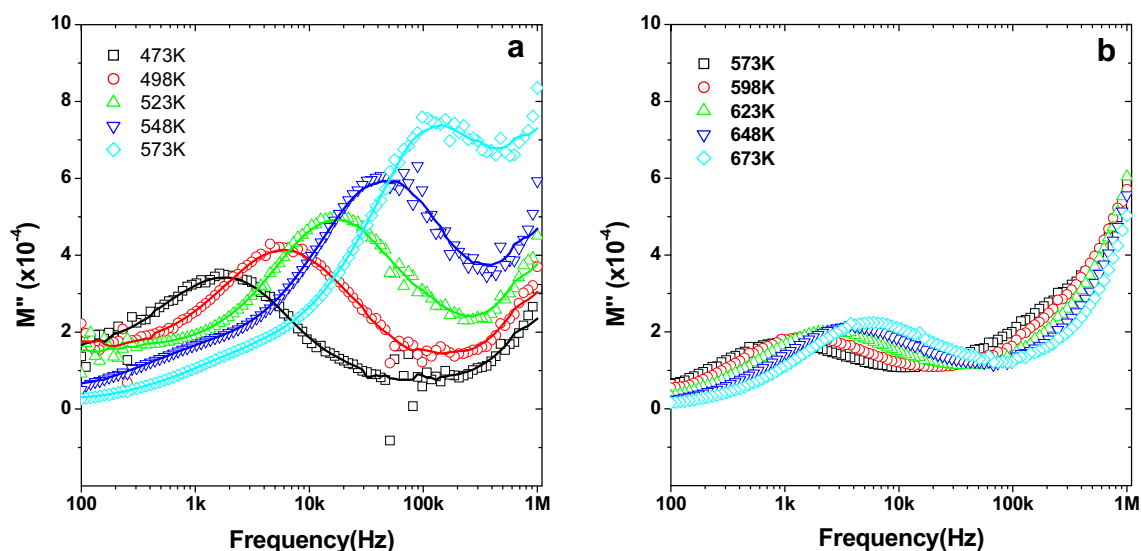
observed indicating multiple relaxations. In the case of the MWS sample, at both lower and higher temperatures, the  $Z''$  peak is symmetric when compared to the CS sample indicating that these curves follow Gaussian distribution function. The  $Z''$  peaks were observed in the lower temperature regime (673–773 K) in the case of the MWS sample when compared to the CS sample (773–873 K). The frequency at which  $Z''$  attains peak value is lower in the case of the MWS sample when compared to the CS sample indicating increased relaxation times.

Figure 4a and b shows the frequency dependent dielectric constant plots for CS and MWS samples, respectively. Variation of dielectric constant above 2 kHz is more or less negligible. However, with decrease of frequency below 2 kHz, the dielectric constant increased and there is dispersion of dielectric constant at a set temperature. The observed higher values of dielectric constant at lower frequencies may be attributed to the space charge polarization effects. With increase of temperature, dielectric constant increases with temperature at lower frequencies and remains almost constant at higher temperatures. This is due to disappearance of space charge polarization effects with temperature.

Figure 5a and b shows the  $Z''$  vs.  $Z'$  (Cole–Cole) plots at different constant temperatures for CS and MWS samples, respectively. The Cole–Cole plots were observed in the lower temperature regime (673–773 K) for the MWS sample when compared to the CS sample (773–873 K). The diameter of the semi-circles indicates the total resistance of the sample is higher in the case of MWS sample. This may be due to the observance of semicircular arcs in the lower temperature regime (673–773 K) when compared to the CS sample (773–873 K). Figure 5c shows the fitted and experimental Cole–Cole plot at 773 K for the MWS sample. The fitting is done using FRA software provided with the PGSTAT 30

impedance analyzer. Equivalent circuit consisting of three parallel  $RC$  combinations in series with each other is found to be the best fit to the experimental data indicating contribution from grain, grain boundary and sample electrode interface effects for samples prepared through CS and MWS routes. The grain resistance is higher than that of the grain boundary and sample electrode interface resistance in the case of the CS sample as shown in figure 6a. Whereas the grain resistance is lower than that of the grain boundary and sample–electrode interface resistance in the MWS sample. The grain, grain boundary and sample electrode resistance are higher for the MWS sample when compared to the CS sample and this may be due to the observance of Cole–Cole plots in the lower temperature regime (673–773 K) for the MWS sample. Linear fitting is done to the experimental data using the Arrhenius relation for resistance as shown in figure 6a and b. From the slope of the linear fitting to experimental data, activation energies for grain, grain boundary and sample–electrode interface conduction are obtained and are shown in figure 5. It is observed that the activation energy for grain conduction for the MWS sample is lower when compared to the CS sample; whereas the activation energy for grain boundary and sample–electrode interface conduction is higher for the MWS sample when compared to the CS sample. This may be attributed to the oxygen vacancy related conduction phenomenon in the MWS sample as explained in previous paragraphs.

Figure 7a and b shows the modulus resonance and anti-resonance plots at different constant temperatures for CS and MWS samples respectively studied under clamped state (in tandem with unknown but constant spring constant). Broad resonance and anti-resonance peaks were observed at lower frequency in the MWS sample when compared to the CS sample. Since the data for the CS sample is scattered smoothing with adjacent averaging is done as shown by coloured lines in figure 7a and these curves are used to obtain the resonance



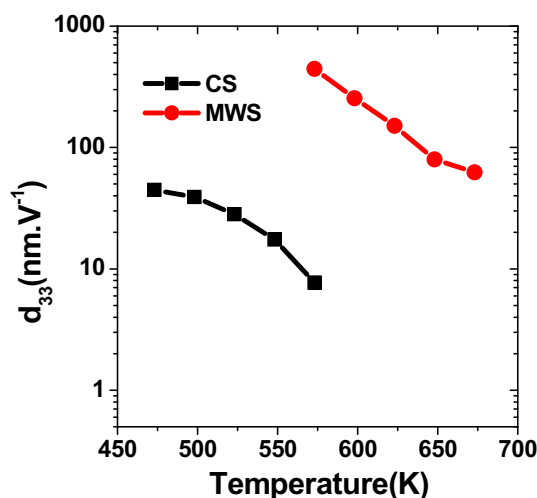
**Figure 7.**  $M''$  vs. frequency plots for (a) CS and (b) MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramics.

**Table 2.** Various parameter values obtained from resonance and anti-resonance studies.

Parameter	Composition $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$	
	CS sample (573 K)	MWS sample (573 K)
$f_r$ (Hz)	141,700.00	932.60
$f_a$ (Hz)	432,900.00	11,500.00
$\Delta f$ (Hz)	291,200.00	10,567.40
$K_t$	0.954	0.997
$d_{33}$ (nm $\text{V}^{-1}$ )	7.72	444.66

and anti-resonance frequency values. The values of thickness mode of electromechanical coupling factor ( $K_t$ ) and piezoelectric charge constant ( $d_{33}$ ) are calculated using the formulas given in the literature [9,16] and are tabulated in table 2. The value of  $K_t$  is found to be 0.954 and 0.997; whereas the value of  $d_{33}$  is 7.72 nm  $\text{V}^{-1}$  (573 K) and 444.66 nm  $\text{V}^{-1}$  (573 K) for CS and MWS samples, respectively. There is almost 57 times enhancement of  $d_{33}$  value in the case of the MWS sample when compared to the CS sample. In MWS more rapid and uncontrolled heating and cooling of the sintered samples takes place when compared to CS samples. Rapid heating and cooling of ceramic samples in MWS lead to the distribution of grains and grain boundary regions with varying sizes and thickness respectively. This in turn makes the ceramics with residual internal stress within the grain and grain boundary regions. Usually internal stress across the grain and grain boundary regions has some effect on the properties under study. In the present case the internal stress developed within the ceramic materials has a positive effect leading to enhanced piezoelectric properties.

Figure 8 shows the temperature dependence of  $d_{33}$  plots for CS and MWS samples. Higher values of  $d_{33}$  were observed



**Figure 8.** Piezoelectric charge constant vs. temperature for CS and MWS  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramics.

for the MWS sample. Both CS and MWS samples showed decrease of  $d_{33}$  value with the increase of temperature. It is known that slope of Arrhenius plot for  $d_{33}$  gives activation energy for domain switching (figure not shown). The values of activation energy for domain switching obtained from Arrhenius plots of  $d_{33}$  for CS and MWS samples are 0.39 and 0.67 eV, respectively.

#### 4. Conclusions

Dielectric studies of  $\text{Ba}_{0.997}\text{Nd}_{0.003}\text{TiO}_3$  ceramic revealed that there is around four times enhancement in the room



temperature dielectric constant in the MWS sample (5250) when compared to the CS sample (1245). Thickness mode of electromechanical coupling factor is over 90% for samples prepared through both the routes. The value of  $d_{33}$  is  $7.72 \text{ nm V}^{-1}$  (573 K) and  $444.66 \text{ nm V}^{-1}$  (573 K) for CS and MWS samples, respectively. MWS has resulted in 57 times enhancement in piezoelectric charge constant ( $d_{33}$ ) when compared to CS ceramic. In the present study, the internal stress developed within the ceramic materials due to rapid cooling in MWS has a positive effect leading to enhanced piezoelectric properties.

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