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*THE GRAIN-SIZE DEPENDENCE OF THE
ELECTROMECHANICAL PROPERTIES IN
LEAD ZIRCONATE - TITANATE CERAMICS*

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The grain-size dependence of the electromechanical properties in lead zirconate – titanate ceramics

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Abstract

The dependence of the electromechanical properties of unmodified lead zirconate-titanate ceramics on the grain size of the ceramic has been determined for materials with compositions on both sides of the rhombohedral/tetragonal boundary. High-density ceramics with average grain diameters from about 1.5 μm to 8 μm were examined. It was found that the dielectric constant before poling, and the dielectric and mechanical losses all decreased with increasing grain size. The coercive field was found to be largely independent of grain size in the range examined.

Introduction

The properties of ceramics and, in particular, those properties of interest for electrical and electronic applications, depend not only on their chemical composition but also on such aspects of their physical structure as the degree of porosity and grain, or crystallite, size. It has been shown, for example, that the electrochemical coupling factor and dielectric constant of lead zirconate-titanate piezoelectric ceramics increase with decreasing porosity (1). Studies on barium titanate piezoelectric ceramics have indicated that very fine-grained materials have higher dielectric constants and lower piezoelectric activity than materials with larger grain sizes (2,3,4). A few investigations of the effects of grain size in lead zirconate-titanate materials have also been reported.

Haertling (5), in a study of the effect of hot-pressing conditions on the properties of lead zirconate-titanate ceramics with added Bi_2O_3 , found that the dielectric constant and coercive field both decreased with increasing grain size of the ceramic. Further investigations by Haertling and Zimmer (6) on another Bi_2O_3 -doped lead zirconate-titanate composition confirmed the earlier observations and indicated also that the dielectric constant and remanent polarization decrease with increasing porosity of the ceramic.

Jonker (7) has quoted results on the composition $\text{PbTi}_{0.90}\text{Zr}_{0.10}\text{O}_3$ that show an increase in electromechanical coupling factor with increasing crystallite size in the range 3 to 12 μm .

Another investigation (8) indicated that, with increasing grain size in lead zirconate-titanate ceramics, there is an increase in remanent polarization and radial coupling factor; on the other

hand, a lowering of the depolarization field was noted with increasing grain size.

Because of the important effects that the grain size has upon the piezoelectric properties of lead zirconate-titanate ceramics, the present investigation was undertaken to extend the previously reported work. Two compositions on each side of the rhombohedral/tetragonal boundary were studied. The investigated properties included dielectric and mechanical losses and frequency constant, as well as dielectric constant, radial coupling factor, remanent polarization and coercive field. Care was taken to ensure, as far as possible, that variations in density, and changes in stoichiometry with respect to the lead oxide content of the material were minimized, since it is known that such variations will affect the observed properties of the materials (9).

Experimental Procedures

Ceramic disks were fabricated from co-precipitated hydroxides (or hydrated oxides) of lead, zirconium and titanium, produced by the method described by McNamara (10). The precipitates were calcined and cold-pressed into disks that were sintered at three different temperatures (1190°C, 1240°C and 1290°C) for three different times (one hour, three hours, and five hours) to give ceramics with a range of grain sizes. Disks with densities lower than 7.59 g/cm³ (cf. theoretical density 8.0 g/cm³) were discarded. The compositions of the materials used, expressed as mole percent zirconate, are given in Table 1, together with the range of densities of the ceramics. No modifiers were added to these compositions.

During the sintering of the ceramics, a small change in weight takes place, part of which may be due to loss or gain of lead oxide by exchange with the furnace atmosphere, in which a partial pressure of lead oxide vapour is maintained by the inclusion of lead zirconate disks. Variations in this weight change reflect variations in the

amount of lead oxide exchanged with the atmosphere. The ranges of observed percentage weight changes during sintering are also given in Table 1. It was considered that, in general, the effects on the electromechanical properties of these variations in density and lead oxide content of the ceramic would be negligible by comparison with those due to variations in grain size. In a few cases, the effects of differences in density and in lead oxide content have been estimated from previously obtained results (1,9), and these estimates support the foregoing assumption.

The ceramics designated in Table 1 as T-1 and T-2 are tetragonal, while those designated as R-1 and R-2 are rhombohedral. Characterization of the powders used to produce these ceramics and of the ceramics fabricated from them under a standard set of conditions have been reported previously (9).

The electrical measurements for determining the properties of interest were carried out using electroded disks, both before poling and 24 hours after poling at 100°C under a field of 35 kV/cm. Most of the methods used have been described previously (11) and are in accordance with the appropriate standards (12). Values of the coercive field (E_c) and of the remanent polarization (P_r) were derived from slow hysteresis loops (approx. 0.25 cps) plotted at 100°C with a maximum applied field of 50 kV/cm. A balanced d-c power supply, manually reversible from maximum positive to maximum negative voltages, was employed as the source for a Sawyer-Tower circuit incorporating the sample; the current through the sample was integrated by a 1 μF capacitor and applied to the Y-axis of an X-Y recorder, while a signal proportional to the applied voltage was applied to the other axis through a voltage divider.

Average grain diameters were determined on etched polished sections by the intercept method, that is, by determining l , the length of a straight line

TABLE 1
Compositions and Ranges in Density and in Weight Change During Sintering of the Materials Studied

Designation	Composition mole % zirconate	Range in Densities (g/cm ³)	Range in Percentage Weight Change during Sintering
T-1	49.5	7.83 to 7.97	0.8
T-2	51.8	7.72 to 7.96	0.3
R-1	53.6	7.61 to 7.98	0.5
R-2	55.9	7.59 to 7.97	0.2

across a portion of the section, divided by the number of grains intersected by that line. In general, twenty lines, each intersecting 10 grains, were measured in various parts of the section. The mean grain diameter* was taken as $1.5 l$, as suggested by Fullman (13).

Experimental Results

The microstructures of some ceramics with composition T-1 are shown in Fig. 1. A range in mean grain diameter from $1.9 \mu\text{m}$ to $8.1 \mu\text{m}$ is illustrated. The ferroelectric domain structure is visible in the larger-sized grains, and it is seen that the domain size is of the same order of magnitude as the grain size in the finest-grained ceramic.

The dielectric constant (K) and dissipation factor ($\tan \delta$), both measured before poling, are shown as functions of the mean grain diameter, in Fig. 2. It is evident that both the dielectric constant and dissipation factor decrease with increasing grain size and, in general, appear to approach a limit at larger grain diameters. For compositions T-1 and R-1, corrections have been estimated to adjust the values of the dielectric constant to an arbitrary density (7.9 g/cm^3) and to an arbitrary percentage weight change during sintering. The adjusted values, also plotted in Fig. 2, indicate that variations in density and in lead oxide content of the ceramic do not significantly alter the principal features of the results.

The radial coupling factor (k_p) and dielectric constant after poling (K_{33}^T) are plotted as functions of mean grain diameter in Fig. 3. The coupling factor increases with increasing grain diameter and appears to approach a limiting value for grain diameters above $5 \mu\text{m}$. The dielectric constant K_{33}^T increases with increasing grain size for the tetragonal materials and decreases with increasing grain size for the rhombohedral materials.

The results presented in Fig. 4 show that the remanent polarization P_r , after application of a field of 50 kV/cm , increases with increasing grain size and approaches a limit at large grain diameters. The coercive field appears to be largely independent of grain size, although a slight drop at small grain diameters is suggested for the tetragonal materials. The mechanical quality factor increases with increasing grain size, but the form of the dependence is uncertain.

The frequency constant (resonance frequency X disk diameter) of the disks remained fairly constant, for a given composition, over the range of grain sizes examined, as indicated in Fig. 5 for two compositions. There appears to be a slight trend towards a lower frequency constant as the grain

* The method of estimating the mean grain diameter used here is different from that used in previous reports (9, 11). The previous results may be converted to values comparable with those used here by multiplying by an empirically determined factor of 1.2.

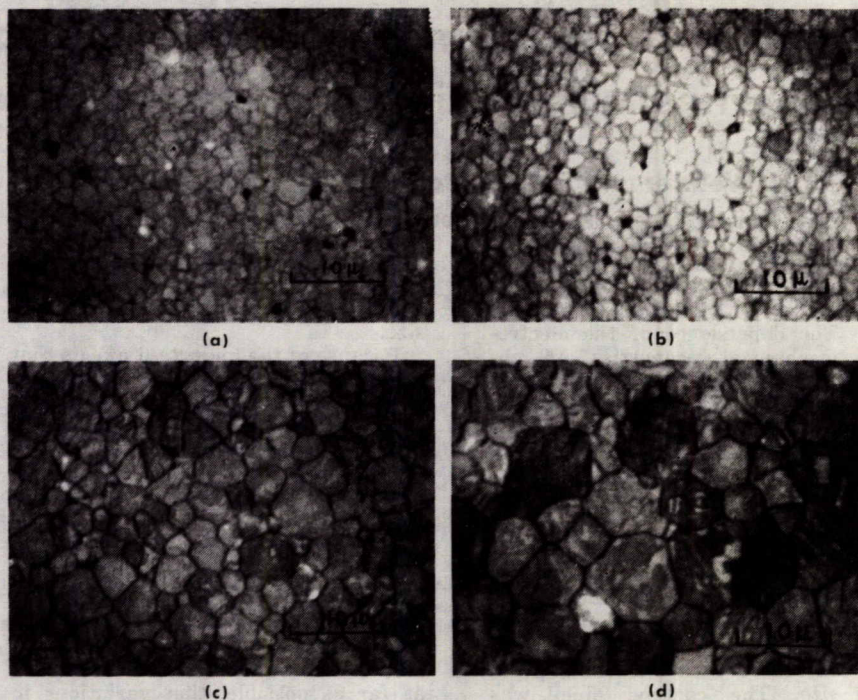


Fig. 1: Microstructures of ceramics of composition T-1. Average grain diameters: (a) $1.9 \mu\text{m}$, (b) $2.5 \mu\text{m}$, (c) $4.7 \mu\text{m}$, (d) $8.1 \mu\text{m}$. Etched with 0.2% HCl: 0.02% HF.

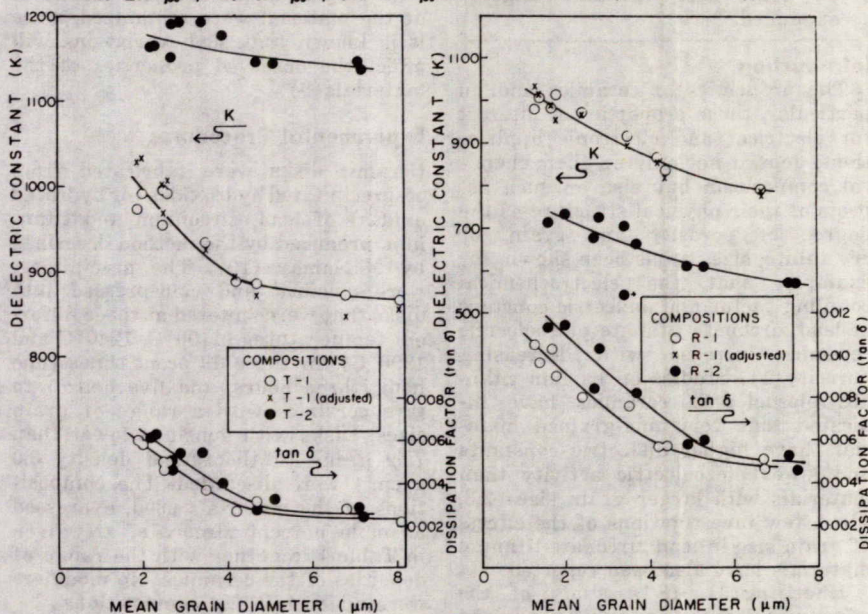


Fig. 2: Variation of dielectric constant and low-field dissipation factor at 1 kHz with ceramic grain-size, prior to poling.

size decreases. This trend persists, even after the results have been adjusted for variations in density and weight change during sintering. However, the effect is small and, over the range examined, is of the order of magnitude of the adjustments.

The dissipation factor determined under a high field (2 kV/cm r.m.s.), measured on poled ceramics, decreases with increasing grain size, as shown in Fig. 5. This is the same general behaviour as was found for the low-field dissipation factor measured before poling. A similar dependency was also shown by the low-field dissipation factor after poling (not plotted), but, in all instances, the dissipation factor after poling was greater than it was before poling.

Discussion

It is generally assumed, as, for example, by Jonker (7), that the re-orientation of the ferroelectric domains becomes difficult when the grain or crystallite size of a ferroelectric ceramic is of the order of, or smaller than, the ferroelectric domain size. The micrographs of the ceramics used in the present investigation indicate that the domain size, as seen in the large-grained ceramic, is of the same order as the grain size in the fine-grained ceramic. Hence it would appear that domain re-orientation in the fine-grained ceramic would be difficult. Such a difficulty in re-orienting the domains would lead to a lower remanent polarization in the fine-grained ceramics, which, in turn, would be reflected in

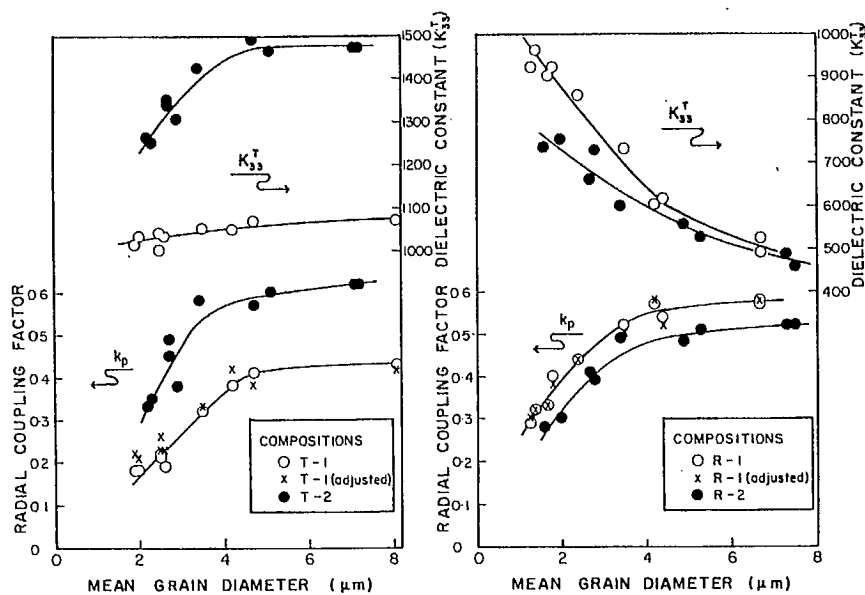


Fig. 3: Variation of dielectric constant after poling and radial electromechanical coupling factor with ceramic grain-size.

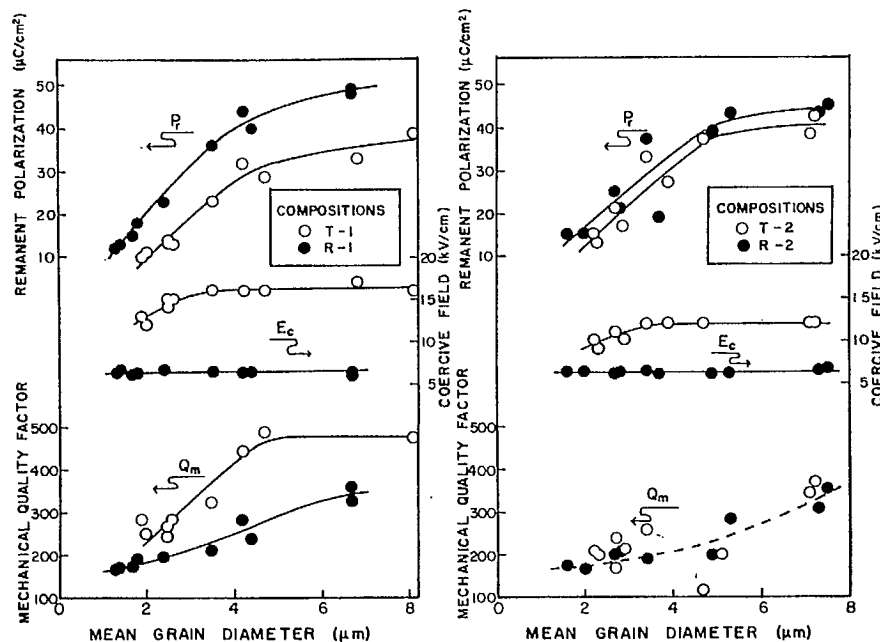


Fig. 4: Variation of remanent polarization, coercive field, and mechanical quality factor with ceramic grain-size.

lower piezoelectric activity, that is, in a decrease in radial coupling factor with decreasing grain size. The observed decrease in remanent polarization with decreasing grain size is in accord with Haertling's results on a composition $\text{Pb}(\text{Zr}_{0.85}\text{Ti}_{0.15})\text{O}_3$ with 2 atom % of added Bi_2O_3 (5). Also, the observed decrease in coupling factor with decreasing grain size is in accord with the results reported by Jonker(7) for the composition $\text{Pb}(\text{Zr}_{0.51}\text{Ti}_{0.49})\text{O}_3$. A similar decrease in piezoelectric activity with decreasing grain size has been observed for pure BaTiO_3 by Egerton and Koonce(2), and by Henry and Ilyn(3).

The increase in dielectric constant with decreasing grain size observed in BaTiO_3 (2,4) has been attributed by Buessem, Cross and Goswami(14) to

internal stresses developed in the ceramic when it is cooled through the Curie temperature. For large-grained ceramics, the stresses can be relieved by the development of a pattern of 90° domains within the grain but, when the domain size is of the order of the grain size, this is not possible.

A similar explanation probably accounts for the observed increase of the dielectric constant K , with decreasing grain size in the lead zirconate-titanate ceramics. A similar increase in dielectric constant with decreasing grain size has been reported by Haertling and Zimmer(6) for a ceramic with the composition $\text{Pb}(\text{Zr}_{0.85}\text{Ti}_{0.15})\text{O}_3$ containing 2 atom % of added Bi_2O_3 .

The behaviour of the dielectric constant after poling can be explained on the basis of the variation with grain

size of the remanent polarization and of the dielectric constant before poling. The dielectric constants (K_{33}^T) of the tetragonal materials increase on poling(9,15). This increase will be smaller when the remanent polarization is smaller. Thus, on poling, the dielectric constant of the large-grained material increases so much more than the dielectric constant of the fine-grained material that the overall behaviour is reversed, and the dielectric constant after poling increases with increasing grain size. On the other hand, it is observed that the dielectric constants of the rhombohedral materials decrease on poling; hence, for the rhombohedral compositions, the decrease in dielectric constant with increasing grain size is accentuated by poling.

The present results indicate that the coercive field is largely independent of grain size. However, the results of Haertling(5), and Haertling and Zimmer(6) indicate a marked increase in coercive field with decreasing grain size. The reason for this discrepancy is not understood; possibly it may be related to the presence of Bi_2O_3 in the compositions used by Haertling.

The dielectric losses, as indicated by the dissipation factor, increase as the grain size is decreased. A similar increase in dielectric loss with decreasing grain size is indicated in the results obtained by Egerton and Koonce (2) on barium titanate ceramics. Possibly one of the mechanisms contributing to the dielectric loss in the unpoled ceramic involves the internal stresses set up within the ceramic due to piezoelectric distortion of the single-domain crystallite grains.

In such small grains, the stresses cannot be relieved by changing the domain configuration. During the stress cycle accompanying the cycle in the electric field, there will be energy loss due to stress-strain hysteresis and this loss will contribute to the dissipation factor. In the poled piezoelectric ceramic, the energy loss will be augmented by the mechanical loss during the vibration cycle of the disk, and, hence, the dissipation factor will be higher in the poled ceramic.

It would thus appear that the dielectric loss is to a considerable extent, dependent on the mechanical loss (as indicated by Q_m^{-1}). As an example, it has been observed(9,15) that, in moving from the tetragonal side to the rhombohedral side of the tetragonal/rhombohedral boundary, both the electrical loss ($\tan \delta$) and the mechanical loss (Q_m^{-1}) increase. Also, it has been noted that some additives, such as Nb_2O_5 (16), which increase the dielectric loss in lead zirconate-titanate ceramics, also decrease the mechanical quality factor, while other additives, such as Fe_2O_3 (17), which decrease the dielectric loss, also increase the mechanical quality factor.

The reason for the decrease in the mechanical quality factor with decreasing grain size (and, hence, specific grain-boundary area) is not clear. Possibly this decrease may be due to vis-

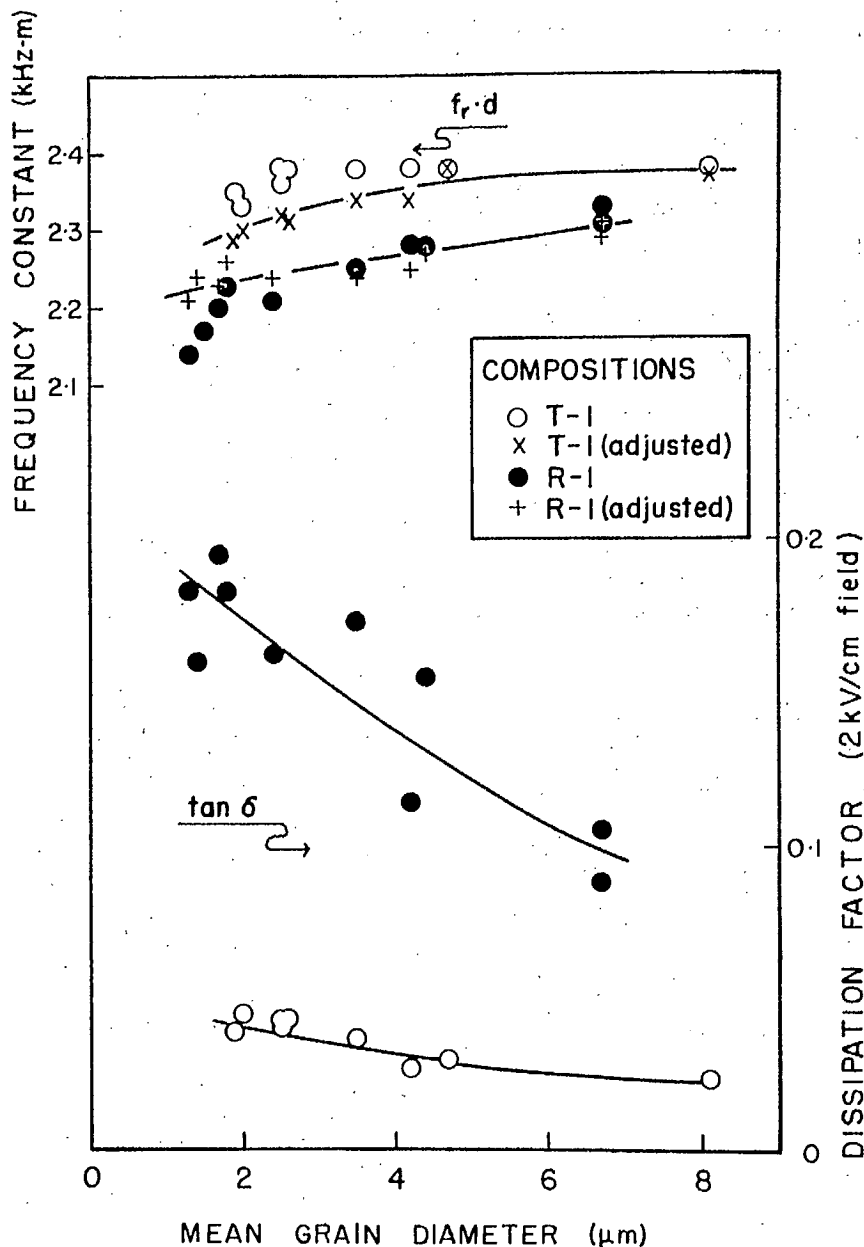


Fig. 5: Variation of frequency constant and dissipation factor (at 1 kHz, 2kV/cm rms field) with ceramic grain-size.

ous flow in the grain boundaries (grain-boundary relaxation), which is one of the mechanisms postulated to account for mechanical losses in ceramics (18). The lack of a significant grain-size effect on the frequency constant is consistent with the observation that, in general, grain size has little effect on the elastic moduli of ceramics (19).

The variations in electromechanical properties of the lead zirconate-titanate ceramics with variations in grain size are, at least qualitatively, the same for both tetragonal and rhombohedral materials. The principal excep-

tion is the behaviour of the poled dielectric constant, K_{33}^T . The variations of the electromechanical properties with grain size indicate the importance of this parameter. If maximum electromechanical coupling and minimum dielectric and mechanical losses are desired, the sintering conditions should be such as to allow for adequate grain growth.

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