Construction and Application of Experimental Formula for Nonlinear Behavior of Ferroelectric Ceramics Switched by Electric Field at Room Temperature during Temperature Rise

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ABSTRACT

A poled lead zirconate titanate (PZT) cube specimen that is switched by an electric field at room temperature is subject to temperature increase. Changes in polarization and thermal expansion coefficients are measured during temperature rise. The measured data are analyzed to obtain changes in pyroelectric coefficient and strain during temperature change. Empirical formulae are developed using linear or quadratic curve fitting to the data. The nonlinear behavior of the materials during temperature increase is predicted using the developed formulae. It is shown that the calculation results can be compared successfully with the measured values, which proves the accuracy and reliability of the developed formulae for the nonlinear behavior of the materials during temperature changes.

Key words : Thermal expansion coefficient, Temperature, Pyroelectric coefficient, Switching, Empirical formula

1. Introduction

Piezoelectric ceramics are widely used in devices and equipment such as ferroelectric memory (FRAM), ultrasonic motors, sonar detectors, and micro electro mechanical systems (MEMS). Research on the application and development of piezoelectric ceramics is also widely pursued. The application of a significant load or electric field to a piezoelectric system can result in excessive concentration of stress or electric fields in the ceramic material due to the complexity of the system or the presence of defects, which causes unexpected domain switching and rapid temperature changes. As a result, the internal structure of the ceramic material often changes to produce macroscopic nonlinear behavior and variations in the material properties. Degradation in system performance is observed due to such unexpected domain switching. In order to prevent system instability due to nonlinear behavior, experimental observation and analysis of nonlinear behavior of piezoelectric ceramic materials under various load conditions must be made. A wide range of related studies have been carried out. Zhou and Kamlah,¹⁾ Liu and Huber,²⁾ and Kim³⁾ observed and analyzed the nonlinear behavior of the materials when electric field and stress are applied at room temperature. Recently, research on the nonlinear behavior of the materials at room temperature has been extended to high temperatures. Lee and Kim⁴⁾ and Selten *et al.*⁵⁾ measured and analyzed the nonlinear behavior of the materials caused by

electric fields at room and high temperatures, while Weber *et al.*⁶⁾ measured and analyzed the nonlinear behavior caused by stresses at room and high temperatures. Grunbichler *et al.*⁷⁾ used the finite element method to predict and understand the nonlinear behavior of piezoelectric actuators due to stress, electric fields, and temperature changes. Also, to develop an empirical formula for predicting experimental observations of piezoelectric materials, Ji and Kim^{8,9,10)} observed and analyzed the nonlinear behavior of the materials when they are subject to stress and electric fields at room and high temperatures.

In the present work, relatively simple empirical formulae for the experiment results of Ji and Kim¹¹⁾ are presented. Moreover, the presented empirical formulae were used to calculate the polarization and strain responses of piezoelectric materials during temperature increases, and comparisons were made with measurements.

2. Experimental Procedure

In the present work, the experimental data of Ji and Kim¹¹⁾ were used to present new formulae for the prediction of ferroelectric ceramic behavior at high temperatures. The experimental method of Ji and Kim¹¹⁾ is presented simply here. For ferroelectric specimens, PZT specimens of regular hexahedron shape with 10 mm sides were used. The followings are the properties of the specimen material, provided by the manufacturer (PZT5H1, Morgan Technical Ceramics, UK): the Curie point is 200°C, coupling factor $k_p = 0.60$, piezoelectric coefficients $d_{31} = -250 \times 10^{-12} \text{ mV}^{-1}$ and $d_{33} = 620 \times 10^{-12} \text{ mV}^{-1}$, elastic compliance coefficients $s_{33} = 21.9 \times 10^{-12} \text{ m}^2\text{N}^{-1}$ and $s_{11} = 17.7 \times 10^{-12} \text{ m}^2\text{N}^{-1}$. Here, the subscript

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Fig. 1. Schematic experimental setup to measure electric displacement and strains of poled PZT cube specimen under electric field at room and high temperatures.

3 refers to the polarization direction; the subscript 1 refers to the transverse polarization direction. Initially, the specimen is poled in the negative direction and a total of 14 electric fields of different magnitude were applied at the reference temperature of 20°C. The range of reference remnant polarization P_3^{R0} induced by an electric field was from -0.26 to $+0.26$ Cm^{-2} . After poling, the leakage current density was measured over 5,000 s and the specimen was stabilized, then followed by temperature increases to 110°C at a rate of $1.2^\circ\text{Cmin}^{-1}$ along with the invar specimen (Product No. 318-0285-3, Danyang, China). During temperature increases, remnant polarization P_3^R and thermal outputs ε_{GIR} and ε_{GIS} of the invar and ceramic specimens were measured. Here, the thermal output changes refer to the variations of strain gage outputs value during temperature rises. Then, thermal expansion coefficients in the longitudinal and transverse directions α_3 and α_1 of the ceramic specimen were calculated using the thermal expansion coefficient of the invar specimen α_R .¹²⁾ Polarization was measured indirectly using the Sawyer-Tower circuit; a Keithley 6514 was used to measure the voltage of the capacitor serially connected to the specimen. Temperature was controlled by placing the specimen in an oil bath (2408 PID controller, EUROTHERM, UK), shown in Fig. 1, filled with an insulating oil (MICTRANS Class1-No2, MICHANG OIL IND. CO., Pusan, Korea), and using a heat coil installed on the bottom of the oil bath. All data were collected at a sampling rate of 100 Hz and the data were processed using the LABVIEW program through a DAQ board (PCI 6221, National Instruments, TX, USA).

3. Results and Discussion

3.1. Pyroelectric Coefficient and Strain Calculations During Temperature Increases

Electric fields of various magnitudes were applied in the direction opposite to the polarization of PZT specimens, causing poling in the negative longitudinal direction at ref-

Fig. 2. Measured polarization P_3^R and longitudinal and transverse thermal expansion coefficients α_3 and α_1 during temperature rise of a ferroelectric ceramic specimen switched by electric field at reference temperature 20°C, (a) P_3^R vs. θ at $P_3^{R0} = -0.256, -0.136, -0.018, +0.136$, and $+0.263$ Cm^{-2} , (b) α_3 vs. θ at $S_3^{R0} = +1.419, -151.7, -287.8, -369.5$, and -458.2×10^{-6} , (c) α_1 vs. θ at $S_1^{R0} = +3.121, +87.20, +151.2, +201.6$, and $+245.2 \times 10^{-6}$.

erence temperature 20°C. Switching is induced by the applied electric field and an internal state of specific reference remnant polarization is obtained. Then, the electric field was removed, and temperature is increased to 110°C. During temperature increases, remnant polarization P_3^R and thermal expansion coefficients in the longitudinal and

transverse directions α_3 and α_1 were measured. Fig. 2(a) shows measured remnant polarization P_3^R , and Figs. 2(b) and (c) thermal expansion coefficients in the longitudinal and transverse directions α_3 and α_1 during temperature increases. Only five states of reference remnant polarization P_3^{R0} are plotted in Fig. 2(a) out of the total 14 remnant polarization states. In Fig. 2(a), it was observed that when P_3^{R0} was negative, the value of P_3^R increased, on the other hand, when P_3^{R0} was positive, P_3^R decreased, with increase in temperature. Additionally, it was observed that P_3^R is almost constant when P_3^{R0} is near zero. As in Fig. 2(a), only five states of longitudinal and transverse remnant strains are plotted in Figs. 2(b) and 2(c) out of fourteen, longitudinal thermal expansion coefficients in the former plot and transverse in the latter. Thermal expansion coefficients of ferroelectric specimens were calculated using the thermal expansion coefficients of the invar specimen, as demonstrated in Ji and Kim.¹¹⁾ In Figs. 2(b), longitudinal thermal expansion coefficient tends to decrease with increase in

temperature, while in Fig. 2(c), transverse thermal expansion coefficient increases and then remain constant. Measured remnant polarization and thermal expansion coefficients are then used to calculate pyroelectric coefficients and strains. First, by estimating the rates of changes in remnant polarizations with temperature, pyroelectric coefficient p_3 is obtained. The values of pyroelectric coefficients, calculated for the temperature range between 20°C to 110°C, for five chosen reference remnant polarization states, are shown as symbols in Fig. 3(a). In the figure, pyroelectric coefficients are plotted with respect to temperature for five constant values of reference remnant polarization P_3^{R0} . The plotted symbols of p_3 fit well with straight line, given by Equation (1) below:

$$p_3 = a_p \theta + b_p, \quad (1)$$

where, a_p refers to the slope of the fitting straight line and b_p refers to the intercept of the line at zero temperature. The values of a_p and b_p are plotted verse P_3^{R0} for the whole range of reference remnant polarization between -0.256 Cm^{-2} and $+0.263 \text{ Cm}^{-2}$ in Fig. 3(b). In the figure, a_p is shown to fit with a straight line and b_p with a parabolic curve, both expressed as

$$\begin{aligned} \hat{a}_p(P_3^{R0}) &= a_{p1}P_3^{R0} + a_{p0}, \\ \hat{b}_p(P_3^{R0}) &= b_{p1}(P_3^{R0})^2 + b_{p1}(P_3^{R0}) + b_{p0}, \end{aligned} \quad (2)$$

Substitution of Eq. (2) into Eq. (1) results in Eq. (3).

$$\hat{p}_3(P_3^{R0}, \theta) = (a_{p1}P_3^{R0} + a_{p0})\theta + [b_{p2}(P_3^{R0})^2 + b_{p1}(P_3^{R0}) + b_{p0}]. \quad (3)$$

Using Eq. (3), one can estimate pyroelectric coefficient p_3 when reference remnant polarization P_3^{R0} and temperature θ are given.

Now turn to the calculation of longitudinal and transverse strains. Thermal expansion coefficient is the rate of change in strain with respect to temperature. Thus, Eq. (4) below can be used to calculate strains from measured thermal expansion coefficients.

$$\begin{aligned} (S_3^R)_{i+1} &= \alpha_3(\theta_i)(\theta_{i+1} - \theta_i) + (S_3^R)_i, \\ (S_1^R)_{i+1} &= \alpha_1(\theta_i)(\theta_{i+1} - \theta_i) + (S_1^R)_i, \end{aligned} \quad (4)$$

Among fourteen measured states, longitudinal and transverse strains are calculated for five specific states of remnant strains and plotted with temperature in Figs. 4(a) and (b), respectively. In Fig. 4(a), as the magnitude of electric field increases, S_3^{R0} changes from zero to negative values. When the values of S_3^{R0} are relatively small, longitudinal strain tends to decrease with increase in temperature; on the other hand, when S_3^{R0} is less than -400×10^{-6} , it increases with temperature. This can be explained by microscopic process of domain switching. When the magnitude of electric field is small, switching is not sufficient and most domains remain parallel to the longitudinal x_3 direction. When electric field is sufficiently large, the ratio of domains with

Fig. 3. Fitting of the changes in pyroelectric coefficient p_3 during temperature rise at different values of reference remnant polarization P_3^{R0} . P_3^{R0} is obtained by application of electric field at reference temperature 20°C. (a) p_3 vs. θ graphs at $P_3^{R0} = -0.256, -0.136, -0.018, +0.136$, and $+0.263 \text{ Cm}^{-2}$ of measured data symbols and fitting of straight lines $p_3 = a_p \theta + b_p$, (b) slopes a_p and intercepts b_p of the fitting of straight lines plotted versus P_3^{R0} and fitting of quadratic and linear curves.

Fig. 4. Measured longitudinal and transverse remnant strains S_3^R and S_1^R during temperature rise of a ferroelectric ceramic specimen switched by an electric field at reference temperature 20°C, (a) S_3^R vs. θ plots at $S_3^{R0} = +1.419, -151.7, -287.8, -369.5,$ and -458.2×10^{-6} , (b) S_1^R vs. θ plots at $S_1^{R0} = +3.121, +87.20, +151.2, +201.6,$ and $+245.6 \times 10^{-6}$.

polarizations parallel to the transverse x_1 axis increases due to electric field-induced switching, leading to increases in S_3^R with temperature rise. Fig. 4(b) shows the variations of transverse strain S_1^R with temperature increase at five chose states of reference remnant transvers strain S_3^{R0} . Here, unlike Fig. 4(a), S_1^R increases with temperature for the five chosen states. The state of maximum S_3^{R0} in Fig. 4(b) corresponds to the state of minimum S_3^{R0} in Fig. 4(a). At the maximum S_3^{R0} state, the magnitude of applied electric field is the largest, which causes the largest switching in the specimen. Most domains arrange in the vertical direction parallel to the x_1 axis, thus resulting in lower increases in S_1^R with temperature than other four state in the figure. The cases of $S_3^{R0} = -458.2 \times 10^{-6}$ in Fig. 4(a) and $S_1^{R0} = +245.6 \times 10^{-6}$ in Fig. 4(b) correspond to the same state at the reference temperature. It is interesting that longitudinal and transverse strains increase simultaneously as temperature increases at the specific state. In the case of isotropic materials, strains change in the same rate in all directions

Fig. 5. Fitting of the changes in longitudinal thermal expansion coefficient α_3 during temperature rise at different values of reference remnant longitudinal strain S_3^{R0} . S_3^{R0} is obtained by application of electric field at reference temperature 20°C, (a) α_3 vs. θ graphs at $S_3^{R0} = +1.419, -151.7, -287.8, -369.5,$ and -458.2×10^{-6} of measured data symbols and fitting of straight lines $\alpha_3 = a_{S3}\theta + b_{S3}$, (b) slopes a_{S3} and intercepts b_{S3} plotted versus S_3^{R0} and their fitting of straight lines.

with temperature increases. The similar increases in longitudinal and transverse strains with temperature in Figs. 4(a) and 4(b) for the specific state, $S_3^{R0} = -458.2 \times 10^{-6}$ in Fig. 4(a) and $S_1^{R0} = +245.6 \times 10^{-6}$, suggest that the specimen behaves like an isotropic material after an application of electric field of sufficient magnitude.

Let us apply the equations in Eqs. (1) - (3) to calculate strains. The same procedure is used for both longitudinal and transverse strains, so only the calculation of longitudinal strain will be dealt with here. The variations of longitudinal thermal expansion coefficient α_3 with temperature for five chosen states of S_3^{R0} are plotted in Fig. 5(a). It is shown that thermal expansion coefficient data in the figure fit adequately with straight lines, whose equations are given by

$$\alpha_3 = a_{S3}\theta + b_{S3}, \quad (5)$$

where a_{S3} refers to the slope of fitting straight line and b_{S3}

the intercept of the line at zero the temperature. The distributions of a_{S3} and b_{S3} over S_3^{R0} from $+1.419 \times 10^{-6}$ to -458.2×10^{-6} are plotted in Fig. 5(b). The data of a_{S3} and b_{S3} , marked with symbols, fit well with straight lines, expressed as

$$\begin{aligned}\hat{a}_{S3}(S_3^{R0}) &= a_{S31}S_3^{R0} + a_{S30}, \\ \hat{b}_{S3}(S_3^{R0}) &= b_{S31}S_3^{R0} + b_{S30},\end{aligned}\quad (6)$$

Substitution of Eq. (6) into Eq. (5) results in Eq. (7) below.

$$\hat{\alpha}_3(S_3^{R0}, \theta) = (a_{S31}S_3^{R0} + a_{S30})\theta + b_{S31}S_3^{R0} + b_{S30}. \quad (7)$$

Using Eq. (7), one can estimate longitudinal thermal expansion coefficient α_3 when reference remnant longitudinal strain S_3^{R0} and temperature θ are given. In a similar manner, one can estimate transverse thermal expansion coefficient when S_1^{R0} and θ are given.

3.2 Comparison of the Proposed Formula and Experimental Results

Pyroelectric coefficient p_3 is the rate of change in remnant polarization P_3^R with temperature θ , so it can be expressed as $p_3 = \frac{dP_3^R}{d\theta}$. Substitution of this relation into Eq. (1) yields

$$\frac{dP_3^R}{d\theta} = \hat{a}_P(P_3^{R0})\theta + \hat{b}_P(P_3^{R0}), \quad (8)$$

Changes in remnant polarization P_3^R during temperature increase can be extracted from Eq. (8) for a constant value of P_3^{R0} .

$$\begin{aligned}P_3^R &= P_3^{R0} + \int_{\theta_0}^{\theta} (a_P\theta + b_P)d\theta, \\ P_3^R &= P_3^{R0} + \frac{a_P}{2}(\theta^2 - \theta_0^2) + b_P(\theta - \theta_0),\end{aligned}\quad (9)$$

Substituting Eq. (2) into Eq. (9) gives Eq. (10) below, in which the variation of remnant polarization P_3^R with temperature θ is determined for given values P_3^{R0} and θ_0 are given.

$$\begin{aligned}P_3^R &= P_3^{R0} + \frac{1}{2}(a_{P1}P_3^{R0} + a_{P0})(\theta^2 - \theta_0^2) \\ &+ [b_{P2}(P_3^{R0})^2 + b_{P1}(P_3^{R0}) + b_{P0}](\theta - \theta_0).\end{aligned}\quad (10)$$

In this work, reference temperature θ_0 is 20°C. The values of all coefficients in Eq. (10) are listed in Table 1. Applying Eq. (10) and Table 1 to the data in Fig. 2(a) gives the prediction results shown in Fig. 6. The symbols in Fig. 6 represent the measured data and the curves represent the calculation results by Eq. (10). Fig. 6(a) shows the plots of changes in remnant polarization P_3^R with temperature θ and Fig. 6(b) the plots of pyroelectric coefficient p_3 with θ . In Fig. 6(a), the measurements and predictions of remnant polarization P_3^R are in a good agreement with each other. The predictions of pyroelectric coefficient were also found to agree approximately well with measurements.

Experimental formulae for longitudinal and transverse

Table 1. Values of the Coefficients in Eq. (10)

Dependent variable	Constants	Units of constants	Values of constants
P_3^R	a_{p1}	10^{-4}	-0.37151
	a_{p0}	10^{-4} Cm^{-2}	-0.0038525
	a_{p2}	$10^{-4} \text{ Cm}^2\text{°C}$	-7.6783
	b_{p1}	10^{-4} °C	-3.6179
	b_{p0}	$10^{-4} \text{ Cm}^{-2}\text{°C}$	0.40011
S_3^R	a_{S31}	10^{-1}	-0.00055716
	a_{S30}	10^{-5}	-0.52243
	b_{S31}	°C^{-1}	-0.0025858
	b_{S30}	10^{-6} °C^{-1}	1.2688
S_1^R	a_{S11}	10^{-1}	-0.00055728
	a_{S10}	10^{-5}	0.10630
	b_{S11}	°C^{-1}	-0.0027053
	b_{S10}	10^{-6} °C^{-1}	3.0889

Fig. 6. Measured and predicted changes in (a) remnant polarization P_3^{R0} and (b) pyroelectric coefficient p_3 during temperature rise. Measured data are represented by symbols and predictions by line segments.

remnant strains S_3^R and S_1^R were also developed in a similar manner, just like Eq. (10). The only difference is the linear and quadratic equations in Eqs. (2)₂ and (6)₂. The values of all coefficients for the strain formulae are found in Table

Fig. 7. Measured and predicted changes in (a, c) remnant longitudinal and transverse strains S_3^R and S_1^R , (b, d) longitudinal and transverse thermal expansion coefficients α_3 and α_1 during temperature rise. Measured data are represented by symbols and predictions by line segments.

1. Fig. 7 shows the calculation results for strains. Fig. 7(a) shows the plots for longitudinal remnant strain S_3^R and Fig. 7(c) for transverse remnant strain S_1^R with respect to θ . S_3^R and S_1^R strain prediction curves match well with measurement symbols. Fig. 7(b) shows longitudinal thermal expansion coefficient α_3 and Fig. 7(d) transverse thermal expansion coefficient α_1 plotted versus temperature θ . The agreement of calculated thermal expansion coefficients with measured ones is relatively good.

4. Conclusions

In the present work, fourteen different electric fields were applied to poled piezoelectric ceramic specimens in the direction opposite to polarization in order to reach a specific state of polarization and strains. Then electric field was removed, and the temperature of specimen was increased, along with that of the invar specimens. Pyroelectric coefficients were calculated using remnant polarizations measured during temperature increase, and strains using thermal expansion coefficient. Then, experimental formulae were developed and used to predict pyroelectric coefficient and strains during temperature rises. The predicted results

were compared with the experimental results. For all fourteen states investigated, polarization and strain variations were predicted accurately. The predictions for pyroelectric and thermal expansion coefficients were in relatively good agreement with experimental results. Thus this study shows that the suggested experiment-based formulae can be used to predict the macroscopic behavior, i.e., polarization and strain changes, of ferroelectric materials during temperature increases, including changes in thermal properties such as pyroelectric and thermal expansion coefficients.

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