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To cite this version:


HAL Id: jpa-00215022
https://hal.archives-ouvertes.fr/jpa-00215022

Submitted on 1 Jan 1972

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PZT-5 UNDER PRESSURE
DIELECTRIC AND PIEZOELECTRIC PROPERTIES

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Abstract. — The permittivity and the piezoelectric coefficients of hot-pressed PZT-5 are studied under variations of the ambient pressure up to 3 kbars and variations of the grain size. Two methods for the piezoelectric coefficients do not agree and it is concluded that one of them (and also the permittivity) is affected by domain wall movements. It is possible that the non-domain portion of $d_3$ is negative.

I. Measurements. — We have been studying the variations with hydrostatic pressure $\pi$ of the polarization of tetragonal Pb(Zr$_{0.52}$Ti$_{0.48}$)$_2$O$_3$ with 1% Nb, (\textit{\textit{PZT-5}}). It has been prepared by hot-pressing to keep the grain size $s$ small; it is then expected that there will be a reduced dependence of the dielectric and piezoelectric properties on $\pi$. The densities of our specimens exceed 99.9% of the ideal value. Applying pressure up to 3 kbars ($3 \times 10^5$ Nm$^{-2}$) in an oil-filled pressure chamber, we found that the permittivity $\varepsilon$ increases 10%. The specimens were poled by 20 kV.cm$^{-1}$ for five minutes, and this produced, surprisingly, a large increase in $\varepsilon$, but only in specimens of relatively large grain size. We have not been able to produce a large range of grain sizes but our range of 6 to 1.4 micron does display some grain-size effects. We have measured $s$ by scanning electron microscope, evaluating it by the correct intersection method. With our smallest grains, the increase on poling was much less, and partly disappears in some hours after removal of the poling voltage; the small-grain specimens are resistant to poling. In these specimens also the $\varepsilon(T)$ peak at the curie temperature $T_c$ is broadened, from 36 K to 69 K, but $T_c = 374 K$ does not decrease; indeed it increases $10^2$ to $20^2$. A similar effect has been reported by Okazaki.

We have been concerned with the piezoelectric coefficient $d$, defined as $\partial P/\partial X$ or $(\partial e/\partial E)_{_T}$, where $e$ is a deformation, and $X$ is a generalized stress; the two definitions are thermodynamically equivalent. Applying hydrostatic pressure of varying amounts, we measured the $P$ change by the electric discharge $Q = AP$. It was necessary to take the measurements 15 minutes after the application of $\pi$, because the oil temperature rises $10^2$ on first application and must be allowed to fall again. Our values are therefore perhaps lower than the true values but we do not believe this effect to be large, and accepted values in the literature are not very different. This method (\textit{\textit{Method 1}}) measure $s$ $d_{3n}$ which is equal to $d_{33} + 2d_{31}$; $d_{31}$ expresses the increase of $P$ on two-dimensional lateral compression, and its sign is opposite to $d_{33}$.

Our \textit{\textit{Method 2}} uses the second definition of $d$; it measures $e$ by straingauge upon the application of a field, either a.c. or d.c. It measures $d_{33}$ and $d_{31}$ separately, but it is less satisfactory than method 1 for determination of $d_{33}$ because $d_{3n}$ is a difference of two numbers ($d_{33}$, and $-2d_{31}$) which are about an order of magnitude larger. We are working close to the limits of accuracy of the straingauges and our $d_{3n}$ values by this method are no better than 20% if the $d_{33}$ and $d_{31}$ values are $\pm 3%$.

We found that $d_{3n}$ increases from $10 \times 10^{-12}$ CN$^{-1}$ to $15 \times 10^{-12}$ CN$^{-1}$ at 3 kbars, and we obtained also values which are 20% greater in the small-grain specimens. But with method 2 we find no detectable change over that range; any change is less than 5%. In addition it seems that the sign of $d_{3n}$ is negative. For the individual components, the precision is good.

<table>
<thead>
<tr>
<th>Table I</th>
<th>Typical data</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>unpoled</td>
<td>poled</td>
</tr>
<tr>
<td>$s = 4.6 \mu$</td>
<td>1435</td>
</tr>
<tr>
<td>$s = 2.6 \mu$</td>
<td>1365</td>
</tr>
<tr>
<td>$s = 1.8 \mu$</td>
<td>1280</td>
</tr>
</tbody>
</table>

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Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphyscol:1972286
enough to observe grain-size effects also, at least for $d_{33}$, in which we observe a 20% decrease in our small-grain specimens. Typical results are given in table I.

For a single domain it is known that $d$ is related to $e$, and it has also been shown that the $XP^2$ term in the free-energy function leads to a linear variation of $1/e$ with $\pi$. In ceramic specimens, these intrinsic $d$ and $e$ contributions are not the only one and the problem is to determine which of the observed behaviours are intrinsic.

II. Interpretations. — We select five points which merit particular attention, of which three (viz points, $a, c, e$) are different from what is to be expected.

Point ($a$): $T_0$ is higher if there are small grains; (b): $d_{33}$ is much smaller if there are small grains, and $d_6$ by method 1 larger; (c): $d_6$ by method 2 may be negative; (d): $e$ increases under pressure, but $d_6$ by method 2 does not; (e): Poling increases $e$, but not if there are small grains.

If it should be true that the intrinsic $d_6$ is negative in our specimens, the physical significance is that the application of hydrostatic pressure to a domain increases its polarization. This would correspond to an increase of $T_0$ under pressure, and a decrease of $e$, and it would be consistent with point $a$, since there will be internal pressure in the small-grain specimens, perhaps of order 10 kbars. But the small grains may be under predominantly lateral compression; that would increase $T_0$ without the hypothesis of a negative $d_6$. Large decreases of $d_{33}$ and $d_{31}$ are not inconsistent with the observed increase of $d_6$, even intrinsically.

Concerning point $d$, we remember that the intrinsic changes of $d$ and of $e$ under pressure are related to one another ($d_{ik} = 2Q_{ik} P_e e_{ik}$ and $Q_{ik} P$ may not vary very strongly with pressure), but we have no way of knowing whether the changes should be large, or so small as to be unobservable. The first suggestion implies a structure-sensitive reduction of $d$, while $e$ is relatively structure-insensitive. It seems unacceptable because it is a supposed reduction of only the extra intrinsic $d$ contribution. The second suggestion is that the intrinsic changes of $d$ or $e$ under pressure are small, but that there is a large extra $e$ contribution under pressure, perhaps due to movements of pressure-induced domain walls, and these movements would also give extra discharge current in method 1, to override the intrinsic effect. This is not opposed to the structure-sensitivity of $d$ because that is an effect of the static presence only of domains and walls, either in its averaging or its clamping form.

The walls postulated as arising under pressure may be of either 180° or 90° type; but they are probably 90° walls, since 180° walls do not relieve stress effects.

Point $e$ is unexpected because perovskites have $e_e$ less than $e_c$ and poling should align more $c$ material. We think that walls may be pinned (inhibited) by grain boundaries and by interacting walls which the poling removes. Since we observed small-grain specimens to be resistant to poling, the extra domains cannot be created when there are small grains, or alternatively, pinning in small grains in due to grain boundaries only, and therefore is not removed by poling.