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# Electrocoloration of donor-doped lead zirconate titanate under DC field stress

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ABSTRACT

Layers of Nd-doped lead zirconate titanate (PZT) with Ag/Pd electrodes were stressed by DC voltage at about 500 °C. Under field, a black "color" front, visible in dark-field optical microscopy, moved from the cathode into the PZT. The PZT layer became highly conducting after some time but degradation was localized to a near-surface zone and could be removed mechanically, leaving an insulating core bulk zone of PZT with the color front still visible. The time-dependent motion of this color front and the electrical properties of the insulating PZT core bulk zone were investigated upon field and during subsequent relaxation. The results suggest that a re-distribution of lead vacancies and built-up of space charge zones at grain boundaries with oxygen vacancy accumulation cause the blackening and conductivity changes. Density of states (DOS) and optical absorption spectra were obtained from density functional theory (DFT) based calculations for several defects in PZT and show that blackening is expected for an increased oxygen vacancy concentration.

## 1. Introduction

Owing to its advantageous ferroelectric, piezoelectric, and pyroelectric properties, perovskite-type lead zirconate titanate (PZT) has found its way into numerous technical applications. PZT is employed in devices as diverse as ferroelectric memories (FeRAM) [1,2], sensor applications [3,4], mobile energy conversion [5], and electrooptics [6]. Particularly in the field of piezoelectric transducers, PZT is the leading material nowadays. Different kinds of bulk and multilayer actuators are used, e.g., for ultrasound generation, nano-positioners, and in fuel injectors for Diesel engines [7,8]. As all applications rely on insulating ceramics, resistance degradation, i.e., the decrease/loss of the insulation resistance upon long times of field stress, is a serious issue limiting the lifetime of electroceramic devices.

Resistance degradation may result from two major sources: first, electrode material may migrate into or onto the ceramics. For operating conditions below 100 °C and some humidity present, especially silver migration from silver-containing electrodes is a well-known phenomenon that leads to dendrite formation at the cathode and finally to electrical shorts [9,10]. Ag filaments were identified as a possible failure mode in PZT capacitors under humid conditions [11]. However, also at higher temperatures (around 500 °C) and thus for negligible humidity-related failure, resistance degradation was reported with silver precipitation on the surface of PZT and along grain boundaries; details on the corresponding degradation mechanism are given in Refs. [12–14]. Similar phenomena with cation motion in oxide thin films and conducive filament formation are further found in room temperature resistive switching cells based on the electrochemical metallization mechanism [15–17].

The second important effect that may cause resistance degradation in oxide electroceramics is the motion of point defects. Oxygen vacancies are of special importance in this respect, as they are generally the most mobile ionic defect much below the sintering temperature of perovskite-type ceramics. Subjected to an electric field, oxygen vacancies can migrate towards the cathode and when being blocked there, characteristic concentration profiles can arise (oxygen stoichiometry polarization). In several studies, the importance of oxygen vacancies in resistance degradation was demonstrated, for example, in acceptor-doped $SrTiO_3$ or $BaTiO_3$ [18–20]. The concentrations of electronic species (holes and electrons) adapt to the changed local oxygen vacancy concentration in order to maintain charge neutrality and the anodic region becomes strongly hole conducting while in the cathodic region high electron conductivity may be found. La-donor-doped $SrTiO_3$, in contrast, does not show resistance degradation since donor doping suppresses the oxygen vacancy formation [18].

PZT and its modifications differ from $BaTiO_3$ or $SrTiO_3$ in that volatile PbO leads to increased and usually unknown cation and anion vacancy concentrations [21]. Hence, even donor-doped PZT may contain oxygen vacancies at a level that might cause significant resistance changes when being redistributed under high fields. In donor-doped PZT under field load, resistance variations up to a factor of about five were reported

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on rather short time scales at high temperatures (ca. 350–500 °C) and attributed to the motion of oxygen vacancies [22,12]. Moreover, by means of impedance spectroscopy, the formation of electroactive interface regions at the electrodes upon cyclic [23,24] or unipolar field stress [25] was shown. However, a major degradation process of donor-doped PZT with silver-containing electrodes at temperatures far above 100 °C is the formation of metallic paths (see above). The relevance of additional defect redistribution in PZT under high fields can easily be masked by the drastic resistance changes due to conductive filament formation, particularly when relying on electrical conductivity measurements only.

Stoichiometry polarization in ionic solids, i.e., the built-up of defect concentration profiles, does not only affect the conductivity but is also often accompanied by changes in the optical appearance (electrocoloration). For $SrTiO_3$ [18], $BaTiO_3$ [26], $LiNbO_3$ [27] and other oxides like yttria-stabilized zircona (YSZ) [28], colored fronts were observed to propagate from the electrodes into the bulk when a voltage was applied. The effects were generally associated with oxygen vacancy motion and their accumulation at the cathode, i.e., with the stoichiometry polarization already discussed above. In PZT, field-induced darkening was also observed at temperatures above the Curie point [22]. Blackening of PZT was further reported to occur without electric field upon annealing in reducing atmospheres [29,30] and was explained by either increased oxygen vacancy concentrations or protons incorporated into the PZT matrix. More systematic investigations on the time, field, and temperature dependence of optical changes in PZT may lead to a substantial gain of knowledge on the motion of defects upon field load and on its relevance for resistance degradation.

In this study, we analyzed color changes in donor-doped PZT layers with Ag containing electrodes at elevated temperatures (above the Curie temperature). Strong resistance degradation due to metal filament formation in near-surface regions are only briefly touched upon; the corresponding results are detailed in a recent series of publications [12–14]. Rather, focus is laid on the processes taking place in the core bulk, which remained highly resistive during resistance degradation of the PZT layer. In order to identify defects or defect complexes that could explain the experimental observations, we further performed *ab initio* density functional theory (DFT) calculations on PZT with a composition of $Pb(Ti_{0.5}Zr_{0.5})O_3$, i.e., near the morphotropic phase boundary, using WIEN2k—an augmented plane wave plus local orbitals program for calculating crystal properties [31–34].

## 2. Experimental

### 2.1. Sample preparation

Samples for degradation experiments were prepared from 1.5 mol% Nd donor-doped PZT multilayer actuator stacks (Epcos OHG, Member of TDK-EPC Corporation, Deutschlandsberg, AT). The polycrystalline PZT layers had a thickness of 80 μm and were separated by interdigital electrodes of silver/palladium (ratio 75/25). Pieces of about $7 \times 5 \times 1$ $mm^3$ were cut from a stack using a Silicon Carbide Cut-off Wheel 10S15 (Struers, Denmark) in a Struers Secotom-10 (feed rate ~0.05 mm/s; Struers, Denmark). In order to access each PZT layer individually, the current collectors of the stacks were removed. Hence, degradation experiments could be separately performed on numerous individual layers within a single sample. Top and bottom sides of the samples were ground manually with SiC grinding paper nos. 1000, 2400, and 4000 (Struers, Denmark) and sometimes additionally polished with 1 μm diamond suspension (DiaPro Nap B; TegraPol-31 in manual operation; Struers, Denmark). Polished samples were cleaned with acetone for 30 s in an ultrasonic bath. A sketch of the resulting sample and the measuring procedure is shown in Fig. 1.

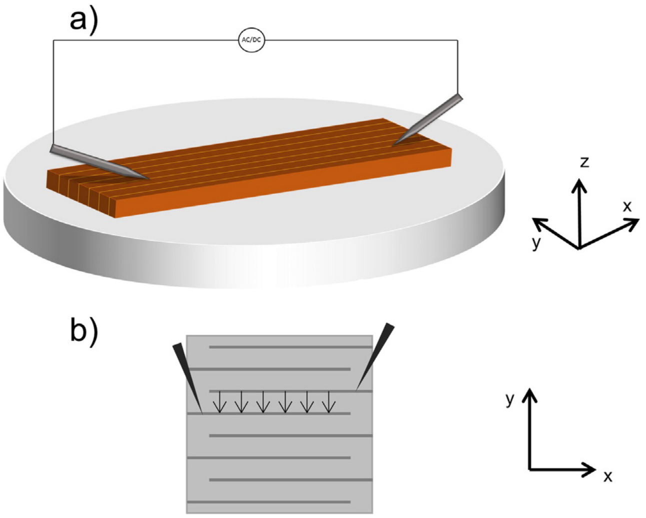

**Fig. 1.** (a) Experimental setup with a PZT sample in a typical capacitor design including interdigital electrodes of a Ag/Pd alloy. The sample is located on a heating stage, tungsten carbide (WC) probe needles were used for contacting the electrodes. (b) Top view of the PZT sample with direction of the applied electrical field.

### 2.2. Field load and resistance degradation

Degradation experiments were carried out in ambient atmosphere. Samples were placed on a ceramic heating stage (Linkam, UK) (see Fig. 1), heated up to a fixed temperature (mostly 500 °C set temperature of the ceramic heater) and (thermally) equilibrated for about 10 min. Note that samples were only heated from the bottom side and hence the top side had a lower temperature due to heat dissipation. The difference to the set temperature is in the range of 30 °C [22,35]. Temperatures stated in the following are set temperatures.

Two adjacent inner electrodes, i.e., one individual PZT layer of the stack, were contacted by tungsten carbide needles (American Probe & Technologies, USA) using micro-manipulators (cf. Fig. 1). During contacting and degradation, the samples were observed via an optical microscope (Mitutoyo, Japan) placed above the heating stage. Before applying a DC load, impedance spectra were acquired with an Alpha-A High Resolution Dielectric Analyzer (Novocontrol, Germany) in the frequency range of $10^6$ Hz to 1 Hz with a rms voltage of 0.01 V. Impedance spectra were evaluated by complex non-linear least square fitting (CNLS) using the software ZView (Scribner, USA).

For the actual degradation, a 2611 System SourceMeter (Keithley, USA) was connected to the sample. An additional series resistor of 100 Ω was employed in order to limit heat dissipation in the final phase of the degradation. Voltages U between 2 V and 100 V were chosen and held constant during degradation. For many experiments, U was set to 10 V, corresponding to an electric field of 1250 kV/cm. Currents ($I$) were limited to $I_{max} = 100$ mA by the hardware—i.e., the voltage was reduced automatically as soon as $I > I_{max}$. For data analysis, sample resistances were calculated according to Ohm's law $R = U/I$, the respective 100 Ω series resistance was subtracted. When the stressed layer reached a stable low-ohmic state, degradation was stopped by quenching to room temperature: contact needles were removed and the sample transferred to a metal surface within 10 s.

### 2.3. Optical and electrical characterization of the degraded layer

Further investigation took place on quenched samples at room temperature after completed degradation. The optical appearance of stressed layers was analyzed by an AxioImager M1m microscope (Zeiss, Germany) in bright-field and dark-field mode. Images of different magnification (50-fold to 500-fold) were acquired with an