journal

J. Am. Ceram. Soc., **88** [8] 2121–2125 (2005)
DOI: 10.1111/j.1551-2916.2005.00418.x

Harmonic Analysis of Polarization Hysteresis of Aged PZTs

Sutham Srilomsak,*,† Walter A. Schulze,* Steven M. Pilgrim,* and Francis A. Williams Jr.

School of Ceramic Engineering and Material Science, Alfred University, Alfred, New York 14802

Many studies have been performed on aging of lead zirconate titanate (PZT), but a single model has not been universally accepted. An aim of this research was to determine whether harmonic analysis could distinguish among the models for the aging of PZTs. Doped and undoped PZT samples were prepared, and the aging behaviors of relative dielectric constant (*K*), planar coupling factor (k_p), dielectric coefficient (d_{33}), and polarization were analyzed by both weak-field and harmonic analysis methods at 37°C. Results indicated that aging behavior, as noted by a harmonic analysis, substantially agreed with the weak-field behavior. This finding suggests that harmonic analysis is a promising new method for studying the aging of PZTs, which may contribute to developing a better aging model for PZTs.

I. Introduction

Lead zirconate titanate (PZT) has been a commercially important piezoelectric ceramic for many decades. Although processed to yield excellent piezoelectric properties, PZT suffers from a long-term aging process in which the piezoelectric properties decrease 0–5% per decade.[1] This means that if the polarization of PZT decreases 5% by the first day, it is expected to have decreased 10% by the 10th day and 15% by the 100th day after poling and so on. Aging is defined as the spontaneous decrease of a property with time, under zero external electric field and isothermal conditions.[1] Most studies of aging in PZTs have concentrated on the aging in the relative dielectric constant and other dielectric properties under weak-field; many models for this aging have been proposed.[2–9] However, there is no universally accepted model to describe the mechanisms of aging. Recently, the work by Leary and Pilgrim[10] and DiAntonio[11] showed that the harmonic content of large-signal polarization versus electric field was a very sensitive indicator of dielectric aging in relaxors. It is the purpose of this study to extend harmonic analysis into the commercially important PZTs, especially to study aging of PZTs at 37°C (body temperature). The results of this study may help define a model to explain the very interesting spontaneous changes in weak- and strong-field properties that accompany aging of PZTs.

II. Methodology

As used here, harmonic analysis is a technique by which high-field polarization data are filtered and processed using discrete fourier transform (DFT) analysis. Fourier analysis is a family of mathematical techniques based on decomposing signals into sinusoids. It is named after Jean Baptiste Joseph Fourier (1768–1830),[12] who showed that any waveform that exists in the real world can be decomposed into an equivalent series of sine waves, as illustrated in Fig. 1(a).

In this work, the input signal (time domain) is decomposed into the output signal (frequency domain), which contains the amplitude and phase of the component sine and cosine waves and a dc bias, as illustrated in Figs. 1(a) and (b). The time (Fig. 1(a)) and frequency domains (Fig. 1(c)) contain the exact same information, but in a different form. Conversion from the time domain to the frequency domain is called "DFT."

The Fourier series (FS) of a function *f* is given by

$$\begin{aligned}\mathrm{FS} = {} & A_0 + A_1 \sin\omega t + A_2 \sin 2\omega t + A_3 \sin 3\omega t \\ & + \cdots + A_n \sin\omega t \ (\text{sine terms}) \\ & + B_1 \cos\omega t + B_2 \cos 2\omega t + B_3 \cos 3\omega t \\ & + \cdots + B_n \cos n\omega t \ (\text{cosine terms})\end{aligned} \tag{1}$$

There are three main parts in function. The first part is the dc term, A_0, which is the average value of the waveform over one full cycle. The second part is a series of sine terms. The third part is a series of cosine terms. In general, it is possible to represent the series entirely as sine or cosine terms by adjusting the phase angles properly. The FS of sine components can be written as

$$\mathrm{FS} = A_0 + \sum_{n=1}^{\infty} A_n \sin(n\omega t + \varphi_n) \tag{2}$$

where A_0 is the zero frequency amplitude or average value, A_n is the specific harmonic component amplitude for harmonic *n*th, ω is the angular frequency, *t* is the time in seconds, and φ is the phase angle in radians.

As shown earlier,[10,11] the FS of a polarization versus electric field test can be mapped as a Devonshire phenomenological expansion.

$$P_i = \varepsilon'_{ij} E_j + \varepsilon'_{ijk} E_j E_k + \varepsilon'_{ijkl} E_j E_k E_l + \cdots \tag{3}$$

where ε'_{ij}, ε'_{ijk}, ε'_{ijkl} are dielectric coefficients and E_j, E_k, E_l are applied electric fields.

In general, experimental electric field is represented by Eq. (4)

$$E = E_0 \ \sin(\omega t \pm \phi) \tag{4}$$

where *E* is the magnitude of the electric field at time *t*, E_0 is the maximum amplitude of the applied electric field, ω is the angular frequency in radians/second (1/s), *t* is the time in seconds, and ϕ is the phase angle in radians.

Equation (4) can be substituted into Eq. (3) to express P_i as

$$\begin{aligned}P_i = {} & \varepsilon'_{ij}(E_0 \ \sin(\omega t \pm \phi)) + \varepsilon'_{ijk}(E_0 \ \sin(\omega t \pm \phi))^2 \\ & + \varepsilon'_{ijkl}(E_0 \ \sin(\omega t \pm \phi))^3 + \varepsilon'_{ijklm}(E_0 \ \sin(\omega t \pm \phi))^4 + \cdots\end{aligned} \tag{5}$$

R. Schwartz—contributing editor

Manuscript No. 10402. Received July 17, 2004; approved February 10, 2005.
This paper was presented at the 105th Annual Meeting of the American Ceramic Society, Nashville, TN, April 30, 2003 (High Strain Piezoelectric Material, Devices and Applications Symposium, Paper Number AM-S10-15-2003).
*Member, American Ceramic Society.
†Author to whom correspondence should be addressed. e-mail: sriloms@alfred.edu

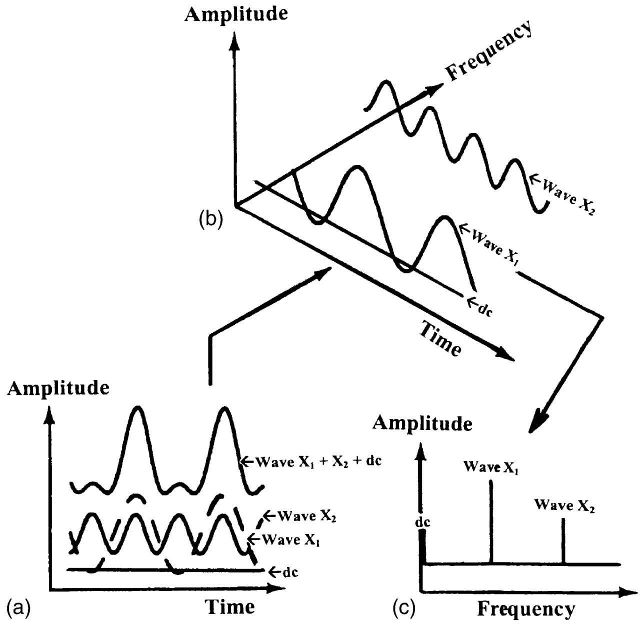

Fig. 1. (1) Any waveform that exists in the real world can be decomposed into an equivalent series of sine waves and a dc component. (2) The time domain (a) and frequency domain (c) contain the exact same information, but in different form (after DiAntonio[11]).

If the ϕ are sufficiently small, use of trigonometry definitions with Eq. (5) yields after rearrangement and truncation at $n = 6$:

$$\begin{aligned} P(E) = {} & \underbrace{\left(\frac{1}{2}\varepsilon'_{ijk}E_0^2 + \frac{3}{8}\varepsilon'_{ijklm}E_0^4 + \frac{5}{16}\varepsilon'_{ijklmno}E_0^6\right)}_{\text{0th harmonic}} \\ & + \underbrace{\left(\varepsilon'_{ij}E_0 + \frac{3}{4}\varepsilon'_{ijkl}E_0^3 + \frac{5}{8}\varepsilon'_{ijklmn}E_0^5\right)\sin\omega t}_{\text{1st harmonic}} \\ & - \underbrace{\left(\frac{1}{2}\varepsilon'_{ijk}E_0^2 + \frac{1}{2}\varepsilon'_{ijklm}E_0^4 + \frac{15}{32}\varepsilon'_{ijklmno}E_0^6\right)\cos 2\omega t}_{\text{2nd harmonic}} \\ & - \underbrace{\left(\frac{1}{4}\varepsilon'_{ijkl}E_0^3 + \frac{5}{16}\varepsilon'_{ijklmn}E_0^5\right)\sin 3\omega t}_{\text{3rd harmonic}} \\ & + \underbrace{\left(\frac{1}{8}\varepsilon'_{ijklm}E_0^4 + \frac{3}{16}\varepsilon'_{ijklmno}E_0^6\right)\cos 4\omega t}_{\text{4th harmonic}} \\ & + \underbrace{\left(\frac{1}{16}\varepsilon'_{ijklmn}E_0^5\right)\sin 5\omega t}_{\text{5th harmonic}} \\ & - \underbrace{\left(\frac{1}{32}\varepsilon'_{ijklmno}E_0^6\right)\cos 6\omega t}_{\text{6th harmonic}} \end{aligned} \quad (6)$$

The Fourier series can be set equal to the polynomial expansion of the polarization (P_i). Therefore, Eq. (2) can be written as

$$\mathrm{FS} = A_0 + \sum_{n=1}^{\infty} A_n \sin(n\omega t + \varphi_n) = P_i$$

$$\begin{aligned} P_i = {} & A_0 && \text{0th harmonic} \\ & + A_1 \sin(1 * \omega t + \phi_1) && \text{1st harmonic} \\ & + A_2 \sin(2 * \omega t + \phi_2) && \text{2nd harmonic} \\ & + A_3 \sin(3 * \omega t + \phi_3) && \text{3rd harmonic} \\ & + A_4 \sin(4 * \omega t + \phi_4) && \text{4th harmonic} \\ & + \cdots \end{aligned} \quad (7)$$

After termwise comparison of Eqs. (6) and (7) and application of the trigonometry identity "sin ($\alpha+\beta$) = sin (α) cos (β)+sin (β) cos (α)," the individual harmonic yields the group of equalities shown as Eq. (8):

$$\begin{aligned} A_1\cos\varphi_1 &= \varepsilon'_{ij}E_0 + \frac{3}{4}\varepsilon'_{ijkl}E_0^3 + \frac{5}{8}\varepsilon'_{ijklmn}E_0^5, \\ -A_2\sin\varphi_2 &= \frac{1}{2}\varepsilon'_{ijk}E_0^2 + \frac{1}{2}\varepsilon'_{ijklm}E_0^4 + \frac{15}{32}\varepsilon'_{ijklmno}E_0^6 \\ -A_3\cos\varphi_3 &= \frac{1}{4}\varepsilon'_{ijkl}E_0^3 + \frac{5}{16}\varepsilon'_{ijklmn}E_0^5, \\ A_4\sin\varphi_4 &= \frac{1}{8}\varepsilon'_{ijklm}E_0^4 + \frac{3}{16}\varepsilon'_{ijklmno}E_0^6 \\ A_5\cos\varphi_5 &= \frac{1}{16}\varepsilon'_{ijklmn}E_0^5, \\ -A_6\sin\varphi_6 &= \frac{1}{32}\varepsilon'_{ijklmno}E_0^6 \end{aligned} \quad (8)$$

The A_i and φ_i are experimentally determined; thus, ε'_{ij}, ε'_{ijk}, ε'_{ijkl}, ε'_{ijklm}, ε'_{ijklmn}, $\varepsilon'_{ijklmno}$ can be calculated. In other words, harmonic analysis enables calculation of the dielectric nonlinearity coefficients.

III. Experimental Procedure

Four compositions of PZT samples, as shown in Table I, were fabricated by using a conventional mixed oxide approach. Each powder was ball milled with zirconia media in isopropanol for 24 h. After drying, the mixtures were calcined at 750°–850°C for 2 h. Next, the powders were ball milled for 24 h to achieve a particle size of ~1 μm. Powders were subsequently mixed with 1% (weight) polyvinyl alcohol as a binder and pressed in a steel mold to make disc-shaped samples. Pellets were then fired to 600°C for 2 h to remove the binder, and sintered at 1300°C for 2 h in doubly sealed alumina crucible. To prevent PbO evaporating from the pellets, two $PbZrO_3$ pellets were inserted into the doubly sealed crucible and the sample was buried under powder, which has the same composition as itself. The density of the pellets as measured by the Archimedes method is more than 90% theoretical. As a final step, pellets were electroded with Dupont 7095 Ag/Pd-paste, fired at 575°C, and stored in a humidity control chamber between tests.

Before each test, the pellets were removed from the humidity control chamber to deage and pole. Deaging is the process to depolarize samples. This was done to assure that samples always started from the same condition. In this experiment, deaging was accomplished by heating the samples from room temperature to 450°C, then holding for at least 2 h, and quenching into methanol at 37±2°C. After deaging, samples were poled by applying dc 3 MV/m at 90°C for 20 min. Once the poling process was completed, samples were electrical shorted and the initial starting time, $t = 0$, in the aging experiments was assigned to samples. Next, the samples were placed in 37°C chambers and tested for aging under open circuit of three properties and polarization for the initial 24 h.

(1) Aging of weak-field relative dielectric constant (K_{wf}).
(2) Aging of planar coupling factor (k_p).

Table I. Chemical Compositions of Samples Prepared in This Work

	Name	Abbreviation	Chemical composition
1	Undoped PZT	UPZT	$PbZr_{0.52}Ti_{0.48}O_3$‡
2	Mn-doped PZT	MnPZT	$Pb(Zr_{0.52}Ti_{0.48})_{0.99}\,Mn_{0.01}O_3$
3	Sr-doped PZT	SrPZT	$(Pb_{0.94}\,Sr_{0.06})(Zr_{0.53}Ti_{0.47})\,O_3$‡
4	Nb-doped PZT	NbPZT	$Pb(Zr_{0.52}Ti_{0.48})_{0.976}\,Nb_{0.024}O_3$‡

‡These chemical compositions are based on those of Table 7A, p. 146 of Jaffe et al.[13]

(3) Aging of piezoelectric constant (d_{33}).
(4) Aging of polarization.

Assessment of aging in weak-field relative dielectric constant (K_{wf}) and planar coupling factor (k_p) was performed under weak field (1 V) by an impedance analyzer, while the assessment of aging in the piezoelectric constant (d_{33}) was performed with a Berlincourt Piezo d_{33} meter inside the second temperature control chamber. Tests 1–3 were considered as weak-field or conventional tests of aging because they were performed under field levels that do not change polarization. Weak-field relative dielectric constant (K_{wf}) was calculated from capacitance, which was measured at a frequency of 1 kHz.

Aging of switchable polarization was assessed by applying a pure sinusoidal electric field (0.5 MV/m), frequency 1 Hz, to the samples. Note that between tests, the samples were maintained at 37°C with open circuit conditions. Polarization was measured by using a modified Sawyer–Tower circuit. The effective relative dielectric constant (K_{eff}) was calculated from the slope of Polarization versus Electrical Field plot. The harmonic analyses of the applied electric field and the polarization signals were performed using a diffuse Fourier transform in Autosignal™ Select (Version 1.0 for Windows, © 1999 AISN Software Inc.). This test method was described in detail by Leary and Pilgrim,[10] Leary,[14] DiAntonio[11] and DiAntonio *et al.*[15] Finally, the ε'_{ij} was calculated by Eq. (8), and calculated relative dielectric constant (K_{cal}) was calculated from:

$$K_{cal} = \varepsilon'_{ij}/\varepsilon_0 \tag{9}$$

IV. Results and Discussion

(1) Weak-field or Conventional Test of Aging

Results of the aging of K_{wf}, k_p, and d_{33} studies are presented in Figs. 2–4. From these figures, it can be seen that K_{wf}, k_p, and d_{33} decreased (aged) as a linear function of log time. The aging behavior follows the logarithmic law, and an aging equation can be written as follows[8]:

$$P_t = P_i - A_p \log(t) \tag{10}$$

where P_i is the property, e.g., K_{wf}, k_p, and d_{33} at the beginning of the test (time equal to zero). The relative aging rate is expressed as

$$R_p = \frac{A_p}{P_i} \times 100\,(\%\text{decade}) \tag{11}$$

Equations printed on each line of the figures are the best-fit aging equations of the samples. Aging rates calculated from Eq. (11) are tabulated in Table II.

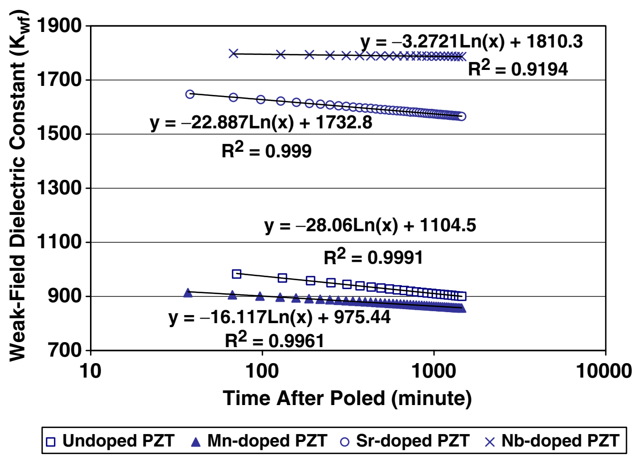

Fig. 2. Aging of weak-field relative dielectric constant (K_{wf}) of PZT samples at 37°C (weak-field method).

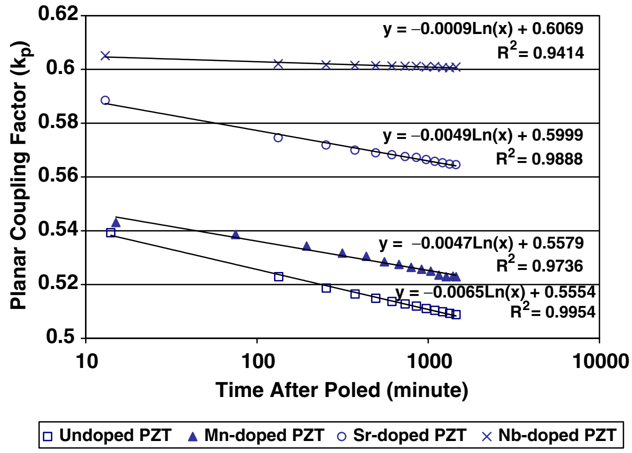

Fig. 3. Aging of planar coupling factor (k_p) of PZT samples at 37°C (weak-field method).

From Table II, aging rates of K_{wf}, k_p, d_{33} for Mn-Doped PZT and Sr-doped PZT were found to be slightly lower than those for undoped PZT, while the aging rate of Nb-doped was substantially lower than undoped PZT. This result is consistent with earlier findings that acceptor doping, e.g., Mn, and isovalent doping, e.g., Sr doping, slightly decreases aging rates of PZT, whereas donor doping, e.g., Nb, significantly decreases the aging rate of PZT.[16–19]

Table III shows the 24 h values of K_{wf}, k_p, d_{33} of the samples aged at 37°C. The k_p values are very close to those reported by other works[16–19] but the K_{wf} and d_{33} are slightly higher. This may be due to the fact that this experiment was performed at 37°C and not at room temperature, as in other works.

(2) Harmonic Analysis Test of Aging

Figure 5 illustrates induced polarization versus applied electric field of UPZT aged at 37°C for different aging times. It can be seen that polarization decreased with time. For clarity, the time domain response of polarization was transformed to the frequency domain and low pass filtered at 6 Hz. The amplitudes of the filtered signals were plotted versus frequency and aging time as shown in Fig. 6. It can be seen for UPZT that: (1) Amplitude of the 1st harmonic was substantially higher than the others. (2) Amplitude 1st and 2nd harmonics decreases with aging time. (3) Amplitude of the 3rd harmonic increases with aging time. Very similar results were found for SrPZT. Substantially similar results were found for MnPZT and NbPZT; the only difference is,

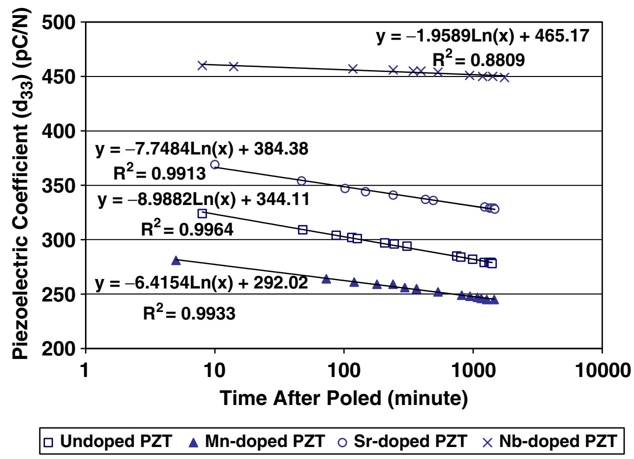

Fig. 4. Aging of piezoelectric coefficient (d_{33}) of PZT samples at 37°C (weak-field method).

Table II. The Aging Rate of K_{wf}, k_p, d_{33} Tested by the Weak-Field Method: K_{eff} and K_{cal} Test by Harmonic Analysis Methods under 0.5 MV/m Applied Field for PZT Samples Aged at 37°C for 24 h

	Weak-field method Aging rate (%/decade) of			Harmonic analysis method Aging rate (%/decade) of	
Materials	K_{wf}	k_p	d_{33}	K_{eff}	K_{cal}
UPZT	5.91	2.69	6.01	12.64	14.27
MnPZT	4.04	1.94	5.06	8.31	10.39
SrPZT	3.16	1.88	4.64	6.90	9.16
NbPZT	0.67	0.34	0.97	1.33	1.61

Table III. The 24 h values of K_{wf}, k_p, and d_{33} Tested by the Weak-field Method: K_{eff} and K_{cal} Test by Harmonic Analysis Method under 0.5 MV/m Applied Field for PZT samples aged at 37°C

	Weak-field method			Harmonic analysis method	
Materials	K_{wf}	k_p (%)	d_{33} (pC/N)	K_{eff}	K_{cal}
UPZT	900	0.51	278	1270	1150
MnPZT	860	0.52	245	1730	1680
SrPZT	1565	0.56	328	2140	1900
NbPZT	1790	0.60	449	3210	3235

The 24 h values of K_{wf}, k_p and d_{33} from Jaffe *et al.*[13] are (1) K_{wf} for UPZT, SrPZT, and NbPZT are 730, 1300, and 1700, respectively; (2) k_p for UPZT, SrPZT, and NbPZT are 0.529, 0.58, and 0.60, respectively; and (3) d_{33} for UPZT, SrPZT, and NbPZT are 223, 289, and 374, respectively.

however, that the amplitude of 1st, 2nd, and 3rd harmonics all decreased with aging.

Harmonic analysis thus suggests that two separate mechanisms are functioning: one in undoped and isovalent-doped PZTs (UPZT and SrPZT) and perhaps two in aliovalent-doped PZTs (MnPZT and NbPZT). Further investigations need to be conducted to confirm this since the amplitude of 3rd harmonic is very small.

Effective relative dielectric constants (K_{eff}) of all PZT samples at different aging times are shown in Fig. 7, and the 24 h values of K_{eff} are tabulated in Table III. Furthermore, calculated relative dielectric constants (K_{cal}) are shown in Fig. 8, and the 24 h values of K_{cal} are tabulated in Table III. From Table III, the K_{eff} and K_{cal} values are higher than the K_{wf} value because there is more extrinsic contribution to K_{eff} and K_{cal} compared with K_{wf}. Moreover, K_{eff} and K_{cal} are obviously different because the harmonics that contribute to K_{eff} and K_{cal} calculations are not the same. For K_{cal}, only the odd harmonics were used in the calculation. However, both odd and even harmonics were used to calculate K_{eff}. The even harmonics in NbPZT are less significant, which is why the K_{eff}–K_{cal} difference in NbPZT is less than the other types of PZT.

Finally, aging rates of K_{eff} and K_{cal} for all samples were calculated and tabulated in Table II. It can be seen that aging rates of K_{eff} and K_{cal} are somewhat more than double the aging rate of K_{wf}. In addition, the aging rates of K_{eff} and K_{cal} are tracked with

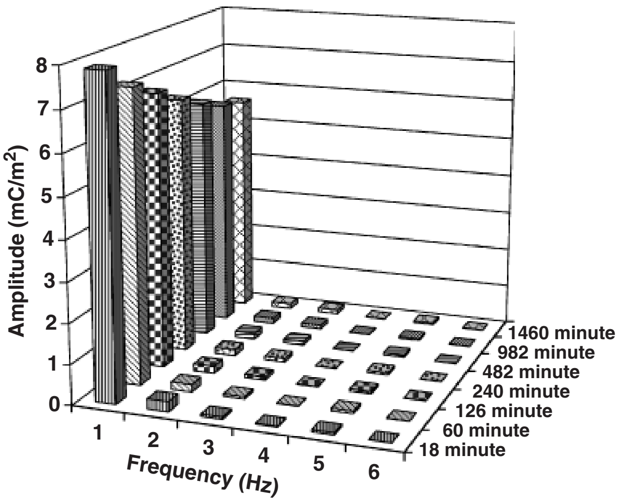

Fig. 6. Frequency domain signal of UPZT aged at 37°C (harmonic analysis method).

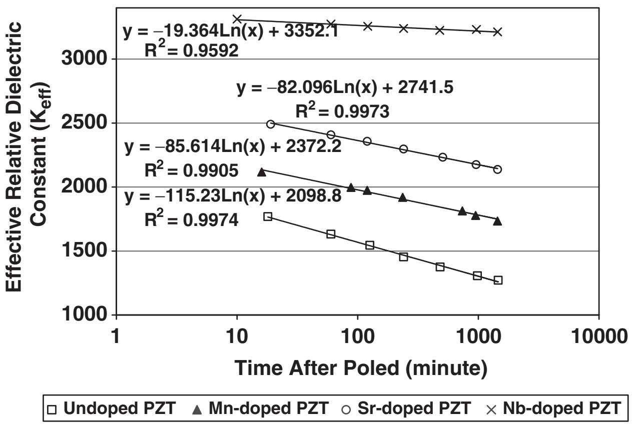

Fig. 7. Aging of effective relative dielectric constant (K_{eff}) of PZT samples at 37°C (hysteresis loop slope) (harmonic analysis method).

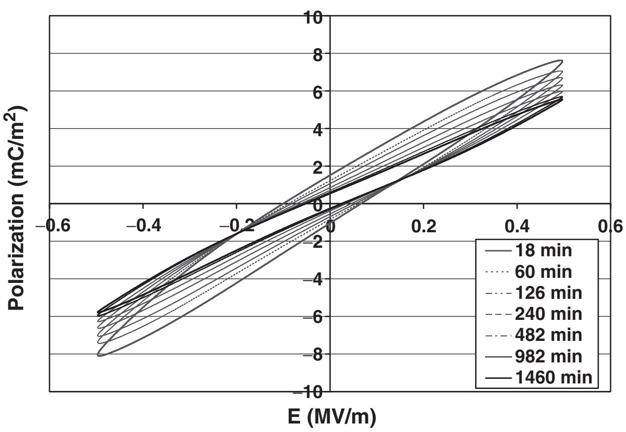

Fig. 5. Polarization versus E-field of UPZT aged at 37°C (harmonic analysis method).

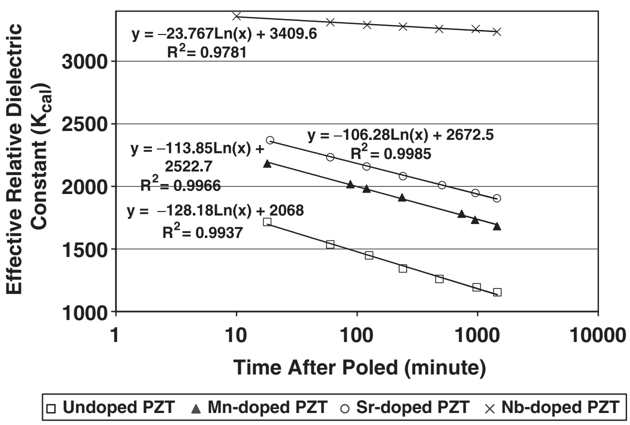

Fig. 8. Aging of calculated relative dielectric constant (K_{cal}) of PZT samples at 37°C (harmonic analysis method).

those of dielectric properties tested by the weak-field method. Although these findings suggest that harmonic analysis can be used to study aging under variable field conditions for both undoped and doped PZTs, this study is restricted to aging for 24 h at 37°C and testing by E-field 0.5 MV/m and 1 Hz. Aging for a longer period is expected to show a similar result because the literature has shown that aging of ferroelectric materials obeys logarithmic law for longer than 24 h. However, further testing using different E-fields is ongoing since it could contribute to a better understanding of the aging of PZTs.

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