Grain-size effects on properties of some ferroelectric ceramics

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Abstract. Hot-pressed ceramics of the lead titanate zirconate system with different grain sizes were prepared and some of their electrical properties measured. The values of the dielectric and piezoelectric properties were analysed together with information on barium titanate ceramics already published in the literature. Many similarities were found between both systems. There are two main contributions to the properties: the single-crystal single-domain intrinsic effect and the contribution of the wall motion. These two effects are active at different values of grain sizes and the $90^\circ$ wall thickness, compared with the grain size, is the 'key' to study their influence.

The intrinsic effect is analysed considering the grains as monodomains. A model is developed which proposes that each grain has a different transition temperature $T_c$. The $T_c$ values are taken as following a Gaussian distribution and the behaviour of the dielectric constant against temperature is computed and checked with experimental results. Measurements show that when the grain size decreases, $T_c$ increases, the maximum of the dielectric constant decreases, the peak widens and room temperature values of the dielectric constant become lower. All these results can be explained qualitatively with our model; a connection between findings and the idea of diffuse phase transitions is outlined.

1. Introduction

Two particular materials have been studied throughout the present work. The well known barium titanate (BT) and the lead zirconate titanate system (PZT). Measurements already published in the literature have been used for BT analysis; additional experiments have been carried out on PZT compositions, and properties of both systems are seen to follow similar behaviour and to fit with the same model.

BT ceramics need no introduction. Their properties have been widely studied and reported (Jaffe et al 1971).

Hot-pressed PZT ceramics ($Zr_xTi_{1-x}O_3 Pb$) become strongly piezoelectric when electrically poled. In particular, compositions near the rhombohedral to tetragonal transition ($x \approx 0.5$) show unusually high values of polarization $P_s$ and piezoelectric constants $d_{13}$ and $d_{15}$ (Jaffe et al 1955, Berlincourt 1960). Some of the properties relevant to their use in transducers improve when these ceramics are modified with pentavalent additives. The addition of Nb$_2$O$_5$ (1% in weight) to the $x = 0.52$ composition proved to be quite successful (Gerson 1960) and gives the well known PZT-5 material.

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The unexpectedly improved properties of these compositions near the morphologic transition are probably a consequence of the very low energy necessary for the interconversion between states on either side (Isupov 1968). The further enhancement of these properties with the addition of Nb_2O_5 has been suggested as being the consequence of increased wall mobility due to the presence of Pb-site vacancies, whose existence can be seen necessary from the general equation of the chemical reaction (Nb occupies a Ti or Zr site):

\[
PbBO_3 + \frac{1}{2}xNb_2O_5 + \frac{1}{2}xPbO(gain) = (Pb_{1+\frac{1}{2}x}V_x)(BNb_x)O_3+3x
\]

where B represents either Ti or Zr and V a vacancy in a Pb site.

Two different aspects have been analysed, both being the extremes of the same problem: grain-size effects on properties. The first one deals with the grain-size effects on room temperature values of dielectric and piezoelectric constants: the second one with the grain-size influence on the transition parameters and their hydrostatic pressure dependence.

In the next two sections data of these effects on BT ceramics (taken from published literature) will be analysed together with new data on PZT-5 obtained during the present work. In §4, a model will be outlined, which can explain simultaneously the behaviour of both compositions, and, we hope, of most ferroelectric ceramics with perovskite structure.

2. Grain-size effect on room temperature properties

2.1. Barium titanate

In spite of some contradictory results, it can be said beyond any doubt that low-frequency room temperature values of the dielectric constant \(\varepsilon'\) increase when the grain size decreases, starting from 5 \(\mu m\) down (Buessem et al 1966). Average values lie around 1500 and they can increase up to 6000 for 1 \(\mu m\) grain ceramics. At larger grain sizes, \(\varepsilon'\) also increases (Demyanov 1967) and can reach values above 2000 (Miller 1967).

The piezoelectric constants \(d_{31}\) and \(d_{33}\) have always been seen to increase with increasing grain size, irrespective of its value.

2.2. Lead titanate zirconate

During the present work, hot-pressed samples with densities better than 99.0% of the theoretical value were prepared. The sintering parameters were varied in a range as wide as possible in order to obtain different grain sizes. However, values ranged from 1–7 \(\mu m\). The failure to achieve larger grains was due to the grain-growth inhibition induced by the presence of Nb additives. This disadvantage is found in all grain-size studies of these compositions.

Samples were hot-pressed under conditions listed in table 1, the pressure being \(7 \times 10^6N m^{-2}\) in all the cases. A further annealing at 1250°C did not seem to help to increase the grain size of sample 1. Longer sintering times were not helpful either, since grains grow at a rate proportional to one third of the power of the sintering time. The hot-press assembly was of a conventional type (Kirby 1968). The die and cylindrical pistons used to press the samples were made of high purity \(Al_2O_3\). The samples were surrounded by spare PZT coarse powder to avoid cracking the die and to provide a PbO saturated atmosphere. The quoted grain sizes were measured from scanning electron-microscope and optical microscope photographs, using the intersection
method with modifications (Anderson 1969). The samples used for optical observations were polished and etched with the usual mixture of HCl and a few drops of HF.

Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sintering temperature (°C)</th>
<th>Time (h)</th>
<th>Grain size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1250</td>
<td>3</td>
<td>4.6 ± 0.3</td>
</tr>
<tr>
<td>2</td>
<td>1150</td>
<td>3</td>
<td>2.6 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>1050</td>
<td>3</td>
<td>1.8 ± 0.3</td>
</tr>
</tbody>
</table>

From hot-pressed blocks, discs 1 mm thick and 12.5 mm diameter were cut and silver deposited on both faces. For poling, an electric field of 3 kV mm⁻¹ was used. Table 2 includes results from measurements performed on these samples; the quoted values are an average of at least six samples for each grain size. The last column corresponds to tan δ, the ratio of the imaginary and real parts of the complex dielectric constant. IRE standards for these measurements were followed (IRE standards 1961).

Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ε''p (before poling)</th>
<th>ε' (after poling)</th>
<th>ε'/ε''p</th>
<th>d31 (10¹² Q N⁻¹)</th>
<th>tan δ (after poling)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1360 ± 40</td>
<td>1780 ± 50</td>
<td>1.30 ± 0.05</td>
<td>179 ± 8</td>
<td>0.016 ± 0.001</td>
</tr>
<tr>
<td>2</td>
<td>1300 ± 40</td>
<td>1620 ± 40</td>
<td>1.24 ± 0.05</td>
<td>161 ± 6</td>
<td>0.018 ± 0.001</td>
</tr>
<tr>
<td>3</td>
<td>1240 ± 40</td>
<td>1390 ± 40</td>
<td>1.12 ± 0.05</td>
<td>145 ± 6</td>
<td>0.019 ± 0.001</td>
</tr>
</tbody>
</table>

Measurements on other compositions of the PZT system (x = 0.65) carried out by Haertling (1966) show that for the same range of grain sizes, ε' decreases with increasing grain size, but at around 10 μm it starts increasing again.

The piezoelectric parameters have always shown an increase with increasing grain size, as in the case of BT.

3. Grain-size effects on transition parameters

3.1. Barium titanate

These effects have not been studied thoroughly, even for BT. Therefore, we had to gather information from different works, in which these effects were not those of main interest, or, in some cases indeed were not explicitly mentioned.

It has been assumed for many years that the maximum in the dielectric constant (ε''max) should decrease with decreasing grain size due to a 'suppression' in the spontaneous polarization. These early assumptions were confirmed by Jonker et al (1962), but they did not detect any variation of Tc and ε''max at all.

Two later works help to solve the problem, both arriving at the same conclusions. Micheron (1972) predicts theoretically and measures experimental values of ε''max increasing and of Tc decreasing with increasing grain size. Berton and Roelandt (1972) find the same behaviour in Ba–Sr titanates. No frequency dependence of any of these parameters has been reported so far.
Therefore, we can say that most experiments on BT lead to the conclusion that on increasing grain size, $\varepsilon'_{\text{max}}$ increases, $T_c$ decreases and the peak broadens.

Hydrostatic pressure effects on BT have been reviewed by Samara (1969). Most of the measurements agree with the well established Devonshire thermodynamic theory, except the fact that $\varepsilon'_{\text{max}}$ increases with pressure for single crystals, but decreases for ceramics, this latter case contradicting the theory.

In single crystals, only $\varepsilon'_c$ is measured and, in ceramics, both $\varepsilon'_c$ and $\varepsilon'_s$ contribute to the value of $\varepsilon'$. Trying to understand the reasons for this different behaviour, Samara proposes two ideas: (i) that some internal stresses among grains may be affecting the macroscopic value of $\varepsilon'_c$ and, (ii) that a peculiar pressure dependence of $\varepsilon'_s$ (not measured when the paper was published) could alter the behaviour of $\varepsilon'$ compared with that of $\varepsilon'_c$.

3.2. Lead zirconate titanate

The study of the ferroelectric transition of these compositions has not been at all thorough, probably due to the high transition temperatures (around 350 °C) and, perhaps, because nobody would expect these compositions to behave differently from better known perovskites.

In very early studies (Shirane 1951) the dielectric anomalies were measured for a wide range of compositions. Those corresponding to $x = 0.75$ and $x = 0.50$ showed quite broad peaks, not typical of Curie–Weiss behaviour, in spite of the author’s claim to the contrary. Later on, Ikeda (1964) commented on ‘rather broad peaks’ without going any further in his analysis.

Our experiments were carried out on samples with the same grain sizes listed in table 1. Figure 1 shows the dielectric constant curves. The experimental set-up was of a conventional type, recording results on a $X-Y$ plotter. The transition temperature $T_c$ was obtained from the graph as the temperature at which the dielectric constant was a maximum. Table 3 includes average values of at least six samples for each grain size. The peak width was measured at half height and no frequency variation was observed in the $10^2–10^5$ Hz region.
Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grain size (µm)</th>
<th>$T_c$ (°C)</th>
<th>$\varepsilon_{max}$ ($\times 10^3$)</th>
<th>$\varepsilon_{max}/\varepsilon_{room temp}$</th>
<th>Width (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.6</td>
<td>373 ± 3</td>
<td>30 ± 3.0</td>
<td>23 ± 2</td>
<td>40 ± 4</td>
</tr>
<tr>
<td>2</td>
<td>2.6</td>
<td>380 ± 3</td>
<td>26.0 ± 2.6</td>
<td>19 ± 2</td>
<td>50 ± 4</td>
</tr>
<tr>
<td>3</td>
<td>1.8</td>
<td>388 ± 3</td>
<td>19.0 ± 1.9</td>
<td>15 ± 2</td>
<td>68 ± 4</td>
</tr>
</tbody>
</table>

Similar qualitative behaviour was observed by Okazaki (1971, 1972, 1973) in different compositions and with different additives. In another very recent paper, Salaneck (1972) measured a shift of $T_c$ with frequency in the $1-10^2$ Hz region. The importance of this result will become clear later on.

As far as hydrostatic pressure effects are concerned, no published information deals with PZT compositions, later than some early papers (Shirane 1951). In the present work, the dielectric peak of PZT-5 was measured under hydrostatic pressure up to $2.8 \times 10^8$ Nm$^{-2}$. A standard design of pressure chamber was used and figure 2 shows a typical example of $\varepsilon'$ curves for one sample. The extent of the pressure dependence of transition parameters did not seem to depend on the grain size of the sample. The measured decrease of $T_c$ with pressure showed an average value of $-5.4 \times 10^{-5}$ °C N$^{-1}$ m$^2$. In most cases the decrease is linear; with respect to the shape of the peak, its width increased by 15–20% under a pressure of $2.8 \times 10^8$ Nm$^{-2}$.

4. Discussion

There are two ways in which grain size can affect ferroelectric properties. One of them is by restricting the motion of domain walls, which are known to contribute to the dielectric constant, piezoelectric and elastic properties. The second one is by affecting the behaviour of each grain taken as a single-crystal single domain. It will be shown that these two effects are active at different grain sizes.
4.1. Motion of walls

Under what conditions can a domain exist inside a grain? Obviously, the wall thickness must be smaller than the size of the grain. If that is the case, walls will be able to move more or less freely under an electric field, affecting in that way the values of some of the properties. One expects the walls to be quite free in very large grains and to be inhibited in their movement as the grain size decreases, since grain boundaries will contribute additional pinning points for the moving walls. If the walls become less mobile, their contribution to the properties will also decrease. If the grain size becomes of the same order as the wall thickness, grains will be either monodomain or will contain very few non-mobile walls.

Our measurements on PZT-5 (from 1-6 μm) and figures published on BT (above 10 μm) and other PZT compositions agree with this idea. The difference in grain-size ranges in which this effect is observed may be due to different wall thicknesses in different compounds.

In BT, values of 0.5 μm for 90° wall thickness have been measured (Little 1955), which would mean that grains larger than 10–20 μm have a rather well developed domain structure. No measurements have been done on PZT-5, but photographs included in Gerson’s paper (1960) suggest that 90° wall may be much thinner.

Furthermore, Gerson also suggests that large values of ε' and d_{ij} in PZT-5 are due to unusual increase in wall mobility due to the presence of Pb vacancies, which release some interdomain stresses between 90° walls.

Another evidence of the domain wall contribution to ε' can be produced by analysing some other results quoted in table 2. On poling, 180° domains are 100% switched, but 90° walls only 20% (Berlincourt and Krueger 1959). Therefore, after poling, the ceramic has a purely 90° domain structure; these walls are now more mobile, since there are no longer any 180° walls to impede their movement. We think that this increased mobility of 90° walls is the reason why ε' increases on poling, overshadowing the intrinsic effect, which will tend to decrease its value (ε'_i is smaller than ε'_a).

In a further stage of the analysis of these figures (table 2), we see that for sample 1, ε' increases 30%, but for sample 3 only 12%; this result implies that 90° domain walls in sample 3 contribute less to ε' than in sample 1. This conclusion agrees with the comments about the pinning effect of the grain boundaries.

The contribution of moving walls to the piezoelectric constants follows similar ideas, and even in BT this contribution keeps on decreasing down to very small grain sizes (1 μm), whereas ε' shows opposite behaviour. Arguments to explain this different behaviour will be seen in §4.2.

Values of tan δ are seen to increase slightly with decreasing grain size. A larger number of asymmetric wall pinning points in small-grained ceramics could explain this behaviour. Walls moving in symmetric, elastic, potential wells do not contribute to the losses.

All these considerations are valid at temperatures well below the transition, near which the intrinsic contribution to the properties becomes large and its influence overshadows the effect of the wall motion.

4.2. Grains as monodomains

In this section, the case in which grains behave as single-crystal single domains will be studied. According to §4.1, PZT-5 shows a behaviour typical of a large domain wall
contribution: therefore the considerations in this section will apply to small-grained BT at room temperature and to all ceramics near the transition.

The idea of monodomain grains was used by Buessem et al (1966) to explain the high values of $\varepsilon'$ for low grain sizes in BT. The main idea is based on the assumption that small grains are subjected to a certain pattern of internal stresses, which cannot be released by the formation of domains at $90^\circ$ (due to the grain size being comparable with the wall thickness). Those stresses may originate when the sample is cooled down through $T_c$ and the ferroelectric deformation tries to develop fully. Due to intergrain contacts this is not possible and some stresses remain unrelieved inside the ceramic.

So far, the model seems to be correct. But then, Buessem argues that ‘the stress system would be of a type forcing the grain back toward the cubic structure’. We consider that this model does not present a real answer to the problem, since that assertion would imply a decrease in $T_c$, which opposes the majority of the reported measurements. Even more, using Buessem’s stress model and Devonshire theory, it can be shown that the mere existence of these stresses would mean a decrease in $T_c$ of around $30-40^\circ$C (Martirena 1973). The proposed stress system consisted in a compression along the $c$ axis and a tension along $a$ and $b$ axes. As will be seen later on, the failure of this model is based on the fact that all the grains see the same type of stress and of the same value. A certain distribution of kinds and intensities of stresses will be the answer to the problem.

The piezoelectric parameters $d_{ij}$ do not show similar behaviour to that of $\varepsilon'$ probably due to the fact that in small-grained ceramics, a poling field does not have many domains to switch; therefore the poling process is not efficient and the macroscopic value of $d_{ij}$ remains small, even if the values for individual grains may be high for the same reason used to explain the large values of $\varepsilon'$.

4.3 Distribution model

In this section it will be seen that another model, based on similar ideas, can explain the contradictions pointed out above and, moreover, can also explain the behaviour of ceramics under hydrostatic pressure and the grain-size dependence of the transition parameters.

In a paper published a few years ago, a model was developed to predict the $\varepsilon'$ against $T$ curves of ceramics based on the idea that grains are monodomains and that $T_c$, for different grains, has values obeying a Gaussian distribution of width $A$ about a conveniently chosen temperature (Diamond 1961). Below each individual $T_c$, grains are supposed to show a constant value of the dielectric constant and above $T_c$, the Curie–Weiss law is taken to be obeyed.

Figure 3 shows the predictions of this model for the particular case of BT ceramics. We can see that $A = 10^\circ$C gives a shape close to the usual Curie–Weiss curves, that is mainly asymmetric. When $A$ increases, the peak broadens, $T_c$ increases and values of $\varepsilon'$ at room temperature also increase; that is, the transition moves away from a typical Curie–Weiss behaviour.

This last point could explain the high values of $\varepsilon'$ in small-grained ceramics at room temperature if $A$ varied with grain size. We propose that as the grain size decreases, the stresses due to ferroelectric deformation become more difficult to release and the remaining internal ones vary in value to a larger extent. As stresses affect the value of $T_c$ in various ways, we can assume that when the stress system values widen in range, values of $A$ also increase. Therefore, we think that there is a direct link between grain size and $A$. Of course, there may be some other reasons for $A$ to vary, but diminishing
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Figure 3. Distribution theory applied to BT ceramics. Dielectric constant against temperature for different values of $A$.

Grain sizes seem to be one of them. In this way, the room temperature behaviour of $\varepsilon'$ for small grained BT ceramics can be explained (see §2) without having to face the contradictions outlined in §4.2. In the next paragraph it will be seen that the same model can also be used to explain the transition features of many ceramics (including PZT), the proposed relationship between $A$ and the grain size being the key point.

Figure 4. Log-log plots of equation (1) for the BT case of figure 3.
To analyse the transition, the following empirical equation is taken to be valid above $T_c$

$$\frac{1}{\epsilon'} = \frac{1}{\epsilon_{\text{max}}} + B(T - T_c)^m$$

(1)

where $m$ and $B$ are constants. When $m = 1$, equation (1) becomes the Curie-Weiss law for first-order transitions. Figure 4 shows plots of equation (1) for our calculations of Diamond's model with $A$ values of 30 and 140, for which $m = 1.75$ and 1.98 respectively. The crosses are the computer calculations for BT ceramics and the straight lines are least mean-square fits of those points. It looks as if Diamond's model predicts a behaviour of $\epsilon'$ similar to (1) for different values of $A$. Experimental measurements published by several authors for BT ceramics show that (1) is obeyed surprisingly well (see Martirena 1973). Figure 5 shows similar results for our PZT-5 experiments.

$$\begin{align*}
100 & \quad 50 \\
5 & \quad 10 \\
\epsilon' & \quad \epsilon_{\text{max}} \\
1 & \quad 5 & \quad 10 \\
T - T_c
\end{align*}$$

Figure 5. Log-log plots of equation (1) for measurements on PZT-5. A: 4.6 $\mu$m, $m = 1.74$; B: 2.6 $\mu$m, $m = 1.82$; C: 1.8 $\mu$m, $m = 1.93$.

These considerations show that ceramics obey, in general, equation (1), where $m$ depends on the grain size. This model explains qualitatively all the features of figure 1: $T_c$ increases, $\epsilon_{\text{max}}$ decreases and the width increases with decreasing grain size; it can also explain the high values of $\epsilon'$ for small-grained ceramics at room temperature.

There are reasons to suppose that $A$ is also dependent on hydrostatic pressure. If that is the case, on application of such a pressure, $A$ would increase and then peaks would become wider and smaller. This behaviour was observed in PZT-5 during the present work and by Samara (1969) in BT ceramics. Therefore, the distribution model, through the pressure dependence of $A$, can also explain this effect. It is worthwhile to remember again that the theoretically predicted and observed behaviour in BT single
crystals is exactly the contrary: peaks become narrower and higher as hydrostatic pressure increases.

The increase of $T_c$ with $A$, given by the distribution model, is a second-order effect compared with the average effect of the pressure on the grains, which tends to decrease $T_c$. However, this second-order effect may be the reason why Samara (1969) measures a smaller rate of decrease of $T_c$ with pressure in ceramics than in single crystals of BT. Samara himself proposes two possibilities to explain this effect: internal stresses or an unexpected behaviour of $\varepsilon_a$. The experiments in the present work clear up the problem: internal stresses are responsible for this effect. Furthermore, in a very recent paper, Samara (1971), finds a normal pressure dependence of $\varepsilon_a$.

4.4. Diffused phase transitions (DPT)

There is a large number of compositions that show a Curie ‘region’ rather than a Curie ‘peak’ (Smolenskii 1970). Besides showing such a broad peak, there are no other characteristics typical of these transitions. Some authors consider it necessary that one of the components should be non-ferroelectric, some expect a frequency-dependent $T_c$, and even comparison of thermal expansion coefficients has been used as a criterion to identify DPT (Rolov 1966).

The main idea on which the concept of diffused phase transition is based consists in the existence of small microregions in the crystal or ceramic that can switch from paraelectric to ferroelectric states in a statistical way, but not interacting, in first approximation, with neighbouring regions; that implies that each region has or may have a different transition temperature. In solid solutions, microscopic variations or deviations of stoichiometry may cause variations of $T_c$ as well.

There has been speculation about the dimensions and stability of these regions. Fritsberg tried to relate their volume to the macroscopic properties (1964), and in another paper (1970) he says that: ‘any factor tending to decrease $V_k$ (the volume of those microregions) must also broaden the DPT. Such factors include the decrease in the average size of the crystallite in a ceramic and the application of high hydrostatic pressure’. The relation of this idea with the present work is obvious.

We do not intend to review the work already published on DPT, but we would like to point out the striking similarities between the concept of DPT and our findings on BT and PZT-5. Both compounds show broad peaks at low grain sizes; these peaks broaden under hydrostatic pressure and when the grain size decreases; some compositions of the PZT system show a frequency dependent $T_c$ (Salaneck 1972). Some completely different materials have been seen to obey equation (1) with $m = 2$ (Smolenskii 1970) and with $m$ between 1 and 2 (Clarke 1973).

At the moment the distribution model has been tried qualitatively only and has worked surprisingly well. It may fail quantitatively since strong approximations and simplifications have been made during its development. But we consider that the concept of a variable distribution of $T_c$ fits very well with the idea of microregions in DPT, with the idea of grains under different stresses, and, even more, with Okazaki’s suggestion of ferroelectric layers (above $T_c$) to explain the decrease of $T_c$ with increasing grain size. Probably, these are different ways of tackling the same problem.

5. Conclusions

After comparing BT and PZT-5 properties, we found that: (a) domain wall motion and
single domain grain effects contribute to the dielectric constant at different ranges of grain sizes; (b) piezoelectric constants are seen to decrease with grain size, whatever the range; (c) $T_c$, $\varepsilon_{\text{max}}$ and the width of the dielectric peak are grain-size dependent; (d) above the transition, $\varepsilon'$ obeys equation (1) in a large number of ceramics, where $m$ depends, among other factors, on the grain size; (e) a model, based on a Gaussian distribution of $T_c$ can explain (a), (c) and (d); and (f) the known decrease of $\varepsilon'_{\text{max}}$ under pressure in ceramics can also be explained using the distribution model.

A link between DPT and the distribution model is suggested, but it is considered that this point needs further clarification.

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