Oxygen ion conduction in Nd\(^{3+}\)-doped Pb\((\text{Zr}_{0.5}\text{Tl}_{0.5})\)O\(_3\) (PZT) was investigated by impedance spectroscopy and \(^{18}\)O-tracer diffusion with subsequent secondary ion mass spectrometry (SIMS) analysis. Ion blocking electrodes lead to a second relaxation feature in impedance spectra at temperatures above 600\(^\circ\)C. This allowed analysis of ionic and electronic partial conductivities. Between 600\(^\circ\)C and 700\(^\circ\)C those are in the same order of magnitude (10\(^{-5}\)-10\(^{-7}\) S/cm) though very differently activated (2.4 eV vs. 1.2 eV for ions and electron holes, respectively). Oxygen tracer experiments showed that ion transport mainly takes place along grain boundaries with partly very high local ionic conductivities. Numerical analysis of the tracer profiles, including a near-surface space charge zone, revealed bulk and grain-boundary diffusion coefficients. Calculation of an effective ionic conductivity from these diffusion coefficients showed good agreement with conductivity values determined from impedance measurements. Based on these data oxygen vacancy concentrations in grain boundary and bulk could be estimated. Annealing at high temperatures caused a decrease in the grain-boundary ionic conductivity and onset of additional defect chemical processes near the surface, most probably due to cation diffusion.

I. Introduction

Large band gap perovskite-type oxides play a functional role in many technological devices such as PTC resistors and multilayer capacitors,\(^1\) generators, motors, ultrasonic transducers, actuators, capacitors, or nonvolatile memories.\(^2\) The analysis of the ionic and electronic conductivity in these oxides is of high relevance for establishing, optimizing, and retaining their functionality. High temperatures (e.g., during production) as well as high electrical driving forces (under working conditions) have a strong influence on the local defect concentrations and thus on the partial conductivities of the charge carriers. For several prominent perovskite-type materials like barium titanate and strontium titanate (STO) many defect chemical studies are available, dealing with defect concentrations and transport properties, but also with field-induced defect chemical phenomena such as stoichiometry polarization and resistance degradation, see Refs. [4–14]. In lead zirconate titanate (PZT), defect-related properties, such as the mixed ionic and electronic conductivity are much less understood, despite their importance for example in piezoelectric applications. This lack of knowledge is partly caused by the limited control of cation stoichiometry due to PbO losses.

Recently, however, an increasing number of studies dealt with the defect chemistry and ion conduction in both nominally undoped and donor-doped PZT.\(^{15–21}\) Defect chemical analysis upon partial pressure changes revealed electron hole conduction not only in nominally undoped PZT,\(^{15}\) but also in nominally donor-doped PZT.\(^{16}\) Impedance measurements on La\(^{3+}\)-doped PZT were interpreted in terms of blocking grain boundaries and hole conduction despite donor doping.\(^{15}\) Impedance spectroscopy is also a powerful tool to separate the electronic and ionic conductivity of a material. Blocking of one charge carrier at the electrodes causes a second relaxation feature\(^{22}\) and in case of Nb\(^{5+}\)-doped PZT this method indeed allowed quantification of ionic and electronic conductivities.\(^{22–24}\) Information on ion transport properties can further be gained from \(^{18}\)O-tracer exchange experiments, and a study on donor-doped PZT at temperatures above 600\(^\circ\)C revealed fast oxygen ion diffusion in near-surface regions and along grain boundaries, but also some ion diffusion in the grain bulk.\(^{20,24}\) The presence of mobile oxygen vacancies in donor-doped PZT can be understood in terms of PbO evaporation during sample preparation or operation\(^{18}\) according to

\[
\text{Pb}_\text{O} + \text{O}_\text{O} \rightarrow \text{V}_\text{Pb} + \text{V}_\text{O} + \text{PbO}^+. \tag{1}
\]

Equilibration with ambient oxygen may consume oxygen vacancies via

\[
\frac{1}{2} \text{O}_2 + \text{V}_\text{O} \rightarrow \text{O}_\text{O} + 2h \tag{2}
\]

and therefore hole conduction can result despite donor doping. According to Eq. (1) some oxygen vacancies are expected in any PZT material, but very little knowledge is available on the absolute amount of vacancies and the exact contribution of bulk and grain boundaries to the total ionic conductivity in PZT.

In this study, we combine impedance spectroscopy (IS) and \(^{18}\)O-tracer exchange measurements with subsequent secondary ion mass spectrometry (SIMS) to address the issues of ionic defects and ion conduction in Nd\(^{3+}\)-doped PZT. Information on electronic and ionic conductivity and their time dependence could be gained from impedance measurements using ion blocking electrodes. In conjunction with the numerical analysis of tracer diffusion profiles, the contribution of grain boundaries to ion conduction could be quantified and defect concentrations could be estimated.

II. Experimental Procedure

(1) Sample Preparation and Impedance Measurements

The polycrystalline PZT (EPCOS OHG, a TDK Group Company, Deutschlandsberg, Austria) consists of 1.5 mol\%

Manuscript No. 36451. Received February 17, 2015; approved June 20, 2015.

H. Chan—contributing editor
Nd-doped Pb\((\text{Zr}_{0.5}\text{Ti}_{0.48})\)O\(_3\) (PZT) in a multi-layer design with 80 µm layer width and Ag/Pd (80/20) inner electrodes. The dopant (Nd\(_2\)O\(_3\)) and a Pb excess of 2 mol% was added during PZT powder preparation, that is, before calcination. The sample was sintered in air at 1100°C together with the inner electrodes, resulting in a ceramic with about 1.3 µm average grain size \((d_{\text{grain}})\), see Fig. 1(b). Pieces of ~8 mm × 8 mm × 1.5 mm were cut from a multilayer stack, resulting in the sample geometry sketched in Fig. 1(a). For surface polishing, diamond suspensions (Dia Pro 9, 3 and 1 µm, Struers, Willich, Germany) were used with MD-disk Largo on a Planopol-3 Pedemax polishing machine (Struers). Contacting for electrical measurements was established on the current collecting outer metallization and thus several PZT layers (about 10 to 20, depending on the size of the sample) were measured in parallel. The sample was heated in ambient air to temperatures between 350°C and 710°C, controlled by a thermocouple positioned next to the sample. After temperature stabilization of ±0.5°C impedance measurements were performed in the range of 10^6 Hz–10^9 Hz using a N4L PSM 1735 frequency analyzer (Newtron4th Ltd, Leicester, UK) with IAI - Impedance Analysis Interface (Newtron4th Ltd) at an amplitude of 100 mV. The impedance measurements were repeated automatically in intervals of 60 s time and 900 s for short-time and long-time measurements, respectively.

(2) 18O Diffusion Experiments and ToF-SIMS Analysis

Information on the oxygen diffusivity of the Nd\(^{3+}\)-doped PZT samples was gained by tracer oxygen exchange experiments and subsequent time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis. The 18O\(_2\) employed for tracer diffusion was purchased from Campro Scientific GmbH (Berlin, Germany) (97.1 atm%; 99.7 vol% chemical purity). To avoid significant changes in the 18O\(_2\) partial pressure during the experiment, the tracer amount in the gas phase was very large compared to the oxygen needed for tracer exchange.\(^{25}\) Two types of measurements were performed:

1. Heating to temperatures between 600°C and 710°C and 18O-tracer exchange was performed for 30 min immediately after reaching constant temperature.
2. Tracer exchange after different annealing times at about 670°C in ambient air (after 1 h, 1 d, 1 week, 3 weeks of annealing). The actual tracer exchange experiments at 670°C took again 30 min.

For each tracer experiment an evacuation step of several minutes was used to reach a pressure of about 10^-7 bar and 18O\(_2\) atmosphere was then established at a partial pressure of 200 mbar. After 30 min in 18O\(_2\) the samples were quenched to room temperature in 18O\(_2\) atmosphere. As evacuation was performed at annealing temperatures, chemical oxygen diffusion processes could not be avoided, but all measured tracer concentrations were so high that any effect caused by chemical 18O diffusion to equilibrate the oxygen stoichiometry in the sample can safely be neglected.

To obtain 18O depth profiles, a TOF-SIMS 5 instrument (ION-TOF, Münster, Germany) was used with a pulsed bismuth primary ion gun (25 keV, Bi\(^{+}\)) working in the “Collimated Burst Alignment” (CBA) mode.\(^{26,27}\) Applying the CBA mode enables an accurate determination of oxygen isotopic fractions and an improved lateral resolution. The 18O fraction \(f_{18O}\) is given by the experimentally obtained 16O\(^-\) and 18O\(^-\) secondary ion intensities \((I_{16O}, I_{18O})\) according to:

\[
 f_{18O} = \frac{I_{18O}}{I_{16O} + I_{18O}}. 
\] (3)

During analysis the primary ion gun scanned a “field-of-view” of 1024 × 1024 pixel, typically in the range of 50 µm × 50 µm, that is, an area within a single PZT layer of the multilayer stack. For depth profiling (up to 1.5 µm) a 2 keV Cs\(^+\) sputter gun rastered an area of 400 µm × 400 µm. The depth of the tracer profiles was calculated by normalizing the sputter times to the sputter crater depths, measured by means of a ZEISS Axio CSM-700 microscope (Oberkochen, Germany). As PZT is poorly conductive, a 20 nm gold layer was sputtered onto the PZT surface (BAL-TEC MED 020 Coating System, BAL-TEC, Germany) and charge compensation was achieved by an electron flood gun (20 eV).

III. Results and Discussion

(1) Analysis of the Partial Conductivities by Impedance Spectroscopy

Impedance spectra were measured at temperatures from 350°C to 710°C. Up to ~600°C only one semicircle can be found in the Nyquist plot, cf. Fig. 2. In this temperature regime the spectra were fitted to a parallel connection of a resistor \(R\) and a constant phase element (CPE) with impedance:

\[
 Z_{\text{CPE}} = \frac{1}{(\text{CPE})^{\text{n}}}Q. 
\] (4)

Fit parameters \(n\) (≈0.93) and \(Q\) can be used to determine a capacitance according to Ref. [28]. The resulting relative permittivity of 830 at 600°C is a reasonable value for a bulk response of PZT.

![Fig. 1. (a) Geometry of the multilayer Ag/Pd-PZT samples (b) SEM image of a part of the PZT layer (thermally etched) for illustrating the microstructure. The average grain size is about 1.3 µm.](image-url)
At temperatures above 600°C two semicircles become visible, see Fig. 2. The small second arc reaches its peak frequency (~10 mHz at 617°C) at measurement frequencies for which at 600°C not even the onset of a second arc is found. From this we conclude that indeed a new feature evolves above 600°C, rather than detecting an always existing second arc that only has been missed at lower temperatures due to the limited frequency range. When roughly analyzing the second arc in terms of an R-CPE element, capacitances of approximately 20 mF/cm² are found. A brick layer model with resistive grain boundaries as the cause of the second arc would thus suggest a grain-boundary thickness in the 0.1 pm range which is far from any realistic value. Hence, an interpretation of the arc in terms of blocking grain boundaries can be excluded in our case, in contrast to a study of La-doped PZT where indeed resistive grain boundaries were found below 500°C. The same is true for an interpretation as Schottky contact at the electrodes: again the measured capacitance is by far too large.

A second semicircle was also found in Ref. [23] for 0.75% Nb-doped PZT and was interpreted in terms of a model with blocked ion conduction at the electrodes and thus a different low and high-frequency sample resistance. The buried Ag electrodes used in our study can also be expected to block ions. Therefore, we interpret our spectra as a result of mixed conduction of oxide ions and electrons with the ionic part being blocked at the metallic (Ag/Pd) electrodes. The meaningfulness of this analysis will be discussed below.

The situation of a mixed conductor with one charge carrier being blocked at the electrodes was treated in detail in a continuum model by Jamnik and Maier. Mobile charge carriers being blocked at the electrodes was treated in detail in a continuum model by Jamnik and Maier. The meaningfulness of this analysis will be discussed below.

The buried Ag electrodes used in our study can also be interpreted as Schottky contact at the electrodes. Depend- ing on the mobilities and concentrations of charge carriers, different simplifications of the model are possible as detailed in Ref. [22]. Chemical capacitances much larger than the double layer capacitance (Cchem ≫ Cion⊥⊥), which is fulfilled in our case, allow an analytical representation of the transmission line Fig. 3(a). The corresponding impedance $Z$ is then given by

$$Z = R_{eon/ion} + (R_{eon} - R_{eon/ion}) \tanh \frac{\sqrt{\frac{\text{ion}}{R_{eon}}}}{\sqrt{\frac{\text{ion}}{R_{eon}}}}$$

$$= R_{eon/ion} + (R_{eon} - R_{eon/ion}) \tanh \frac{\sqrt{\text{R}_{chem}(R_{eon} + R_{ion})}}{\sqrt{\text{R}_{chem}(R_{eon} + R_{ion})}}$$

(5)

The serial resistor in Eq. (5), $R_{eon/ion}$, refers to the sample resistance relevant for high frequencies, that is, a parallel connection of the electronic ($R_{eon}$) and ionic ($R_{ion}$) resistances:

$$R_{eon/ion} = (R_{eon})^{-1} + (R_{ion})^{-1}$$

(6)

$L$ is the sample (PZT layer) thickness (80 μm) and $D_{chem}$ the chemical (ambipolar) diffusion coefficient of electronic and ionic species. The second term in Eq. (5) corresponds to a finite Warburg impedance. $W_s$ with a DC resistance ($R_{eon} - R_{eon/ion}$) and thus the circuit of Fig. 3(a) can be simplified to Fig. 3(b). When applying this model to our experimental data, an additional offset resistor and an inductance, both caused by wiring and contacts, have to be added and a CPE instead of the geometrical capacitance $C_{geo}$ is used. A good agreement between fit data according to the circuit in Fig. 3(c) and measured data is found [Fig. 4(a)]. The remaining deviations, especially at the onset of the second arc may result from nonideal electrodes with some resistance for electron transfer.

For an interpretation of the resistance contributions, the spectrum is again plotted in Fig. 4(b) after subtracting the measurement artifacts of $R_{offset}$ and $L_{setup}$. The DC resistance reflects the current carried by electronic charge carriers—here electron holes—and thus equals $R_{eon}$. The diameter of the high-frequency arc represents the resistance with both ionic and electronic rail being effective, that is, $R_{eon/ion}$. The size of the second arc can therefore be interpreted as the resistance reduction by including the ionic rail for high frequencies. Thus, it is possible to determine the ionic resistance and also the ionic conductivity from the impedance data.
Eq. (6) we obtain:

$$R_{\text{ion}} = \frac{R_{\text{eon}}/\text{ion} \cdot R_{\text{eon}}}{R_{\text{eon}} - R_{\text{eon}}/\text{ion}}$$

(7)

with $R_{\text{eon}}/\text{ion}$ and $R_{\text{eon}}$ being available from the fit result. $R_{\text{eon}}$ and $R_{\text{eon}}$ can now be used to determine the ionic ($\sigma_{\text{ion}}$) and the electronic ($\sigma_{\text{eon}}$) conductivity of PZT. In the specific case at 707°C we get $\sigma_{\text{ion}} = 2.5 \times 10^{-5} \text{ S/cm}$ and $\sigma_{\text{eon}} = 4.6 \times 10^{-5} \text{ S/cm}$ and thus a total conductivity of $7.1 \times 10^{-5} \text{ S/cm}$. This analysis can be done for all temperatures above 600°C and thus we obtain an Arrhenius plot of electronic and ionic conductivities [Fig. 5]. For temperatures of 600°C and lower only one arc is found and interpreted in terms of electronic conductivity; those data are also plotted in Fig. 5(a). Most probably this electronic conductivity is carried by holes; this is concluded from a recent study on the partial pressure dependence of a very similar PZT composition. Hole conduction is caused by a surplus of cation vacancies compared to the donor doping due to PbO evaporation during sintering.

All conductivity values are considered to represent PZT samples with frozen-in cation defect concentrations—determined during sintering—and oxygen surface exchange frozen-in due to measurement times being small compared to the time needed for complete oxygen equilibration. The ionic conductivity exhibits a high activation energy of 2.36 eV, compared to the electronic activation energy of 1.19 eV. Similar activation energies of electron conduction in PZT are reported in literature, with values mostly in the range of about 1 eV and this suggests a trapping reaction being involved, rather than only hopping conduction. However, ionic conductivity is much higher activated in our material compared to the few existing literature data, where values between 0.6 and 1 eV are reported in the range from 500°C to 700°C. Different doping situations (acceptor vs. donor doped) and preparation routes may lead to very different activation energies for ionic conductivity. Furthermore, the location of ionic conductivity (grain or grain boundary) may differ from that in our study, see detailed analysis below. Our high ionic activation energy is also the reason for no longer finding an ionic contribution in spectra measured at lower temperatures.

From the fit model in Fig. 3(b) and Eqs. (5) and (6) it is possible to extract the chemical capacitance $C_{\text{chem}}$ of our PZT sample. The chemical capacitance mainly reflects the concentration of the minority charge carrier involved in stoichiometry changes and assuming this to be oxygen vacancies we get.

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Fig. 4. (a) Impedance response of a PZT sample (several layers) at 707°C (symbols) and fit result from the equivalent circuit Fig. 3(c) (red line). (b) Interpretation of the resistive contributions according to Ref. [22]; $L + R_{\text{offset}}$ are subtracted.

Fig. 5. (a) Arrhenius plot of electronic and ionic conductivity obtained by IS measurements. Electronic and ionic conductivity exhibit activation energies of 1.19 and 2.36 eV, respectively. Value pairs between 613°C and 707°C are from a fit to the circuit model in Fig. 3(c). Electronic conductivities without ionic counterpart (600°C and below) are obtained from the single semicircle in the complex impedance plane (b) Arrhenius plot of $C_{\text{chem}} \cdot T$ normalized to the sample volume in the temperature range with measurable ionic conductivity.
with $V$ denoting the volume of the sample, $T$, $e$, and $k_b$ the annealing temperature, elementary charge and Boltzmann’s constant, respectively, and $c_V$ the oxygen vacancy concentration. All chemical capacitance values are shown in an Arrhenius-type diagram in Fig. 5(b), $C_{chem}$ and $T$ exhibits much larger scatter than $R_{ion}$ (for unknown reasons) but still a trend is given and nominally a temperature dependence with an activation energy of 1.07 eV. At 673°C, for example, Eq. (8) yields an oxygen vacancy concentration of about 4.6 ppm with respect to oxide ion sites.

The ionic conductivity is given by

$$\sigma_{ion} = 2 \cdot e \cdot c_V \cdot \nu_v$$

(9)

and includes two temperature-dependent terms: mobility $\nu_v$ and $c_V$. As $c_V$ is proportional to $C_{chem}$, the difference in activation energy of $\sigma_{ion}$ and $C_{chem}$ has to be attributed to $\nu_v$. We get a difference of 1.3 eV and taking into account that $C_{chem}$ values significantly scatter, this is acceptably close to typical values found for $\nu_v$ of perovskite-type materials (0.7...0.9 eV$^{10(1)}$). From Eq. (9) and the calculated $c_V$ value, the mobility $\nu_v$ for oxygen vacancies can be estimated to $1.5 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ at 673°C. Nernst–Einstein’s equation $D_V = (\nu_v k_b T)/(2e)$ can now be used to determine the oxygen vacancy diffusion coefficient $D_V$ and we finally receive a diffusion coefficient of $D_V = 6.3 \times 10^{-6}$ cm$^2$s$^{-1}$ for 673°C.

However, this analysis according to Ref. [22] is based on the assumption of ion conduction in the bulk of PZT without fast grain-boundary transport. A situation with fast ionic transport in grain boundaries, electron conduction primarily in the grain bulk and the chemical capacitance being mainly determined by oxygen vacancies in grain boundaries should lead to the same equivalent circuit model. Then the activation energy of $C_{chem}$ ($c_V$) could reflect an internal defect chemical reaction. In the case of fast ionic grain-boundary transport, only the volume of grain boundaries has to be considered in Eq. 8 and thus the vacancy concentration (in grain boundaries) would be larger than 4.6 ppm by a factor of $d_{grain}^{-2}$ (i.e., ~1000 ppm assuming a grain-boundary width $d$ of 2 nm). Accordingly, $\sigma_{ion}$ from $R_{ion}$ has to be referred to the grain-boundary area and the local grain-boundary conductivity $\sigma_{gb}$ would then be enhanced by $d_{grain}^{-2} \approx 325$, that is, $\sigma_{gb} = 3.2 \times 10^{-2}$ S/cm for 673°C. Then for vacancies in grain boundaries $\nu_v = 2.3 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ and $D_V = 9.5 \times 10^{-6}$ cm$^2$s$^{-1}$ result. Both cases, that is, grain-boundary conduction and grain conduction, lead to very realistic $\nu_v$ values for perovskite-type oxides ($\nu_v$ in STO is $\approx 3 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ for 673°C$^{10(1)}$).

(2) Analysis of Oxide Ion Transport by Oxygen Exchange Experiments

In order to get a more detailed mechanistic insight into oxide ion conduction in PZT, $^{18}$O-tracer exchange experiments were performed between 500°C and 676°C. The resulting $^{18}$O-tracer profiles were monitored by ToF-SIMS. Figure 6 shows results of $^{18}$O-tracer exchange experiments performed at these temperatures in linear and logarithmic plots. Neither of the curves can be described by the simple solution of the diffusion equation

$$\frac{\partial f_{18O}}{\partial t} = D \frac{\partial^2 f_{18O}}{\partial x^2}$$

(10)

$x = \text{depth}$, $t = \text{diffusion time}$, $D = \text{homogeneous diffusion coefficient}$ with a surface exchange factor $k$, that is, by

$$f_{18O} - f_{18O}^0 = \left(1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right) - \frac{e^{x^2/2}}{\left[1 - \left( \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) + k \sqrt{t/D} \right) \right]}$$

(11)

with $f_{18O}^0$ being the fraction of tracer oxygen in the gas phase and $f_{18O}^0$ the natural abundance of tracer oxygen. For low temperatures at least the near-surface part can be approximated by Eq. (11) (exact procedure is shown below). However, deviations are found in some depth, the natural abundance level is not reached. The high-temperature profiles are partly rather box-like close to the surface and thus far from shapes expected for Eq. (11).

Pronounced box-like profiles were also reported in Ref. [24] for similar PZT samples and were interpreted in terms of a near-surface space charge layer. An accumulation of oxygen vacancies in this zone was assumed to be responsible for the increased tracer fraction in the vicinity of the surface. At first glance the substantial width of the box-like profile part in Fig 6 seems to be too large for a space charge layer. However, the majority charge carriers, that is, Nd$^{3+}$ dopants and the charge balancing cation vacancies, are expected to be frozen-in at the diffusion temperature (at least on the time scale of 30 min). Therefore, the Debye length ($\lambda$), which can be used to estimate the space charge width, becomes determined by a minority charge carrier, either oxygen vacancies or electrons or electron holes. Electron holes result from the slight excess of cation vacancies compared to donor dopants due to PbO evaporation during sintering (see above) but depending on temperature also electrons may be relevant. The Debye length is defined as

$$\lambda = \left( \frac{e k_b T}{2\epsilon \nu_v \epsilon_0} \right)^{1/2}$$

(12)

with $\epsilon$ being the absolute permittivity, $z$ the relative charge, and $\epsilon_0$ the bulk concentration of the accumulated charge carrier. For a bulk oxygen vacancy concentration of 2 ppm and $\nu_v$ of about 830, for example, we get a Debye length of approximately 220 nm at 600°C.

We regard it as highly probable that also in our case the near-surface part of the high-temperature profiles reflects a space charge zone with varying oxygen vacancy concentration $c_V$. Therefore, the tracer diffusion coefficient ($D^*$), being a function of the vacancy concentration ($D^* = f_e D_k c_V$ with correlation factor $f_e$), becomes spatially varying, according to

$$D^*(x) = D_k \frac{c_V(x)}{c_V(\infty)}$$

(13)

While analytical fit models cannot be used for extracting the bulk diffusion coefficient $D_k$ numerical analysis of the profiles including space charge layers is still possible. The exact function describing $c_V(x)$ depends on the type of space charge, that is, whether there is an accumulation or depletion of the space charge determining charge carriers or even an inversion layer.$^{30}$ Several situations may cause an accumulation of oxygen vacancies and owing to the lack of knowledge regarding the space charge determining charge carriers in our samples, we assume a Gouy–Chapman-type approximation of the oxygen vacancy accumulation in accordance with Ref. [24]. This means that the surface is negatively charged, whereas the space charge is positive, a situation not uncommon in donor-doped perovskites, cf. PTC resistors.
The solution of Poisson’s equation leads to the concentration distribution of the accumulated charge carrier (here) according to

\[ \frac{c_v(x)}{c_v(\infty)} = \left( \frac{D_b^*}{D_b} \right)^{\frac{1}{2}} \left( \frac{\exp(\xi) + \theta}{\exp(\xi) - \theta} \right)^{\frac{1}{2}} \]

(14)

with \( \xi \) being \( x/\lambda \) and \( \theta \) defined as

\[ \theta = \tanh \left( \frac{e(\Delta \phi^0)}{2k_bT} \right) \]

(15)

Symbol \( \Delta \phi^0 \) denotes the space charge potential. In the following analysis, the more box-like near-surface profiles were thus quantified by numerically solving Fick’s second law of diffusion

\[ \frac{\partial c_v}{\partial t} = D^* \left( D_b^* \frac{\partial c_v}{\partial x} \right) \]

(16)

with \( D^* \) from Eq. (14) and appropriate initial and boundary conditions, including an oxygen exchange factor at the surface due to limited surface kinetics \( (k*) \). \( D_b^*, \Delta \phi^0, k^* \) and the Debye length \( \lambda \) were the free parameters in the corresponding finite element calculations (COMSOL AB, Stockholm, Sweden) and were varied to get an agreement between measured near-surface profile and calculated profile.

The long diffusion tails with substantial tracer concentrations strongly resemble those usually found in samples with fast grain-boundary diffusion. Indeed, similar to measurements in Ref. [24] a spatially resolved \(^{18}\)O-distribution image measured at 676°C unambiguously shows high tracer concentrations in grain boundaries, see Fig. 7, and proves existence of fast grain-boundary diffusion. This fast transport may either take place in the core of the grain boundary or it is again a space charge effect, see discussion below. Hence, we have to analyze a profile governed by two parallel diffusion paths, grain diffusion (with additional near-surface space charge effects) and fast grain-boundary diffusion. This is sketched in Fig. 8(a). Unfortunately, the short part of the depth profile with predominant grain-boundary diffusion may still include contributions from grain diffusion [path (1)] and the near-surface region could be affected by fast grain-boundary diffusion [path (2)]. To account for this problem we carried out an iterative analysis of both profile parts. The exact procedure is described in Supplementary Information. The grain-boundary diffusion coefficient \( D_{gb}^* \) was obtained by using the equation of Whipple and Le Claire.

\[ D_{gb}^* = \frac{1.322}{\delta} \left( \frac{D_b^*}{D_b} \right)^{\frac{1}{2}} \left( \frac{\partial \ln f_{isc}}{\partial x^*} \right)^{\frac{1}{2}} \]

(17)

\( D_{gb}^* \) denotes the grain-boundary diffusion coefficient. Figure 8(b) indicates the first step of the grain-boundary fitting procedure, before subtracting the near-surface part of the profile, for achieving better accuracy. This grain-boundary fit was then subtracted from the original data for numerically quantifying the near-surface region including the space charge layer, see Fig. 8(b). In this manner both parts of the profile could be quantified and Tab. 1 shows the ‘fit’ values for all measurements.

The space charge potential \( \Delta \phi^0 \) seems to increase from 80 mV at 600°C to 200 or 350 mV at 680°C. An exact reason for this increase remains unknown yet but it might be related to temperature-dependent variations of electronic charge carrier concentrations, see also below. Some defect chemical differences between the samples may also be the reason for variations in fit parameters found at 550°C and 676°C, despite nominally identical sample preparation. Moreover, it should be emphasized that the approximation of the near-surface part by finite element calculations was not a true nonlinear least square fit but more a variation in the four parameters to approximate the given shape. It was not intended to determine exact \( \Delta \phi^0 \) values or deducing whether the space charge is Mott–Schottky or Gouy–Chapman like, but rather the space charge approximation was a tool to determine reasonable \( D_b^* \) and \( D_{gb}^* \) values.

Figure 9(a) presents the Arrhenius plots for \( D_b^* \) and \( D_{gb}^* \) (for \( \delta = 2 \) nm). Bulk diffusion coefficients show a comparatively weak dependence on temperature, exhibiting an activation energy of 0.65 eV. Taking the fitting complexity into account, this is reasonably close to typical activation energies of oxygen vacancy mobilities in perovskite-type oxides, for example, circa 0.7 to 0.9 eV for SrTiO\(_3\). The low value also suggests little change in the bulk vacancy concentration with increasing temperature. The grain-boundary diffusion coefficients are several orders of magnitude higher than \( D_b^* \) with the difference becoming even larger with increasing temperature. An activation energy of about 2.15 eV is found for grain boundaries (excluding the data point for 500°C, which was extracted from tracer fractions close to the natural abundance). This is close to the activation energy calculated for the ionic conductivity contribution in IS (2.36 eV). This already suggests that the electrically measured ion conductance above 600°C [Fig. 5(a)] is mostly carried by grain boundaries.

To further analyze this hypothesis, we calculated ionic conductivities from tracer diffusion coefficients via...
The resulting bulk conductivities \( \sigma_{\text{ion}} \) are given in Table I. These values are about three orders of magnitude lower than \( \sigma_{\text{ion}} \) determined by IS. Grain-boundary conductivities calculated from Eq. (18) and \( D_{\text{gb}} \), on the other hand, are impressively high and reach ca. 10\(^{-2}\) S/cm at 676 °C. This corresponds to the ionic conductivity of yttrium stabilized zirconia. To also compare the grain-boundary conductivity \( \sigma_{\text{gb}} \) determined from \( D_{\text{gb}} \) with \( \sigma_{\text{ion}} \) from IS we have to consider effective grain-boundary conductivities \( \sigma_{\text{eff,gb}} \). Those are obtained from a normalization of the true local conductivity to the total sample geometry according to

\[
\sigma_{\text{eff,gb}} = \frac{A_{\text{gb}}}{A_{\text{total}}} \sigma_{\text{gb}}
\]

(19)

\( A_{\text{gb}}, A_{\text{total}} \) are the effective grain-boundary cross-sectional area and the total area with \( A_{\text{gb}}/A_{\text{total}} \approx 2\delta / \text{grain size} \). When combining Eqs. (17–19) \( \delta \) cancels and effective grain-boundary conductivities become independent of any grain-boundary thickness assumption. Values resulting for 1.3 μm grain size are included in Table I.

Owing to the very high grain-boundary diffusion coefficient, the effective grain-boundary conductivity is indeed much larger than the bulk conductivity and this proves that ion conduction is almost exclusively due to grain boundaries. Figure 9(b) compares the effective grain-boundary conductivity calculated from the tracer grain-boundary diffusion coefficient (which essentially equals the effective total ionic conductivity \( \sigma_{\text{eff,gb}} + \sigma_{\text{b}} \) due to \( \sigma_{\text{eff,gb}} \gg \sigma_{\text{b}} \)) with ionic conductivity values from IS. The two conductivity values are in good agreement, particularly in consideration of the complex analysis of the tracer diffusion profiles. This strongly supports the validity of the analysis of EIS data as well as of tracer diffusion profiles.

Therefore, we conclude that the “onset” of high ionic conductivity upon temperatures above 600 °C has its origin in the grain-boundary region of PZT and is caused by a strong increase in the oxygen vacancy concentration in grain boundaries with increasing temperature, cf. Eq. (9) and discussion of \( c_V \) and \( u_V \) in Section III(1). Moreover, the agreement of conductivities from IS and tracer diffusion studies also shows that the temperature dependence of \( D_{\text{gb}} \) is not caused by chemical equilibration of near-surface grain boundaries with

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**Fig. 7.** (a) Tracer distribution image (top view) measured after a tracer exchange experiment at 676°C (30 min) clearly showing high tracer fractions at grain boundaries and thus indicating fast grain-boundary diffusion in PZT (b) Cross section of the same tracer distribution revealing the near-surface (space charge) region with high tracer fractions and enhanced tracer concentrations along grain boundaries.

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**Fig. 8.** (a) Sketch of the model used for quantifying tracer diffusion profiles based on two diffusion paths. The grain-boundary transport [path (2)] might either take place in the grain-boundary core or along a space charge layer with oxygen vacancy accumulation. Path (1) includes a near-surface space charge layer (SCL). (b) Fitting procedure showing the first fit of the grain-boundary contribution [1st fit of path(2)] and the data after subtracting the first fit of path (2), together with a fit curve from finite element (FEM) calculations of the near-surface region with space charge zone.
the gas phase, which is unavoidable in tracer experiments due to the much higher chemical diffusion coefficient compared to $D^\ast$. Rather, the entire grain-boundary network (seen by electrical IS measurements) seems to exhibit a strongly temperature-dependent vacancy concentration.

Fast ion conduction may take place in the grain-boundary core or in a space charge layer with accumulation of mobile vacancies. In the core, transport of oxide ions might include a de-trapping of oxygen vacancies from associates with negative ionic species (e.g., segregated donors). In this case, a high concentration of vacancies always exists in the core but becomes mobile only at high temperatures and the high activation energy of the grain-boundary ionic conductivity is a combined effect of mobility and defect association energy. If a space charge layer with oxygen vacancy accumulation is responsible for fast grain-boundary transport, the high activation energy indicates a very strong change in the space charge potential with temperature. Even though a certain temperature dependence of the space charge barrier height is quite common, such a huge variation requires an explanation: Possibly, a complete change in the space charge polarity takes place above 600°C, due to a change in the space charge determining bulk species.

For example, for electrons becoming the predominant mobile bulk species above 600°C, a positive space charge with negative core charge is very realistic (cf. e.g., PTC resistors) and this causes an oxygen vacancy accumulation in the space charge region. Those vacancies might originate from the core where they could be much less mobile. This assumption of a severe change in space charges above a certain temperature would also be in agreement with the strong temperature dependence of the space charge potential deduced for the near-surface region (Table I). If above 600°C electrons took over control of the near-surface and grain-boundary space charges, simultaneous appearance of space charge effects in both region is expected and indeed effects in terms of strongly changed oxygen vacancy concentrations are experimentally found in grain-boundary and near-surface regions. The good agreement of the estimated “grain boundary” mobility $u_v$ with typical bulk mobilities in STO also supports assumption of a space charge effect within the undisturbed perovskite lattice rather than a transport along the structurally different grain-boundary core. However, additional measurements of partial pressure and temperature-dependent conductivities are required to verify this hypothesis. Anyway, the estimates of effective charge carrier concentrations from $C_{chem}$ (see above) most probably reflect vacancy concentrations in grain-boundary zones (either core or space charge) and locally they are thus in the 0.1% range with respect to lattice sites at ~670°C.

Assuming the same $D_v$ (or $u_v$) value of grain boundary (space charge) and bulk also allows an estimate of the bulk vacancy concentration $c_{V,gb}$ from $D_{gb}/D_b^\ast = c_{V,gb}/c_{V,b}$. For 0.1% vacancies (with respect to oxygen lattice sites) and the $D^\ast$ values of Table I we get a bulk vacancy fraction of ~0.01 ppm at ~670°C, at least in the near-surface bulk part seen in the tracer study. This would cause a Debye length in the μm range. Accordingly, the Debye length of Table I seems to be due to another charge carrier than oxygen vacancies, for example electrons.

### (3) Time Dependence of Partial Conductivities Measured by Impedance Spectroscopy

So far only transport properties measured immediately after reaching the corresponding temperature have been discussed. However, time-dependent measurements revealed that the sample properties significantly change with time, at least at $T > 600°C$. In Fig. 10 the time dependence of the impedance response at 707°C annealing temperature is shown. Two semicircles can be found, with the high-frequency semicircle increasing for advanced annealing time. The low-frequency semicircle decreases and finally vanishes after long annealing. The total resistance (reflecting $\sigma_{con}$) stays almost con-

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**Table 1. Fit Parameters for PZT Tracer Diffusion Profiles at Different Temperatures, Also Effective Grain-Boundary Conductivities Are Given. Grain-Boundary Values at 500°C have a Large Level of Uncertainty**

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$k_\ast$ (cm/s)</th>
<th>$\lambda$ (nm)</th>
<th>$\Delta\psi_0$ (mV)</th>
<th>$D_{gb}^\ast$ (cm$^2$/s)</th>
<th>$D_b^\ast$ (cm$^2$/s)</th>
<th>$\sigma_{gb}$ (S/cm)</th>
<th>$\sigma_{gb,eff}$ (S/cm)</th>
<th>$\sigma_b$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>1.9 × 10$^{-9}$</td>
<td>—</td>
<td>—</td>
<td>8.5 × 10$^{-14}$</td>
<td>2.3 × 10$^{-11}$</td>
<td>3.3 × 10$^{-5}$</td>
<td>1 × 10$^{-7}$</td>
<td>5.2 × 10$^{-8}$</td>
</tr>
<tr>
<td>550</td>
<td>6.5 × 10$^{-9}$</td>
<td>—</td>
<td>—</td>
<td>6.2 × 10$^{-14}$</td>
<td>3.1 × 10$^{-10}$</td>
<td>1.8 × 10$^{-4}$</td>
<td>5.4 × 10$^{-7}$</td>
<td>3.6 × 10$^{-8}$</td>
</tr>
<tr>
<td>550</td>
<td>7.0 × 10$^{-9}$</td>
<td>—</td>
<td>—</td>
<td>3.4 × 10$^{-14}$</td>
<td>3.7 × 10$^{-10}$</td>
<td>2.1 × 10$^{-4}$</td>
<td>6.6 × 10$^{-7}$</td>
<td>2.0 × 10$^{-8}$</td>
</tr>
<tr>
<td>600</td>
<td>1.6 × 10$^{-8}$</td>
<td>110</td>
<td>80</td>
<td>1.1 × 10$^{-13}$</td>
<td>2.3 × 10$^{-9}$</td>
<td>1.3 × 10$^{-3}$</td>
<td>3.9 × 10$^{-6}$</td>
<td>6.0 × 10$^{-7}$</td>
</tr>
<tr>
<td>676</td>
<td>3.2 × 10$^{-8}$</td>
<td>140</td>
<td>200</td>
<td>8.0 × 10$^{-14}$</td>
<td>5.8 × 10$^{-9}$</td>
<td>2.9 × 10$^{-3}$</td>
<td>9.0 × 10$^{-6}$</td>
<td>4.0 × 10$^{-8}$</td>
</tr>
<tr>
<td>676</td>
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<td>270</td>
<td>350</td>
<td>5.0 × 10$^{-13}$</td>
<td>6.3 × 10$^{-8}$</td>
<td>3.2 × 10$^{-2}$</td>
<td>9.7 × 10$^{-5}$</td>
<td>2.5 × 10$^{-7}$</td>
</tr>
</tbody>
</table>
constant. The impedance spectra can again be analyzed by the model described in Section III(1). Ionic resistances were calculated using Eq. (7) and transformed into ionic conductivities. Figure 11 presents the resulting electronic and ionic conductivities over time.

After an initial decrease in the oxide ion conduction a temporary plateau is reached, partly even a slight increase is found. On a long-time scale a continuous decrease in the ionic conductivity is visible until $\sigma_{\text{ion}}$ can no longer be separated by IS. Within the entire period, also the electronic conductivity changes but these changes are much less pronounced. Owing to the decrease in the ionic transference number, the total conductivity soon largely reflects the electronic conductivity. Exact (defect) chemical reasons of the small changes in the (bulk) electronic conductivity are not known yet. Some defect chemical equilibration of the oxygen stoichiometry may be present in the first hours but long-time changes most probably also involve cation motion.

The strong variation in the ionic conductivity with annealing time has to be caused by changes in the grain-boundary defect chemistry due to predominant ion conduction via grain boundaries, at least in the first period. Exact reasons are again unknown but the first sharp drop might be due to chemical diffusion of oxygen in grain boundaries, the second period (“plateau”) could indicate chemical bulk diffusion and the strong long-time decrease most probably also involves cation diffusion.

It is again worth emphasizing that the ionic conductivity reaches almost 30% of the total conductivity at the immediate start of the analysis, which is quite unexpected for nominally donor-doped PZT (cf. transference number in Fig. 11).

The fast initial decrease of $\sigma_{\text{ion}}$ and the fact that the start of the measurement was “delayed” by several minutes to ensure constant temperature conditions, let us assume that the oxygen vacancy conductivity was possibly even larger than the electronic one in the very beginning of the experiment. However, this high ionic transference number is not a consequence of simple bulk defect chemistry but is a grain-boundary-related phenomenon.

(4) Time-Dependent Ion Transport Investigated by Oxygen Tracer Exchange Measurements

To get a more detailed insight into the strong loss of ionic conductivity over time above 600°C, $^{18}$O tracer exchange experiments were conducted at different time stages of annealing at 676°C. 30 min exposure to $^{18}$O tracer atmosphere was performed after 1 day, 1 week and 3 weeks of annealing, respectively. The resulting tracer profiles are given in Fig. 12. Again, the profiles show strong deviation from simple bulk diffusion according to Eq. (11) with a pronounced box-shaped profile in the near-surface region and contributions extending deep into the material. However, the tracer level in some depth is strongly reduced after one week and almost reaches natural abundance after three weeks. The near-surface profile found after three weeks also clearly differs from all the others.

In a first step, the part of the profile which is attributed to grain-boundary diffusion can be compared to the conductivity behavior over time given in Fig. 11. After 24 h the ionic conductivity has decreased and this reduction finds its counterpart in the increased slope of the tracer profile, that is, less pronounced grain-boundary diffusion. Measurements performed after 1 week show a drastic decrease in the ionic conductivity and much less tracer ions in the profile part reflecting grain-boundary diffusion. After 3 weeks the ionic contribution has vanished completely in impedance measurements and results from tracer experiments do not longer show clear indication of ionic conductivity within grain boundaries, tracer concentrations near the natural abundance level are reached in ~1 μm depth.

The quantitative analysis of diffusion coefficients was performed in the same way as described in Section III(2). Table II presents the results for the time-dependent measurements at 676°C. Bulk diffusion coefficients are not much affected, but the near-surface space charge contribution seems to be reduced during annealing. The grain-boundary diffusion coefficient is reduced by about two orders of magnitude after 1 d. $D_{\text{gb}}$ values deduced for 1 and 3 weeks of annealing have to be taken with care due to the low tracer level. All together, these results support the interpretation given so far, namely only slight changes in bulk defect chemistry but strong grain-boundary modifications during annealing. Mechanistic explanation of the changes in the grain boundaries cannot be given yet, but additional information
(see below) clearly shows that the changes are not limited to a region near to the surface. The sample annealed for three weeks showed a near-surface profile which differed significantly from all others not only in terms of grain-boundary part (essentially missing) but also in the near-surface part. The much thicker near-surface box could no longer be described by a space charge effect solely, that is, Eqs. (13) and (14) were not sufficient. Therefore, the first 200 nm from the surface—showing an almost linear decrease of $f_{l^{18}O}$—were treated as an individual layer with a different (high) diffusion coefficient. Only after 200 nm the space charge layer was assumed to set in. Figure 13(a) shows the results of such a fit approach. The first 200 nm have a diffusion coefficient which is more than one order of magnitude higher than the bulk diffusion coefficient in the remaining layer ($D_{200\,nm}^*$ = $6.8 \times 10^{-13}$ cm$^2$/s at 676°C).

The rather good agreement already for this very simple model of an additional layer with fixed $D_{200\,nm}^*$ suggests that indeed after three weeks an additional process has strongly modified the near-surface region. Irreversible changes in this region are most probably the reason. Onset of PbO evaporation from the surface, accompanied by lead diffusion from the bulk to the surface, is a very realistic explanation, as it would indeed result in an enhanced vacancy concentration in the near-surface region, thus increasing the tracer diffusion coefficient within the first 200 nm. This Pb diffusion should again cause a spatially varying oxide ion diffusion coefficient but owing to the lack of a kinetic model for describing this process we did not try to refine the fit model. A first approximation with \( L = \sqrt{Dt} = 200\,nm \) yields a chemical lead oxide diffusion coefficient of about $2 \times 10^{-16}$ cm$^2$/s at 676°C. The change in defect concentrations in this very first 200 nm compared to the remaining bulk can again lead to a space charge (with accumulated vacancy concentrations) and such a space charge was indeed required to reproduce the profile.

To verify this assumption of a strongly modified near-surface zone, the sample was grinded and polished, thus removing many micrometers of the material. Immediately after this preparation step a second tracer exchange experiment was performed at 670°C. The result is given in Fig. 13(b). Significant changes in the tracer fraction in the grain-boundary region are not found (values are still close to the natural abundance). However, strong deviations can be observed in the near-surface part and results are very close to those found after one week and thus before appearance of the 200 nm zone. Hence, our assumption of long-time changes in the near-surface region due to PbO evaporation are supported by this experiments. Moreover, this clearly shows that

### Table II. Fit Parameters for Tracer Profiles in PZT Measured After Different Annealing Times

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>$k^*$ (cm/s)</th>
<th>$D^b_0$ (cm$^2$/s)</th>
<th>$\lambda$ (nm)</th>
<th>$\Delta\phi^0$ (mV)</th>
<th>$D^b_{gb}$ (cm$^2$/s)</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>$3.2 \times 10^{-8}$</td>
<td>$8.0 \times 10^{-14}$</td>
<td>140</td>
<td>200</td>
<td>$1.3 \times 10^{-8}$</td>
</tr>
<tr>
<td>24</td>
<td>$2.0 \times 10^{-8}$</td>
<td>$8.0 \times 10^{-14}$</td>
<td>150</td>
<td>90</td>
<td>$4.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>168</td>
<td>$3.8 \times 10^{-8}$</td>
<td>$7.0 \times 10^{-14}$</td>
<td>100</td>
<td>70</td>
<td>$(1.9 \times 10^{-10})$</td>
</tr>
<tr>
<td>504†</td>
<td>$2.6 \times 10^{-8}$</td>
<td>$4.8 \times 10^{-14}$</td>
<td>120</td>
<td>100</td>
<td>$(2.2 \times 10^{-11})$</td>
</tr>
</tbody>
</table>

†Analysis only of the box-shaped profile beginning at approx. 200 nm.

Fig. 13. Measurement of a tracer profile after 3 weeks of annealing at 670°C. (a) Measured data and fit from the modified fitting routine including a 200 nm layer with $D_{200\,nm}^*$ to describe the near-surface part of the profile. (b) Comparison of profiles found at the original surface after 3 weeks annealing and in the same sample after grinding and additional 30 min tracer exchange at 676°C.
The combination of impedance spectroscopy measurements and tracer diffusion in Nd\(^{3+}\)-doped PZT revealed many details on ion conduction in this material:

1. Nd\(^{3+}\)-doped PZT shows a substantial partial ionic conductivity above 600°C with transference number up to several 10%. This is reflected by a second arc in impedance spectra.

2. Oxygen tracer exchange measurements clearly showed that mainly grain boundaries are responsible for this high ionic conductivity.

3. For quantitative analysis of the tracer depth profiles an assumption of a near-surface space charge with enhanced vacancy concentration was required at higher temperatures. An iterative analysis considering regions with predominant space charge effect and regions reflecting grain-boundary diffusion yielded quantitative data of \(D_g\), \(D_{gb}\), and space charge potentials. The effective ionic conductivity calculated from \(D_{gb}\) is in good agreement with ionic conductivities measured by IS.

4. Activation energies of grain-boundary conduction are above 2 eV and thus much larger than those of the bulk ion conduction. Oxygen vacancy mobilities similar to those in SrTiO\(_3\) are found and the high activation energy of grain boundaries therefore indicates a strong temperature-dependent mobile oxygen vacancy concentration.

5. Effective vacancy concentrations (in the order of 2 ppm at 670°C), calculated from IS are caused by much higher vacancy concentrations found in grain boundaries (in the range of 10\(^{-5}\)). In the bulk, oxygen vacancy fractions in the 0.01 ppm range are estimated.

6. Time-dependent changes found in IS and tracer exchange measurements reflect a drastic decrease in ionic conductivity within grain boundaries during annealing. Bulk properties do not significantly change.

7. Additional near-surface effects found in tracer profiles after long annealing times are possibly caused by PbO evaporation and allow an estimate of the ambipolar lead diffusion coefficient in PZT.

Acknowledgment

The authors gratefully acknowledge Christian Doppler Society for funding.

Supporting Information

Additional Supporting Information may be found in the online version of this article:

Data S1. Supplementary material.

References


