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The energy level of the Fe$^{2+/3+}$-transition in BaTiO$_3$ and SrTiO$_3$ single crystals

Issei Suzuki,*‡ Leonard G. Gura,§ and Andreas Klein

An approach to determine the defect energy levels of the Fe impurities in BaTiO$_3$ and SrTiO$_3$ single crystals using electrical conductance measurements is presented. The defect levels are obtained from the dependence of the activation energy of electrical transport on the oxygen vacancy concentration, which is varied by stepwise re-oxidation of a reduced sample. An energy level at 0.7–0.8 eV below the conduction band minimum $E_{CB}$ is identified for BaTiO$_3$, which can be assigned to the Fe$^{2+/3+}$-transition in good agreement with literature. In contrast, the conductivity of Fe-doped SrTiO$_3$ does not show a defect energy level in the upper half of the band gap, indicating that the Fe$^{2+/3+}$-transition in SrTiO$_3$ is near the conduction band minimum. The often reported alignment of defect energy levels, which is fulfilled for the Fe$^{3+/4+}$-transition in BaTiO$_3$ and SrTiO$_3$, does not hold for the Fe$^{2+/3+}$-transition in these compounds. This limits the applicability of Fe-doped SrTiO$_3$ as a model system for studying resistance degradation in acceptor-doped high-permittivity dielectrics.

1 Introduction

The increase of insulation resistance of high-permittivity dielectrics (resistance degradation), which occurs at elevated temperatures under applied electric field and which is governed by oxygen vacancy migration at temperatures above $\sim 100^\circ$C, remains a major obstacle for high-temperature application of multilayer ceramic capacitors. Acceptor-doped BaTiO$_3$ is widely used for such applications. The increase of the leakage current of such capacitors is well described by assuming internal field-driven rearrangement of oxygen vacancies. A strong chemical reduction of the dielectric near the cathode, which has been observed by different techniques, is likely related to a removal of oxygen from the dielectric. This must occur at the anode under operation conditions.

The change of oxygen content of a material by oxygen extraction and incorporation is affected by ionic space charge regions, which are determined by the difference in Fermi energy in the bulk and at the surface. The latter is determined by the Schottky barrier at the electrode interface and can be measured directly using photoelectron spectroscopy. The Fermi level in the bulk is, on the other hand, determined by the concentrations and energy levels of defects, such as (un)intentional impurities (dopants), and intrinsic defects, such as cation and anion vacancies or interstitials.

The energy levels of defects are related to the change of valence. Depending on the valence relative to the host site (lattice or interstitial position), an impurity can act as an electron source (donor) or trap (acceptor). The controlled doping of semiconductors is the basis for almost all electronic devices and relies on shallow defect states, which can be easily ionized at room temperature. As such materials are good electronic conductors, the energy levels of the defects can be determined by electrical transport measurements, for example using the Hall effect. Oxygen vacancies in BaTiO$_3$ and SrTiO$_3$ are also shallow defects, with energy levels near the conduction band minimum.

In contrast to this, transition-metal impurities generate deep defect levels. In electronically conducting materials, the energy levels of such defects can still be identified using electrical measurements, such as deep level transient spectroscopy (DLTS) or admittance spectroscopy. In dielectric materials, such as BaTiO$_3$, these techniques cannot be applied due to their low electrical conductivity.

Transition-metal impurities cannot be avoided in high-permittivity dielectrics. In BaTiO$_3$, for example, Fe is the most abundant impurity, which occurs in concentrations between 5 and 10 ppm.
100 ppm,24–26 corresponding to 0.3–6 · 10^{18} Fe atoms per cm^3. These impurities participate, for example, in the photorefective effect of BaTiO_3.25 Other transition-metals, such as Mn, are intentionally inserted in BaTiO_3 ceramics in order to reduce the leakage current in multilayer ceramic capacitors.3

Regarding the energy levels of Fe in BaTiO_3 and SrTiO_3, the Fe^{3+/4+} transition is well established in both materials.17,27–32 The charge transition occurs at an energy of 0.8–0.9 eV above the valence band maximum. In contrast to this, the Fe^{2+/3+} transition is considered only in BaTiO_3 with an energy level of ~2.4 eV above the valence band maximum.27,28,33 There is, however, also evidence from Mössbauer spectroscopy and infrared absorption for the presence of Fe^{2+}, either in reduced or in La co-doped Fe-doped SrTiO_3.34–36 An impedance study of degraded Fe-doped SrTiO_3 single crystals by Bayer et al. indicated the presence of an electron trap in the cathode region with an activation energy of 1.01 eV.37 If this trap is related to the Fe^{2+/3+} transition, it would be at a similar energy as the same transition in BaTiO_3. Such an alignment of defect energy levels has been reported for other systems, such as transition-metal impurities in III-V semiconductors,20–22 hydrogen impurities38 and oxygen vacancies39 and would therefore not be unexpected.

In this study, we present an approach to determine the defect energy levels using electrical conductance measurements. The defect level of Fe in a BaTiO_3 single crystal is obtained from the dependence of the activation energy of transport on the oxygen vacancy concentration. The latter is varied by stepwise re-oxidation of a reduced sample. An energy level at 0.7–0.8 eV below the conduction band minimum E_{CB} is identified, being in good agreement with literature on the Fe^{2+/3+} transition. In contrast, the conductivity of Fe-doped SrTiO_3 does not show a defect energy level in the upper half of the band gap.

2 Defect Model and Activation Energy

The defect chemistry of acceptor-doped BaTiO_3 is extensively described in literature.24,27,32,40–42 The relevant defect reactions are the oxygen exchange reaction, electron-hole pair generation and the ionization reactions of the acceptor. Partial de-ionization of oxygen vacancies into a singly charged and a neutral charge and the ionization reactions of the acceptor. Partial de-ionization are the oxygen exchange reaction, electron-hole pair generation 24,27,32,40–42. In good agreement with literature on the Fe^{3+} transition, has been set to 0.8 eV below the conduction band minimum in order to be comparable to the experimental results reported below. The energy level of the Fe^{3+/4+} transition has been set to 0.9 eV above the valence band maximum in order to distinguish the activation energies related to the two levels. The results of the calculations are comparable to those reported by Wechsler and Klein and by Maier and Randall for differently doped BaTiO_3.27,32

The mobilities of electrons in dependence on temperature is given by Ihrig33 and the oxygen vacancy mobility from diffusivity data reported by Kessel and coworkers.44 The latter have also been used by Maier and Randall.32

\[
\begin{align*}
\mu_c &= 8080 \cdot T^{-1.5} \cdot \exp(-0.021/k_BT) \\
\mu_h &= \frac{1}{2} \cdot \mu_c \\
\mu_{V_0}^{\text{free}} &= \frac{2e}{k_BT} \cdot D_{V_0} = \frac{2e}{k_BT} \cdot 6.4 \cdot 10^{-3} \cdot \exp(-0.7/k_BT)
\end{align*}
\]

Following Chan et al.45 we estimate the hole mobility, which is not relevant in this work as the hole conductivity does not contribute significantly to the conduction in the measured samples, as half the electron mobility. The total conductivity of the sample is finally obtained by summing up all three contributions:

\[
\sigma_{\text{tot}} = qn \mu_c + qp \mu_h + 2q \left( V_0^* \right) \mu_{V_0}^{\text{free}}
\]
In principle, it would be necessary to add polaron transport by hopping of electrons between the Fe centers. As the concentration of Fe is rather low in the studied samples (\(c(\text{Fe}) = 3 \cdot 10^{17} \text{ cm}^{-3}\)), this contribution can be neglected. The resulting partial conductivities are displayed in Fig. 1c).

The activation energy, which is shown in Fig. 1d)–e) in dependence oxygen vacancy concentration, Fermi level and conductivity, respectively, are obtained by calculating the defect concentrations and carrier mobilities at two different temperatures, 200 and 220°C. The activation energy clearly shows three different regions: At low, medium and high oxygen vacancy concentration, the activation energy is determined by the Fe\(^{3+/4+}\) and the Fe\(^{2+/3+}\) transitions and by the oxygen vacancies, respectively. The activation energies of the former two are exactly the energy differences between the transition levels and the valence and conduction band, respectively. The negative activation energies for strongly reduced samples result from the fact that the oxygen vacancies are rather shallow donors, which are completely ionized at the measurement temperature. The concentration of ionized oxygen vacancies, and therefore also that of the electrons, does therefore not depend on temperature. The activation energy of electrical conductivity is then completely determined by the temperature dependence of electron mobility, which is given by equation 7. As the carrier mobility decreases with increasing temperature, a negative activation energy results.

### 3 Experimental details

Nominally undoped BaTiO\(_3\) and 0.05 wt.\% Fe-doped SrTiO\(_3\) single crystals with a dimension of \(5 \times 5 \times 0.5 \text{ mm}^3\) were purchased from Alineason Materials Technology GmbH, Frankfurt, Germany and from MaTeck GmbH, Jülich, Germany, respectively. Both crystals have [100] orientation. The BaTiO\(_3\) samples had a slightly yellowish appearance while the Fe-doped SrTiO\(_3\) crystals exhibit a light brownish colour. Impurity concentrations of the BaTiO\(_3\) crystals were measured by using Glow Discharge Mass Spectrometry (GDMS). The most relevant impurity concentrations are given in Table 1. A complete list of concentrations is included in the supplementary information.\(^7\) The Fe concentration in SrTiO\(_3\) corresponds to \(2.75 \cdot 10^{19} \text{ cm}^{-3}\).

<table>
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<td>Fe</td>
<td>4.7</td>
<td>(3.0 \cdot 10^{11})</td>
</tr>
<tr>
<td>Al</td>
<td>0.26</td>
<td>(3.5 \cdot 10^{16})</td>
</tr>
<tr>
<td>Mn</td>
<td>0.11</td>
<td>(7.2 \cdot 10^{15})</td>
</tr>
<tr>
<td>Mg</td>
<td>0.66</td>
<td>(9.8 \cdot 10^{16})</td>
</tr>
<tr>
<td>Ni</td>
<td>0.36</td>
<td>(2.2 \cdot 10^{16})</td>
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The samples for the electrical measurement were prepared as follows; the crystals were sonicated in acetone, isopropanol and
ethanol for 5 mins each. Subsequently, the crystals were then equilibrated at 900°C for 12 h in air and quenched to room temperature with a high cooling rate of \( \sim 60 \text{K/s} \). No cracks were detected after the quench. The first BaTiO\(_3\) sample (sample 1) was then coated with Pt electrodes of 50 nm thickness on both top and bottom surfaces by DC magnetron sputtering. The crystal was then reduced by annealing in vacuum at \( \sim 5 \cdot 10^{-5} \text{Pa} \) at 700°C for 12 h resulting in a slightly bluish appearance. In-situ X-ray photoelectron spectroscopy (XPS) measurements of crystals treated this way exhibit a Fermi energy close to the conduction band minimum.\(^{46}\) A second BaTiO\(_3\) crystal (sample 2) was reduced by annealing in glass tube with 5% H\(_2\) and 95% Ar mixture flow of 60 sccm at 600°C for 12 h. SrTiO\(_3\) crystals were reduced by heating in H\(_2\)/Ar at 1000°C for 14 hours. Pt electrodes were deposited on both surfaces afterwards. The reducing conditions for SrTiO\(_3\) were set in order to obtain sufficiently high electrical conductivity. The stronger reducing conditions required for SrTiO\(_3\) as compared to BaTiO\(_3\) are reasonable due to the higher Fe concentration.

The re-oxidation and electrical measurement of the samples were simultaneously conducted in the furnace illustrated in Fig. 2. In order to re-oxidize the samples, they were heated up and cooled down repetitively with a rate of 2.5 K/min. Between heating and cooling, the samples were stored at the maximum temperature for a couple of minutes. The dc conductivity of the samples was continuously recorded with a Keithley 6487 picoammeter/voltage source (Keithley Instruments Inc., Ohio, USA), which was connected to the sample surfaces with a mechanically attached gold wire. The voltage applied was ranging from 10 to 100 mV depending on the resistivity of the sample. A low voltage was chosen to avoid polarization of the sample during measurement.

4 Results and Discussion

4.1 BaTiO\(_3\)

Figure 3 shows the Arrhenius plot of the conductivity measured during consecutive heating and cooling of a BaTiO\(_3\) single crystal reduced by heating in vacuum (sample1). At the beginning, the sample exhibits a conductivity of \( \sim 10^{-2} \text{S/cm} \). Taking a carrier mobility of 0.5 cm\(^2\)/Vs, this corresponds to an electron concentration of \( \sim 10^{17} \text{cm}^{-3} \), indicating that the oxygen vacancy concentration is only slightly higher than the Fe concentration. The sample is clearly n-type (Samples showing a conductivity which decreases/increases with increasing oxygen content are denominated as n-/p-type as common in defect chemistry and confirmed by Seebeck measurements\(^{47}\) and dominated by electron conduc-

The first cycle was conducted in vacuum (\( \sim 1 \cdot 10^{-5} \text{Pa} \)). The conductivity during heating in vacuum is identical to the one measured during cooling, indicating that the oxygen vacancy concentration does not change during the cycle. Hence no oxygen was incorporated during the temperature cycle. For temperatures < \( 128^\circ \text{C} \), which is the temperature at which the ferroelectric polarization of the crystal vanishes, the conductivity decreases with increasing temperature. This corresponds well to the negative activation energy in Fig. 1(d-f), which is a consequence of the temperature dependence of carrier mobility. In the respective temperature region, the conductivity also exhibits a power law dependence with a temperature exponent of \( \sim 1.8 \), which roughly agrees with the expected dependence from Eq. 7. Contrastingly, for temperatures > \( 128^\circ \text{C} \), the conductivity increases with increas-
ing temperature. A similar change in slope has been reported by Berglund and Baer. However, the temperature dependence of mobility according to Eq. 7 is expected to prevail particularly above the Curie temperature. Increasing the concentration of electronic carriers is also not expected to cause the change in slope, as all oxygen vacancies should be ionized already at room temperature due to their low ionization energy.

The change in slope is obviously related to the phase transition from the tetragonal ferroelectric to the cubic paraelectric phase. Measurements performed on reduced Fe-doped SrTiO$_3$ (see section 4.2) show a negative temperature coefficient at all temperatures, corresponding to the behaviour of BaTiO$_3$ in the ferroelectric phase. The origin of the behaviour of reduced BaTiO$_3$ is not clear yet. Schottky barriers at the contacts, which depend on polarization, could contribute to the effect and may explain the positive temperature coefficient in the paraelectric phase. However, Schottky barriers at the electrode interface do not seem to play a role in the measurements. This will be addressed more extensively in section 4.2.

All subsequent cycles were performed in ambient pressure in an atmosphere containing 99% N$_2$ and 1% O$_2$. During the first oxidation cycle, the conductivity follows the course of the vacuum cycle during heating up to 250°C. For $T > 250°C$, the conductivity starts to increase more slowly with temperature before it even decreases with temperature. During the cooling, the conductivity is substantially lower than the one during heating up. The decrease of conductivity is a clear indication for oxygen incorporation into the sample, which decreases the electron concentration and therefore the conductivity. In addition to the decrease of conductivity, the slope of the curve at lower temperature also increased. The activation energy determined at 200°C increased from $\sim 0.08$ to $\sim 0.16\,\text{eV}$.

In the following, the sample was repetitively re-oxidized in the N$_2$/O$_2$ atmosphere. In every measurement cycle the conductivity increases linearly with increasing temperature up to $\sim 250°C$. At higher temperatures the conductivity increases slower and then decreases, resulting in a significantly lower conductivity during cooling. With increasing cycle number, the conductivity continuously decreases. Concurrently, the activation energy increases with decreasing conductivity. To ensure the reproducibility of this re-oxidation experiment, an additional measurement was conducted on a second sample, which was reduced by heating in H$_2$/Ar. The resulting behaviour is comparable (see Fig. S1 in the supplementary information). The situation in the presented experiments is different as the regime of high oxygen activity is not reached. The homogenization time is estimated to be $\tau < 8.6h$. Considering the slow heating and cooling rates of 2.5K/min, the fact that homogenization already occurs at temperatures above 250°C and that oxygen vacancy concentrations are close to the Fe concentration, it appears reasonable to assume a largely homogeneous distribution of oxygen vacancies in the sample.

The calculation of the chemical diffusivity does not take electron/hole trapping into account, which can substantially slow down the diffusion of ionic species if their concentration becomes too low to charge balance the ionic motion. In Fe-doped SrTiO$_3$, the effect becomes pronounced at high oxygen pressure and low temperature when the oxygen vacancy concentration is low compared to the Fe concentration. The situation in the presented experiments is different as the regime of high oxygen activity is not reached. The activation energies we extract are for concentrations of oxygen vacancies larger than half the Fe concentration.

The calculation of the chemical diffusivity $D_\delta^O$ for $T = 250 \text{ and } 300°C$ is shown in Fig. 4 as a function of oxygen vacancy concentration. For high oxygen vacancy concentration, $D_\delta^O$ approaches the value of $3 \cdot D_\delta^{\text{Fe}}$ ($3.5 \cdot 10^{-9} \text{cm}^2/\text{s}$ at 250°C and $1.3 \cdot 10^{-8} \text{cm}^2/\text{s}$ at 300°C according to Eq. 9), in agreement with the expression derived by de Souza.$^{11} D_\delta^O$ exhibits pronounced maxima at $c(V_O) \approx c(\text{Fe})$ and $c(V_O) \approx \frac{1}{4}c(\text{Fe})$ and is $> 10^{-8} \text{cm}^2/\text{s}$ for a wide range of concentrations around these values. Therefore, the homogenization time is estimated to be $\tau < 8.6h$. Considering the slow heating and cooling rates of 2.5K/min, the fact that homogenization already occurs at temperatures above 250°C and that oxygen vacancy concentrations are close to the Fe concentration, it appears reasonable to assume a largely homogeneous distribution of oxygen vacancies in the sample.

Another important question is how much ionic conductivity contributes to the measured conductivity. Platinum electrodes are considered as being oxygen blocking. But, oxygen incorporation may still take place at the triple phase boundaries at the edges of Pt contacts. Using the same sample geometry, we could record time independent currents with dc voltages for $\gamma$-stabilized ZrO$_2$.
(YSZ) with Pt electrodes. The current through YSZ is only possible by ionic transport. Hence, a contribution of ionic transport to the current through the crystal cannot be excluded. The magnitude of the measured current is, however, much higher than expected for ionic conductivity. The calculation shown in Fig. 1(c) reveals an ionic conductivity at 200°C of 10^{-9}–10^{-8} S/cm. Such low conductivities are only observed during the very last cycles in Fig. 3. Even at this low conductivity, the conductivity is not necessarily determined by ionic motion.

The activation energies are determined from linear approximation of ln(σT) in the temperature range 150–200°C. The results obtained for the 2 investigated BaTiO_3 samples are shown in Fig. 5 as a function of conductivity at 200°C. Both samples show a very similar behaviour with a rise of the activation energy in the conductivity range S = 10^{-3}–10^{-5} S/cm. This corresponds well to the dependence calculated in section 2, indicating that the experimental approach is valid for the determination of the energy level of defects. The activation energy exhibits a clear plateau at ~0.8 eV. Within the assumed defect model this plateau can be assigned to the Fe^{2+/3+}-transition. The derived energy level is in good agreement with the values reported in literature.\textsuperscript{17,27,28}

4.2 SrTiO_3

Hall effect measurements in van der Pauw geometry of reduced SrTiO_3 crystals revealed electron concentrations and mobilities of ~10^{18} cm^{-3} and ~6 cm^{2}/Vs, respectively. Assuming that the electron concentration is equal to c(V_{O}^\prime) = c(Fe_{Ti}^{\prime\prime}), the oxygen vacancy concentration is less than 10% higher than the Fe concentration of 2.75 · 10^{19} cm^{-3}.

The evolution of electrical conductivity measured in parallel plate geometry with Pt electrodes is shown in Fig. 6 in the course of stepwise re-oxidation. In general higher temperatures are required to re-oxidize the Fe-doped SrTiO_3 in comparison to the unintentionally doped BaTiO_3. This is reasonable as the total amount of oxygen to be incorporated is much higher due to higher dopant concentration.

As for the BaTiO_3 crystals, the first cycle shows a conductivity of ~10^{-2} S/cm and a negative temperature coefficient. How-
ever, in contrast to BaTiO$_3$, the negative temperature coefficient of conductivity, which corresponds to a temperature independent carrier concentration, persists with decreasing conductivity. Only at a conductivity of $\sim 2 \cdot 10^{-8}$ S/cm, indicated by the red line in Fig. 6, the sample suddenly changed to a behaviour with a rather high activation energy of $>1.3$ eV. This activation corresponds to approximately half of the energy gap. Such an activation is expected when the oxygen vacancy concentration is exactly half of the Fe concentration. Slightly different activation energies will already reduce the activation energy as indicated by the defect model calculations in section 2. In the following cycles, the conductivity increases from cycle to cycle. This indicates that the sample became p-type, which indicates that $c(V'O) < \frac{1}{2}c(Fe)$.

The evolution of activation energy in the course of re-oxidation is shown in Fig. 7. The abrupt jump from a negative temperature coefficient to an activation energy corresponding to approximately half the energy gap and a subsequent p-type behaviour is observed in all samples and clearly different from the case of BaTiO$_3$. The transition from n-type to p-type behaviour seems to be less sharp for the undoped SrTiO$_3$ sample included in Fig. 7. This has to be taken with caution, however, as there is only a single data point with an intermediate activation energy. In contrast to BaTiO$_3$, the activation energy of the undoped SrTiO$_3$ sample does not exhibit a plateau, which is required to clearly identify a defect transition.

The activation energies measured for SrTiO$_3$ has two main implications: i) ionic conductivity cannot contribute to the measurements. Otherwise the activation energy can’t be that high (see Fig. 1); ii) In contrast to BaTiO$_3$, there is no evidence for the existence of an Fe$^{2+/3+}$ defect level in the band gap of SrTiO$_3$.

The origin of the different behaviour of the Fe impurity in BaTiO$_3$ and SrTiO$_3$ is not clear. It is, however, consistent with literature on defect properties of these materials, which take the Fe$^{2+/3+}$ transition into account for BaTiO$_3$ but not for SrTiO$_3$. One possible origin of this discrepancy is the fact that defect properties of SrTiO$_3$ are mostly investigated at high temperature, where the effect of the second charge transition may not be evident. The present study indicates, however, that the difference persists down to room temperature.

The impedance study of degraded Fe-doped SrTiO$_3$ single crystals by Bayer et al. indicated the presence of an electron trap in the cathode region. The cathode region is oxygen depleted due to the field-driven migration of oxygen vacancies towards the cathode in the course of degradation. By comparison with BaTiO$_3$, it seems straightforward to associate the observed activation energy of 1.01 eV to the Fe$^{2+/3+}$-transition. The present study does, however, not support this. A Fe$^{2+/3+}$-transition at 1.01 eV below the conduction band should also show up as a plateau of the activation energy in the n-type regime. This is evidently not observed.

The present study does not only rule out the Fe$^{2+/3+}$-transition as origin of the activation energy of 1 eV in the cathode region of degraded crystals, it could not identify an activation of electron transport in reduced Fe-doped SrTiO$_3$ at all. The presence of the p-n junction and a potentially stronger reduction in the cathode region of the degraded crystals compared to the homogeneously reduced single crystals used in this study may be related to the different behaviour.

There are literature reports providing experimental evidence for the presence of Fe$^{2+}$ in either reduced, or donor (La) co-doped, Fe-doped SrTiO$_3$. The observation of Fe$^{2+}$ in these studies and the apparent absence of the same in the present study could be consistently explained if the Fe$^{2+/3+}$-transition is energetically close to the conduction band edge. This is also in good agreement with a recent DFT study by Baker and coworkers. If the Fe$^{2+/3+}$-transition is energetically close to the conduction band edge in SrTiO$_3$, they can not be easily distinguished from oxygen vacancies in electrical measurements.

Another difference between SrTiO$_3$ and BaTiO$_3$ is the temperature coefficient of conductivity in the cubic phase at higher conductivity, which is positive in the case of BaTiO$_3$ and negative for SrTiO$_3$. A negative temperature coefficient is generally not expected in 2-point measurements, as Pt forms a Schottky barrier on these materials. These are expected to be negligibly small at room temperature, due to the negligible band discontinuity between SrTiO$_3$ and BaTiO$_3$. The observation of a negative temperature coefficient of conductivity therefore clearly rules out that Schottky barriers at the electrode interface are affecting the measurements.

The reason why ohmic contacts are obtained despite high Schottky barriers for electrons may lie in the Schottky barrier itself. As oxygen vacancies are mobile in the heated samples, they will accumulate adjacent to the interface and form an ionic space charge layer due to the difference in electrostatic potential. If the Schottky barrier is high the Fermi energy at the interface will be lower than in the bulk, at least in the early stages of the experiments where the conductivity is not too low. Assuming a potential difference of 0.5 V and, for simplicity, Boltzmann statistics, the concentration of oxygen vacancies at the interface will be enhanced compared to that in the bulk by $\exp \left(0.5 eV / k_B T \right)$, which amounts to $\sim 10^5$ at 200 °C. With such a high oxygen vacancy concentration, the space charge region at the electrode interface will become narrow enough that tunnelling can provide an ohmic contact. This does not conflict with rectifying current-voltage...
curves obtained with Pt contacts on Nb-doped SrTiO$_3$ as oxygen vacancies are minority defects in Nb-doped SrTiO$_3$. The presence of ohmic contacts, despite nominally high Schottky barriers, has also been observed for SnO$_2$. In this case, the absence of electron blocking interfaces has been related to the large contact area and to charge transport only along small parts such as grain boundaries. Grain boundaries are excluded in the present situation but dislocations may also contribute to the formation of an ohmic contact.

The energy levels of the Fe$^{3+/4+}$- and the Fe$^{2+/3+}$-transition are illustrated in Fig. 8. According to literature, the energy levels of transition-metal impurities in different materials are aligned if the energy bands are arranged according to their energy band alignment. This has been particularly demonstrated for III-V semiconductors. As shown in Fig. 8, the valence band maxima of SrTiO$_3$ and BaTiO$_3$ are very close in energy. This has been derived from photoelectron spectroscopy studies and is reasonable according to the very similar electronic structures of both materials. Due to this, one could expect that the energy levels of the Fe impurity in SrTiO$_3$ and SrTiO$_3$ are also aligned. This is indeed the case for the Fe$^{3+/4+}$-transition, which is 0.8–0.9 eV above the valence band maximum in both materials. In contrast, the Fe$^{2+/3+}$-transition in BaTiO$_3$ is $\sim$ 0.8 eV below the conduction band minimum, while it is close to the conduction band minimum in SrTiO$_3$. The difference could be related to the ionic radius of Fe$^{2+}$, which is slightly larger than that of Ti$^{4+}$. While the larger Ba ion leaves more space in the center of the oxygen octahedra to accommodate a larger cation, an Fe$^{2+}$ ion might induce a substantial lattice relaxation in SrTiO$_3$. However, additional studies are required to resolve the origin of the higher energy of the Fe$^{2+/3+}$-transition in SrTiO$_3$.

5 Summary and Conclusions

An approach to determine the energy levels of defects in high-permittivity dielectrics from the observation of the activation energy of electronic transport in the course of stepwise oxidation of reduced crystals has been presented. Nominally undoped BaTiO$_3$ single crystals containing $3 \cdot 10^{17}$ cm$^{-3}$ Fe impurities and 0.05 wt.% Fe-doped SrTiO$_3$ single have been studied. The conductivity is measured in parallel plate geometry with Pt electrodes and using direct current. The applied voltage was kept low in order to avoid polarization of the samples.

After reduction, the samples contained oxygen vacancy concentrations slightly higher than the Fe concentration, making them n-type electronic conductors. The samples were slowly heated in N$_2$/O$_2$ atmosphere up to temperatures where the conductivity starts to decrease by oxygen incorporation and cooled down again after a certain holding time. This allows for a controlled slow oxidation of the samples. A homogeneous vacancy distribution is enabled by a high thermodynamic factor for oxygen diffusion, as the oxygen vacancy concentration is close to the Fe concentration.

A contribution of ionic transport to the measurements can clearly be excluded in the case of SrTiO$_3$ and is also not likely to affect the measurement in the case of BaTiO$_3$. The study reveals a plateau of the activation energy at $\sim$ 0.8 eV for BaTiO$_3$. In the context of defect models provided in literature, this energy level can be associated to the Fe$^{2+/3+}$-transition of the Fe impurity. In contrast, the conductivity of Fe-doped SrTiO$_3$ abruptly changes from n-type with a temperature independent carrier concentration to p-type behaviour with a high activation energy. This rules out the presence of a Fe$^{2+/3+}$-transition at an energy substantially below the conduction band minimum. Very likely, this transition is energetically located near the conduction band minimum. While the energy level of the Fe$^{3+/4+}$-transition is at similar energy in BaTiO$_3$ and SrTiO$_3$, this rule does not hold for the Fe$^{2+/3+}$-transition. The origin of the higher energy of the Fe$^{2+/3+}$-transition in SrTiO$_3$ is not clear at present. Lattice relaxations might contribute to the effect.

According to the presented results, it seems unlikely that the electron trap observed in impedance studies in the cathode region of degraded Fe-doped SrTiO$_3$ is caused by the Fe$^{2+/3+}$-transition. Moreover, due to the different defect energy levels, acceptor-doped SrTiO$_3$ cannot generally be used as a model system for studying degradation behaviour of high-permittivity dielectrics.

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