

DIELECTRIC PROPERTIES AND AGING OF FAST-FIRED BARIUM TITANATE

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Abstract — The dielectric properties and their aging rate of three chemically prepared BaTiO₃ compositions, from Ba-rich to Ti-rich fast fired to 1450°C, were measured from 470 K down to 225 K. Ba-rich samples, in spite of their similar sintering behavior when compared to stoichiometric samples, exhibited the highest dielectric constant values of all compositions. The 1 kHz dissipation factor values in Ba-rich and stoichiometric samples were not observed to decrease with increasing fired density of the samples. High density samples of all three stoichiometries exhibited fairly small losses just above the Curie temperature, while Ba-rich and stoichiometric samples exhibited a marked decrease in the dissipation factor below 260 K.

Keywords — Fast-firing, sintering, barium titanate, dielectric, aging.

I. INTRODUCTION

Some work has been done in the past studying the effect of microstructure on the dielectric properties of polycrystalline BaTiO₃. A strong dependence of the permittivity of the ferroelectric phases with average grain size in this material has been reported for fine-grained samples. Room-temperature dielectric constant values ranging from 3500 up to 5500 have been reported for dense polycrystalline ceramics with averages grain sizes at around 1 μm (Kniekamp and Heywang, 1954; Kinoshita and Yamaji, 1976).

Prior studies have tried to optimize densification and control grain growth phenomena in order to produce samples with high permittivity and small dielectric losses by using sintering aids or particular sintering conditions (Mostaghaci and Brook, 1981; Yoo *et al.*, 1987).

Fast firing has received some attention since this technique allows for an increase in densification while minimizing grain growth by establishing temperature conditions in which the mass-transport mechanisms available for densification during sintering are favored over those leading to grain growth. This method involves, basically, heating rapidly through the low temperature region, with heating rates as high as 500°C/min, to relatively high sintering temperatures where the ceramic is held for a short period of time. Fast firing has been successfully applied to a variety of materials (Harmer *et al.*, 1978; Morell and Hermosin, 1980).

Besides the microstructure benefits, fast firing can be favored over other techniques, such as grain growth inhibitors— Ta₂O₅, Nb₂O₅, ZrO₂ (Jonker and Noorlander,

1962; Harkulich *et al.*, 1966)- or hot pressing (Mostaghachi and Brook, 1983; Sharma and McCartney, 1974), because of its simple set-up as well as the potential of decreased production times due to the relatively short firing cycles employed.

Fast firing applied successfully to BaTiO₃ requires a highly homogeneous starting powder, since the existence of localized stoichiometry differences may result in discontinuous grain growth (Yoo *et al.*, 1987) even with Ba-rich chemically prepared powders (see Fig. 1) that render uniform microstructures when conventionally sintered (Alles *et al.*, 1989).

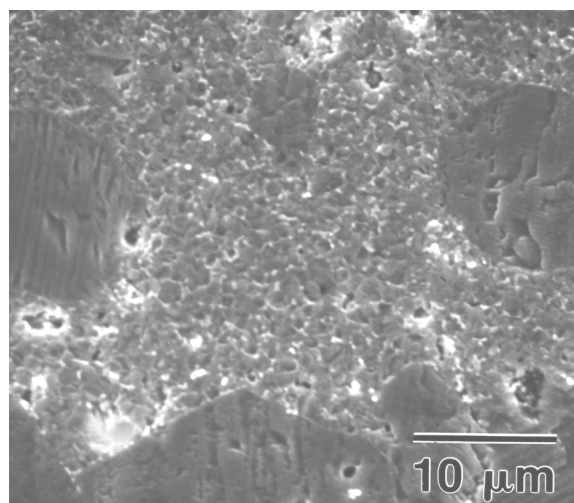


Figure 1. SEM (SE) 2000X micrograph of the fired surface of a chemically prepared barium titanate sample with a Ba/Ti ratio of 1.01 fired at 500°C/minute to 1450°C and held for 5 minutes.

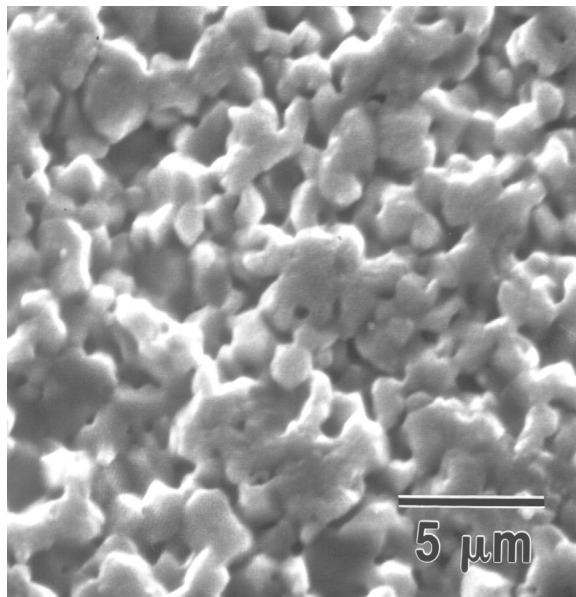


Figure 2. SEM (SE) 4000X micrograph of a polished and thermally etched sample with a Ba/Ti ratio of 0.999 fired at 500°C/min heating rate and soaked at 1450°C for 2 minutes.

The presence of excess TiO_2 in BaTiO_3 promotes the formation of a Ti-rich liquid phase at about 1320°C that causes rapid densification and coarsening. Upon cooling, a second phase, identified as BaTi_3O_7 (Sharma *et al.*, 1981) or $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ (Negas *et al.*, 1974), remaining from the sintering process, is normally observed at triple-grain junctions. Because of the rapid cycle used in fast firing, a liquid phase forms in those regions whose stoichiometry is found to be Ti-rich causing a bimodal grain size distribution, in spite of the beneficial effect that the presence of liquid phase sintering may have on the final properties of the samples (Alles and Burdick, 1991; Alles and Burdick, 1993).

The presence of porosity not only decreases the value of the permittivity but also increases the dissipation factor (Herbert, 1985; Fang *et al.*, 1993), particularly if diffusion promotes the access of moist air into the pores. This is markedly important for Ba-rich samples since the excess barium, that has limited solubility in the barium titanate lattice, segregates as a second phase as Ba_2TiO_4 (Hu *et al.*, 1985) and it is susceptible to be attacked by water.

Variations in composition, as well as the presence of small impurities, can drastically affect the dielectric properties of BaTiO_3 , thus a high purity, highly homogeneous powder coupled with high fired density values and small grain-size microstructures are required to obtain ceramics with high permittivity and small losses.

It is the objective of this work to observe the effect on the dielectric properties and on their aging rate of using fast firing methods on high purity organically prepared BaTiO_3 powders with stoichiometries ranging from Ba-rich to Ti-rich.

II. EXPERIMENTAL PROCEDURE

Three chemically prepared high purity (see Table 1) barium titanate powders (Transelco Division, Ferro Corp) with Ba/Ti ratios essayed to be 1.007, 0.999, 0.993 ± 0.0025 respectively were ball-milled. Standard tape-casting manufacturing techniques were employed to produce samples of 12 mm x 6 mm x 1 mm. A full description of the procedure followed is given elsewhere (Alles *et al.*, 2001).

Binder burnout was conducted in a conventional furnace at 650°C followed by sample sintering at 1450°C in a fast firing furnace with a ramp rate of 500°C/h for heating and cooling with soaking times ranging between 0 and 80 minutes (Alles *et al.*, 2001).

The dielectric properties of the samples were measured by using an HP 4192 (Hewlett Packard) impedance analyzer with a HP 3488A switch scanner (Hewlett Packard) after applying electrodes by evaporation of a thin layer of chromium followed by a layer of gold. Dielectric properties were measured at preset frequencies of 1 kHz and 100 kHz from 470 K down to 225 K at a cooling rate of 2 K/min.

Aging measurements were conducted at $353.0 \text{ K} \pm 0.2 \text{ K}$ for all samples and their dielectric properties were measured at the preset frequencies of 1 kHz and 100 kHz. Sample temperature was monitored by an RTD detector. All samples were de-aged at 473 K for 30 minutes, immediately placed in the aging sample holder, and the aging run started within a few seconds after the samples reached 353 K. Each aging experiment was monitored for 10^4 minutes by measuring the capacitance and the loss tangent.

Table 1. Chemical analysis and impurity level of barium titanate 219-9 series powder (Transelco Division – Ferro Corporation), mole ratio Ba/Ti = 0.993.

Specie	Concentration	Specie	Concentration
BaO	65.43%	SnO ₂	< 30 ppm
TiO ₂	34.33%	Bi ₂ O ₃	< 10 ppm
Al ₂ O ₃	< 10 ppm	CuO	< 10 ppm
CaO	< 30 ppm	Li ₂ O	< 10 ppm
Fe ₂ O ₃	< 30 ppm	MnO ₂	< 10 ppm
MgO	< 50 ppm	Nb ₂ O ₅	< 30 ppm
Na ₂ O	30 ppm	PbO	< 50 ppm
NiO	< 30 ppm	SiO ₂	10 ppm
SO ₃	50 ppm	SrO	< 10 ppm

Table 2. Fired density, average grain size, and 353 K dielectric constant and dielectric loss values for barium titanate samples fired at 1450°C.

Ba/Ti ratio	Soaking (min.)	Density (%)	Grain size (μm)	Dielectric constant		Dielectric loss	
				1 kHz	100 kHz	1 kHz	100 kHz
1.007	1	84	1.0	2210	2030	0.039	0.028
	2	88	1.5	2460	2230	0.047	0.026
	5	92	2.0	2900	2570	0.060	0.034
	10	93	3.0	3740	3290	0.047	0.055
	20	96	5.0	3250	2870	0.048	0.054
	40	98	9.0	3340	2900	0.042	0.063
	80	100	11.0	3170	2750	0.042	0.063
0.999	1	84	1.0	1980	1860	0.029	0.021
	2	89	1.5	2080	1930	0.036	0.021
	5	91	1.5	2430	2260	0.037	0.021
	10	92	3.0	2770	2510	0.052	0.032
	20	96	4.0	2870	2610	0.038	0.048
	40	96	9.5	3150	2840	0.029	0.047
	80	99	10.0	2930	2690	0.027	0.045
0.993	0	96	24.5	2080	2020	0.009	0.070
	1	97	24.0	1860	1800	0.016	0.081
	2	98	25.0	1910	1850	0.017	0.080
	5	97	25.0	1860	1800	0.018	0.078
	10	97	25.0	1910	1850	0.013	0.086
	20	97	28.0	1910	1810	0.037	0.091

III. RESULTS AND DISCUSSION

Ba-rich and stoichiometric samples behaved similarly upon sintering, reaching relatively high density values at longer soaking times (see Table 2 and Fig. 2).

Although both compositions differed less than 1 at. % of excess barium, the above result did not fully agree with previous reports (Mostaghaci and Brook, 1986). Also, here was no apparent liquid-phase formation in these samples to induce rapid densification, in spite of earlier reports (Yoo *et al.*, 1987), and sample densification and grain growth proceeded by solid-state diffusion mechanisms (see Fig. 3).

A distinct second phase was not found under SEM observation, however, some evidence was obtained that the grain boundary region could have a different composition than the bulk when compared to stoichiometric samples (Alles *et al.*, 2001).

In contrast to the other two compositions, Ti-rich samples exhibited remarkably high fired densities with short soaking times and relatively coarse but uniform microstructures (see Fig. 4). A sample fired at 1400°C without soaking was observed to be 94% dense with an average grain size of 21 μm and uniform microstructure. It should be kept in mind that, in principle if some small thermal inertia effects are disregarded (Alles *et al.*, 2001), this sample remained above the eutectic temperature of 1320°C for about 20 seconds only.

Ti-rich samples fired at 1450°C exhibited an average grain size of about 25 μm and about 96% density in spite of longer soaking times indicating that the sintering process was exhausted, as well as secondary recrystallization phenomena proceeded with a fairly low time dependence under the prevalent conditions (see Fig. 3) similarly to other ceramic systems (Alles and Burdick, 1991; Alles and Burdick, 1993).

As expected, the dielectric constants of the different samples depended strongly on grain size and porosity (see Table 2 and Fig. 5). Since both characteristics influence the relative permittivity in opposite directions exceedingly high values of the dielectric constant were not observed in this work.

In spite of similar sintering behavior when compared to stoichiometric samples, Ba-rich specimens exhibited higher values of the dielectric constant and the dissipation factor when compared with stoichiometric as well as Ti-rich samples. This could suggest that barium-rich second phases, perhaps present as a Ruddlesden-Popper intergrowth structure (Ruddlesden and Popper, 1958) segregated at the grain boundaries, in spite of its low dielectric constant value improve the dielectric characteristics of the grains. Also, no significant differences were observed in the extrapolated Curie-Weiss temperature values between barium-rich and stoichiometric samples (Alles *et al.*, 2001), a fact that

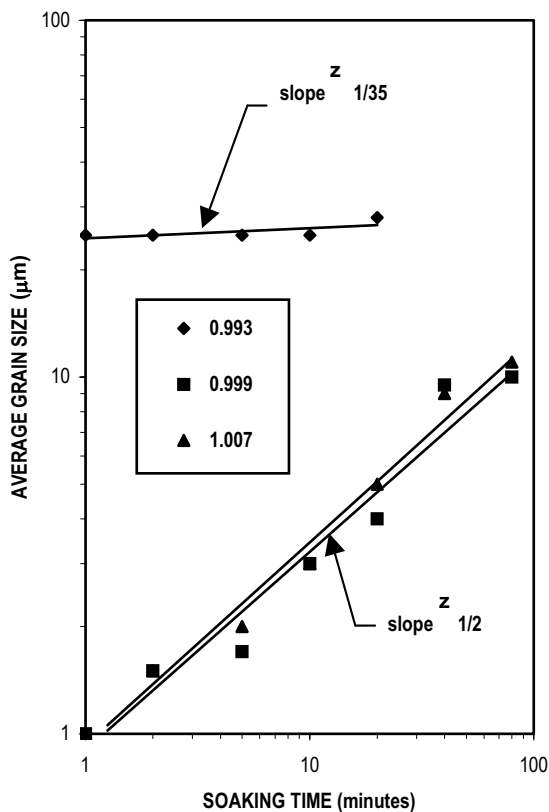


Figure 3. Average grain-size values for samples fired at 500°C/min heating rate and soaked at 1450°C.

could suggest the presence of a continuous low permittivity second phase located at the grain boundaries in Ba-rich samples.

The orthorhombic to tetragonal phase transition was observed to be broader and shifted to higher temperatures values in Ba-rich and stoichiometric samples when compared to Ti-rich samples (see Fig. 5). This could indicate that a higher degree of stress (Buessem *et al.*, 1966a) could be present in the former polycrystalline samples when compare to the latter samples, in spite of the relatively broad range of average grain sizes of the former, e.g. from about 1 μm up to 11 μm.

Ti-rich samples exhibited a fairly constant value of about 2200 for the room-temperature dielectric constant, as expected since the average grain size of these samples exceeded the value of 10 μm (Buessem *et al.*, 1966b; Arlt, 1987). However, this value is somewhat higher than the recognized value of 1500 (Buessem *et al.*, 1966a,b; Hu *et al.*, 1985; Arlt, 1987;) for samples of these characteristics.

Barium-rich and stoichiometric samples exhibited similar dissipation factors. The 1 kHz losses were observed to remain relatively constant with increasing soaking times for these samples in spite of decreasing

porosity, while 100 kHz losses increased with increasing density (see Table 2).

The losses of barium-rich and stoichiometric samples exhibiting higher density values were observed to decrease significantly in the temperature interval of about 40K above the Curie point, while samples with higher porosity exhibited a marked increase in the dissipation factor values after a sharp reduction just above the critical temperature (see Fig. 6).

Ti-rich samples exhibited the lowest values of the dissipation factor of all fired samples, as well as losses were observed, once again, to decrease significantly above the critical temperature (see Fig. 7). In fact, high density samples of all three stoichiometries, in the temperature range around 40 K above the critical temperature, exhibited very small negative loss-tangent values (inductive) probably because of experimental error and the virtually zero value of the dissipation factors (see Figs. 6-7). This suggests that the losses in dense samples in the ferroelectric region could be caused chiefly by hysteretic domain-wall motion (Arlt, 1987).

Upon cooling from 260 K down to about 225 K well within the orthorhombic region, Ba-rich and stoichiometric samples exhibited a strong decrease in losses which is not completely paralleled by a decrease in the dielectric constant values (see Figs. 5-6). This sharp decrease in the loss factor is also not observed in Ti-rich samples (see Fig. 7). Considering that in fine grain materials, under 10μm of average grain size, the hysteretic domain-wall motion should contribute more

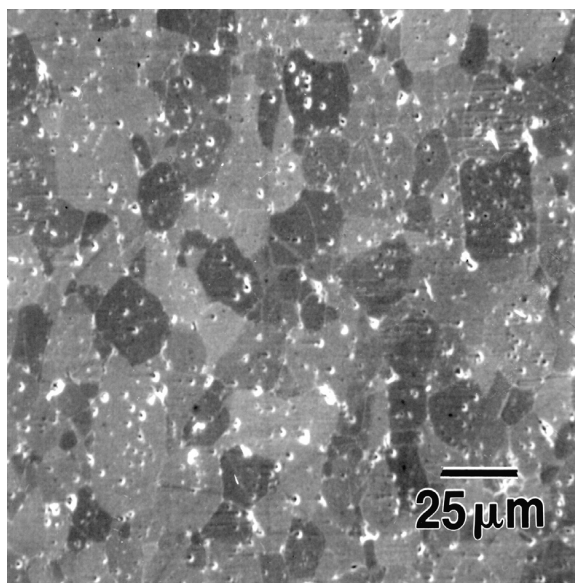


Figure 4. SEM (SE) 400 X micrograph of a polished and thermally etched sample with a Ba/Ti ratio of 0.993 fired at 500°C/min heating rate and soaked at 1450°C for 2 minutes.

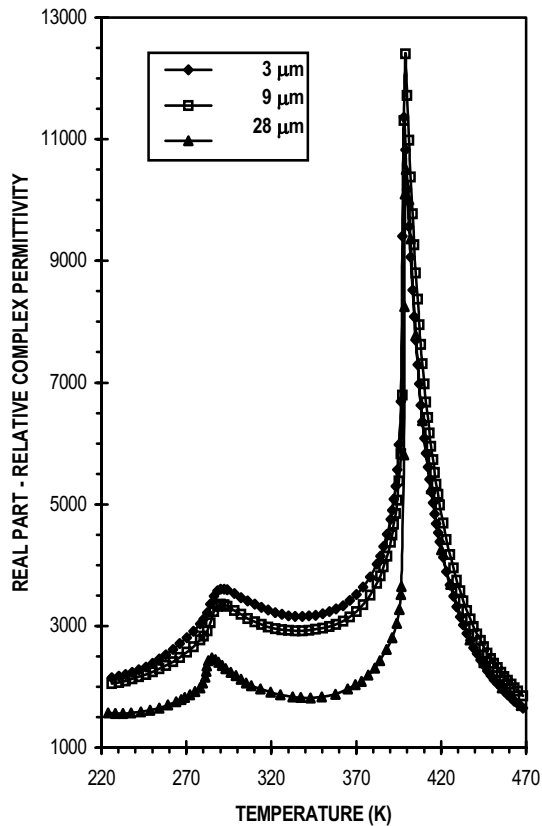


Figure 5. Dielectric constant at 1 kHz versus temperature characteristics for samples fired at 1450°C with 1.007 Ba/Ti ratio and average grain sizes of 3.0 μm and 9.0 μm , and with 0.993 Ba/Ti ratio and average grain size of 28 μm .

heavily to the dissipation factor than to the dielectric constant value, this could suggest a change in the thermally activated response of the walls below 260 K.

In general, in the paraelectric region well above the Curie point, the increase in the dissipation factor values observed in all the samples (see Figs. 6-7) may be attributed to thermally activated conduction losses due to hole hopping- if the acceptor nature of common impurities in barium titanate materials is taken into account- or polaron conduction if a slight oxygen deficiency prevails in the structure.

In general, for all three stoichiometries the samples with higher density values exhibited higher losses at 100 kHz of applied electric field when compared to an applied signal of 1 kHz of frequency. Contrary to this for barium-rich and stoichiometric samples, lower density samples were observed to have higher losses at 1 kHz comparatively to those observed at 100 kHz (see Table 2).

In the paraelectric region, the Curie-Weiss constant values for Ba-rich and stoichiometric samples were

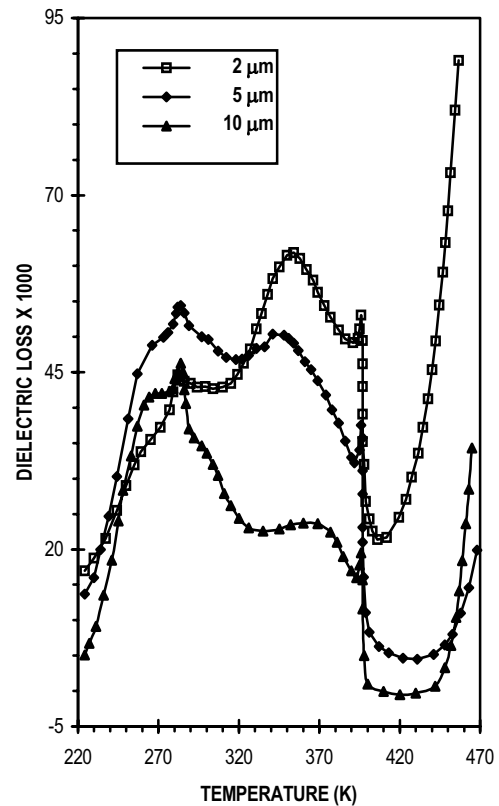


Figure 6. Dielectric loss versus temperature characteristics at 1 kHz for samples fired at 1450°C with 1.007 Ba/Ti ratio and average grain sizes of 2.0 μm , 5.0 μm , and with 0.999 Ba/Ti ratio and an average grain size of 10 μm .

strongly influenced by porosity (Alles *et al.*, 2001) exhibiting values ranging from 0.87×10^5 K to about 1.50×10^5 K. The Curie-Weiss temperature was found to exhibit values ranging from 378 K to 390 K for Ba-rich samples and stoichiometric samples, reaching maximum values for the comparatively higher density samples. Ti-rich samples exhibited fairly constant values for these two parameters observed to be 1.27×10^5 K and 389 K for the Curie-Weiss constant and temperature respectively.

The aging rate of the different samples is presented in Table 3. As expected, the dielectric loss was observed to age more rapidly than the dielectric constant, with the lower aging rate of the latter observed in Ti-rich samples consistent with their larger average grain size and a state of less general of stress. Domain-wall motion is expected to contribute more heavily to the losses than to the dielectric constant, and since domain-size growth in barium titanate should reduce the total amount of domain-wall area per unit volume, a faster aging rate of the dissipation factor should be observed.

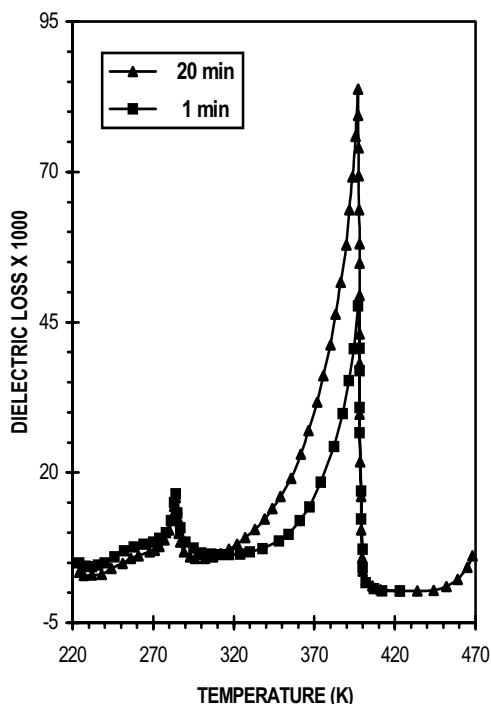


Figure 7. Dielectric loss versus temperature characteristics at 1 kHz for samples fired at 1450°C with 0.993 Ba/Ti ratio and two different soaking times.

IV. CONCLUSIONS

1. Ba-rich and stoichiometric samples behaved similarly during sintering resulting in uniform microstructures.
2. Evidence of transient liquid-phase formation in Ba-rich and stoichiometric samples was not found, and sintering as well as grain growth proceeded by solid-state mass-transfer mechanisms.
3. Ba-rich samples exhibited comparatively higher values for the dielectric constant of all the samples.
4. Dielectric losses at 1 kHz in the different samples were not observed to decrease with decreasing porosity, while 100 kHz losses increased with increasing density.
5. For all three compositions, high density samples exhibited exceedingly small dissipation factors just above the Curie point, while losses started to increase significantly in these specimens at about 50 K above the Curie point.
6. Ba-rich and stoichiometric samples were observed to have a sharp decrease in the dissipation factor between 260 K and 225 K, and a relatively moderate decrease of the dielectric constant value in this temperature range.
7. As expected, the loss factor was observed to age more rapidly than dielectric constant.

Table 3. Aging rate at 353 K for the dielectric constant and dielectric loss of BaTiO₃ samples fired at 1450°C with different compositions and soaking times.

Ba/Ti ratio	Soaking (min.)	Dielectric constant aging rate (%/decade)		Dielectric loss aging rate (%/decade)	
		1 kHz	100 kHz	1 kHz	100 kHz
1.007	1	5.7	5.0	8.8	8.6
	2	5.3	4.7	7.3	4.6
	5	4.4	3.8	6.1	4.0
	10	6.1	5.3	6.0	16.7
	20	6.8	5.6	9.5	12.7
	40	7.1	5.8	7.0	16.5
	80	6.9	5.6	8.4	15.0
0.999	1	5.5	5.1	10.2	7.8
	2	5.4	5.5	9.3	8.7
	5	5.1	4.7	10.9	4.6
	10	3.4	3.3	12.2	5.1
	20	6.4	5.5	8.6	8.5
	40	6.3	3.6	8.5	12.9
	80	6.1	5.5	10.5	11.1
0.993	0	3.5	3.2	11.5	6.4
	1	3.9	3.6	9.4	3.8
	2	3.9	3.7	13.7	7.6
	5	4.0	3.8	14.4	7.8
	10	3.8	3.6	12.1	7.0
	20	4.3	3.7	16.3	9.9

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