Nonlinear behavior of ferroelectric ceramics during mechanical depolarization at room and high temperatures: experiment and prediction by an experimental formula

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The strain changes during temperature rise in a poled lead titanate zirconate rectangular parallelepiped specimen switched by compressive stress at room temperature are measured using an invar-specimen. First-order differential equations were derived by analyzing the observed polarization and strain data and solved to give an experimental formula for remnant polarization and remnant strain changes during temperature rise. Then the dependence of pyroelectric and thermal expansion coefficients on remnant state variables and the relations between reference remnant state variables were obtained through experiments. Using the relations and the experimental formula, the strain behavior during mechanical depolarization at a high temperature was predicted from a polarization behavior at the same temperature. It was found that the predictions compared favorably with the measured behavior.

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1. Introduction

Piezoelectric ceramics such as lead titanate zirconate (PZT) or lanthanum-doped lead zirconium titanate (PLZT) are widely used as sensors, actuators, thermistors, non-volatile memory, capacitors, and so on. The wide application is thanks to interesting properties of the materials called piezoelectricity, pyroelectricity, ferroelectricity, and ferroelasticity. Piezoelectricity is the linear electromechanical interaction between the mechanical and the electrical state in the materials. When subjected to an electric field, the materials generate mechanical strain. In reverse, they create electricity when subjected to a mechanical stress. Pyroelectricity is interpreted as the ability of materials to generate a temporary voltage when they are heated or cooled. The change in temperature slightly modifies the positions of the atoms within the crystal structure of materials, leading to the changes in the polarization of materials. Ferroelectricity is a property of the materials that the spontaneous polarization of the materials is reversed by the application of an external electric field. The polarization of the material is also changed by the application of stress, a process called ferroelasticity. In the applications of the material, piezoelectric devices are often subjected to strong electric and stress fields and large temperature change so that unnecessary domain switching is caused in the material. The domain switching leads to degradation of the thermo-electro-mechanical properties of the materials, which may end in failure of the piezoelectric devices. To prevent unwanted deterioration of the functions of piezoelectric devices, a sufficient amount of experimental data should be accumulated first on the nonlinear behavior of the material under large electric and stress fields at different high temperatures. Then a reliable constitutive model must be developed to enable prediction of the observed nonlinear behavior of the material. Incorporating the developed constitutive model into an analysis tool such as finite element analysis software would result in an efficient and reliable design of piezoelectric devices. In the construction of a constitutive model of the ferroelectric ceramic materials, macroscopic variables such as remnant polarization and remnant strains are often used as state variables to describe the evolution of the internal domain structure in the material. It is necessary to understand the dependence of material properties on remnant state variables and the relations between the state variables themselves.

The dependence of material properties on remnant state variables has been studied by researchers. Liu and Huber1) and Selten et al.2) applied electric field and/or compressive stress to ferroelectric ceramics at room temperature large enough to induced domain switching. During the domain switching, they measured the changes in polarization and strains, estimated the material properties of permittivity, piezoelectric coefficients, and elastic moduli,

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and plotted these against remnant state variables, studying their dependence on the state variables. The nonlinear strain behavior of ferroelectric ceramics under different loading conditions of electric field and stress is obtained and used to study the effect of residual stress on domain switching under applied loads by Achuthan and Sun. They found that the mechanism of polarization reversal due to cyclic electric fields at the morphotropic phase boundary is two successive 90° domain switches rather than a direct 180° domain switching. In the work of Zhou et al., measured polarization and strains are divided into two parts, reversible and irreversible. Taking the so-called partial unloading method, they found that the material properties depend on the loading history of electric field and compressive stress and discussed the use of irreversible strain and irreversible polarization as internal variables for constitutive modeling. The study of material properties and remnant state variables has been extended to high temperatures. The nonlinear behavior of a soft lead zirconate titanate under large compressive stress at high temperatures was measured by Weber et al., and a strong dependence of ferroelastic switching on temperature was observed. Full hysteresis loops of the relaxor ferroelectric 8/65/35 PLZT at room and high temperatures were measured by Rauls et al. and the changes from open loops to linearity with increases in temperature were observed. The temperature dependent behavior of PZT wafers under electrical and mechanical loading at room and high temperatures was studied by developing an internal energy-based model and incorporating it into a 3D finite element framework by Anand and Arockiarajan. They compared the simulated results with experiments and conducted a parametric study using macro-state variables such as remnant polarization and remnant strains. Grunbichler et al. carried out a parametric study for the constitutive law reported in the literature and applied it to the prediction of ferroelectric and ferroelastic behavior of piezoelectric materials at high temperatures. Kungl and Hoffman studied the temperature dependence of the poling strain and the strain under high electric fields in a morphotropic PZT and its relation to changes in structural characteristics. The opposite behavior of remnant strain and field-induced strain under unipolar cycling is observed by analyzing X-ray diffraction patterns. A new switching model to account for the temperature effect on domain switching in PZT materials was proposed and implemented into a finite element code by Senousy et al. The model is shown to have good agreement with experimental results at different temperatures and loading conditions. Changes in the shapes of full hysteresis loops of a soft lead zirconate titanate bulk ceramic at different temperatures were measured, and the power-law temperature scaling relations were proposed by Ymmirun et al. The piezoelectric coefficient and permittivity of a ferroelectric single crystal were measured as functions of temperature and compressive stress at various frequencies by Schader et al. Their observations show the combined influence of stress and temperature on the electromechanical properties and stress-induced phase transitions in relaxor ferroelectric PIN-PMN-PT single crystals. Kim and Ji applied electric field and compressive stress to a poled ferroelectric ceramic specimen at room and high temperatures, estimated linear material properties from electric displacement and strain responses, and studied the dependence of the material properties on remnant state variables and the relations between remnant state variables. The dependence of thermal properties such as pyroelectric and thermal expansion coefficients on remnant state variables was studied for ferroelectric ceramics switched by compressive stress at a room temperature by Ji and Kim. Assuming constant thermal properties in a temperature range of interest, an experimental equation was proposed to predict the changes in polarization and strains during temperature increase of ferroelectric ceramics switched by electric field at a room temperature by Ji and Kim, which was then extended to allow variable thermal properties with temperature by Ji and Kim. Ji and Kim studied the effect of the overall switching rate on the dependence of material properties on remnant state variables and the relations between remnant state variables at room and high temperatures.

In this work, the work of Ji and Kim based on their experimental data is generalized to enable thermal properties to vary with temperature in the derivation of an experimental formula, which is developed to predict the material behavior during temperature increase of ferroelectric ceramics switched by compressive stress at a room temperature. The thermal outputs of the strain gauge grid from a ferroelectric specimen and an invar specimen are measured during temperature increases. Thermal expansion coefficients are calculated from the measured thermal outputs, which are then integrated to yield strains. Analyzing the data for strains and polarization, first-order differential equations are derived to govern the polarization and strain changes during temperature increase. The solution function of the differential equations is shown to predict the observed data reliably and accurately. To test the developed experimental formula, the measurement and strain behavior of the material during mechanical depolarization at room and high temperatures are obtained experimentally. It is shown that the experimental data are adequately predicted by the developed experimental formula.

2. Experimental procedure

The thermal output data measured by Ji and Kim for a ferroelectric specimen switched by compressive stress at reference temperature $T_0 = 20^\circ C$ are used to obtain the changes in thermal expansion coefficients during a temperature increase from 20 to 110°C. A soft PZT ferroelectric specimen provided by Morgan Technical Ceramics of the United States is used as a specimen for experiments. The dimensions of the specimen are 10 mm x 10 mm x 12 mm with electrodes on the 10 mm x 10 mm faces. The specimen is poled in the 12 mm direction, which is designated $-\alpha_3$ and called the longitudinal direction. The directions
orthogonal to the longitudinal $x_3$ axis are designated $x_1$ and $x_2$ and referred to as transverse directions. The three orthogonal axes $x_1$, $x_2$, and $x_3$ are often called the 1, 2 and 3 axes, respectively. Longitudinal and transverse thermal outputs are measured by one biaxial strain gauge attached to a side face of specimen. A fully encapsulated constantan strain gauge (WA-03-062TT-350, VISHAY, Germany) is used for measurements. According to the VISHAY manual, longitudinal and transverse thermal expansion coefficients are obtained from the measured thermal outputs. In the calculation of thermal expansion coefficients, the thermal expansion coefficient of an invar specimen is used. An invar specimen (Product No. 318-0285-3) with a thermal expansion coefficient of $0.75 \times 10^{-6}$°C$^{-1}$ is provided by Danyang City Kaixin Alloy Material Co., LTD of China (www.kaixinhejin.cn).

In order to test a developed experimental formula for the high temperature behavior of ferroelectric ceramics switched by compressive stress at the reference temperature, a poled ferroelectric specimen is subjected to loading and unloading of compressive stress with a magnitude of 300 MPa at 20 and 80°C. The magnitude of stress changes at a rate of 10 MPa s$^{-1}$. Longitudinal electric displacement $D_3$ of the specimen is measured using a Sawyer-Tower bridge with a Keithley 6514 electrometer. To increase the temperature of a PZT specimen, it is immersed into a bath of transformer oil (MICTRANS Class1-No2, MICHANG OIL IND. CO., Pusan, Korea) and then the temperature of the oil is controlled using an electric heat coil installed in the bottom plate of the bath and a temperature control unit (2408 PID controller, EUROTERM, UK). In all experiments, equipment output signals pass through a data acquisition board (PCI 6221, National Instruments, TX, USA) and are manipulated by a LABVIEW software. For further details, one may refer to Ji and Kim.16)

3. Results and discussion

3.1 Measurement and the differential equation of polarization and strain changes during temperature increases

The data obtained by Ji and Kim16) for a ferroelectric specimen switched by compressive stress at room temperature 20°C, called the reference temperature, are revisited, modified and analyzed to construct a first-order differential equation and develop an empirical formula for polarization and strain changes during pure temperature rise. To begin with polarization data, Fig. 1 shows the changes in polarization during temperature rise of a ferroelectric specimen switched by compressive stress at 20°C. Eight different values for remnant polarization $P_{3r}^0$ were obtained by different magnitudes of compressive stress at the temperature. Temperature rise experiments from 20 to 110°C were repeated for the eight states of reference remnant polarization, with only three of them for $P_{3r}^0 = -0.341$, $-0.421$, and $-0.499$ Cm$^{-2}$ plotted in Fig. 1(a). The slope of change in polarization in the figure corresponds to

![Fig. 1](image-url)
It was evaluated at intervals of five degrees along each curve of the constant $P_{3}^{0}$, yielding nineteen estimations from 20 to 110°C. The changes in $P_{3}$ are then plotted versus remnant polarization at a constant temperature. Among the nineteen temperatures between 20 and 110°C, the $P_{3}$ plots at only three temperatures 30, 60, and 90°C are shown in Fig. 1(b). It is observed that the data for $P_{3}$ fit well with the straight lines below $S_{3}^{0}$ due to the large compressive stress at every temperature in the figure. A linear fitting of the data of $P_{3}$ to the left of $S_{3}^{0}$ is made by the standard least squares method, with the R-squared value larger than 0.9560 in Fig. 1(b). The slopes $a_{P_{3}}$ and the vertical axis intercepts $b_{P_{3}}$ of the fitting lines in the figure are then obtained and plotted versus temperature in Fig. 1(c). The two obtrusive peaks at 20 and 90°C in the figure mean that the magnitudes and slopes of the fitting lines in Fig. 1(b) at the temperatures are larger than those at other temperatures. A possible explanation may be found in the manner of controlling the temperature of the specimen. The temperature of the heat coil is controlled by a PID controller based on the temperatures measured by a temperature sensor. The occurrence of overshooting high and low in the rate of change of the specimen temperature is inevitable. When the specimen temperature changes slowly, a longer time is allowed for polarization and strain changes with temperature; on the contrary, when temperature increases rapidly, only a shorter time is available. The differences in the available time at different temperatures may lead to the fluctuations in the slopes $a_{P_{3}}$ and the vertical axis intercepts $b_{P_{3}}$ of the straight fitting lines in the figure. Fortunately, the data in Fig. 1(c) also fit well with the straight lines, their R-squared values larger than 0.8728. Thus one may represent $a_{P_{3}}$ and $b_{P_{3}}$ as linear functions of temperature given by the following equation:

\[
S_{3}^{0} = -1470 \times 10^{-6} -708 \times 10^{-6} -1470 \times 10^{-6}
\]
\[
\begin{align*}
  \alpha_p &= \alpha_{p0}\theta + \alpha_{p0}, \\
  b_p &= b_{p0}\theta + b_{p0},
\end{align*}
\]
where \(\alpha_{p0}\) and \(b_{p0}\) are the slopes of the straight fitting lines and \(\alpha_{p0}\) and \(b_{p0}\) the intercepts of the fitting lines with vertical axis at zero temperature in Fig. 1(c). Combining Eq. (1) with the equation \(p_3 = a_{p3}P_{03}^R + b_p\) in Fig. 1(b) gives
\[
p_3 = (a_{p0}\theta + a_{p0})P_{03}^R + (b_{p0}\theta + b_{p0}).
\]  

Equation (2) gives an estimate of pyroelectric coefficient \(p_3\) for given values of remnant polarization \(P_{03}^R\) and temperature \(\theta\). Remnant polarization \(P_{03}^R\) in Eq. (2) is obtained when a ferroelectric specimen poled in the \(-x_3\) direction is switched by compressive stress at reference temperature 20°C, and its temperature is then increased to 110°C. The range of \(P_{03}^R\) over which Eq. (2) is valid is \(P_{03}^R \leq -0.32 \text{ Cm}^{-2}\) for the tested ferroelectric specimen. Note that the same process of derivation of Eq. (2) can also be applied to a ferroelectric specimen poled in the \(+x_3\) direction. In that case, the slope \(a_p\) remains the same, but the sign for intercept \(b_p\) is reversed. Combining \(p_3 = dP_{03}^R/\theta\) from the definition of the pyroelectric coefficient with Eq. (2) yields a first-order differential equation given by
\[
\frac{dP_{03}^R}{d\theta} = (a_{p0}\theta + a_{p0})P_{03}^R = \pm(b_{p0}\theta + b_{p0}).
\]  

where the plus sign on the right hand side refers to a ferroelectric specimen poled in the \(-x_3\) direction and the minus sign to a specimen poled in the \(+x_3\) direction at the reference temperature. Now it is obvious that fitting of the data in Figs. 1(b) and 1(c) by simple linear function is necessary and useful in constructing solvable first-order differential equations.

Before solving the differential equation in Eq. (3), let’s turn to the discussion of strain. As demonstrated by Ji and Kim,\(^{18}\) the strain changes during temperature increase are obtained by measuring and integrating the thermal expansion coefficients. To measure the thermal expansion coefficient \(\alpha_S\) of a ferroelectric specimen, strain gauges are attached to the ferroelectric specimen and an invar specimen. The thermal outputs of the strain gauge grids on the ferroelectric specimen and the invar specimen are designated \(\varepsilon_{G/S}\) and \(\varepsilon_{G/R}\), respectively. For an accurate measurement of \(\alpha_S\), the value of thermal expansion coefficient \(\alpha_S\) of the reference invar specimen must be relatively small and constant in the temperature range of interest. According to the VISHAY manual,\(^{20}\) \(\alpha_S\) can be calculated from the following:
\[
\alpha_S - \alpha_R = \frac{\varepsilon_{G/S} - \varepsilon_{G/R}}{\Delta\theta},
\]  

where \(\Delta\theta\) is the range of temperature within which the thermal expansion coefficient is measured. Applying Eq. (4) to the measured data of thermal outputs in Ji and Kim\(^{16}\) gives the distributions of longitudinal thermal expansion coefficient \(\alpha_3\) of a ferroelectric specimen over temperature, which are shown in Fig. 2(a) for three states of \(S_{3}^{R}, -1470 \times 10^{-6}, -708 \times 10^{-6}\) and \(1.67 \times 10^{-6}\), at the reference temperature 20°C. Integrating \(\alpha_3\) in the figure gives the changes in remnant longitudinal strain \(S_3^R\) with temperature, as shown in Fig. 2(b). \(\alpha_3\) can be obtained by estimating the slopes of \(S_3^R\) curves in Fig. 2(b). Plotting them versus \(S_3^R\) in Fig. 2(c) for three typical temperatures, 30, 60 and 90°C, shows that the data for \(\alpha_3\) fit well with the straight lines, much like those of \(p_3\) in Fig. 1(b). The equations for the straight lines with slopes \(a_{3}\) and intercepts \(b_{3}\) are shown in the figure. Figure 2(d) shows the plots of \(a_{3}\) and \(b_{3}\) over temperature denoted by symbols, which are also fitted with straight lines. Denoting the slopes and vertical axis intercepts of the straight fitting lines by using subscripts \(S\) and \(S_0\), respectively, and taking the equation \(\alpha_3 = a_{30}S_3^R + b_{30}\) shown in Fig. 2(c) yields the estimates for \(\alpha_3\) using
\[
\alpha_3 = (a_{330}\theta + a_{330})S_3^R + (b_{330}\theta + b_{330}).
\]  

Though it is derived for a ferroelectric specimen poled in the \(-x_3\) direction, Eq. (5) can be applied well to a specimen poled in the \(+x_3\) direction. Combining the definition of longitudinal thermal expansion coefficient \(\alpha_3 = dS_3^R/\theta\) with Eq. (5) leads to a first-order differential equation given by
\[
\frac{dS_3^R}{d\theta} = (a_{330}\theta + a_{330})S_3^R = b_{330}\theta + b_{330}.
\]  

Equation (6) governs the changes in longitudinal remnant strain \(S_3^R\) during temperature increase of a ferroelectric specimen switched by compressive stress at reference temperature. The process of derivation of the differential equation for \(S_3^R\) can also be applied to transverse remnant strain \(S_3^R\), yielding the same type of differential equation for \(S_3^R\) with the subscript 3 replaced by 1 in Eq. (6). Finally, it is interesting to compare the differential equation for \(P_{03}^R\) in Eq. (3) with that for \(S_3^R\) in Eq. (6). The two differential equations are closely parallel. The former can be converted to the latter just by replacing \(P_{03}^R\) by \(S_3^R\) and the subscript \(P\) with \(S\). This means that the differential equations for \(P_{03}^R\), \(S_3^R\) and \(S_3^R\) are of the same form, yielding the same form of an empirical formula for the polarization and strain behavior during temperature increases. The values of all coefficients in Eq. (3) through Eq. (6) are listed in Table 1.

### 3.2 Prediction of polarization and strain changes during temperature rises by an empirical formula

The first-order differential equations in Eqs. (3) and (6) can be represented together as follows:
\[
\frac{dY}{d\theta} = (a_{0}\theta + a_{0}) = b_{0}\theta + b_{0},
\]  

where \(Y\) is either \(P_{03}^R\) or \(S_3^R\), \(a_{0}\) is either \(a_{p0}\) or \(a_{s0}\) or \(a_{s0}\), and so on. The general solution of Eq. (7) is found to be the following:
\[
Y(\theta) = \exp\left(\frac{a_{0}}{2} \theta^2 + a_{0}\theta\right)[c + I(\theta)].
\]
Table 1. Values of coefficients in differential equations in Eqs. (3) and (6), estimated from the straight fitting lines in Figs. 1(c) and 2(d)

| Differential equations for | Constants | Units of constants | Values of constants |
|---------------------------|-----------|--------------------|---------------------|
| $P^R$ in Eq. (3)          | $a_0$     | $10^{-4}$          | $-0.90067$          |
|                           | $b_0$     | $10^{-5}$          | $-0.29706$          |
|                           | $b_{33}$  | $10^{-3}$          | $-0.14018$          |
| $S^F$ in Eq. (6)          | $a_{33}$  | $10^{-3}$          | $1.2344$            |
|                           | $b_{33}$  | $10^{-6}$          | $-0.11696$          |
| $S^I$                     | $b_{33}$  | $10^{-6}$          | $4.3306$            |

where $c$ is an integration constant and $I(\theta)$ is an indefinite integral given by

$$
I(\theta) = \frac{1}{2(a_0b_0)^{1/3}} \exp\left( -\frac{a_0}{2} \theta^2 - a_0\theta \right)
\times \left[ -\sqrt{2\pi} \exp\left( \frac{(a_0\theta + a_0)^2}{2a_0} \right) [a_0b_0 - a_0b_0] \right]
\times \text{erf}\left( \frac{a_0\theta + a_0}{\sqrt{2a_0}} \right) - 2\sqrt{a_0b_0}. \tag{9}
$$

The error function $\text{erf}(x)$ is defined by

$$
\text{erf}(x) = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{x} \exp(-t^2) dt. \tag{10}
$$

The integration constant $c$ is determined for a given boundary condition of $(\theta_1, Y_1)$ by

$$
c = Y_1 \exp\left( -\frac{a_0}{2} \theta_1^2 - a_0\theta_1 \right) - I(\theta_1). \tag{11}
$$

The particular solution $Y(\theta)$ of Eq. (7) with a boundary condition $(\theta_1, Y_1)$ is obtained by inserting Eq. (11) into Eq. (8):

$$
Y(\theta) = \exp\left( \frac{a_0}{2} \theta^2 + a_0\theta \right) \left[ Y_1 \exp\left( -\frac{a_0}{2} \theta_1^2 - a_0\theta_1 \right) + I(\theta) - I(\theta_1) \right]. \tag{12}
$$

where $I(\theta)$ is given by Eq. (9). It should be noted that the values and signs of the coefficients in Eq. (7) should be extracted carefully depending on the kind of dependent variable and the direction of poling of the ferroelectric specimen concerned.

Now the empirical formula in Eq. (12) is used to predict the measured behavior of remnant polarization and strains during temperature increases in a ferroelectric ceramic switched by compressive stress at the reference temperature. The boundary conditions for the differential equation are obtained by measuring the values for $P^R$, $S^F$, and $S^I$ induced by compressive stress at reference temperature $\theta_0$. They are denoted by $(P^{R0}, S^{F0}, S^{I0})$ at $\theta = \theta_0$. Temperature increase experiments were carried out for eight different sets of $(P^{R0}, S^{F0}, S^{I0})$ by Ji and Kim. Only five of them were plotted and denoted as symbols in Fig. 3 for $P^{R0} = -0.500, -0.463, -0.422, -0.379$ and $-0.341 \text{Cm}^{-2}$. $P^R$, $S^F$ and $S^I$ are plotted in Figs. 3(a)–3(c), respectively. The calculation results obtained by the empirical formula in Eq. (12) are plotted as solid lines in the figures for comparison purposes. The coincidence between the calculations and the measurements in the
The empirical formula can also be used to compare the switching processes during mechanical depolarization at different temperatures. Since remnant variables, such as remnant polarization and remnant strains, are often used as state variables to describe an internal domain structure in a ferroelectric specimen, it is necessary and important to investigate the evolutions of remnant state variables during temperature increases. Figure 4(a) shows the variations of remnant longitudinal and transverse strains $S_{R3}^P$ and $S_{R1}^P$ over remnant polarization $P_{R3}^P$ at four temperatures, 20, 50, 80 and 110°C. The symbols in the figure represent the measured values of remnant state variables, the data at 20, 50, 80 and 110°C denoted by solid square, right triangle, circle, and gradient symbols, respectively. The empty symbols in Figs. 4(a) and 4(c) represent those which are not included in the derivation of Eq. (12), as in Fig. 1(b). But they are denoted by solid symbols in Figs. 4(b) and 4(d). It is shown that remnant strains $S_{R3}^P$ and $S_{R1}^P$ are almost linearly proportional to remnant polarization $P_{R3}^P$ at the four temperatures in Fig. 4(a). The line segment data in the figure are obtained by applying Eq. (12) to the corresponding data at reference temperature 20°C. The calculation data at 50, 80 and 110°C are in good agreement with the corresponding measured data at the three temperatures. This means that the evolution paths of remnant state variables in $(S_{R3}^P - P_{R3}^P)$ or $(S_{R1}^P - P_{R1}^P)$ spaces at different temperatures coincide with one another. Figure 4(b) shows the relations between $S_{R3}^P$ and $S_{R1}^P$ at four temperatures. The measured data of remnant state variables are in good coincidence with the calculated data at four temperatures, again supporting the presence of the same switching processes at different temperatures.

On the contrary, the empirical formula in Eq. (12) is applied to the measured data of remnant state variables at three high temperatures 50, 80 and 110°C to obtain the corresponding data at reference temperature 20°C. The calculated data for 50, 80 and 110°C are plotted as a right triangle, circle, and gradient symbol in the $(S_{R3}^P - P_{R3}^P)$, $(S_{R1}^P - P_{R1}^P)$ and $(S_{R1}^P - S_{R3}^P)$ spaces in Figs. 4(c) and 4(d), respectively. Except for the empty symbols in the range of
Eq. (13)\(^1\) with the expression by the second-order polynomial equation in For example, the \(\alpha\) determining the mechanical depolarization behavior of ferro-
test the developed empirical formula in Eq. (12) by pre-
values of \(\alpha\) listed in Table 2.

3.3 Application to mechanical depolarization behavior at high temperatures
The empirical formula in Eq. (12) is applied to predict strain behavior during mechanical depolarization at high temperatures. In order to test the formula, it is necessary first to determine the dependences of the piezoelectric and elastic compliance coefficients on remnant polarization and the relations between reference remnant state variables. A ferroelectric specimen poled in the \(\alpha\) direction at reference temperature is subjected to successive pulses of compressive stress whose magnitude increases, as shown in Fig. 6(a). The magnitude of the stress pulse increases up to \(-300\) MPa in ten pulses. The rate of increase in stress magnitude during loading and unloading is 10 MPa s\(^{-1}\). Figures 5(b) and 5(c) show the electric displacement, longitudinal and transverse strain responses at 20°C, respectively. The same experiments were also conducted at a high temperature of 80°C, which are not shown here. At the first instance of each stress pulse, piezoelectric coefficient \(d_{33}\) is evaluated by dividing the change in electric displacement by the change in stress. At the same time, elastic compliance coefficients \(s_{13}\) and \(s_{31}\) are estimated by dividing the changes in longitudinal and transverse strains by the change in stress, respectively. The estimated material properties are then plotted versus remnant polarization \(P_{33}^R\) in Figs. 6(a) and 6(b), \(d_{33}\) in Fig. 6(a) and \(s_{31}\) and \(s_{13}\) in Fig. 6(b). The data at 20°C are denoted by solid square symbols, and those at 80°C by empty circle symbols in the figures. The relations between remnant state variables at reference temperature 20°C are plotted in the \((S_{33}^R - P_{33}^R)\) or \((S_{31}^R - P_{31}^R)\) spaces in Figs. 6(c) and 6(d), respectively. In all the figures of Fig. 6, the symbol data are shown to fit well with quadratic or cubic curves, Figs. 6(a), 6(c) and 6(d) by quadratic curves and Fig. 6(b) cubic curves. The fitting curves are expressed by the polynomial equations of the form given by the following:

\[
y = ax^2 + bx + c,
\]
\[
y = ax^3 + bx^2 + cx + d.
\]

For example, the fitting quadratic curve in Fig. 6(c) is expressed by the second-order polynomial equation in Eq. (13)\(^1\) with \(x = P_{33}^R\) and \(y = S_{13}^R\) and with the values of the coefficients \(a\), \(b\) and \(c\) listed in Table 2. The estimated values of coefficients for all fitting curves in Fig. 6 are listed in Table 2.

With the fitting curves in Fig. 6, we are now ready to test the developed empirical formula in Eq. (12) by predicting the mechanical depolarization behavior of ferro-
electric ceramics at high temperatures. The polarization and strain changes during the loading and unloading of compressive stress at 20 and 80°C are measured. Figure 7(a) shows the polarization responses measured during stress loading and unloading of magnitude 100 MPa, the response at 20°C represented by solid lines and that at 80°C by dashed lines. Remnant polarization \(P_{33}^R\) is obtained by inserting the quadratic equation for \(d_{33}\) in Eq. (13)\(^1\) into the following equation:

\[T_{13} = \frac{\Delta P_{33}^R}{\Delta S_{33}}\]
The changes in $P_{3}^{R}$ during mechanical depolarization at 20 and 80°C are obtained by solving the resultant quadratic equation in Eq. (14). Then, the data of remnant polarization $P_{3}^{R}$ at 80°C are transformed to reference remnant polarization $P_{3}^{R0}$ at 20°C by using the formula in Eq. (12). At 20°C, $P_{3}^{R}$ is equal to $P_{3}^{R0}$ by the definition of $P_{3}^{R0}$. The calculated data of $P_{3}^{R0}$ are plotted in Fig. 7(b). It is observed in the figure that the graphs of $P_{3}^{R0}$ at 20 and 80°C are coincident with each other, which means the processes of domain switching during mechanical depolarization at the two temperatures are essentially the same from the viewpoint of reference remnant state variables. Using the quadratic equations for the reference remnant state variables of the fitting curves in Figs. 6(c) and 6(d), the changes in $S_{3}^{R0}$ and $S_{1}^{R0}$ during mechanical depolarization are calculated. $S_{3}^{R0}$ (or $S_{1}^{R0}$) is equal to $S_{3}^{R}$ (or $S_{1}^{R}$) at 20°C. The data for $S_{3}^{R0}$ and $S_{1}^{R0}$ at 80°C are transformed to those of $S_{3}^{R}$ and $S_{1}^{R}$ at 80°C using the empirical formula in Eq. (12). Then, as a last step in the calculation procedure, the following equation is used to obtain the changes in strains $S_{3}$ and $S_{1}$ during mechanical depolarization:

\[
P_{3}^{R} = D_{3} - d_{33}T_{3},
\]

(14)

\[
S_{3} = S_{3}^{R} + s_{33}T_{3},
\]

(15)

\[
S_{1} = S_{1}^{R} + s_{13}T_{3},
\]

where $s_{33}$ and $s_{13}$ are given by the fitting curves in Fig. 6(b) and the cubic equations of $P_{3}^{R}$ in Eq. (13). The calculated values of $S_{3}^{R}$ and $S_{1}^{R}$ are shown in Figs. 7(c) and 7(d) at 20 and 80°C, respectively. In the figures, the measured strains are denoted by solid lines and the calculated strains by dashed lines. The comparisons in Figs. 7(c) and 7(d) show that the procedure presented for predicting the strain behavior during mechanical depolarization at high temperatures from a corresponding polarization behavior at the same temperature is accurate and reliable.

4. Conclusions

Previously measured data for polarization and strain changes during temperature increases of a poled ferroelectric ceramic specimen switched by compressive stress at a reference temperature 20°C are analyzed again to construct first-order differential equations governing the behavior of polarization and strains during temperature increase. An experimental formula is derived by solving the differential equation and applied to predict the changes in polarization.
and strains during temperature rise. A comparison between measured and predicted results shows that the derived experimental formula works very well for compressive stress of relatively small magnitudes. When viewed in the \( P_3^{0} - S_3^{0} \), \( P_3^{0} - S_1^{0} \) and \( S_3^{0} - S_1^{0} \) spaces, the relations between remnant state variables at different temperatures are shown to be the same, implying the same mechanism of domain switching during mechanical depolarization at different temperatures in the temperature range of interest.

The developed formula is applied to predict the strain behavior of ferroelectric ceramics at high temperatures based on the polarization behavior at the temperature. As a preliminary stage, stress pulses of increasing magnitude are applied to poled ferroelectric ceramics at 20 and 80°C. The changes in piezoelectric and elastic compliance coefficients during mechanical depolarization are estimated, plotted versus remnant polarization, and expressed
as functions of remnant polarization. Then compressive stress of magnitude 300 MPa is loaded and unloaded to obtain mechanical depolarization responses from poled ferroelectric ceramic specimens at 20 and 80°C. From the dependence of material properties on remnant polarization and the relations between reference remnant polarization and reference remnant strains, the strain responses during mechanical depolarization at 80°C are predicted from the polarization responses at the same temperature. The predicted strains are in good agreement with the measured ones, demonstrating the reliability and accuracy of the proposed empirical formula. Knowledge of the behavior of material moduli and remnant state variables during mechanical depolarization at room and high temperatures would be of great help in the development of a constitutive model for linear and nonlinear behavior of ferroelectric ceramics.

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