Prediction of high temperature behavior of ferroelectric ceramics with state dependent thermal moduli

Dae Won JI and Sang-joo KIM

Department of Mechanical and Information Engineering, University of Seoul, Dongdaemun-gu, Seoul 130–743, Korea

A poled lead titanate zirconate rectangular parallelepiped is subjected to an electric field at a room temperature called reference temperature to reach a specific value of polarization. Then the temperature of specimen is raised at the specific value of polarization under no electric field, measuring polarization and strain changes in the specimen. Pyroelectric and thermal expansion coefficients are estimated from measured responses. A set of modeling equations is proposed to predict the dependence of the thermal moduli on remnant state variables and the relations between remnant state variables at high temperatures.

Key-words: Pyroelectric, Thermal expansion, High temperature, Remnant polarization, Ferroelectric

1. Introduction

Piezoelectric ceramics such as lead titanate zirconate (PZT) have been used widely in the fields of actuators and sensors. In these applications, it is important to predict the performance or reliability of piezoelectric devices. The predictions are usually made by using finite element methods, which require a reliable constitutive model for the materials. A construction of constitutive equations for the linear and nonlinear behavior of piezoelectric materials is often based on the knowledge of the evolution of remnant state variables and the dependency of linear material properties on remnant state variables, where remnant state variables are macroscopic variables such as polarization and strains under no electric and stress fields.

Much research activity has been reported on the dependency of linear material properties on remnant state variables. Selten et al.1) and Liu and Huber2) described linear moduli as functions of remnant state variables at room temperature. The nonlinear creep behavior of the materials at room temperature under electric fields was observed by Zhou and Kamlah3) and Liu and Huber.4) However, all these studies are limited to room temperature only. As reported by Sakai and Kawamoto,5) 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 investigating the high temperature behavior of the materials and developing the constitutive equations effective at high temperatures. Recently, much research work has been made for both observing experimentally and predicting theoretically the behavior of piezoelectric materials at high temperatures. Yimniran et al.6) proposed temperature scaling laws for hysteresis responses of soft lead zirconate titanate bulk ceramic by fitting observed temperature-dependence of hysteresis area, remnant polarization, and coercive field. Grunbichler et al.7) used the concept of plasticity to develop a constitutive law for nonlinear behavior of ferroelectric ceramics and calculated the hysteresis and butterfly responses of the materials at ambient temperature. A temperature-dependent two-step domain-switching model is proposed by Senousy et al.8)

where domain switching occurs at a critical value of energy barrier. Their switching model is based on that of Hwang et al.9) and has temperature-dependent energy barrier. The performance characteristics of 1–3 piezocomposites with different fiber volume fractions at high compressive stress and temperatures are measured and simulated by a thermodynamically consistent uni-axial model.10) Effective material properties of the piezocomposites at various temperatures are measured and predicted by an analytical homogenization technique based on equivalent layered approach. A polarization constitutive model is proposed to predict time-dependent behavior of ferroelectric materials at various histories of electric field and at ambient temperatures by Muliana.11) Wang et al.12) observed temperature-dependence of the electro-mechanical properties of piezoelectric materials and suggested that material degradation was primarily caused by mechanical stresses in the materials. Weber et al.13) measured and characterized the nonlinear switching behavior of a soft lead zirconate titanate by compressive stress at high temperatures, observing a strong temperature dependency of ferroelastic switching. The pyroelectric and transverse thermal expansion coefficients of the PZT wafer after electric field loading and unloading were shown to depend on remnant polarization and remnant transverse strain at various constant values of reference remnant polarization.14) A PZT rectangular parallelepiped specimen was subjected to various types of compressive stress loading at room and high temperatures.15–18) The dependency of linear moduli on remnant state variables and temperature and the evolution of remnant state variables during domain switching were obtained and analyzed.

In this work, a PZT rectangular parallelepiped specimen is subjected to an electric field at reference temperature so that it may obtain a specific value of remnant polarization. The specimen temperature is raised under no electric and stress fields, and polarization and strain changes are measured during temperature rise. The pyroelectric and thermal expansion coefficients at the specific remnant polarization are evaluated from measured responses. Then a set of modeling equations is proposed by assuming constant thermal moduli in the temperature range of present interest and fitting the observed data of thermal moduli and remnant state variables at reference temperature. Using the
modeling equations, the dependency of thermal moduli on remnant state variables and the relations between remnant state variables at higher temperatures are predicted. The predictions are compared with experimental observations.

2. Experiment

A soft PZT rectangular parallelepiped (PZTSH1, 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 12 mm direction. The 12 mm direction is referred to as 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⋅m\(^{-3}\), the coupling factor is \( k_p = 0.60 \), the piezoelectric charge coefficients are \( d_{31} = -250 \times 10^{-12} \text{mV}^{-1}\text{C}^{-1} \) and \( d_{33} = 620 \times 10^{-12} \text{mV}^{-1}\text{C}^{-1} \), and the elastic compliance coefficients at constant electric field \( s_{33} = 21.9 \times 10^{-12} \text{m}^2\text{N}^{-1} \), \( s_{11} = 17.7 \times 10^{-12} \text{m}^2\text{N}^{-1} \), and \( s_{12} = -5.7 \times 10^{-12} \text{m}^2\text{N}^{-1} \).

A PZT specimen initially saturated (or poled) in the \(-x_3\) direction is subjected to an electric field in the positive \(+x_3\) direction to obtain a specific domain structure at the so-called reference temperature \( \theta_0 = 20^\circ\text{C} \). Due to material symmetry, transverse strain \( \varepsilon_1 \) in the \( x_1 \) direction is equal to transverse strain \( \varepsilon_2 \) in the \( x_2 \) direction. The reference configuration for strain measures is the poled state at reference temperature \( \theta_0 \). A specific internal domain state obtained after an electric field loading and unloading at reference temperature \( \theta_0 \) is assumed to be specified by polarization, longitudinal strain, and transverse strain under no electric field at the temperature, which are referred to as reference remnant polarization \( P_{0}^{R} \), reference remnant longitudinal strain \( S_{0}^{R} \), and reference remnant transverse strain \( S_{0}^{T} \), respectively. Then, at the specific state, the specimen temperature is raised under no electric field from 20 to 110°C at a rate of 1.08°C per minute for 5000 s. While temperature rises, remnant polarization \( P_{ij}^{R} \), remnant longitudinal strain \( S_{ij}^{R} \), and remnant transverse strain \( S_{ij}^{T} \) are measured. The same temperature experiments are repeated for other twenty seven states represented by different values of \( T_{0}^{R} \).

To raise the temperature of a PZT specimen, it is immersed into a bath of transformer oil (MICTRANS ClassI-No2, MICHANG OIL IND. CO., Pusan, Korea). The temperature of the oil is controlled using an electric heat coil equipped at the bottom plate of the bath and a temperature control unit (2408 PID controller, EUROTHERM, UK), whose schematic diagram can be found in several published papers.\(^{15,19}\) Electric displacement in longitudinal direction is measured using a Sawyer-Tower bridge, where a reference capacitor (metallized polypropylene capacitor) of capacitance 100μF is connected to the specimen in series. This is 1000 times larger than the PZT specimen capacitance 0.1μF. The voltage across the reference capacitor is measured by 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-03-062T-350, VISHAY, Germany) that can be used for the temperature range between −75°C and +205°C. All equipment output signals pass through a data acquisition board (PCI 6221, National Instruments, TX, USA) and are manipulated using a LABVIEW software.

Before measuring polarization and strain changes during temperature rise, it is necessary to check if there is any current leakage or unknown spontaneous polarization change during the long period of time 5000 s of temperature rise. For that purpose, spontaneous polarization change under zero electric field at \( \theta_0 = 20^\circ\text{C} \) is measured for 5000 s. It is reasonable to assume that the measured spontaneous polarization changes also take place in the same way during the long time of temperature rise experiments. Throughout the paper, the spontaneous polarization changes observed at \( \theta_0 = 20^\circ\text{C} \) are removed from measured polarizations during temperature rise.

3. Results and discussion

3.1 Measured polarization and strains during temperature rise

Measured remnant polarization \( P_{ij}^{R} \) is shown in Fig. 1(a); remnant longitudinal strain \( S_{ij}^{R} \) and remnant transverse strain \( S_{ij}^{T} \) are shown, respectively, in the lower and upper parts of Figs. 1(b) and 1(c), during temperature rise from 20 to 110°C. \( S_{ij}^{R} \) and \( S_{ij}^{T} \) for negative values of \( P_{ij}^{R} \) are shown in Fig. 1(b) and those for positive \( P_{ij}^{R} \) in Fig. 1(c). The nine different values of reference remnant polarization \( P_{ij}^{R0} \) in Fig. 1 correspond to different domain structures induced by electric fields of nine different magnitudes. For example, the curves of \( P_{ij}^{R0} = -0.530 \text{Cm}^{-2} \) in Figs. 1(a) and 1(b) correspond to the initial negatively saturated (or poled) state; those of \( P_{ij}^{R0} = +0.523 \text{Cm}^{-2} \) in Figs. 1(b) and 1(c) a state near to the positively saturated state. In Fig. 1(a), it is shown that the amount of decrease in the magnitude of \( P_{ij}^{R} \) during temperature rise is larger at larger magnitudes of \( P_{ij}^{R0} \). Considering the rate of temperature rise is the same for all nine tests in the figure, the magnitude of \( P_{ij}^{R} \) decreases at the fastest rate at the saturated states \( P_{ij}^{R0} = -0.530 \text{ or } +0.523 \text{ Cm}^{-2} \). On the other hand, it tends to remain constant at the states with smaller magnitudes of \( P_{ij}^{R0} \). For example, the magnitude of \( P_{ij}^{R} \) is almost constant at \( P_{ij}^{R0} = +0.002 \text{ Cm}^{-2} \). Strains are set to be zero at the saturated states and reference temperature, as shown in Figs. 1(b) and 1(c). With rising temperature, a specimen contracts longitudinally but elongates transversely for all values of \( P_{ij}^{R0} \) in the figure, resulting in negative longitudinal strain \( S_{ij}^{R} \) and positive transverse strain \( S_{ij}^{T} \). The magnitudes of longitudinal and transverse strain changes during temperature rise tend to increase with increasing magnitude of \( P_{ij}^{R0} \) getting larger near the saturated states but smaller near the state of \( P_{ij}^{R0} = +0.002 \text{ Cm}^{-2} \) in the figure.

In order to have a graphical picture for the dependency of polarization and strain changes on reference remnant polarization \( P_{ij}^{R0} \), the changes in \( P_{ij}^{R} \), \( S_{ij}^{R} \), and \( S_{ij}^{T} \) during temperature increase from 20 to 110°C, denoted by \( \Delta P_{ij}^{R} \), \( \Delta S_{ij}^{R} \), and \( \Delta S_{ij}^{T} \), respectively, are plotted with respect to \( P_{ij}^{R0} \) in Fig. 2. They are marked, respectively, by solid circle, solid square, and empty square symbols in the figure. It is seen that the data symbols are fitted quite well by a solid straight line for \( \Delta P_{ij}^{R} \) and dashed quadratic curves for \( \Delta S_{ij}^{R} \) and \( \Delta S_{ij}^{T} \). The fitting straight line for \( \Delta P_{ij}^{R} \) is, approximately, point-symmetric with respect to the origin of graph. The fitting quadratic curves for \( \Delta S_{ij}^{R} \) and \( \Delta S_{ij}^{T} \) are also approximately symmetric with respect to the vertical axis at \( P_{ij}^{R0} = 0 \), though shifted slightly leftward. At the saturated states near \( P_{ij}^{R0} = \pm 0.530 \text{ Cm}^{-2} \) in the left and right parts of the figure plane, the magnitudes of \( \Delta P_{ij}^{R} \), \( \Delta S_{ij}^{R} \), and \( \Delta S_{ij}^{T} \) are larger than they are at the states near \( P_{ij}^{R0} = 0 \) in the center part of the figure plane.

The macroscopic behavior of \( P_{ij}^{R} \), \( S_{ij}^{R} \), and \( S_{ij}^{T} \) during temperature rise at different values of \( P_{ij}^{R0} \) in Figs. 1 and 2 can be explained in terms of the change in microscopic domain structure by electric field at reference temperature. At the saturated states \( P_{ij}^{R0} = \pm 0.530 \text{ Cm}^{-2} \), the crystallographic \( c \) axes of most lattice
elements in the specimen are orientated as close as possible to the longitudinal \( x_3 \) axis. When an electric field is applied in the opposite direction to the poling, some lattice elements switch to transverse directions with their crystallographic \( c \) axes perpendicular to the longitudinal axis, reducing the magnitude of \( PR_0^{3z} \). Remember that a lattice element elongates in the crystallographic \( c \) axis but contracts in the crystallographic \( a \) axis, when temperature rises. As a result, the magnitudes of \( SR_0^{3z} \) and \( SR_1^{3z} \) are larger at the saturated states than at the state of \( PR_0^{3z} = 0 \). The magnitude of \( PR_0^{3z} \) is also larger at the saturated states and smaller near the state of \( PR_0^{3z} = 0 \). It is because near the state of \( PR_0^{3z} = 0 \), the increasing polarization in the lattice elements orientated in the \( +x_1 \) direction during temperature rise is canceled by the decreasing polarization in the lattice elements orientated in the \( -x_1 \) direction.

\[ \frac{\partial C_1^{SR_3}}{\partial PR_0^{3z}} \] at \( PR_0^{3z} = 0 \) in Fig. 2 means that the number of the lattice elements orientated in the \( -x_3 \) direction is nearly equal to that of the lattice elements orientated in the \( +x_3 \) direction. It is also expected from \( \frac{\partial C_1^{SR_3}}{\partial PR_0^{3z}} < 0 \) and \( \frac{\partial C_1^{SR_1}}{\partial PR_0^{3z}} > 0 \) at \( PR_0^{3z} = 0 \) that the fraction of vertically orientated lattice elements is not large enough to make \( SR_0^{3z} \) positive or \( SR_1^{3z} \) negative at \( PR_0^{3z} = 0 \).

### 3.2 State-dependent thermal moduli and modeling equations

It was reported in the author’s previous work\(^{14}\) that pyroelectric and thermal expansion coefficients could be expressed as functions of remnant polarization and remnant transverse strain for a poled PZT wafer subjected to a through-thickness electric field. The relations between remnant state variables in the wafer during temperature rise were also studied. In the present work, their point of view is taken. Pyroelectric coefficient in the longitudinal \( x_3 \) direction \( \rho_3 \) and longitudinal and transverse thermal expansion coefficients \( \alpha_3 \) and \( \alpha_1 \) are evaluated from the measured responses to temperature rise in Fig. 1. It is shown in the figure that polarization and strains change in proportion to a rise in temperature. The rates of change in polarization and strains with respect to temperature are equal to the values of pyroelectric and thermal expansion coefficients, respectively. The evaluated thermal moduli at \( \theta_0 = 20°C \) are plotted with respect to \( P_{3z}^{R} \) and \( S_{3z}^{R} \) in Figs. 3(c) and 3(d). They are also plotted with respect to \( P_{3z}^{R}, S_{3z}^{R} \) and \( S_{3}^{R} \) at four temperatures 20, 50, 80, and 110°C from Figs. 4(c) to 4(f). In addition, measured remnant state variables are plotted in Figs. 3 and 4: \( (S_{3z}^{R}, S_{3}^{R}) \) and \( (P_{3z}^{R}, S_{3z}^{R}) \) data at 20°C are plotted in Figs. 3(a) and 3(b), respectively, and \( (P_{3z}^{R}, S_{3z}^{R}), (P_{3z}^{R}, S_{3}^{R}) \) and \( (S_{3z}^{R}, S_{3}^{R}) \) data at four temperatures 20, 50, 80, and 110°C in Figs. 4(a) and 4(b). In Fig. 4, the plotted data of
thermal moduli and remnant state variables at 20, 50, 80, and 110°C are marked by filled circle, empty diamond, filled right triangle, and empty square symbols, respectively. Remnant polarization and strains are often used as macroscopic state variables to describe the evolution of microscopic domain structure during domain switching. The plotted data symbols in Figs. 4(a) and 4(b) are produced while raising temperature at a constant value of $P_{R0}^3$, where $P_{R0}^3$ is obtained by an electric field at reference temperature $\theta_0$. Thus it is not certain that the same data are produced while applying an electric field at a constant high temperature. Nevertheless, the observed evolution relations between remnant state variable in Figs. 4(a) and 4(b) are useful in understanding the evolution of domain structure during an electric field-induced switching at a constant temperature. Remnant strain data symbols, both $S_{R3}^0$ and $S_{R1}^0$, are found to have, approximately, quadratic relations with remnant polarization $P_{R3}$ at every temperature in the figure. The magnitudes of remnant longitudinal and transverse strains grow large with rising temperature. In Fig. 4(b), $S_{R3}^0$ and $S_{R1}^0$, are shown to have linear relations with each other at four temperatures. Turning to thermal moduli, it is shown in Figs. 4(c) and 4(d) that the data symbols of pyroelectric coefficient $\beta_3$ are linearly related to remnant polarization and quadratically related to remnant strains at each constant temperature. Thermal expansion coefficients $\alpha_3$ and $\alpha_1$ are also plotted with respect to $P_{R3}^0$ and $S_{R3}^0$ in Figs. 4(c) and 4(f), respectively. In Fig. 4(e), $\alpha_3$ and $\alpha_1$ data symbols have quadratic dependences on $P_{R3}^0$ and linear dependences on $S_{R3}^0$ and $S_{R1}^0$ at each constant temperature. Similar linear dependences of $\beta_3$ on $P_{R3}^0$ and $\alpha_1$ on $S_{R1}^0$ at four temperatures were also observed and reported for a PZT wafer.

It would be interesting and useful if one could predict the relations between remnant state variables and the dependency of thermal moduli on remnant state variables at high temperatures by using some modeling equations at a reference temperature. To make a mathematical modeling possible, some of the observed behaviors of the materials are idealized. The first idealization is to assume that polarization and strains measured during temperature rise in Fig. 1 are proportional to temperature. The assumption looks acceptable in all figures in Fig. 1, except transverse remnant strain in the temperature range between 20 to 40°C. In the narrow temperature range, transverse remnant strain $S_{R1}^0$ remains almost constant. The unexpected strange behavior is not understood yet. It may be due to an inherent error in temperature compensation factors of used strain gauges. However, within a
Fig. 4. Measured remnant state variables, evaluated thermal moduli, and calculated straight lines or quadratic curves at 20, 50, 80 and 110°C, respectively, denoted by filled circle symbols and solid lines, empty diamond symbols and dashed lines, filled right triangle symbols and dashed and dotted lines, and empty square symbols and long-dashed lines, (a) $S_{1}^{R}$ and $S_{3}^{R}$ versus $P_{3}^{R}$ graphs, (b) $S_{1}^{R}$ versus $S_{3}^{R}$ graphs, (c) $P_{3}$ versus $P_{3}^{R}$ graphs, (d) $P_{3}$ versus $S_{3}^{R}$ and $S_{1}^{R}$ graphs, (e) $\alpha_{1}$ and $\alpha_{3}$ versus $P_{3}^{R}$ graphs, and (f) $\alpha_{1}$ and $\alpha_{3}$ versus $S_{3}^{R}$ and $S_{1}^{R}$ graphs.
limited margin of error, a linear variation in transverse strain over the whole temperature range will be assumed in constructing basic modeling equations. Then remnant polarization and remnant longitudinal and transverse strains can be given as linear functions of temperature by

\[ P_R^x = P_{R0}^x + p_1(\theta - \theta_0), \]
\[ S_R^x = S_{R0}^x + a_1(\theta - \theta_0), \]
\[ \tilde{S}_R^x = S_{R0}^x + \tilde{a}_1(\theta - \theta_0), \]

where \( p_1, a_1, \) and \( \tilde{a}_1 \) are pyroelectric, longitudinal thermal expansion, and transverse thermal expansion coefficients, respectively. As stated before, they are taken to be constant at a fixed value of \( P_{R0}^x \) in the whole temperature range between 20 and 110°C. Next it is necessary to introduce modeling equations between remnant state variables \( S_{R0}^y, S_{R0}^z, P_{R0}^x \) and \( P_R^x \) at reference temperature \( \theta_0 = 20^\circ \text{C} \). Figures 3(a) and 3(b) show the \( S_{R0}^y - S_{R0}^z \) and \( P_{R0}^x - S_{R0}^z \) graphs at \( \theta_0 = 20^\circ \text{C} \), respectively. The measured \( (S_{R0}^y, S_{R0}^z) \) and \( (P_{R0}^x, S_{R0}^z) \) data points are marked by filled circle symbols, and they are fitted by a straight line and a quadratic curve, respectively. The equations of the fitting line or curve constitute a part of the modeling equations and given by

\[ S_{R0}^y = a_{11}S_{R0}^y + b_{11}, \]
\[ S_{R0}^z = a_{12}(P_{R0}^x - b_{12})^2 + c_{12}, \]

where \( a_{11}, b_{11}, a_{12}, b_{12}, \) and \( c_{12} \) are the slope of the fitting straight line in Fig. 3(a), the intercept of the straight line with the vertical axis at \( S_{R0}^y = 0 \), the second order coefficient of the fitting quadratic curve in Fig. 3(b), and \( (b_{12}, c_{12}) \) is the coordinates of the peak point of the quadratic curve in the \((P_{R0}^x, S_{R0}^z)\) plane. By the definition of reference configuration for strain measures, the fitting straight line in Fig. 3(a) should pass through the origin of the \((S_{R0}^y, S_{R0}^z)\) plane, that is, \( b_{11} = 0 \). However, it is not exactly zero in the figure, though negligibly small compared to the typical magnitude of transverse remnant strain. The small nonzero value of \( b_{11} \) is neglected here to improve the accuracy of modeling calculations and predictions. The last equations needed for a complete modeling system of equations are those from pyroelectric and thermal expansion coefficients. Figure 3(c) shows the distribution of pyroelectric coefficient \( p_1 \) over \( P_{R0}^x \), and Fig. 3(d) those of longitudinal thermal expansion coefficient \( a_1 \) and transverse thermal expansion coefficient \( \tilde{a}_1 \) over \( S_{R0}^z \), both figures drawn at reference temperature \( \theta_0 = 20^\circ \text{C} \). In the figures, the three data symbols are fitted well by straight lines, which are expressed as

\[ p_1 = a_{p1}(P_{R0}^x)^2 + b_p, \]
\[ a_1 = a_{a1}S_{R0}^y + b_{a1}, \]
\[ \tilde{a}_1 = a_{\tilde{a}1}S_{R0}^y + b_{\tilde{a}1}, \]

where \( b_p \) is the value of pyroelectric coefficient \( p_1 \) at \( P_{R0}^x = 0 \). The value of \( b_p \) is, though very small, negative in Fig. 3(c), which means that zero polarization at \( \theta_0 = 20^\circ \text{C} \) decreases to negative values with rising temperature. This interesting phenomenon may be due to the fact that the initial zero polarization state at \( \theta_0 = 20^\circ \text{C} \) is obtained by a positive electric field applied to a negatively poled specimen. On the contrary, if the zero polarization state were obtained by a negative electric field applied to a positively poled specimen, then the value of \( b_p \) would be positive, which means that zero polarization at \( \theta_0 = 20^\circ \text{C} \) increases to positive values during temperature rise, which was observed and discussed for a PZT wafer. Now all eight modeling equations from Eq. (1) to (3) constitute the complete system of modeling equations that will be used to predict the relations between remnant state variables and the dependency of thermal moduli on remnant state variables at room and high temperatures. The number of constants in the eight equations from Eq. (1) to (3) is eleven, and they are evaluated from four fitting straight lines and one quadratic curve in Fig. 3. The results of evaluation are tabulated in Table 1.

### Table 1. The values of constants for fitting straight lines and quadratic curve in Fig. 3

| Equations | Constants | Units of constants | Values of constants |
|-----------|-----------|--------------------|---------------------|
| \( S_{R0}^y = a_{11}S_{R0}^y + b_{11} \) | \( a_{11} \) | \(-\) | \(-0.43652\) |
| \( S_{R0}^z = a_{12}(P_{R0}^x - b_{12})^2 + c_{12} \) | \( b_{11} \) | \(10^{-4}\) | \(-7.3994\) |
| \( a_{12} \) | \(10^{-6} \text{C}^{-1} \text{m}^2\) | \(2246.3\) |
| \( c_{12} \) | \(\text{C}^{-1}\) | \(-0.038367\) |
| \( \tilde{a}_1 = a_{\tilde{a}1}S_{R0}^y + b_{\tilde{a}1} \) | \(a_{\tilde{a}1} \) | \(10^{-4}\) | \(-623.41\) |
| \( b_{\tilde{a}1} \) | \(\text{C}^{-1}\) | \(-12.476\) |
| \( b_p \) | \(\text{C}^{-1}\) | \(-0.47418\) |
| \( a_{p1} \) | \(10^{-4} \text{C}^{-1}\) | \(-0.0065843\) |
| \( b_p \) | \(10^{-6} \text{C}^{-1}\) | \(-4.38035\) |

### 3.3 Comparison of measurements and predictions

In this section, the proposed eight modeling equations from Eq. (1) to (3) are used to calculate the behavior of remnant state variables and thermal moduli at high temperatures. All the predictions obtained from the modeling equations are drawn in Fig. 4 by using solid, dashed, dashed and dotted, and long-dashed line patterns for four temperatures 20, 50, 80, and 110°C, respectively. Symbols in the figure are either measured remnant state variables or thermal moduli estimated from measured responses at four temperatures. Figures 4(a) and 4(b) show the relations between remnant state variables at four temperatures 20, 50, 80 and 110°C. Measured \( (P_R^x, S_R^y) \) and \( (P_R^x, S_R^z) \) data are marked as symbols in the lower and upper parts of Fig. 4(a), respectively, and measured \( (S_R^y, S_R^z) \) data in Fig. 4(b). The fitting straight line for \( (S_R^y, S_R^z) \) data and the fitting quadratic curve for \( (P_R^x, S_R^y) \) data at \( \theta_0 = 20^\circ \text{C} \) were already used to construct modeling equations. The calculated quadratic \( P_R^x - S_R^z \) and \( P_R^x - S_R^y \) curves agree relatively well with measured \( P_R^x, S_R^y \) and \( P_R^x, S_R^z \) data symbols at all four temperatures in Fig. 4(a), though measured remnant transverse strains are smaller than the calculated curves at 50 and 80°C in the upper part of the figure. It is shown in Fig. 4(a) that both measured remnant strain data symbols and calculated curves are shifted leftward slightly at all four temperatures in the figure. It may also be attributed to a positive electric field applied to a negatively saturated specimen to obtain a specific value of \( P_{R0}^x \) at which temperature is raised. The same argument was used to explain the observed negative
value of $b_p$ in Eq. (3). The quadratic relations between $P_3^R$ and $S_3^R$ at four temperatures in the upper part of Fig. 4(a) are quite similar to the observed data for a PZT wafer in Fig. 3(a) of Kim and Kim.\(^{14)}\) The calculated $S_3^R - S_3^R$ straight lines for three high temperatures 50, 80 and 110°C are shown in Fig. 4(b). It is seen that the three calculated straight lines are evenly placed from the fitting straight line at reference temperature 20°C. It is observed that measured $(S_3^R, S_3^R)$ data symbols at 50 and 80°C are below the calculated lines. The difference between measurements and calculations is because transverse thermal expansion coefficient $\alpha_t$ is assumed to be constant in modeling equations, as discussed before introducing Eq. (1).

Pyroelectric coefficient $p_3$ estimated from measured polarization is plotted with respect to remnant polarization $P_3^R$ and remnant strains $S_3^R$ and $S_3^R$ in Figs. 4(c) and 4(d), respectively. In Fig. 4(c), it is shown that $p_3$ is proportional to $P_3^R$ at four temperatures. The slope of change in $p_3$ over $P_3^R$ is steeper at higher temperatures in both measured data symbols and calculated straight lines. $p_3$ is also plotted with respect to $S_3^R$ and $S_3^R$ in Fig. 4(d). Quadratic curves calculated from modeling equations fit well with measured pyroelectric coefficients. The same linear dependence of $p_3$ on $P_3^R$ at four temperatures was observed and reported for a PZT wafer in Fig. 7(a) of Kim and Kim.\(^{14)}\) Approximately, measured data symbols of $\alpha_3$ and $\alpha_3$ show quadratic dependences on remnant polarization in Fig. 4(e) and linear dependences on remnant strains in Fig. 4(f). The observed dependences of the data symbols of $\alpha_3$ and $\alpha_3$ on $P_3^R$, $S_3^R$ and $S_3^R$ are predicted quite well by the calculated quadratic curves and straight lines in Figs. 4(e) and 4(f), respectively. The linear and quadratic dependences of $\alpha_3$ on $P_3^R$ and $S_3^R$ at four temperatures are coincident with the previous observations\(^{14)}\) for a PZT wafer.

4. Conclusions

A soft PZT rectangular parallelepiped specimen poled in the $-x_3$ direction is subjected to various magnitudes of longitudinal electric field in the $+x_3$ direction. Then the specimen temperature is raised from 20 to 110°C under no electric field, measuring longitudinal polarization and longitudinal/transverse strains. Estimated pyroelectric coefficient was shown to have linear dependences on remnant polarization and quadratic dependences on remnant strains; thermal expansion coefficients linear dependences on remnant strains and quadratic dependences on remnant polarization. A set of eight modeling equations is proposed to predict the variations of remnant polarization and remnant strains and the dependency of pyroelectric and thermal expansion coefficients on remnant state variables at high temperatures. The predictions of the modeling equations are compared well with measured data.

The state-dependency of thermal moduli is found to be necessary for predicting high temperature behavior of ferroelectric ceramics. The successful prediction leads us to extend the proposed modeling method to the materials under combined loads of electric and compressive stress fields, which would allow the prediction of high temperature behavior of piezoelectric actuators subjected to preliminary compressive stress. In addition, the research outputs are of general utility and can be transferred to other piezoelectric materials. The modeling equations on thermal moduli and remnant state variables would be useful in the development of constitutive laws for the linear and nonlinear behavior of the materials at high temperatures as well as in the application of piezoelectric actuators and sensors.

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