Room Temperature Polarization Phenomena in Nanocrystalline and Epitaxial Thin Films of Gd-Doped Ceria Studied by Kelvin Probe Force Microscopy

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Thick films of nanocrystalline, acceptor doped ceria have in the past been of interest of intensive study due to their unique physical characteristics such as high electrical conductivity1–4 and distinguished oxide ion and proton transport characteristics.5–8 as well as increased chemical reactivity. Ceria thin films can be employed in different high and intermediate temperature applications such as micro-solid oxide fuel cells9,10 or gas sensors.11 Just from these applications, low temperature usage of doped ceria nanoparticles or thin films has increased in the last 25 years, especially in the area of catalysis12,13 and even for pharmaceutical applications.14,15

The electrochemical characteristics of acceptor doped ceria thin films have already been investigated as a function of grain size, temperature and oxygen or water partial pressure. It was established that with decreasing grain size the electronic conductivity increases while the oxide ion conductivity decreases,4 resulting in an increased total conductivity and decreased activation energy.4,8,16

Interestingly, it has been shown that Ce cations are strongly reduced at free surfaces.17 For example, electron magnetic resonance (EMR) measurements carried out on ceria nanoparticles detected ca. 18% of the cerium cations to be fully reduced.18 Electron energy-loss spectroscopic (EELS) imaging in scanning transmission electron microscopy (STEM), relying on characteristic valence-sensitive features of the Ce-M4,5 edges revealed a Ce-reduction in proximity of the free surface in both nanoparticles as well as in gadolinium doped thin films.19–21

A combination of surface potential mapping using Kelvin probe force microscopy (KPFM) and polarization experiments has recently been established as experimental technique to access polarization properties of oxide ion conductors at low temperatures.22–25 In contrast to more established measurement techniques, surface potential mapping using Kelvin probe force microscopy has a very high spatial resolution, thus yielding not only information about the effect of polarization but also about size and intensity of the introduced chemical gradient and velocity of the relaxation process.

Negative polarization of the AFM tip leads to a decrease of the local surface potential.26 Near the tip-sample contact while positive polarization leads to an increase of the surface potential with respect to the pristine, non-polarized state. This effect is completely reversible within a certain voltage threshold. It is supposed that positive polarization of the AFM tip locally ionizes defects and leads to the local oxidation of Ce3+ to Ce4+. Negative polarization of the AFM tip can cause a mobilization of partially ionized defects by locally increasing the Ce3+ concentration. A local oxidation of cerium ions as well as higher concentrations of oxygen vacancies (V O ) will lead to a higher surface potential while a local reduction of cerium ions as well as transport of V O or V O will lower the surface potential.27

There have already been polarization-KPFM studies on the relaxation behavior of doped ceria thin films,22 pellets and single crystals.23,24 Such investigations revealed for example that the diameter of the introduced gradient increases to a certain degree with increasing applied bias and increasing application time.22 Furthermore, the relaxation rate of the gradient after the end of polarization was observed to be faster for single crystalline materials than for pellets23 and even faster for polycrystalline thin films.22 In addition, a slower relaxation for positive than for negative polarization was found for all three material types and an increase of the polarization rate was detected with increasing temperature22,24 while the relaxation rate was found to increase with increasing oxygen partial pressure of the surrounding.22

Apart from these KPFM-related studies, Farrow et al. studied the spatial variation of conductance of a ceria thin film on the nanometer scale by AFM current-voltage mapping. Chen et al.25 and Doria et al.26 published studies of space charge regions in Sm-doped ceria with a related AFM technique (electrochemical strain microscopy, ESM), where very short bias pulses were used to map the local vertical strain within the sample. This local change of strain was found to be directly related to changes in the local defect concentration. The authors were able to show locally resolved evidence for the existence of space charge regions at ceria grain boundaries and at the sample surface.27 Yang et al. used a similar setup to study the effect of absorbed water on the surface of ceria thin films during polarization with high applied biases in the range of several volts.28,29 and Kumar et al. demonstrated that this technique could also be used to monitor the local oxygen reduction (or evolution) on Pt-decorated YSZ30 or to detect the change of electrochemical processes on Sm-doped ceria thin films during polarization with high biases under variation of temperature.31

The effects on the surface potential introduced by changing the steady state of an acceptor doped ceria system by polarization were at first explained by an ionization process leading to the local oxidation of Ce3+ to Ce4+.24 Negative polarization was thought to cause a mobilization of partially ionized defects by relocalization of higher Ce3+.
concentrations. A local oxidation of cerium ions as well as higher concentrations of $V_{O}^{\delta}$ were assumed to lead to a higher surface potential while a local reduction of cerium ions as well as transport of $V_{O}^{\delta}$ or $V_{O}$ was assumed to be the reason for a locally lowered surface potential.24

**Preliminary Studies of Gd-Doped Thin Films**

A study of the influence of epitaxial crystal growth on the low temperature polarization behavior has not been conducted so far, although it is known, that epitaxial thin films have different characteristics compared to polycrystalline thin films, which can be industrially relevant. For pure ceria, it has been found, for example, that the catalytic activity of epitaxial ceria thin films on Pt wafers is strongly reduced in comparison to polycrystalline thin films.13 At the same time, the electrical conductivity is enhanced effectively.16 Generally, for doped and undoped ceria thin films, dopant/impurity concentrations, grain/grain boundary ratio, crystallinity and film thickness play crucial roles in determining the electric transport properties of such systems.2–8

Comprehensive studies on the characteristics of Gd-doped thin films have already been conducted in literature.3,6,16,32 The thin films used in the investigations presented here were produced in a similar manner like the materials used in these publications: in these studies, 10 mol% Gd-doped thin film samples were measured in the high temperature range. They showed a conductivity behavior which was governed by ionic conductivity. Epitaxial thin films showed – as expected – a very high electrical (ionic) conductivity (3.6 S/cm at 700°C for a 186 nm thick film32) On the contrary, polycrystalline thin films showed a much smaller conductivity (0.98 S/cm at 700°C for a 230 nm thick film16) and also significantly higher activation energies. This effect was attributed to the conductivity of the material being governed by negatively charged (oxide ion transport blocking) space charge layers at the grain boundaries perpendicular to the direction of transport.16

For polycrystalline thin films, the conductivity behavior was found to vary strongly depending on the film thickness and grain size of the materials.8 For nanocrystalline samples, which were produced under similar conditions like the nanocrystalline sample presented here, Göbel et al.3 found a significant influence of electronic conductance despite of the considerable acceptor dopant concentration. Such a behavior resulted from an increased space charge potential at grain boundaries and the comparably small grain/grain boundary ratio.7

For very small thin films the conductivity was found to be governed by the interface between material and substrate, which plays a dominant part regarding the overall electrical conduction properties.

In the present study the thickness of the films is much larger than the thickness that is typically observed to be influenced by the interface properties. It is therefore assumed that the effects in our measurements are mainly governed by the sample material itself.

**Theoretical Considerations**

Comparing the response to polarization of nanocrystalline and epitaxial materials with the same dopant concentration is expected to yield information about the effect of grain boundary induced space charge region on the polarization behavior of the ceria thin film samples. Several groups have already pointed out that the electrochemical behavior of nanocrystalline samples is mainly governed by the influence of grain boundary related space charge layers.3,16,32–35 It is widely accepted that a positively charged grain boundary core in acceptor doped ceria leads to a reduced ionic conductivity at the grain boundaries and simultaneously to an increase of the electronic conductivity.

Because of the comparably good electron conductivity, the nanocrystalline material in our investigations should show only a moderate to small surface potential deviation $\Delta \Phi_{SP}$ after polarization, as electrons should be redistributed faster during polarization than in materials with larger grains.25 Also, the diameter of the introduced grain should be comparably small.

The epitaxial film, on the other hand should behave similarly to a monocrystalline material23,24 as there are no blocking grain boundaries which would improve the electron transport. Monocrystalline Ce$_{0.9}$Gd$_{0.1}$O$_{2.4}$ and Ce$_{0.9}$Y$_{0.1}$O$_{2.3}$ in previous studies showed 2–3 times larger diameters of the surface potential gradient after polarization and also $\Delta \Phi_{SP}$ was 2–3 times increased compared to polycrystalline materials with the same acceptor dopant concentration.25,24 At the same time, the relaxation was found to be significantly faster for monocrystalline materials than for polycrystalline materials.

In the present study, a time constant (relaxation time, $\tau_{in}$) was deduced from an exponential fit of the results of Kelvin probe potential relaxation measurements. Said time constant is the time, at which the surface potential has reached the value $\Phi_{SP}^{-1}$ with $\Phi_{SP}$ being the surface potential difference at the end of polarization (roughly 36.8% of the initial value). In such a bulk polarization situation, the experimentally determined time constant $\tau_{in}$ can be expressed in terms of chemical capacitance $C$ and chemical resistance $R$:36

$$\tau_{in} = R^h \cdot C$$

where

$$R^h = R_{ion} + R_{con}$$

Furthermore, $\tau_{in}$ can be used to determine the chemical diffusion coefficient

$$D^h = \frac{L^2}{\pi^2 \tau_{in}}.$$  

which – as in the case of acceptor-doped ceria – results from the diffusion coefficients of the mobile ionic and electronic species, as follows

$$D^h = \frac{\sigma_{ion}}{\sigma} D_{con} \chi_{con} + \frac{\sigma_{ion}}{\sigma} D_{con} \chi_{con}.$$  

Here, the factors $\chi_{con}$ and $\chi_{con}$ denote the corresponding trapping factors and $\sigma_{ion}$ and $\sigma_{con}$ the ionic and electronic conductivities. In the case of largely acceptor doped CeO$_2$, such as Ce$_{0.9}$Gd$_{0.1}$O$_{2.3}$, in which the ionic conductivity is larger than the electronic one by several orders of magnitude ($\sigma_{ion} \gg \sigma$) and $D_{con}$ is not negligible, the bulk chemical diffusion coefficient reduces to

$$D^h \cong D_{con} \chi_{con}.$$  

$$D^h \cong \frac{\mu_{con} k_B T}{\varepsilon} \chi_{con}.$$  

**Experimental**

Two different thin films with the composition Ce$_{0.9}$Gd$_{0.1}$O$_{2.4}$ and a thickness of 200 nm were fabricated on an Al$_2$O$_3$ (0001) substrate using pulsed laser deposition (PLD) as described elsewhere:19 one was produced at room temperature, yielding nanocrystalline material (CGnano) with a grain size in the area of 10 nm. The other one was prepared at a substrate temperature of 720°C, yielding an epitaxial microstructure (CGepi).3,16,32

For polarization and KPFM mapping, the samples were contacted with a silver paste back contact and Pt wire. The working contact for the polarization was an AFM tip (PPP-NCSST-Pt) with Pt coating, which was used simultaneously as probe during KPFM mapping (cf. Fig. 1). Experiments were conducted with a Keysight 5500 AFM in KPFM-AM mode. As no absolute surface potential values can be obtained with this method without extensive calibration, we took the pristine state of the surface potential before polarization as 0 V for normalization of measurement values. The samples were first mapped in the pristine state for reference. Subsequently, the sample was polarized with up to ±5 V (with regard to the AFM tip) for up to 300 s. Directly after the end of the polarization experiment continuous surface potential mapping was started.

The difference of the root mean square surface potential of the KPFM images in the pristine state between both samples was in the
Figure 1. Schematic of the experimental setup.

range of 10–20 mV. As this is a similar range as the noise in the images, both materials can be assumed to have a similar initial surface potential state.

Results and Discussion

Polarization of CGnano.—Both the negative and the positive polarization experiments were completely reversible and did not lead to a detectable change in the surface topography. This is consistent with previous studies by Farrow et al.,27 who reported irreversible surface damage only for polarization of ceria films with currents higher than 1 nA. As the bias was kept between +5 and –5 V, the currents were below this threshold in our study.

Here, the negative polarization for CGnano led to well-defined circular areas of decreased surface potential of about 150–200 nm in diameter (cf. Fig. 2). The image quality for these measurements was affected by the very high scan velocity, because the introduced effects vanished very fast (see overview in Fig. 6). The change of surface potential was completely reversible.

The size of the introduced gradients after positive polarization was in the same range as for negative polarization, but the effects relaxed somewhat more slowly (10 minutes relaxation time for positive compared to 6 minutes for negative polarization, see overview in Fig. 6), which is in good accordance to published findings for acceptor doped ceria.22–24 The gradient sizes observed for CGnano are also consistent with the results of Lee et al.,22 who found a slightly larger diameter of the gradient (about 500 nm FWHM) for polarization of a ∼100 nm thick Ce0.8Gd0.2O2–δ thin film with up to ±3 V for 60 s at room temperature.

Polarization of CGepi.—In comparison to the nanocrystalline thin films, the relaxation time of the epitaxial thin films was considerably higher for both negative as well as positive polarization. Positive polarization of CGepi with +3 V for 300 s led to a more or less circular shape of the gradient, which had an elevated surface potential. The relaxation process was slower for positive than for negative polarization: the observed average relaxation time was around 42 minutes compared to 35 minutes for polarization with –3 V for 300 s (cf. Fig. 3 and Fig. 6).

Positive polarization with +5 V for 300 s led to irreversible changes of the surface potential (cf. Fig. 4). In two experiments, the area of increased surface potential was found to be visible even after 24 h, although the intensity decreased somewhat compared to the initial state. At the same time, a slight change of the mechanical vibration phase of the cantilever in this area was observed, which was also irreversible. This can be a hint for the occurrence of textural changes of the material itself, which were introduced by the polarization. The surface topography signal however showed no changes. Because of these findings, only a limited number of experiments with +5 V were performed and application of –5 V was not considered.

Negative polarization of CGepi with –3 V for 300 s led to slightly hazy areas with lowered surface potential. The triangular shape (especially obvious in the first image after polarization in Fig. 3) is due to the direction of the scan (in this case from bottom to top), because the potential difference was vanishing faster than the scan velocity in y-direction. The broad area with decreased surface potential vanished relatively fast (about three minutes), leaving a small spot with decreased potential at the direct contact area during the polarization. This spot showed a much slower relaxation behavior (cf. Fig. 6).

Furthermore, the epitaxial thin film exhibited also a very fast charge transport along a large surface area in the direct contact area, which was detectable for about 200 s. Doped ceria single crystals and doped ceria pellets, which have been investigated previously23,24 did not
show these features, although test measurements with similar technical parameters as used for the thin films were performed on these samples.

**Discussion.**—Figs. 4 to 6 summarize the results of the polarization experiments, of which a few representative AFM images were displayed in Fig. 2 to Fig. 4. As it can be seen here, the relaxation curves of the whole set of measurement show that $\Delta \Phi_{sp}$ is higher for the epitaxial samples (CGepi) than for the nanocrystalline samples (CGnano). This was already anticipated from studies on microcrystalline and monocristalline materials.23,24 Besides, by comparing positive and negative polarization, a slower relaxation was found after positive polarization (cf. Table I), which is in good accordance to previous findings for polarization of ceria.23,24

Apart from this, the behavior of the epitaxial and nanocrystalline samples during polarization is different. The nanocrystalline samples showed well-defined circular areas while for the epitaxial thin film exhibited two distinct effects: (i) a spot showing a high surface potential gradient directly at the electrode contact area and (ii) a slightly hazy area, where the surface potential was increased or decreased in similar direction to the polarization bias (see Fig. 3 to Fig. 5). Furthermore, the polarization with $\pm 5$ V was reversible for the nanocrystalline samples, whereas for CGepi an irreversible effect was observed. This feature is also recognizable in the relaxation curves, as the surface potential does not go back to the initial state of zero potential, but remains in the range of $\pm 250$ mV (cf. Fig. 6).

In comparison to the polarization behavior of previously investigated Gd-doped pellets,23 both thin films showed different characteristics. For the pellets, a slow relaxation of the gradient after polarization lasting up to 1 hour depending on dopant composition was observed (see the bright blue star symbols in Fig. 6). The corresponding polarization maps always showed well-defined circular areas with a diameter of about 1–1.5 $\mu$m. Here instead, the diameter of the gradient of CGnano was roughly 150–200 nm, while for CGepi, the fast-relaxing large-area polarization gradient had a size of several $\mu$m while the slower-relaxing polarization gradient had a diameter in the same range as CGnano.

Interestingly, also the polarization behavior of a previously studied $\text{Ce}_{x}\text{Gd}_{1-x}\text{O}_{2-\delta}$ single crystal24 (cf. Fig. 7) was much slower than the relaxation of the thin films. Furthermore, the induced gradients for CGnano have roughly half the diameter of the gradients observed in the single crystal with the same bias ($\sim 350–400$ nm),24 while for CGepi the fast-relaxing, large-area effects are significantly larger.

Such a faster relaxation of the thin films is in good accordance to findings by Lee et al., who also observed a fast relaxation after polarization of polycrystalline thin films with composition $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$.22

For a more detailed discussion of the data of the present study, let us first consider the CGepi thin film. Its dual relaxation behavior with a faster and slower relaxation points toward the presence of two distinct polarization mechanisms involving distinct portions of the sample. We first deal with the slower relaxation process which exhibits a time scale comparable with the one of the relaxation occurring in the CGnano film (roughly 2–3 times higher, although the applied potential was lower than for CGnano), as it is shown in Table I, which summarizes the time constants as well as the respective chemical diffusion coefficients $D^\delta$ of the two samples (calculated according...
to Eqs. 1–3). Interestingly, only small differences in terms of $D^0$ can be recognized among the two samples, despite the fact that the nanocrystalline film has an effective electronic conductivity which is comparable to the ionic one at room temperature.\(^1\)\(^3\)\(^8\)

As far as the epitaxial film is regarded (in the bulk of which the ionic conductivity is predominant), for the chemical diffusion, Eqs. 5a and 5b hold. In order to verify whether the chemical diffusion associated to the polarization experiments is a bulk effect, we can estimate the bulk electronic diffusion coefficient for 10 mol\% Gd doped ceria. By taking literature values of the mobility of electrons in CeO\(_2\)\(^9\) (namely, migration enthalpy $\delta = 0.4$ eV, pre-exponential factor $\delta e_0$), where $ue_0 = 0.039$ m\(^2\) K/(V·s) and $T = 293$ K, we obtain

$$D_{\text{eon}} = 4 \times 10^{-13} \text{ m}^2/\text{s}. \quad [6]$$

According to this result, a trapping coefficient $\chi_{\text{eon}} = 10^{-4}$, which is not unexpected for such a large dopant concentration and low experimental temperature,\(^4\)\(^1\)\(^3\)\(^4\) would suffice to yield a chemical diffusion $D^0$ on the order of $10^{-17}$ m\(^2\)/s. Thus, we can conclude that for the CGepi film, the slower relaxation behavior can be due to a bulk polarization, which is limited by the electron diffusion coefficient.

The fast relaxing relaxation process, which was detectable for only about 200 s (cf. Fig. 3 to Fig. 5), can be assigned to a charge transport occurring in proximity of the free surface, in which almost all cerium cations are fully reduced.\(^1\)\(^7\)\(^–\)\(^9\) In such a case, Eq. 4a becomes

$$D^0 \cong D_{\text{eon}} \chi_{\text{eon}} \quad [4b]$$

Since in this case $L$ corresponds to the thickness of the space charge region (on the order of 1–2 nm) and $D_{\text{eon}}$ is at room temperature on the order of $10^{-14}$ m\(^2\)/s,\(^9\) one recognizes that, depending on trapping, the polarization effect occurring at the surface can be more or less visible. Here, a trapping factor of $10^{-4}$–$10^{-5}$ would correspond to a $\tau_{\text{fit}}$ of about 10–100 s, which is in line with our experimental findings.

The above plausible considerations ignore however the possibility of a contribution of a space charge profile. We show in the following that the observed polarization can be rationalized by the presence of a space charge situation. In such a case the overall polarization behavior can be modeled by two RC elements in series comprising chemical circuit elements ($R^c$, $C^c$), in which the first resistance in parallel to the first capacitor represent the space charge properties and the second resistance in parallel to the second capacitor the bulk properties. In such a system, the fast polarization process is determined by the space charge properties, since, at the beginning of the polarization, the second capacitor corresponding to the bulk capacitive properties (which is larger than the space charge capacitor) is short-circuited. As the polarization proceeds, in the considered model, the space charge capacitor is fully charged while the bulk capacitor becomes relevant. In such a case, as shown in Ref. 42 the charge concentration splitting occurring within the space charge region leads to a lowering of the effective chemical diffusion coefficient. The process can be described by essentially a space-charge-limited bulk polarization, in which the chemical capacitance is bulk-like but the chemical resistance distinctly increases as a consequence of the depressed oxygen vacancy concentration within the space charge region. It is noted that the space-charge-limited bulk polarization is in line with the reduced value of $D^0$ compared to $D_{\text{eon}}$ (6) without the need to invoke for trapping factors.

Therefore, the presence of a space charge situation at the surface of the film would explain the occurrence of two relaxation time constants, one of which pertaining to the space charge polarization and the other to a space-charge-limited bulk polarization.

Comparing the findings of this study to the findings by Doria et al.\(^2\)\(^6\) who used short voltage pulses with up to 30 V to study the effect of grain boundaries in an epitaxial 20 mol\% Sm-doped thin film and a corresponding nanocrystalline material, the relaxation times found for our material are much longer (hundreds of s vs. some ms). This can be attributed to much longer polarization times used in our study: the polarization time was chosen to be long enough to receive a stable current signal in previous tests. Also, Doria et al.\(^2\)\(^6\) found differences for the polarization behavior of grains vs. grain boundary regions which they ascribed to an increase of the migration energy for oxygen vacancies at the grain boundaries due to the existence of a space charge layer. In our case, the introduced defect gradient was in all cases larger than single grains of CGnano, therefore effects of grains and grain boundaries during polarization were not clearly separable.

Nevertheless, as far as the CGnano sample is regarded, we can clearly recognize that its situation is dominated by a large volume fraction of grain boundaries, at which space charge effects are known to be predominant.\(^2\)\(^9\)\(^3\)\(^5\) Thus, the observation of a single relaxation behavior with a lowered chemical diffusion can be explained by space charge effects occurring at the grain boundaries of the nanocrystalline sample, which is in good accordance to the findings by Doria et al.\(^2\)\(^6\)

**Conclusions and Outlook**

It has been shown that by variation of the microstructure of doped ceria thin films the local polarization behavior of acceptor doped ceria can be altered significantly. The main part of the results from this Kelvin probe force microscopy study is in good accordance with previous findings on similar compositions. Here, the polarization experiments allowed us for estimating the chemical diffusion coefficient to be on the order of $10^{-17}$ m\(^2\)/s at room temperature. Only small differences of $D^0$ were found between the nanocrystalline and the
Figure 5. Exemplary cross cuts through KPFM surface potential $\phi_{sp}$ maps of CGnano after polarization with $+5$ V (A) and $-5$ V (B) and of CGepi after polarization with $+3$ V (C) and $-3$ V (D) as well as $+5$ V (E). It can be seen, that the gradients are 2–3 times larger for CGepi than for CGnano. Additionally, for CGepi, a surface potential change several $\mu$m away from the point of contact can be found. Here, the surface potential is increased for negative and decreased for positive polarization (indicated by arrows in C–E). Taking into account the error for referring to the initial state as zero and the error of detection, a standard deviation of 7% for the respective single values was calculated. Dashed line marks pristine state as reference.

epitaxial sample, despite the fact that the nanocrystalline thin film is known to have an effective electronic conductivity, which is comparable to the ionic one at room temperature.

Interestingly, the polarization behavior of the CGepi film can be explained by two distinct situations: (1) a bulk situation with cerium reduced at the surface and (2) a bulk situation with a space charge region at the surface. Both considerations give plausible results. The relaxation behavior observed for CGnano, which showed a lowered chemical diffusion can be explained by space charge effects occurring at the grain boundaries, as predicted initially.

Figure 6. Relaxation behavior of $\phi_{sp}$ taken from the area of the thin films in direct contact with the tip after polarization with $\pm 5$ V for CGnano and $\pm 3$ V for CGepi. Polarization experiments of CGepi with $+5$ V showing irreversible character are presented as well. The surface potential values are referred to the pristine material as 0 V. Error bars show standard deviation for set of experiments. Dotted lines represent an exponential fit of the data points.

Figure 7. Relaxation behavior of the reversible polarization effects of CGnano and CGepi in comparison to pellets with the composition $\text{Ce}_{0.8}\text{Gd}_{0.19}\text{Pr}_{0.01}\text{O}_{2-\delta}$ and single crystalline material with the composition $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ from Ref. 23, 24. Error bars show standard deviation for set of experiments.
With this study, it has been shown that the combined polarization-KPFM method is able to produce consistent results for evaluation of room temperature chemical diffusion processes. In the future, a compilation of similar experiments with variation of temperature, humidity, gas surrounding etc. could also help to further study not only the role of the microstructure but also the influence of the environment on the polarization properties of other industrially relevant oxides.

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