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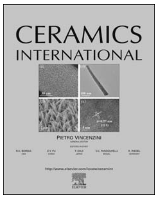

Effects of temperature on aging degradation of soft and hard lead zirconate titanate ceramics

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ABSTRACT

This paper aims to study the effects of heat treatment temperatures on the aging degradation of piezoelectric properties, i.e. piezoelectric coefficient (d_{33}) and planar electromechanical coupling factor (k_p), in soft and hard PZT ceramics. Aging degradations of d_{33} and k_p of the samples were measured for 192 h prior to heat treatments. The samples were then treated at various temperatures equivalent to 0.3, 0.4, 0.5, 0.6, 0.7 and 0.8 times of the materials' Curie temperatures. Aging degradations of d_{33} and k_p of the heat-treated samples were observed continuously for 1128 h. The piezoelectric properties of the un-treated samples gradually decreased with aging time. Attenuation of d_{33} and k_p in the samples immediately after heat treatment increased with increasing heat treatment temperature. Moreover, aging degradation rate and relaxation time of the samples measured after heat treatments increased with increasing heat treatment temperature. Comparing to hard PZT ceramics, soft PZT demonstrated greater change of d_{33} and k_p immediately after heat treatments. Soft PZT also showed greater aging rate and aging time than those of hard PZT. From the overall results, it can be concluded that both material type and heat treatment temperature have effects on aging behaviors of PZT materials. Aging degradation was more pronounced in soft PZT and the samples treated at high temperatures. The observed aging behaviors of PZT materials were explained by the interaction between domains and defects of oxygen vacancies that leads to volume, domain and grain boundary effects.

1. Introduction

Lead zirconate titanate (PZT) is a piezoelectric ceramic with excellent electromechanical properties. It is commonly used in the applications of piezo-transducers, actuators and sensors [1–4], occupying more than 90% of the bulk piezoelectric device market [5]. PZT ceramics are usually glued to other electronic parts using conductive adhesive that can be cured at high temperature. The heat treatment used in such assembly process could cause degradation of piezoelectric properties in the PZT ceramics, subsequently affecting the performance of the devices [6–8]. The adhesive is usually cured at the range of 80–120 °C. Since the working temperature of piezoelectric ceramics cannot exceed 50% of Curie points (T_C), this curing process can accelerate the aging degradation of piezoelectric properties and worsen the performance of actuator [7,8].

Aging degradation of piezoelectric ceramics depends on the material type, poling process, and heat treatment conditions [9,10]. Aging behavior of piezoelectric ceramics can be quantified by a mathematical model based on a stretched exponential decay function [11–14]. To date, few researches have investigated the effects of heat treatment temperature on the aging behavior of piezoelectric ceramics. This work focuses on the effects of heat treatment temperature on the aging degradation of soft and hard PZT ceramics. Heat treatments at different temperatures from 30% to 80% of T_C were applied to the PZT samples. The aging of piezoelectric coefficient (d_{33}) and planar electromechanical coupling factor (k_p) of the PZTs were measured after heat treatment. The mathematical model based on a linear logarithmic stretched exponential function that reflects the polarization-defect dipole interaction during aging was used to describe the effects of temperature on the aging behavior. The results from this work will be

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useful for improving the manufacturing process of PZT actuators.

2. Experiment

Two types of $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) ceramics were used in this study. They were soft PZT that doped with Nb (PZT-5A type), and hard PZT that doped with Fe (PZT-4 type). Curie temperatures (T_C) of the soft and the hard ceramics are 360 and 325 °C, respectively. The ceramics were polished into a pellet shape with thickness of 1 mm and diameter of 10 mm. The ceramics were annealed at 500 °C for 2 h to remove any residual stress due to the polishing process. Silver electrodes were painted on the parallel surfaces using a colloidal silver paste. The samples were submerged in silicone oil and poled under a DC electric field of 3 kV/mm, which is equivalent to 1.7 coercive field (E_c) and $2E_c$ of the soft and the hard ceramics, respectively, for 10 min at 100 °C. Piezoelectric coefficient (d_{33}) and planar electromechanical coupling factor (k_p) of the poled samples were then measured 7 times with time interval of 24 h. After that, the samples were annealed at the temperatures of 30%, 40%, 50%, 60%, 70% and 80% of the ceramics' T_C for 10 min. After heat treatment, the d_{33} and k_p values of the ceramics were measured 7 times with time interval of 24 h. The measurements were continuously performed for 4 times with time interval of 1 week. Six samples from each type of the ceramics were tested to give averaged results on the measured values. The d_{33} values of the samples were measured by a d_{33} meter (APC product inc. S5865). Polarization-electric field (*P-E*) hysteresis loops at different states were measured by a Sawyer-Tower circuit. In the *P-E* measurement, the poled samples were placed into a sample holder, where the positive polarity of the samples was opposite to the positive field. X-ray diffraction (XRD) patterns were collected using X-ray diffraction instrument (D2 PHASER, Bruker, USA). Microstructures of the fracture surfaces were observed by a scanning electron microscope (JSM-6010V, JEOL, Japan). Electrical impedance was measured at the frequency range from 1.5 to 3 kHz via an impedance/gain-phase analyzer (Solartron). The impedance was plotted as a function of frequency by a ZPlot-impedance software. The resonance (f_m) and the anti-resonance (f_n) frequencies, which are the frequencies of the minimum and the maximum impedances, respectively, were applied to calculate a k_p value using the following equation [15],

$$k_p \cong \sqrt{[(2.51(f_n - f_m)/f_n) - ((f_n - f_m)/f_n)^2]} \tag{1}$$

3. Results and discussion

3.1. Piezoelectric coefficient

Piezoelectric coefficient (d_{33}) values of the soft and hard PZT prior to the aging process were measured to be 375 and 315 pC/N respectively, which can be used to normalize the subsequent measured d_{33} values. Plots of the normalized d_{33} values before and after heat treatments at various temperatures are shown in Fig. 1(a) and (b), respectively. For both ceramics, the normalized d_{33} value measured before heat treatment (at aging time < 168 h) decreased gradually with increasing aging time. In this period (aging time < 168 h), aging degradation of the soft ceramic was faster than that of the hard ceramic. The d_{33} of both ceramics decreased rapidly after the heat treatment. The decrease in d_{33} was greater when the ceramics were heat treated at higher temperature. At each heat treatment temperature, change in the normalized d_{33} of the soft PZT is greater than that of the hard PZT. The normalized d_{33} measured after heat treatments (at aging time ≥192 h) of both ceramics decreased exponentially with aging time.

In order to determine the effects of heat treatment temperatures on the aging rates of both ceramics, time dependence of the normalized d_{33} after heat treatments is expressed as a logarithmic function, as in the following equation [16],

$$aging \quad rate = \frac{1}{\log(t_2) - \log(t_1)}\left(\frac{p_2 - p_1}{p_1}\right) \tag{2}$$

where t_1 and t_2 are the numbers of hours just after heat treatment (192 h) and after an aging process (1344 h), respectively. p_1 and p_2 are the piezoelectric properties measured at t_1 and t_2, respectively. Aging rates of the ceramics are listed in Table 1. It shows that for both soft and hard ceramics, aging rate increases with increasing heat treatment temperature. Moreover, aging rate of the soft ceramic is faster than that of the hard ceramic.

In order to determine the aging characteristics, the time dependence of the normalized d_{33} after heat treatments is fitted to an exponential law, as in the following equation [11,13],

$$p_{33} = p_{33_\infty} + p_{33_1}\exp[-(t/\tau)^\upsilon] \tag{3}$$

where p_{33_∞} is the piezoelectric property which is time independent, therefore, the second term on the right-hand side of the equation is also time dependent. t is the aging time. τ is the characteristic relaxation time, which relates to aging rate. υ is the stretching exponent. The fitting parameters of the ceramics are listed in Table 2. Relaxation time τ of the samples heated at higher temperatures are less than those samples heated at lower temperature. At each heat treatment temperature, relaxation time of the soft ceramic is longer than that of the hard ceramic.

3.2. Electromechanical coupling factor

Planar electromechanical coupling factor (k_p) values were normalized to the k_p values measured at the beginning of the aging process. The aging behaviors represented by the normalized k_p values before and after heat treatments are shown in Fig. 2(a) and (b), respectively. For both ceramics, the normalized k_p value degraded rapidly after heat treatment and gradually decreased with increasing aging time. The time dependences of the normalized k_p after heat treatments (at aging time ≥192 h) were fitted to the logarithmic and the exponential functions as in Eqs. (2) and (3), respectively. The fitting parameters are listed in Tables 1 and 2. For both soft and hard PZT ceramics, the aging rate increased while the relaxation time decreased with increasing heat treatment temperature. At each heat treatment temperature, the aging rate and relaxation time of the soft PZT are greater than that of the hard PZT.

3.3. Discussion

Theoretically, three major mechanisms have been proposed to explain the aging behavior of ferroelectric materials [17]. These mechanisms are: (1) defect dipole effect (or volume effect), (2) domain effect, (3) grain boundary interface effect. All these aging mechanisms were mostly dominated by oxygen vacancies formed during the high temperature process. In the case of volume effect, the defect dipole is formed by the different potentials of the polarities between acceptor ions and oxygen vacancies. This defect dipole can interact with the lattice polarization in the domain and thus hinder the polarization switching. For domain effect, oxygen vacancies diffuse toward and pin the domain walls. For gain boundary interface effect, oxygen vacancies further diffuse toward grain boundaries. It is known that the concentration of oxygen vacancies in soft PZT is lower than that in hard PZT [18]. This leads to a lower number of defects that contribute to the aging of the soft PZT as compared to that of the hard PZT. Based on the effects of oxygen vacancies, therefore, the soft PZT could exhibit a greater aging degradation of piezoelectric properties as compared to the hard PZT. An aging model based on the response of oxygen vacancies at different scales, i.e. volume, domain and grain boundary effects is described in the following discussion.