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Effect of electrical fatigue on the electromechanical behavior and microstructure of strontium modified lead zirconate titanate ceramics

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ABSTRACT

The fatigue behavior of strontium doped lead zirconate titanate (PSZT) ceramics is investigated. Different compositions near the antiferroelectric–ferroelectric (AF–F) phase boundary are synthesized by tape casting and sintering route. The influence of electric field-induced AF to F phase transition on piezoelectric and strain behaviors is studied. Very high maximum polarization (~41 μC/cm^2) and ultrahigh strain (0.8%) are seen for some of the PSZT compositions near the morphotropic phase boundary. The samples are subjected to low frequency (30 Hz) electric field up to 10^7 cycles. Although the maximum polarizations of most of the PSZT ceramics showed fatigue-free behavior (less than 10% degradation), the strains in most of them showed degradation as high as over 50%. Electron microscopy of the fractured surface of the electrically cycled samples showed some intergranular fracture below the electroded surface. Results indicated that diffusion of silver electrode into the PSZT ceramics is responsible for the electro-coloration and degradation in strain response with fatigue cycles. Thermal annealing and removal of the damaged layer under the electrode showed the complete recovery of the strain to its original as-sintered value. X-ray diffraction technique is used before and after the fatigue cycles to investigate the influence of electrical cycles on the changes at the crystal structure level, which are also related to the fatigue-induced changes to electromechanical properties of PSZT ceramics.

1. Introduction

Lead zirconate titanate (PZT) ceramics are extensively used as piezoelectric sensors, transducers, and actuators in a variety of applications because of their excellent electromechanical response. There has been great interest in the Zr-rich end of the PZT phase diagram, close to the AF–F phase boundary (Zr/Ti ≈ 95/5), where the switching between AF–F can be accomplished by the application of a suitable electric field, temperature or pressure [1]. Strontium is an antiferroelectric phase stabilizer resulting in a long morphotropic phase boundary (MPB), where phase transition from AF to F can be accomplished by applying an electric field. It is shown that compositions close to the MPB shows polarization as high as 33 μC/cm^2 and field-induced strain as high as 0.5% [2–4]. The reliabilities of these piezoelectric and ferroelectric sensors and actuators depend on the time-dependant retention of their electromechanical properties. The requirement for actuators is 10^5–10^{11} cycles before failure of the device occurs, and the memory devices require life of more than 10^{12} switching cycles. The mechanisms of polarization fatigue are presently not well understood. Fatigue may be due to external driving forces [5], mechanical embrittlement [6], micro- and macrocracking [7]. Fatigue is also agreed to be the result of charge injection and the accumulation of space charge that pins domain switching [8–10]. Some tried to explain fatigue by appearance of microcracks formed during the large change in strain during the continuous switching [5]. Lanthanum doped PZT ceramics near the morphotropic phase boundary showed only 15% loss in switchable polarization under unipolar load after 10^6 cycles, but the degradation reached 30% under bipolar load only after 2×10^5 cycles [11]. It was also shown that purely electrostrictive rhombohedral compositions neither fatigues under bipolar nor unipolar cycling up to 10^6 cycles.

One of the most widely seen degradation mode in ferroelectric ceramics is called "electro-coloration". Two ionic mechanisms have been proposed for dc degradation [12–15]. Protons from water and anion vacancies (oxygen vacancies) are injected from the anode of an open system and they migrate through the grain boundary region towards cathode. These charged species create electronic carriers by reducing Ti^{4+} to Ti^{3+} (dark color) and eventually induced breakdown. The same effect is seen in ac electric field where the polarity changes in every cycle. The electro-coloration has been observed for different electrode materials Al [13], Ag [16,17] and Au [12]. For all the metallic electrode materials, the same results have been observed. In the regions close to the electrodes, the grain boundaries constitute paths of partial conductivity. Oxygen vacancies under applied electric fields are drawn to the grain

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Table 1
Summary of PSZT compositions, simplified forms, density and lattice parameters.

Composition	Simplified form	Density (gm/cm^3)	Theoretical density (gm/cm^3)	Grain size (μm)	Lattice parameters				
					a (Å)	c (Å)	α (°)	c/a	Vol. (Å^3)
$(Pb_{0.9}Sr_{0.1})(Zr_{0.75}Ti_{0.25})O_3$	10/75/25	7.622	7.69	6.78 ± 1.82	4.118	4.118	89.76	1	69.83
$(Pb_{0.9}Sr_{0.1})(Zr_{0.865}Ti_{0.135})O_3$	10/86.5/13.5	7.77	7.9	2.96 ± 0.66	4.158	4.119	90	0.9906	71.21
$(Pb_{0.9}Sr_{0.1})(Zr_{0.9}Ti_{0.1})O_3$	10/90/10	7.78	7.93	2.75 ± 0.74	4.163	4.123	90	0.9903	71.45

boundaries and weaken this part of the microstructure. In the depth of the sample no conducting paths are present. The charged defects agglomerate to planar structures within the grains. These agglomerates, in turn, are responsible for the strongly reduced mobility of the domain system in this part of the sample. During electrical cycles these pinned domains reduce the overall electromechanical behavior of the ferroelectric or electrostrictive ceramics resulting in fatigue. To reduce or eliminate this effect, a series of oxide electrodes have been used [18–21]. A recent study on Sr doped PZT 50/50 thin film has shown that Sr addition enhances the stability of oxygen ions and suppresses the oxygen vacancies [22]. This results in improved fatigue endurance of these thin films. The group found out that with Sr doping, the PZT films are practically polarization fatigue free up to 10^{10} voltage cycles.

Another very important correlation being made to ferroelectric fatigue is the diffusion of electrode material in the ceramic under cyclic electric fields. It has been shown before that silver as an electrode material has a high diffusivity in $(Pb_{0.95}Sr_{0.05})(Zr_{0.53}Ti_{0.47})O_3$ + 1 mol% Nb_2O_5 ceramics and the diffusion path being the grain boundary [23]. The diffusion depth for silver was found to be as high as 1 mm during electroding at 750 °C. With the application of external electric field, diffusion of silver was reported to be more. The diffusion coefficient was found to follow an Arrhenius law with effective diffusion coefficient of silver was calculated to be 3.7×10^{-11} cm^2/s. Silver diffusion was also observed in $(Pb_{0.9}La_{0.1})(Zr_{0.65}Ti_{0.35})O_3$ ceramics using a secondary ion mass spectroscopy study (SIMS) [24]. It was proposed that an interfacial reaction layer is formed when the diffused silver reacts with the bulk PLZT ceramics. Intergranular fracture was also observed in samples where silver had penetrated. They proposed that silver penetration makes the grain boundary weak, resulting in the intergranular fracture.

The objectives of this study are to observe and analyze systematic changes in the electromechanical and other physical properties of Sr modified PZT ceramics up to 10 million electrical cycles at low frequency. Efforts are also been made to clarify and separate the dominant factors for such changes and to understand the mechanism of fatigue degradation.

2. Experimental

Three compositions (△) along the horizontal line were prepared with different Zr/Ti ratio with fixed Sr^{2+} content as shown in Fig. 1. The details of the compositions are provided in Table 1. PSZT powders were prepared through modified mixed oxide route. The details of the preparation is published elsewhere [25]. Polycrystalline PSZT ceramics were prepared by tape casting and sintering route [3,4]. Compositions were selected so that one of them was on the ferroelectric–rhombohedral F_R side $(Pb_{0.9}Sr_{0.1})(Zr_{0.75}Ti_{0.25})O_3$ [10/75/25], one of them on the AF–F boundary $(Pb_{0.9}Sr_{0.1})(Zr_{0.865}Ti_{0.135})O_3$ [10/86.5/13.5], and one totally on the A_T side $(Pb_{0.9}Sr_{0.1})(Zr_{0.9}Ti_{0.1})O_3$ [10/90/10].

The rectangular sintered samples were ground by 600 grit silicon carbide paper to a thickness less than 0.5 mm and polished to mirror finish using diamond polishing paste. The polished samples were chemically etched to reveal a clear microstructure. Grain size and morphology of the individual compositions were measured by SEM analysis. Phase analysis of the sintered samples was done using X-ray diffractometer (Philips X'Pert θ–θ powder diffractometer, 50 mA 40 kV) with Cu Kα radiation in the 2θ range of 20–60° at 0.6°/min. XRD peaks were indexed according to a pseudo-cubic perovskite cell having a structure *P*4*mm*. The unit cell parameters of AF and F phases were calculated from angular positions of (1 1 0), (2 0 0) and (0 0 2) components according to conventional relations for quadratic forms ($1/d^2$) regarding tetragonal and rhombohedral cases [26].

Silver paste was applied to the surfaces and sintered at 550 °C for 30 min to have a continuous electrode. The polarization (P) versus electric field (E) was measured using a modified Sawyer and Tower circuit [2,27]. The voltage was supplied using a high-voltage amplifier (Model 601C, Trek Incorporated). To eliminate arcing, the samples were immersed in an insulating silicon oil (Aldrich Chemical Company). The longitudinal strains of the PSZT ceramics were obtained using MTI-2000 Fotonic Sensor. All P–E and longitudinal strain curves were obtained using an amplified sinusoidal waveform at 0.1 Hz, created by a function generator.

Fatigue tests were done by applying 30 Hz sinusoidal wave at the electric field up to saturation polarization of the materials for 10^7 cycles. The PSZT ceramics were electroded at the faces except near the edge and immersed in Silicone oil for the whole length of the experiment to reduce electric arcing and resultant physical damage to the sample. Polarization and strain data were collected at different time intervals to observe the progressive changes in the electromechanical properties of each of these compositions. After the fatigue cycles, the silver electrodes were removed chemically by using diluted nitric acid solution. This was done to eliminate the mechanical damage and to retain any stress generated during voltage cycling. X-ray diffraction on the cycled samples was done using the same technique as above. Small portions of the sam-

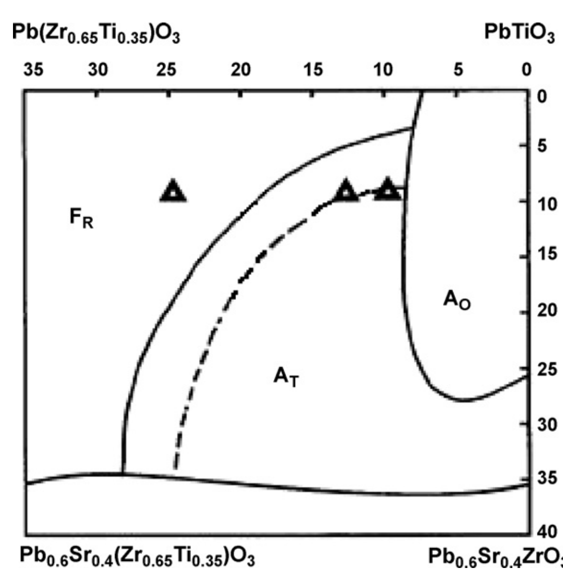

Fig. 1. $PbTiO_3$–$PbZrO_3$–$SrTiO_3$–$SrZrO_3$ phase diagram. The dotted line shows the modified A_T–F_R phase boundary from previous study [2]. (△) indicates the compositions selected.