Compressive stress-induced depolarization in ferroelectric ceramics at room and high temperatures: experiment and prediction

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A poled lead titanate zirconate rectangular parallelepiped is subjected to compressive stress-induced switching at room and high temperatures. From measured electric displacement and strains, piezoelectric and elastic compliance coefficients are estimated and plotted versus remnant state variables. Then a set of modeling equations is proposed to predict the high temperature behavior of the material reported in one of the authors’ previous work.9 The equations are applied to the present work to calculate the evolutions of reference remnant state variables during mechanical depolarization. Finally, the high temperature behavior of the material during mechanical depolarization is compared with the behavior during electric field-induced polarization reversal in terms of reference remnant state variables.

Key-words : Compressive stress, Depolarization, Linear moduli, High temperature, Reference remnant, Ferroelectric ceramics

1. Introduction

Some piezoelectric ceramics such as lead titanate zirconate (PZT) have high coercive fields, low piezoelectric coefficients, and low dielectric loss. They are strong enough to withstand high levels of mechanical and electrical loading. Hence, it is often used as high voltage or high power generators and transducers. In these applications, the piezoelectric devices are usually subjected to excessive electric field and compressive stress at high temperatures. For example, it was reported by Sakai and Kawamoto3) that a piezoelectric stack actuator was heated more than 75°C while it was operated at 130 Hz driving frequency at a surrounding temperature of 120°C. This implies the importance of predicting the switching behavior of the materials at high temperature for the development of efficient and accurate piezoelectric devices. The predictions are usually made by finite element method, which requires a complete constitutive model of the materials. A sufficient amount of experimental data and knowledge at high temperatures should be accumulated and analyzed to construct a reliable constitutive model of the materials. A domain structure of a ferroelectric specimen is often represented by macroscopic state variables such as remnant polarization or remnant strains.5,6,7 It is therefore useful to investigate the evolutions of those remnant state variables and the dependence of material properties on remnant state variables in the materials at room and high temperatures.

Evolutions of material properties during domain switching of ferroelectric materials have been investigated from the macroscopic point of view. Selten et al.5) applied electric field and compressive stress and measured electric displacement and strains, from which dielectric permittivity, Young’s modulus, and piezoelectric coefficient are estimated and plotted versus remnant polarization. Liu and Huber5) described linear moduli as functions of remnant state variables at room temperature and plotted the relations between remnant polarization and remnant longitudinal strain, when the piezoelectric materials are switched under the combined loads of electric field and compressive stress. The nonlinear creep behavior of the materials under static electric fields and/or compressive stresses was observed by Zhou and Kamlah9) and Liu and Huber,5) where remnant state variables were used as internal variables. Kim and Lee8) studied the creep behavior of a poled PZT wafer under longitudinal tensile stress and through-thickness electric field and discussed the effect of electrical boundary conditions on the tensile creep behavior of the materials. However, all these studies have been made at room temperature only. Recently, some research works have been made at high temperatures. Weber et al.7) measured and characterized the nonlinear switching behavior of a soft lead zirconate titanate by compressive stress at high temperatures, observing a strong temperature dependence of ferroelastic switching. The evolutions of linear material properties and remnant state variables were calculated from measured responses at high temperatures as well as room temperature. Rauls et al.9) measured the responses of a relaxor ferroelectric PLZT to electric fields at room and high temperatures and discussed the dependence of polarization hysteresis and butterfly strain loops on temperature. Ji and Kim9) applied various magnitudes of compressive stress at room temperature and induced a ferroelastic switching. Then the stress is removed and temperature is increased, during which polarization and strains are measured. From the measurements, pyroelectric and thermal expansion coefficients are estimated and the relations among remnant state variables are studied. Ji and Kim10) also applied electric field pulses of increasing magnitude to induce polarization reversals at room and high temperatures. They obtained permittivity and piezoelectric coefficients at various temperatures and calculated the so-called reference remnant state variables to compare the behavior of materials at different temperatures. Recently, Ji and Kim11) applied electric fields of sufficient magnitude at room temperature and then increased the temperature of specimen under no electric field, estimating

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pyroelectric and thermal expansion coefficients. They proposed a set of modeling equations to predict the high temperature behavior of the material.

The present work is divided into two parts, prediction and experiment. In the part of prediction, a new set of eight modeling equations is proposed by modifying those of Ji and Kim. Instead of relative remnant polarization, the so-called reference remnant polarization is chosen for analysis. The proposed equations are applied to the measured data of Ji and Kim to predict the relations among remnant state variables and the dependence of thermal properties on remnant state variables at high temperatures. The second part of the work begins by applying compressive stress cycles (or pulses) of increasing magnitude to a poled PZT specimen at room and high temperatures. Electric displacement and strains are measured, and piezoelectric and elastic compliance coefficients are estimated and plotted versus reference remnant state variables. Finally, in terms of reference remnant state variables, the switching behavior of the material during compressive stress-induced mechanical depolarization is discussed and compared with the behavior during electric field-induced polarization reversal, the latter behavior being measured by Ji and Kim.

2. Experiment

A soft PZT rectangular parallelepiped (PZT5H1, Morgan Technical Ceramics, UK) of dimensions 10 mm × 10 mm × 12 mm is taken as a specimen for experiments. The PZT specimen has electrodes on the 10 mm × 10 mm faces and is poled along the longitudinal 12 mm direction. The 12 mm direction is referred to as the longitudinal direction and designated as \( x_3 \); two mutually orthogonal directions perpendicular to the longitudinal \( x_3 \) axis are called transverse directions and designated as \( x_1 \) and \( x_2 \), respectively. From the manufacturing company, the Curie point of the material is 200°C; the density is 7400 kg/m³, the coupling factor is \( k_p = 0.60 \), the piezoelectric coefficients are \( d_{31} = -250 \times 10^{-12} \text{m/N} \) and \( d_{32} = 620 \times 10^{-12} \text{m/V} \), and the elastic compliance coefficients at constant electric field \( s_{12} = 21.9 \times 10^{-12} \text{m} \cdot \text{N}^{-1} \), \( s_{11} = 17.7 \times 10^{-12} \text{m} \cdot \text{N}^{-1} \), and \( s_{13} = -5.7 \times 10^{-12} \text{m} \cdot \text{N}^{-1} \). It should be noted that these material properties provided by manufacturing companies are usually measured under small signal and high frequency conditions, whereas in the present work, they are measured in the conditions of large signal and low frequency. The latter is more relevant to typical actuator and sensor applications and gives more useful information to realistic predictions of the material behavior for a variety of possible loading profiles.

A PZT specimen is saturated (or poled) by applying 1.0 MV/m\(^{-1}\) in the \(-x_3\) direction at the so-called reference temperature \( \theta_0 = 20°C \). The value of polarization at the poled state is \( P_{30} = -0.530 \text{ C/m}^2 \), and strain gauges are set to be zero at the poled state. The reference configuration for all strain measurement is, therefore, the poled state at reference temperature \( \theta_0 \). Before measurements, a constant preloading stress of \(-15 \text{ MPa}\) is applied for stable measurements of strains. Then compressive stress of cyclic type is added to the preload stress to induce mechanical depolarization. The magnitudes of stress cycles (or pulses) increase gradually from 20 to 200 MPa at an interval of 20 MPa, making ten stress cycles in total. The rate of stress loading and unloading is 10 MPa/s, and three seconds of stop time are given after each stress cycle, as shown in Fig. 3(a). Since the specimen remains isotropic with respect to the \( x_3 \) direction, transverse strain \( S_3 \) in the \( x_1 \) direction is equal to transverse strain \( S_1 \) in the \( x_2 \) direction. During compressive stress-induced depolarization at \( \theta = \theta_0 \), longitudinal electric displacement \( D_3 \) and longitudinal and transverse strains \( S_1 \) and \( S_1 \) are measured and plotted in Figs. 3(b) and 3(c), respectively. After the stress-induced depolarization experiment at \( \theta = \theta_0 \), the specimen is subjected to a poling electric field \( E_3 = -1.0 \text{MV/m} \) to restore the initial poled state. The initialization procedure to restore the same initial saturated state is described in the authors’ previous works. Then the temperature of specimen is increased to a high temperature. Just like the stress-induced depolarization experiment at reference temperature, the preloading stress of \(-15 \text{ MPa}\) is given first, and then the stress cycles in Fig. 3(a) are applied to induce depolarization at the high temperature. Similar experiments are repeated for three high temperatures 50, 80, and 110°C, though not shown here.

The temperature of a PZT specimen is controlled by immersing it into a bath of transformer oil (MICTRANS Class-1 No-2, MICHANG OIL IND. CO., Pusan, Korea) and controlling the temperature of the oil. The oil is heated using an electric heat coil equipped at the bottom plate of the bath and a temperature control unit (2408 PID controller, EUROTHERM, UK). Electric displacement in longitudinal direction is measured using a Sawyer-Tower bridge, using a Keithley 6514 electrometer. Both longitudinal and transverse strains are measured by only one biaxial strain gauge attached in a side face of specimen. The used biaxial strain gauge is a fully encapsulated constantan strain gauge (WA-10, VISHAY, Germany) that can be used for the temperature range between \(-75°C\) and \(+205°C\). Measured strain data at high temperatures have been compensated according to a manufacturer’s manual. All equipment output signals pass through a data acquisition board (PCI 6221, National Instruments, TX, USA) and are manipulated using a LABVIEW software. More details on experiments and measurements can be found in the authors’ other works.

3. Results and discussion

3.1 Predictions for high temperature behavior during temperature rise after compressive stress-induced switching at room temperature

In a previous work of the authors, a set of simple modeling equations was proposed from their experimental observations on a PZT specimen subjected to temperature rise subsequent to electric field-induced switching at reference temperature, predicting the high temperature behavior of the materials. In the present work, a similar set of modeling equations is proposed and applied to predict the high temperature behavior of the same specimen which is subjected to compressive stress-induced domain switching at reference temperature. The proposed modeling equations are applied to the previous experimental data of Ji and Kim. In their work, all experimental data were arranged and analyzed by using the so-called relative remnant polarization \( P_3^R/P_3^{sat} \), where \( P_3^{sat} \) is the magnitude of remnant polarization at the saturated state obtained by a restoring electric field. In the present work, however, \( P_3^{R}/P_3^{sat} \) is replaced by reference remnant polarization \( P_3^{sat} \). The replacement can be justified by deriving a relation between \( P_3^{R}/P_3^{sat} \) and \( P_3^{R} \). From the definition of pyroelectric coefficient \( p_3 \), \( P_3^{sat} \) can be expressed as a function of temperature given by:

\[
\begin{align*}
\hat{p}_3^R(\theta) &= P_3^{R0} + p_3(\theta - \theta_0), \\
\hat{p}_3^{sat}(\theta) &= P_3^{sat0} - p_{3sat}(\theta - \theta_0),
\end{align*}
\]

where \( P_3^{R0}(>0) \) and \( p_{3sat}(>0) \) are the magnitudes of \( P_3^{R0} \) and pyroelectric coefficient at the saturated state, respectively. \( p_3^{sat} \) has been introduced to compare the behavior of the materials at different temperatures. Assuming that pyroelec-
Eq. (2), and Eq. (3) is reduced to

\[ \Delta p_3 = a_3 p_3^{Ro} + b_p \]

and combining Eq. (2) with Eq. (1), we get

\[ \frac{P_R^R}{P_{3Sat}^R} = \frac{1 + a_3 \Delta \theta - \theta_0}{P_{3Sat}^{Ro} - P_{3Sat}(\Delta \theta - \theta_0)} p_3^{Ro} + \frac{b_3 \Delta \theta - \theta_0}{P_{3Sat}^{Ro} - P_{3Sat}(\Delta \theta - \theta_0)}. \]

Eq. (3) shows that \( P_R^R / P_{3Sat}^R \) does not have a one-to-one correspondence with \( p_3^{Ro} \) but it depends on temperature \( \Delta \theta \). If \( b_p \) is zero, or equivalently if \( \Delta p_3 = 0 \) at \( p_3^{Ro} = 0 \), then \( a_p = \frac{P_{3Sat}}{P_{3Sat}^{Ro}} \) from Eq. (2), and Eq. (3) is reduced to

\[ \frac{P_R^R}{P_{3Sat}^R} = \frac{P_{3Sat}^{Ro}}{P_{3Sat}^{Ro}}. \]

In other words, if \( \Delta p_3 \) is a linear function of \( p_3^{Ro} \) having zero value at \( p_3^{Ro} = 0 \), then \( P_R^R / P_{3Sat}^R \) has a one-to-one relation with \( p_3^{Ro} \) and it can be used as a state variable to compare the thermal behavior of the materials at different temperatures. As clearly shown in Fig. 3(c) of Ji and Kim, \( \Delta p_3 \) has the form of \( \Delta p_3 = a_p p_3^{Ro} \) with \( b_p = 0 \) when the temperature of a specimen is increased after it is switched at reference temperature by an electric field. However, as observed in Fig. 5(a) of Ji and Kim, it is not so during temperature rise after compressive stress-induced switching at reference temperature, thereby \( p_3^{Ro} \) being a proper state variable instead of \( P_R^R / P_{3Sat}^R \) in the case of compressive stress-induced switching.

Now a system of eight modeling equations are proposed to analyze the data of Ji and Kim in terms of reference remnant state variables such as \( P_{3Sat}^{Ro} \) and \( s_{3Sat}^{Ro} \). The first three modeling equations give the changes in remnant state variables \( P_{3Sat}^R \), \( s_{3Sat}^R \) and \( S_{3Sat}^R \) during temperature increase, which are already introduced by the authors as follows.

\[ P_{3Sat}^R \approx P_{3Sat}^R + \Delta p_3(\Delta \theta - \theta_0), \]

\[ S_{3Sat}^R = S_{3Sat}^R + \Delta \alpha_3(\Delta \theta - \theta_0), \]

\[ S_{3Sat}^R = S_{3Sat}^R + \Delta \beta_3(\Delta \theta - \theta_0), \] (5)

where \( \Delta p_3 \), \( \Delta \alpha_3 \), and \( \Delta \beta_3 \) are pyroelectric, longitudinal thermal expansion, and transverse thermal expansion coefficients, respectively. They depend on remnant state variables at reference temperature, as expressed in Eq. (6) below, but they are constant between 20 and 110°C independent of temperature. \( \Delta \alpha_3 \) and \( \Delta \beta_3 \) are plotted versus \( s_{3Sat}^{Ro} \) and \( S_{3Sat}^{Ro} \), which are obtained by Ji and Kim for a PZT specimen during pure temperature rise subsequent to compressive stress-induced domain switching at reference temperature. It is shown in Fig. 1 that the data symbols of measured thermal properties are fitted well by either straight lines or quadratic curves. For modeling purpose, the three thermal properties are expressed by polynomial equations of \( s_{3Sat}^{Ro} \) given by

\[ \Delta p_3 = a_3(s_{3Sat}^{Ro}) + b_3, \]

\[ \Delta \alpha_3 = a_3(s_{3Sat}^{Ro}) + b_3, \]

\[ \Delta \beta_3 = a_3(s_{3Sat}^{Ro})^2 + b_3(s_{3Sat}^{Ro}) + c_3, \] (6)

where \( \Delta p_3 \) and \( \Delta \alpha_3 \) are linear functions and \( \Delta \beta_3 \) a quadratic function of \( s_{3Sat}^{Ro} \), respectively. The last two modeling equations come

![Fig. 1. Measured thermal properties and reference remnant state variables fitted by eight polynomial equations of Eqs. (5), (6) and (7), (a) \( p_3 \) versus \( S_{3Sat}^{Ro} \), (b) \( \alpha_3 \) and \( \alpha_1 \) versus \( S_{3Sat}^{Ro} \), (c) \( S_{3Sat}^R \) versus \( P_{3Sat}^R \), and (d) \( S_{3Sat}^R \) versus \( S_{3Sat}^{Ro} \) plots.](image-url)
from the relations between reference remnant state variables. Figure 1(c) shows the plot of \( S_{3}^{R} \) versus \( P_{3}^{R} \) and Fig. 1(d) that of \( S_{1}^{R} \) versus \( S_{3}^{R} \). \( S_{3}^{R} \) is fitted well by a cubic polynomial function of \( P_{3}^{R} \) in Fig. 1(c) and \( S_{3}^{R} \) by a quadratic function of \( S_{3}^{R} \) in Fig. 1(d). So remnant state variables at reference temperature are related to one another by the polynomial equations

\[
S_{3}^{R} = a_{3}(P_{3}^{R})^3 + b_{3}(P_{3}^{R})^2 + c_{3}(P_{3}^{R}) + d_{3},
\]

\[
S_{1}^{R} = a_{1}(S_{3}^{R})^2 + b_{1}(S_{3}^{R}) + c_{1},
\]

and

\[
S_{1}^{R} = a_{1}(S_{3}^{R})^2 + b_{1}(S_{3}^{R}) + c_{1}.
\]  \( \text{(7)} \)

Thus the proposed set of modeling equations consists of three equations in Eq. (5) representing linear variations of remnant state variables with temperature, three equations in Eq. (6) expressing linear or quadratic dependence of thermal properties on \( S_{3}^{R} \), and finally two equations in Eq. (7) assuming cubic or quadratic relations between reference remnant state variables. The total fourteen coefficients from \( a_{3} \) to \( c_{1} \) in Eqs. (6) and (7) are evaluated from the five fitting curves drawn in Fig. 1, which are listed in Table 1.

Now we predict the high temperature behavior of thermal properties in a PZT specimen subjected to stress-induced switching at reference temperature shown in Fig. 5 of Ji and Kim\(^9\) by using the modeling equations from Eqs. (5) to (7), which is similar to a previous work for a PZT specimen subjected to electric field-induced switching.\(^11\) The symbols in Fig. 2 represent measured remnant state variables or estimated thermal properties when the temperature of a PZT specimen is increased after compressive stress-induced switching at reference temperature. Filled circle, empty diamond, filled right triangle, and empty square symbols stand for the data at 20, 50, 80, and 110°C, respectively. The solid, dashed, dashed and dotted, and long square symbols stand for the data at 20, 50, 80, and 110°C, respectively. The proposed set of modeling equations consists of three equations in Eq. (5) representing linear variations of remnant state variables with temperature, three equations in Eq. (6) expressing linear or quadratic dependence of thermal properties on \( S_{3}^{R} \), and finally two equations in Eq. (7) assuming cubic or quadratic relations between reference remnant state variables. The total fourteen coefficients from \( a_{3} \) to \( c_{1} \) in Eqs. (6) and (7) are evaluated from the five fitting curves drawn in Fig. 1, which are listed in Table 1.

Table 1. The values of constants for fitting straight lines and quadratic curve in Fig. 5

<table>
<thead>
<tr>
<th>Equations</th>
<th>Constants</th>
<th>Units of constants</th>
<th>Values of constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_{1} = a_{1}(S_{3}^{R}) + b_{1} )</td>
<td>( a_{3} )</td>
<td>( 10^{6} \text{ Cm}^{-2} \text{C}^{-1} )</td>
<td>0.00375523</td>
</tr>
<tr>
<td>( p_{3} = a_{3}(S_{3}^{R}) + b_{3} )</td>
<td>( h_{3} )</td>
<td>( 10^{-2} \text{Cm}^{2} \text{C}^{-1} )</td>
<td>6.87614</td>
</tr>
<tr>
<td>( a_{3} )</td>
<td>( a_{3} )</td>
<td>( \text{[°C]}^{-1} )</td>
<td>-0.00523946</td>
</tr>
<tr>
<td>( b_{3} )</td>
<td>( b_{3} )</td>
<td>( 10^{-6} \text{C}^{-1} )</td>
<td>-3.35792</td>
</tr>
<tr>
<td>( p_{1} = a_{1}(S_{3}^{R})^2 + b_{1}(S_{3}^{R}) + c_{1} )</td>
<td>( a_{1} )</td>
<td>( 10^{6} \text{C}^{-1} )</td>
<td>0.00000602631</td>
</tr>
<tr>
<td>( h_{1} )</td>
<td>( h_{1} )</td>
<td>( \text{[°C]}^{-1} )</td>
<td>0.00374985</td>
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<tr>
<td>( a_{1} )</td>
<td>( a_{1} )</td>
<td>( 10^{-6} \text{C}^{-1} )</td>
<td>2.81033</td>
</tr>
<tr>
<td>( b_{1} )</td>
<td>( b_{1} )</td>
<td>( 10^{-6} \text{C}^{-1} )</td>
<td>147745</td>
</tr>
<tr>
<td>( c_{1} )</td>
<td>( c_{1} )</td>
<td>( 10^{-6} \text{C}^{-1} )</td>
<td>187742</td>
</tr>
<tr>
<td>( d_{1} )</td>
<td>( d_{1} )</td>
<td>( \text{[°C]}^{-1} )</td>
<td>69237.3</td>
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<tr>
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<td>( c_{1} )</td>
<td>( 10^{-6} )</td>
<td>0.569409</td>
</tr>
</tbody>
</table>

The values of remnant state variables, such as remnant polarization \( P_{3}^{R} \), remnant longitudinal strain \( S_{1}^{R} \), and remnant trans-

3.2 Measurement and analysis for compressive stress-induced switching at room and high temperatures

In the previous section, the eight modeling equations in Eqs. (5), (6), and (7) are proposed and applied to predict the behavior of a ferroelectric specimen during pure temperature increase subsequent to compressive stress-induced domain switching at room (or reference) temperature, as shown in Fig. 2. It is interesting to apply the proposed equations to the behavior of compressive stress-induced switching at high temperatures. Figure 3(a) shows a cyclic profile of applied compressive stress at reference temperature 20°C. The magnitude of stress cycles (or pulses) increases from about 20 to 200 MPa during ten cycles of stress loading. Figures 3(b) and 3(c) are, respectively, the electric displacement and strain responses of the specimen during the stress loading in Fig. 3(a). The value of electric displacement is shown to increase from about −0.5 to −0.28 Cm−2, that of longitudinal strain to decrease down to about −2400 × 10−6, and that of transverse strain to increase up to some 1100 × 10−6, with the level of stress pulse. The same experiments are also made at three high temperatures 50, 80, and 110°C, though the responses are not shown here.

The values of remnant state variables, such as remnant polarization \( P_{3}^{R} \), remnant longitudinal strain \( S_{1}^{R} \), and remnant trans-
verse strain $S_{R}^p$, of a one-dimensional ferroelectric specimen are obtained by averaging those of polarization and strains of constituent grains in the specimen. Thus remnant state variables $P_{R}^3$, $S_{R}^3$, and $S_{R}^1$ are considered to represent the domain structure of the specimen. An application of large compressive stress causes domain switching in a ferroelectric specimen and changes the values of remnant state variables in the specimen. A unique set of remnant state variables corresponds to a unique domain structure of the specimen, which motivates us to investigate the evolutions of material properties during switching in terms of remnant state variables. From the measured responses in Figs. 3(b) and 3(c), piezoelectric coefficient $d_{33}$ and elastic compliance coefficients $s_{33}$ and $s_{13}$ are estimated by dividing the changes of electric displacement and strains by the change of compressive stress, respectively. The linear material properties are estimated at the instant of time when each stress pulse increases from the preload stress $-15$ MPa. The change in electric displacement for 1.5 s is divided by the change in stress for the same period of time, yielding the value of $d_{33}$ at that instant of time. Similar estimates are also made for three high temperatures 50, 80, and 110°C as well as reference temperature 20°C. Estimates of $d_{33}$ are plotted versus $P_{R}^3$, $S_{R}^3$, and $S_{R}^1$ for all four temperatures in Figs. 4(a) and 4(c), respectively. Similarly, elastic compliance coefficients $s_{33}$ and $s_{13}$ are estimated by dividing the changes in longitudinal and transverse strains by the change in stress for 1.5 s. The estimates of $s_{33}$ and $s_{13}$ are plotted versus $P_{R}^3$, $S_{R}^3$, and $S_{R}^1$ for all four temperatures.

Fig. 2. The previous measured data in Ji and Kim" represented by symbols and the prediction curves calculated from the eight modeling equations in Eqs. (5), (6) and (7) at four temperatures, (a) $S_{R}^p$ versus $P_{R}^3$, (b) $S_{R}^p$ versus $P_{R}^1$, (c) $P_{R}^3$ versus $P_{R}^1$, (d) $P_{R}^3$ versus $S_{R}^3$, (e) $a_{R}^3$ and $a_{R}^1$ versus $P_{R}^3$, and (f) $a_{R}^3$ and $a_{R}^1$ versus $S_{R}^3$ and $S_{R}^1$ plots.
temperatures in Figs. 5(a) and 5(c), respectively. It is useful to plot again the estimated linear moduli $d_{13}$, $s_{33}$, and $s_{13}$ versus reference remnant state variables $P_{0}^{PR}$, $S_{0}^{PR}$, and $S_{1}^{PR}$, for comparison purpose. The values of remnant state variables $P_{0}^{PR}$, $S_{0}^{PR}$, and $S_{1}^{PR}$ at temperature $\theta$ can be transformed to the corresponding values of reference remnant state variables $P_{0}^{SR}$, $S_{0}^{SR}$, and $S_{1}^{SR}$ at reference temperature $\theta_{0}$ in this way: first, insert Eq. (6) into Eq. (5) to get

$$S_{1}^{SR} = \frac{S_{1}^{PR} - b_{13}(\theta - \theta_{0})}{1 + a_{13}(\theta - \theta_{0})}. \tag{8}$$

then put Eq. (8) into Eqs. (6), and finally insert them into Eqs. (5) and (5) to obtain $P_{0}^{SR}$ and $S_{0}^{SR}$, respectively. Thus, the values of $P_{0}^{PR}$, $S_{0}^{PR}$, and $S_{1}^{PR}$ at $\theta_{0}$ are obtained from the given values of $P_{0}^{SR}$, $S_{0}^{SR}$, and $S_{1}^{SR}$ at $\theta$. The linear moduli in Figs. 4(a), 4(c), 5(a) and 5(c) are plotted again versus $P_{0}^{PR}$ in Figs. 4(b) and 5(b) and versus $S_{0}^{PR}$ and $S_{1}^{PR}$ in Figs. 4(d) and 5(d), for four temperatures 20, 50, 80, and 110°C.

Turning to Fig. 4, it is shown that piezoelectric coefficient $d_{13}$ remains negative for all levels of compressive stress applied in the experiment. The magnitude of $d_{13}$ looks proportional to the magnitude of polarization; it is saturated to zero with mechanical depolarization at four temperatures; and it is smaller at lower temperature for a fixed value of $P_{0}^{PR}$ or $P_{0}^{SR}$ in Figs. 4(a) and 4(b). The difference in the magnitude of $d_{13}$ between different temperatures gets smaller when it is plotted versus $P_{0}^{PR}$ in Fig. 4(b) than when plotted versus $P_{0}^{SR}$ in Fig. 4(a). When $d_{13}$ is plotted versus $S_{1}^{PR}$ and $S_{0}^{PR}$ in Fig. 4(c), the linear dependence of $d_{13}$ on them is clearly observed, but the rate of change in $d_{13}$ with respect to $S_{1}^{PR}$ and $S_{0}^{PR}$ is larger at higher temperatures. When it is plotted versus $S_{1}^{SR}$ and $S_{0}^{SR}$ in Fig. 4(d), all data of $d_{13}$ at four temperatures, interestingly, appear to be fitted by one single straight line. In Figs. 5(a) and 5(b), dependence of elastic compliance coefficients $s_{33}$ and $s_{13}$ on $P_{0}^{SR}$ and $P_{0}^{PR}$ are shown to be quadratic at four temperatures, respectively. The value of $s_{33}$ is always positive but that of $s_{13}$ negative, both being saturated to certain fixed values with increasing $P_{0}^{PR}$ and $P_{0}^{SR}$, or equivalently, with increasing magnitude of compressive stress. It is because the domain structure in a specimen is saturated to a certain ideal state at the end of stress-induced mechanical depolarization. The magnitudes of $s_{33}$ and $s_{13}$ are larger at higher temperatures in both Figs. 5(a) and 5(b). When they are plotted versus $S_{1}^{PR}$ or $S_{0}^{PR}$ in Fig. 5(c), they have the same values for the same $S_{1}^{PR}$ or $S_{0}^{PR}$ for four different temperatures. Figure 5(d) shows that the dependence of $s_{13}$ and $s_{33}$ on $S_{0}^{SR}$ or $S_{0}^{PR}$ can be expressed as a single function of $S_{0}^{SR}$ or $S_{0}^{PR}$ for all temperatures in the figure.

Finally, the measured and/or calculated data of reference remnant state variables during compressive stress-induced domain switching are plotted in the planes of $S_{0}^{SR}$ or $S_{0}^{PR}$ versus $P_{0}^{SR}$ and $S_{0}^{PR}$ or $S_{0}^{PR}$ in Figs. 6(a) and 6(b), respectively. The data of filled circle symbols are obtained from the measured data in Figs. 2(a) and 2(b), which are obtained from a specimen during pure temperature increase subsequent to compressive stress-induced switching at reference temperature.9) The values of remnant state variables $P_{0}^{SR}$, $S_{0}^{SR}$ and $S_{1}^{SR}$ for four temperatures in Figs. 2(a) and 2(b) are transformed to those of reference remnant state variables $P_{0}^{PR}$, $S_{0}^{PR}$, and $S_{1}^{PR}$ at reference temperature by applying Eq. (5). A remarkable thing is that the relations among remnant state variables are shown to be different at different temperatures in Fig. 2, but those among reference remnant state variables are the same independent of temperature in Fig. 6. It means that from the viewpoint of reference remnant state variables, remnant state variables keep the same relations among themselves at different temperatures, i.e., the relations among remnant state variables are actually the same independent of temperature. The values of reference remnant state variables plotted as empty square symbols in Fig. 6 are obtained by applying Eq. (8) to the measured data in Fig. 3, where a specimen is under compressive stress and thermal loading. In the former case, compressive stress is applied first at reference temperature and then temperature
is increased; in the latter, temperature is increased to a high temperature first, and then compressive stress is applied at the high temperature. As in the data of filled circle symbols, the relations among reference remnant state variables, calculated from the data of remnant state variables at high temperatures and plotted as empty square symbols, are approximately the same independent of temperature. Hence the relations among remnant state variables during compressive stress-induced switching at different temperatures are actually the same regardless of temperature from the viewpoint of reference remnant state variables.

A major difference between filled circle data and empty square ones is that the magnitudes of strains are usually smaller in the latter than in the former. The difference may be due to the difference sequence of stress and thermal loading. Compressive stress is applied after temperature is increased in the empty square data, whereas compressive stress is applied first at reference temperature and then temperature is increased in the filled circle data.

The data in Figs. 1 and 2 are obtained by first applying compressive stress at room temperature and then increasing temperature; and those in Fig. 3 to Fig. 6 by increasing temperature first and then applying compressive stress. That is, all data from Fig. 1 to Fig. 6 are associated with compressive stress-induced switching at room and/or high temperatures. In a previous work of the authors, compressed electric field was used instead of compressive stress, and similar analysis and calculations were made to compare the behavior of material during electric field-induced domain switching at different temperatures. It is interesting to compare the behavior of reference remnant state variables for both loading cases in the same figure plane. The data in Fig. 6 are plotted again in Fig. 7, where filled square symbols are used for temperature increase after compressive stress-induced switching at reference temperature and empty triangle symbols for stress application after temperature increase. The data of reference remnant state variables associated with electric field-induced switching are also plotted in Fig. 7. The changes in reference remnant state variables during temperature increase subsequent to electric field-induced switching at reference temperature are denoted by filled circle symbols, and those during electric field-induced switching at high temperatures by empty right triangle symbols. A first glance at Fig. 7 shows that the magnitudes of reference remnant strains associated with stress-induced switching are much larger than those associated with electric field-induced switching. The magnitudes of reference remnant polarization associated with stress-induced switching are also shown to be much smaller than those associated with electric field-induced switching. The second thing to be noted is that the evolution paths of reference remnant strains and along reference remnant polarization are the same independent of temperature. It means that the procedure of domain switching at different temperatures is the same independent of temperature from the viewpoint of reference remnant state variables. The last thing to be mentioned in the figure is that the effect of the sequence of loading on the shape of the plots of reference remnant state variables is not significant. For example, the change of along during temperature increase subsequent to compressive stress-induced switching at reference temperature is very close to that during stress-induced switching after temperature increase to high temperature. The loading sequence...
independence is also observed in the case of electric field-induced switching in the figure. When electric field is applied after temperature rise, the SR$_{03}^{0}$–PR$_{03}^{0}$ and SR$_{01}^{0}$–PR$_{03}^{0}$ data symbols move leftward only just a little, as shown by empty right triangle symbols in Fig. 7(a).

4. Conclusions
A set of modeling equations is proposed to predict the high temperature behavior of ferroelectric ceramics during temperature increase subsequent to compressive stress-induced switching at room temperature. The modeling equations are composed of three equations based on the assumption of constant thermal properties in the temperature range of interest, two equations relating three remnant state variables at reference temperature, and three equations on the dependence of thermal properties on reference remnant longitudinal strain. The proposed equations are successfully applied to predict the high temperature behavior and thermal characteristics of the specimen subjected to compressive stress-induced switching at reference temperature and temperature increase in succession, which are reported in the work of the...
The calculated reference remnant state variables are shown to keep the same relations among themselves independent of temperature. It means that the relations among $P_{30}^0$, $S_{03}^0$ and $S_{13}^0$ are the same independent of temperature.

The temperature of a ferroelectric specimen is increased from room temperature to high temperatures, and the specimen is subjected to compressive stress of cyclic type with increasing magnitude. During depolarization switching by compressive stress, polarization and strains are measured at room and high temperatures. Piezoelectric coefficient $d_{33}$ and elastic coefficients $s_{33}$ and $s_{13}$ are estimated and plotted versus reference remnant state variables $P_{30}^0$, $S_{03}^0$ and $S_{13}^0$ at four temperatures. As compressive stress increases, it is seen that $d_{33}$ appears to be saturated to zero and $s_{33}$ and $s_{13}$ to some nonzero constant values at four temperatures. The dependence of the linear moduli on $S_{03}^0$ and $S_{13}^0$ looks the same independent of temperature. Finally, in the plots of reference remnant state variables, it is observed that both the effect of loading sequence on the relations among reference remnant state variables is not significant. The relations among reference remnant state variables is also shown to be the same independent of temperature, implying the same procedure of domain switching at different temperatures from the viewpoint of reference remnant state variables.

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References