Electrical response during indentation of piezoelectric materials: A new method for material characterization

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The electrical responses of piezoelectric materials subjected to spherical microindentation are evaluated. Theoretical analysis based on normal indentation of a transversely isotropic, linear piezoelectric solid by a conducting steel sphere with zero potential bias is compared to experimental results. The materials considered are PZT-4 and (Ba$_{0.917}$Ca$_{0.083}$)TiO$_3$. Effects of poling, poling direction, indentation velocity, and polarization loss due to annealing were investigated. All the basic trends predicted by the theory are confirmed by the experiments. The current induced into the indentor due to the polarized layer on the contact surface of the piezoelectric specimen increases with time as the contact area increases. Experimentally, observed power dependence of current to indentation velocity is close to the theoretical value of 1.5. The relation between induced current and indentation time is specific to the properties of the material. It is demonstrated that in addition to some of the material constants, the poling direction and the aging behavior of piezoelectric ceramics can be determined by spherical indentation. © 1999 American Institute of Physics.

I. INTRODUCTION

Many poled polycrystalline ferroelectric materials can be described as transversely isotropic. The dihexagonal polar piezoelectric crystals (6 mm) also fall in this category. These materials have axisymmetric properties around the direction of polarization. Materials with higher symmetry (e.g., cubic) could also be treated as having particular cases of transverse isotropy. Rocks and minerals exhibit piezoelectric effects. Some of the well-studied piezoelectric minerals with hexagonal symmetry include β-quartz (β-SiO$_2$), turmaline, nepheline, cancrinité (3Na.AlSiO$_4$.CaCO$_3$), greennockite (β-CdS), cadmoselite (β-CdSe), bromellite (BeO), zincite (ZnO), and ice (H$_2$O). Piezoelectric minerals with cubic symmetry include sphalerite (ZrS), wurtzite (α-ZnS), sheelite (ZnSe), ammonium chloride (NH$_4$Cl), and sodalite (Na$_8$[Cl(AI$_2$SO$_4$)$_6$]).

The most important piezoelectric ceramics crystallize in the perovskite structure. This is a cubic cell with a large cation at the corners (e.g., Ba$^{2+}$ or Pb$^{2+}$), a smaller cation in the body center (e.g., Ti$^{4+}$ or Zr$^{4+}$) and oxygen anions in the face centered positions. The structure is a network of corner-linked oxygen octahedra, with the smaller cation filling the octahedral holes. Poling results in moving the small cation in phase with the applied electric field leading to polarization and in a simultaneous change of the crystal structure, creating anisotropic physical properties. In polycrystalline materials, a strong applied electric field aligns the polarization of favorably oriented domains.

Many factors, such as porosity, impurities, and grain size, influence the properties of piezoelectric materials. The piezoelectric properties are strongly temperature dependent and degrade just below the Curie point. The dielectric and elastic constants change as a result of a change in crystal structure. Additives (e.g., La for Pb and Nb for Zr or Ti) may increase the electric conductivity and lead to undesirably high dielectric losses. Ultrafine grains and certain dopants weaken the piezoelectric constants because they pin the domain walls and inhibit poling of the materials. Inadequate electric fields result in poling below saturation, producing very different piezoelectric constants than the ones typically reported for saturated poling conditions. Piezoelectric properties are also sensitive to isovalent substitutions of the large cations and formation of solid solutions.

In the examination of charged surfaces of ionic crystals, as well as other materials such as ice, the piezoelectric approach offers a good theoretical basis for analysis. When surfaces become charged, an equal and opposite space charge in a layer just inside the surface will develop. An electrical potential is then set up between the surface and the interior of the crystal. An additional potential of comparable magnitude exists across the first few layers of ions because of the relaxation of the ionic positions perpendicular to the surface. Under these conditions, linear piezoelectricity is expected to hold when internal friction is independent of load.

When indented, surfaces with negatively distributed charges produce higher absolute electrostatic forces reacting to the indentor’s motion than surfaces with positively distributed charges. This was found to be the case of contact electrification of thin silicon oxide films. Because of prior electron or ion deposition on the free surface, the film can be electrically polarized with the polarization vector normal to the surface. The present analysis explains why the negatively
distributed charges produce higher absolute electrostatic forces than surfaces with positively distributed charges.

Young examined the mechanical weakening and breaking effect of high frequency electric current applied to dielectric rock fragments. Tests were reported on low grade disseminated copper ore, granite (quartz monzonite) waste, limestone, shale, sandstone, aplit, quartz porphyry, chalcopyrite, rhodinite, and rhodochrosite. Utilization of pulse power from discharging capacitor banks was partly successful because of the spalling at the electrode contact. Young attributed the phenomenon to the piezoelectric effects of the rocks. However, no conclusions could be drawn because of a lack of in-depth analysis, except for empirical values of the voltage magnitude and frequency, as well as the electrode positioning. Crankshaw and Arnold showed that compression of PZT-4 up to 500 kg/cm² can generate open circuit fields in the range of 5–15 kV/cm. Such electric fields can provide the spark for gasoline motors. Other applications of piezoelectrically generated sparks are for ignition explosives and for butane and natural gas in space heaters, cooking stoves, brazing torches, and cigarette lighters. Gradual compression gives multiple sparks for a single application of force. Voltages up to 100 kV or more have been generated by applying near destructive compression to poled ferroelectric ceramics.

Enomoto and Hashimoto tested several kinds of rocks, by indenting them with electro-conductive Rockwell-type indenter which served as an electrode to collect charged particles during indentation. They found that indentation induced cracking was associated with high electric signals. Such emission of charged particles due to fracture has been found to accompany earthquakes. Lowell and Rose-Innes recognized that contact electrification may be related to the deformation and the surface electric poling of many piezoelectric insulators. Horn and Smith found an apparent adhesion between dissimilar materials (mica and silica) in non-sliding normal contact. The work required to separate the charged surfaces was estimated to be comparable to the fracture energies of ionic-covalent materials.

This study investigates the use of mechanical indentation with a conducting spherical indenter (with zero potential bias) as a novel method for characterizing piezoelectric materials. Force and induced charge in the indenter are continuously monitored during the indentation. The electrical and mechanical response are linked to the elastic, piezoelectric, and dielectric properties of the specimen. In a mechanical indentation test these properties are extracted from the depth versus force behavior. The mechanical response shows that the stiffness depends on the material condition (polled vs unpolled) and the type of indenter (conducting vs insulating). This article focuses on the electrical response with the objective of addressing the questions:

1. How does the experimentally observed indentation induced current compare with theoretical predictions for two well-studied piezoelectric materials, namely, PZT-4 and (Ba₀.₉₁Ca₀.₀₉)TiO₃?
2. Is the method able to detect poling direction?
3. Is the method able to detect depolarization as, for example, that arising from aging?

II. THEORY

A general theory for axisymmetric indentation of linear piezoelectric solids has been presented by Giannakopoulos and Suresh. Here those issues directly pertaining to the electrical response are first briefly summarized, in an attempt to develop a basis for examining and interpreting the experiments. The solution to the problem of indentation was approached by using cylindrical coordinates (r, θ, z), were Oz is the vertical axis (Fig. 1). The polarization axis is the z axis, which is also the axis of transverse isotropy and the loading axis.

The stress equilibrium equations without body or inertia forces are

$$\text{div} \sigma_{ij} = 0,$$

where $\sigma_{rr}$, $\sigma_{r\theta}$, $\sigma_{\theta\theta}$, and $\sigma_{rz}$ are the nonzero stress components.

In the absence of volume electric charges, the Maxwell electrostatic equation is

$$\text{div} D_i = 0,$$

where $(D_r, D_z)$ is the electric-displacement vector.

Spherical elastic indentation justifies the use of small strains and small electric displacements. The small-strain geometric relations are

$$e_{ij} = \text{sym} (\text{grad} u_i),$$

where $(u_r, u_z)$ is the displacement vector.

The electric flux is given by the Gauss equation:

$$\text{curl} E = -\text{curl} (\text{grad} \phi) = 0,$$

where $\phi$ is electric potential and $(E_r, E_z)$ is the electric flux vector.

In addition to the fundamental Eqs. (1)–(4), the following constitutive equations hold for a linear piezoelectric material:

$$\sigma_{rr} = c_{11} E_r + c_{12} E_\theta + c_{13} E_z - e_{31} E_z,$$

$$\sigma_{r\theta} = c_{12} E_r + c_{11} E_\theta + c_{13} E_z - e_{31} E_z,$$
TABLE I. Pertinent physical properties of PZT-4 and (Ba$_{0.47}$Ca$_{0.03}$)TiO$_3$ (see Ref. 13). Superscript E refers to elastic constants measured in short circuit condition. Superscript T refers to dielectric constant measured with no mechanical constraint.

<table>
<thead>
<tr>
<th>Property</th>
<th>PZT-4</th>
<th>(Ba$<em>{0.47}$Ca$</em>{0.03}$)TiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (10$^3$ kg m$^{-3}$)</td>
<td>7.5</td>
<td>5.7</td>
</tr>
<tr>
<td>Curie temperature (K)</td>
<td>601</td>
<td>388</td>
</tr>
<tr>
<td>Elastic Constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}^E$ (GPa)</td>
<td>139</td>
<td>158</td>
</tr>
<tr>
<td>$C_{33}^E$ (GPa)</td>
<td>115</td>
<td>150</td>
</tr>
<tr>
<td>$C_{12}^E$ (GPa)</td>
<td>77.8</td>
<td>69</td>
</tr>
<tr>
<td>$C_{13}^E$ (GPa)</td>
<td>74.3</td>
<td>67.5</td>
</tr>
<tr>
<td>$C_{44}^E$ (GPa)</td>
<td>25.6</td>
<td>45</td>
</tr>
<tr>
<td>$C_{66}^E$ (GPa)</td>
<td>30.6</td>
<td>45</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e_{11}^T$ (10$^{-9}$ F m$^{-1}$)</td>
<td>6.461</td>
<td>8.850</td>
</tr>
<tr>
<td>$e_{33}^T$ (10$^{-9}$ F m$^{-1}$)</td>
<td>5.620</td>
<td>8.054</td>
</tr>
<tr>
<td>Piezoelectric constants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$e_{31}$ (C m$^{-3}$)</td>
<td>0.52</td>
<td>-3.1</td>
</tr>
<tr>
<td>$e_{33}$ (C m$^{-3}$)</td>
<td>15.1</td>
<td>13.5</td>
</tr>
<tr>
<td>$e_{15}$ (C m$^{-3}$)</td>
<td>12.7</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Equations (5)–(8) are the Duhamel–Neumann relations in the absence of thermal strains and Eqs. (9)–(10) are the elastic displacements under the influence of strain and electric flux. From Eqs. (5)–(10) it is seen that there are five elastic constants ($C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, and $C_{44}$), two dielectric constants ($e_{11}^T$ and $e_{33}^T$), and three piezoelectric constants ($e_{31}$, $e_{33}$, and $e_{15}$). The elastic mechanic, dielectric and piezoelectric properties of the material are completely characterized by these ten constants. Table I lists these constants for PZT-4 and (Ba$_{0.47}$Ca$_{0.03}$)TiO$_3$.

The indenting punch is assumed to be frictionless, rigid, and spherical with diameter $D$, indenting normally the piezoelectric half space by transferring a total normal load, $P$. The nonconformal contact advances monotonically with load, and if $h$ is the penetration depth measured from an initially flat surface, then $dP/dh>0$ for $h>0$. The contact area is a circular disc with radius $a$. The following mechanical boundary conditions must be satisfied at the surface:

\[ u_z(r,0) = h - \frac{r^2}{D}; \quad 0 \leq r < a, \]  
\[ \sigma_{zz}(r,0) = 0; \quad r \geq 0, \]  
\[ \sigma_{zz}(r,0) = 0; \quad r > a. \]  

The electrical boundary conditions assume that the indenting punch is a perfect conductor with a constant potential $\phi_0$. Outside the contact area, the electric charge is zero. Hence, the following electrical boundary conditions are obtained at the surface ($z = 0$):

\[ \phi(r,0) = \phi_0; \quad 0 \leq r < a, \]  
\[ D_z(r,0) = 0; \quad r > a. \]  

Finally, the principal quantities ($u_z$, $u_r$, and $\phi$) must have continuous derivatives and must decay to zero asymptotically, sufficiently far away from the contact area.

\[ (u_z, u_r, \phi) \rightarrow (0,0,0), \quad \frac{\text{~}}{\sqrt{1 + r^2}} \rightarrow 0 \]  

provided that the contact radius $a$ is much smaller than any other dimension of the specimen. A solution to Eqs. (1)–(10) under the conditions imposed by Eqs. (11)–(16) was found by Giannakopoulos and Suresh. Only the final equations for the dependence of charge ($Q$) versus penetration depth ($h$) are reproduced here. The mechanical displacement induces a polarization on the piezoelectric specimen at the contact area. By integrating the electric charge distribution under the indenter, an expression for the mechanically induced total charge is found:

\[ Q = \frac{16}{3} M_1 M_2 \frac{a^3}{D^2} + 2 \pi a \left[ \phi_0 M_2 - M_1 \left( 1 - \frac{2a^2}{D} \right) \right]. \]  

The charge distribution under the indenter is due to the strained contact area and will not be sustained if the contact area is fixed. However, in the case of an advancing contact (i.e., spherical indentation with increasing load), the charge buildup increases due to the increase in strained area. If the indenter is conducting and is grounded, a charge opposing that of the specimen would develop. The dynamic change in the charge at the indenter needed to sustain charge neutrality can be measured as a quasistatic current.

The constants $M_1$ and $M_2$ depend in a complicated way on the five elastic ($C_{ij}$), two dielectric ($e_{ij}^T$), and three piezoelectric ($e_{ij}$) constants that characterize the material. The relation between the contact radius, $a$, and the displacement $h$, corresponding to a rigid sphere of diameter $D$, is given at $\phi_0 = 0$ by the classical condition of linear elastic contact mechanics:

\[ h_{\text{rigid}} = \frac{2a^2}{D}. \]  

If the potential of the indenting punch is maintained at zero ($\phi_0 = 0$), Eqs. (17) and (18) give

\[ Q = \frac{16}{3} M_1 \sqrt{\frac{h_{\text{rigid}}}{8}}. \]  

By using a correction factor accounting for the nonrigidity of the indenting punch, the ideally rigid displacement can be substituted by the actual measured displacement $h_{\text{actual}}$. If a constant indentation velocity, $v$, is used, then the measured displacement is $h_{\text{actual}} = vt$, assuming that the indentation starts at zero time, $t=0$. The correction factor is

\[ h_{\text{actual}} = h_{\text{rigid}} + \frac{E_{\text{specimen}} (1 - v_t^2)}{E_{\text{indenter}} (1 - v_{\text{indenter}}^2)} K_{\text{corr}}, \]  

where $E_{\text{specimen}}$ and $E_{\text{indenter}}$ are the Young’s modulus of the specimen and indenter, respectively, $v_t$ and $v_{\text{indenter}}$ are the indentation and indenter velocity, and $K_{\text{corr}}$ is the correction factor.
where $E_{\text{indentor}}$ and $v_{\text{indentor}}$ are Young’s modulus and Poisson’s ratio, respectively, of the indentor and $E_{\text{specimen}}$ and $v_{\text{specimen}}$ are the Young’s modulus and Poisson’s ratio, respectively, of the specimen.

During indentation, the total absolute charge under the punch will increase due to the increase in contact radius $a$. The change in total charge under the punch with time is related to the change in contact area and thereby to the change in displacement. By electrically grounding the punch, a charge of the same magnitude but opposite polarity will be induced in the punch on the other side of the contact area in order to maintain charge neutrality (see Fig. 1). The model assumes that no charge transfer takes place between the punch and the specimen (since the specimen is mainly dielectric, the surface charges are bounded). The increase in total charge between two close times $t_1$ and $t_2$ can be viewed in the limit as a quasistatic electric current:

$$\frac{Q_2 - Q_1}{t_2 - t_1} = \lim_{\Delta t \to 0} \frac{\Delta Q}{\Delta t} = \frac{\partial Q}{\partial t},$$

(21)

$$\frac{\partial Q}{\partial t} = \left( \frac{4}{K_{\text{corr}}} \right) \tilde{M}_1 \sqrt{\frac{v^2 D t}{2}}.$$ 

(22)

Equation (22) shows that the quasistatic current would vary with a power of 3/2 with the indentation velocity $v$. The constant, $\tilde{M}_1$, has been solved by using finite element analysis by Giannakopoulos and Suresh, and was found to be 3.35 and 2.69 C/m² for PZT-4 and (Ba0.87Ca0.13)TiO₃, respectively.

If the indentation is carried out with a constant acceleration, $v'$, then $h_{\text{actual}} = v'^2 t'/2$ and the quasistatic current is given by

$$\frac{\partial Q}{\partial t} = \left( \frac{2}{K_{\text{corr}}} \right) \tilde{M}_1 \sqrt{(v')^3 D t^2}.$$ 

(23)

The above equations, Eqs. (22) and (23), essentially correspond to electrodes that operate into a circuit of admittance $Y$ (for direct currents $Y = 1/R_c$, where $R_c$ is the electrical resistance of the circuit), hence

$$I = \frac{\partial Q}{\partial t} = 2\pi \int_0^a D_r d r = \pm Y V,$$

(24)

where ± depends on the orientation of the poling axis.

III. MATERIALS

PZT-4 and a solid solution of barium titanate were the materials selected as specimens for measuring the current induced in a conducting spherical punch during indentation. The exact chemical composition of PZT-4 (mole %) is 47 PbTiO₃ + 47 PbZrO₃ + 6 SrZrO₃ and the composition of the barium titanate solution is 91.7 BaTiO₃ + 8.3 CaTiO₃. The reason for choosing these materials is twofold. First, the piezoelectric, dielectric and elastic constants are readily available in literature (Table I). Second, specimens processed through standardized techniques with known and reproducible microstructures were commercially available.

IV. METHODOLOGY

The side of the specimen to be indented was polished to a surface finish of 0.05 μm. The first step of the polishing procedure involved the use of 1 μm diamond paste and subsequent steps involved the use of Al₂O₃ slurry. The reason for limiting the initial step to a 1 μm grit was to minimize depoling and damage of the surface layer caused by deformation due to the grit.

In order to enforce experimentally the condition of zero electrical potential far away from the indentor, the surface opposite to that being indented was coated with silver. The experimental setup is shown in Fig. 2. The lower cross head on which the specimen was placed and the indentor were both electrically grounded. The indentor was a half sphere of stainless steel 316 with a diameter of 10 mm. A Keithley-614 electrometer, connected between the indentor and the ground, was used to measure the quasi-static current induced into the punch.

Indentation experiments were conducted using a mechanical testing machine (commercially available as Model 4505 from Instron Corporation, Canton, MA) for constant velocity indentation. The device allows simultaneous measurements of the load and the corresponding depth of penetration. Load is measured with a load cell and penetration is obtained with a fotonic sensor (MTI-2000) and mirror. The
measured load, penetration depth and electric current are stored in a computer with a scan rate of 10^3/s.

Four indentation velocities of 5, 10, 20, and 50 μm/min were used. In order to avoid permanent deformation (the risk increasing with penetration depth and load) the tests were limited to a maximum load of 300 N. Indentation velocities greater than 50 μm/min reached this limit so rapidly that useful data could not be gathered. Since the current decreases with decreasing indentation velocity, the measured signal becomes too small for velocities below 1 μm/min with the present setup.

The effect of rapid aging at elevated temperatures was studied for (Ba_{0.917}Ca_{0.083})TiO_{3} since the results could be compared to literature.\textsuperscript{14} Partially depoled (Ba_{0.917}Ca_{0.083})TiO_{3} specimen were obtained by annealing the samples for 3, 14, and 25 h in flowing argon atmosphere at 373 and 363 K. In order to confirm the effect of temperature, an additional specimen was annealed at 383 K for 14 h. Different samples were used for the three temperatures. When investigating the effect of a given annealing temperature, the same sample was reheated three times and the cumulative time of 14 h was used as the annealing time. In order to make sure that there were no effects due to long time temperature cycling, a specimen heated to 373 K for 14 h in one heating cycle was compared to a specimen heated to 373 in two cycles (3+11 h). No appreciable difference was found. The specimens were cut into different surface shapes with areas varying from 1 to 3 cm². The results were independent of the specimen shape, in accordance with the theory.

The material constant, $\bar{M}_1$, was extracted from the measured $I$ vs $t$ curves according to the following procedure; first, the area under the curve was evaluated numerically for a given time interval. A constant, $A$, was then evaluated with the equation:

$$A = \frac{3}{2(t_2^{3/2} - t_1^{3/2})} \int_{t_1}^{t_2} I dt$$  \hspace{1cm} (25)$$

by performing trapezoidal numerical integration with the $I$-$t$ experimental points. Equation (22) was integrated with respect to the same time interval. $\bar{M}_1$ was then calculated from $A$:

$$\bar{M}_1 = A \left( \frac{4}{K_{corr}} \sqrt{\frac{v^2D}{2}} \right)^{-1}$$ \hspace{1cm} (26)$$

This procedure proved to minimize experimental errors.

V. RESULTS AND DISCUSSIONS

A. Indentation velocity and poling direction

The induced-quasistatic current in the stainless steel punch was measured for three distinct cases for PZT-4 and (Ba_{0.917}Ca_{0.083})TiO_{3}: indentation along the poling direction, indentation against the poling direction, and indentation on an unpoled sample. Figures 3 and 4 show the induced current as a function of time after contact had commenced between punch and specimen. The poling direction coincides with the coercive electric flux necessary for the material polarization.

When indenting towards the poling direction the induced current increases in magnitude with time, first rapidly and then slowly [Figs. 3(a) and 4(a)]. This increase is to be expected since the contact area increases with time. The induced current is a result of the electrically polarized contact area. Higher velocities are expected to result in greater currents. This is because at higher velocities, larger displacements would have been obtained, for a given time period, resulting in larger contact areas. As seen from Figs. 3(a) and 4(a), the results are consistent with this prediction.

Unpoled PZT-4 and (Ba_{0.917}Ca_{0.083})TiO_{3} [Figs. 3(b) and 4(b)] do not, as expected, result in any induced current. This is because there is no preferred orientation for the ferroelectric domains and hence no net polarization change upon mechanical deformation.

When indenting along the poling direction, the change in magnitude of the induced current is similar to the case of indenting towards the poling direction. As seen in Figs. 3(c) and 4(c) the sign of the current is opposite to that in Figs. 3(a) and 4(a). This is to be expected since the electrical dipoles at the contact area are oriented in the opposite direction compared to the case of indenting along the poling direction.

The expected induced current during indentation is calculated from Eq. (23), using the values for the constant $\bar{M}_1$ reported by Giannakopoulos and Suresh.\textsuperscript{12} The correction

![FIG. 3. Current vs time after indentation for PZT-4: (a) indentation towards the poling direction; (b) unpoled specimen; (c) indentation along the poling direction.](image-url)
TABLE II. Data used to calculate the nonrigid correction for displacement, $K_{\text{corr}}$.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$E_{\text{specimen}}$</th>
<th>$\nu_{\text{specimen}}$</th>
<th>$K_{\text{corr}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-4</td>
<td>67 GPa</td>
<td>0.3–0.5</td>
<td>1.3–1.6</td>
</tr>
<tr>
<td>(Ba$<em>{0.91}$Ca$</em>{0.083}$)TiO$_3$</td>
<td>117 GPa</td>
<td>0.3</td>
<td>1.6</td>
</tr>
<tr>
<td>Sphere</td>
<td>$4E_{\text{indenter}}$</td>
<td>$\nu_{\text{indenter}}$</td>
<td></td>
</tr>
<tr>
<td>Stainless steel 316</td>
<td>208 GPa</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 4. Current vs time after indentation for (Ba$_{0.91}$Ca$_{0.083}$)TiO$_3$: (a) indentation towards the poling direction; (b) unpoled specimen; (c) indentation along the poling direction.
and therefore characterization of thin films and thin strips is made possible without any need of sample preparation.

B. Characterization of polarization loss

Mason\textsuperscript{14} investigated the aging of the properties of barium titanate and found that aging affects not only the dielectric constants (total reduction by 15\% in 1 year) but also the remnant frequency, the electromechanical coupling factor, and the electrical and mechanical dissipation factor. His investigation was connected with a gradual depolarization process having an activation energy between 15 and 19 kcal/mole for temperatures between 110 and 70 °C, respectively. Furthermore, the aging process was consistent with an equilibration of the domain structure brought about by thermal energy which was also directly observed. Linear piezoelectricity was found to hold for uniaxial compressive stresses up to 6.9 MPa. Strong nonlinearity due to stress induced depolarization was found to start at a uniaxial compressive stress of 35 MPa.\textsuperscript{14} The average tensile residual stress of barium titanate in full polarity was estimated to be 433 MPa.\textsuperscript{14}

In order to investigate whether polarization loss would be measurable with the present indentation technique, (Ba\textsubscript{0.917}Ca\textsubscript{0.083})\textsubscript{TiO\textsubscript{3}} samples were annealed in flowing argon at 363 and 373 K for 3, 14, and 25 h and at 383 K for 14 h. The quasistatic current was then measured for the annealed samples with an indentation velocity of 5 \( \mu \)m/min. The constant \( \bar{M}_1 \) which combines the piezoelectric, dielectric, and elastic properties of the material was then extracted from the current versus time behavior using Eqs. (25) and (26). A decrease in \( \bar{M}_1 \) after an annealing treatment is assumed to be associated with the enhanced rate of polarization loss at elevated temperature. The measured difference between \( \bar{M}_1 \) before annealing (\( \bar{M}_{1\text{(initial)}} \)) and after (\( \bar{M}_{1\text{(final)}} \)) is presented in Fig. 7. The essential behavior of loss in \( \bar{M}_1 \) vs annealing time (\( t_{\text{heat}} \)) is similar to the loss in dielectric constant versus annealing time observed by Mason.\textsuperscript{14} In both cases, there is an initial fast drop of \( \bar{M}_1 \) from \( \bar{M}_{1\text{(initial)}} \), followed by an exponential asymptotic behavior towards a final value \( \bar{M}_{1\text{(final)}} \). By interpolation according to the following equation, as by Mason,\textsuperscript{14} the activation energy is estimated to be 15 kcal/mole at 373 K.

TABLE III. Slopes of ln \( I \) vs ln \( v \).

<table>
<thead>
<tr>
<th>Material</th>
<th>Indenting direction</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT-4</td>
<td>Towards poling direction</td>
<td>1.32</td>
</tr>
<tr>
<td>PZT-4</td>
<td>Along poling direction</td>
<td>2.28</td>
</tr>
<tr>
<td>(Ba\textsubscript{0.917}Ca\textsubscript{0.083})\textsubscript{TiO\textsubscript{3}}</td>
<td>Towards poling direction</td>
<td>1.22</td>
</tr>
<tr>
<td>(Ba\textsubscript{0.917}Ca\textsubscript{0.083})\textsubscript{TiO\textsubscript{3}}</td>
<td>Along poling direction</td>
<td>1.74</td>
</tr>
</tbody>
</table>
The experimental results reproduce the basic features predicted by the analytical results based on the piezoelectric, dielectric and mechanical properties of the materials. The current increases during indentation first rapidly and then slowly. Increasing the indentation velocity enhances the absolute magnitude of the current. Switching the poling direction of the specimen with respect to the indenting direction changes the polarity of the current. In the case of (Ba$_{0.917}$Ca$_{0.083}$)$_3$TiO$_3$, the quantitative agreement between calculations and experiments is adequate. There is a difference of a factor of 2 between calculations and experiments for PZT-4 which is attributed to deviations in material properties from the assumed values as well as to indentation induced mechanical and/or electrical damage. The presented quasistatic indentation method is practical with piezoelectric materials having high permittivity and low conductivity that minimize power drain due to internal leakage of charges.

Depoling of (Ba$_{0.917}$Ca$_{0.083}$)$_3$TiO$_3$ enhanced by polarization loss at elevated temperatures (393, 383, and 373 K) was investigated with the current technique and the resulting activation energy due to depoling agree, with values given in the literature. Therefore, indentation is a viable tool for assessing the aging of piezoelectric material.

Linear elastic indentation with simultaneous measurements of load, displacement, and electrical current is a non-destructive, quick technique for characterization of piezoelectric specimens. It may offer great advantages in the research, as well as in practice for characterization of the electric properties of piezoelectric materials.

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