Electrical conductivity of synthetic mullite single crystals

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ABSTRACT

The electrical conductivity of 2/1-mullite (approximate composition 2Al₂O₃ · SiO₂) was measured using plane parallel, polished plates cut perpendicular to [100], [010] and [001] from a large single crystal grown by the Czochralski method. Impedance spectra were recorded in the 1 Hz to 1 MHz frequency range at temperatures from 550 °C to 1400 °C in air. The conductivity versus temperature curves display changes of their slope between 850 °C and 950 °C depending on the crystallographical direction. The low temperature region (T < 850 °C) of conductivity is characterized by low electrical conductivities (σ_{av} ≈ 5.4 · 10⁻² Ω⁻¹cm⁻¹, average conductivity at 550°C) with σ_{[010]} > σ_{[100]} > σ_{[001]} and low activation energies (≈ 0.66 eV, average value). In the high temperature region (T > 950 °C) the electrical conductivity is significantly higher (σ_{av} ≈ 1.1 · 10⁻⁵ Ω⁻¹cm⁻¹, average conductivity at 1400 °C) with σ_{[001]} > σ_{[100]} ≈ σ_{[010]}, and with higher activation energies (≈ 1.6 eV). While the conductivity in the low temperature region essentially is electronic, ion conductivity dominates the conductivity in the high temperature region. We believe that the ionic conductivity is essentially due to hopping of oxygen atoms from structural sites linking the tetrahedral double chains in mullite towards adjacent oxygen vacancies especially in c-axis direction. These oxygen hoppings are associated with complex structural re-arrangements, which control and slow down the velocity of the processes. Thus the electrical conductivity of mullite at high temperature is much lower than e.g. that of Y-doped zirconia, but is significantly higher than that of α-alumina.

Keywords: mullite, single crystals, electrical conductivity, high temperature
INTRODUCTION

In spite of the fact that mullite occurs only very seldomly in natural rocks it is certainly one of the most widely studied materials in oxide ceramics. This is due to its outstanding properties, especially at high temperatures. Among these properties are the high thermal and chemical stability and the excellent thermo-shock and creep behavior which make mullite a promising candidate for many high temperature applications (see e.g. Schneider and Komarneni, 2005, and the references therein).

The crystal structure of mullite can best be described by means of the structurally closely related but more simple sillimanite. The key features of the crystal structure of sillimanite (Figure 1) are edge-sharing octahedral AlO$_6$ chains running parallel to the c-axis (Fischer and Schneider, 2005). The octahedral chains are linked by double chains of corner-sharing MO$_4$ tetrahedra (also parallel e), with an ordered distribution of the tetrahedral cations Al$^{3+}$ and Si$^{4+}$. Perpendicular to the c-axis the situation is different, with a sequence of AlO$_6$ octahedra and AlO$_4$ and SiO$_4$ tetrahedra occurring parallel to the a- and b-axis (Figure 1). The average structure of mullite can be derived from the one of sillimanite by the coupled substitution Si$^{4+}_{tet}$ by Al$^{3+}_{tet}$ (tet = tetrahedral) and simultaneous Al$^{3+}$ and Si$^{4+}$ disordering over the tetrahedral sites. The excess negative charge in mullite produced by the substitution of Si$^{4+}$ by Al$^{3+}$ is compensated by the formation of oxygen vacancies (see e.g. Fischer and Schneider, 2005). It involves removal of oxygens bridging two adjacent tetrahedra in the sillimanite structure (O(C) oxygen atoms), with the number of vacancies corresponding to the $x$-value of the general formula of the mullite-type alumino silicates Al$_{4+2x}$Si$_{2-2x}$O$_{10-x}$. The formation of vacancies causes associated tetrahedral sites TS to be displaced to positions designated as TS$^*$, so that the formerly bridging O(C) oxygen atoms become threefold coordinated and form T$_3$O groups (the so-called tetrahedral triclusters, TS$^*$, according to literature the TS position is favorably occupied by Al, see Figure 1).
A few preliminary studies exist on the electrical conductivity of mullite at high temperatures. Rommerskirchen et al. (1994), on the basis of electromagnetic fields (EMF) measurements on mullite ceramics provided data for an extremely high ionic conductivity of mullite being even superior to that of CaO-stabilized ZrO$_2$ solid electrolytes at temperatures between 1400°C and 1600°C. Chaudhuri et al. (1999) carried out DC (direct current) measurements to determine the electrical resistivity of undoped and transition metal-doped mullite ceramics at 1400°C. Chaudhuri and coworkers found a much lower electrical conductivity lying in between those of α-alumina and CaO-doped zirconia. Results of Faradaic current studies published by Mata-Osoro et al. (2012) at voltages up to 1000 V on mullite single crystals, ceramics and cermets showed small but measurable currents even at room temperature.

The determination of the nature of charge carriers in highly resistive materials is a challenge in general. For mullite, it has been suggested that below about 1000 °C, n-type electronic conduction might be expected to dominate (Buchanan, 2004). Using ab initio calculations, Aryal et al. (2012) showed that the 2/1-mullite single crystal is a large band gap insulator with a direct gap at the Brillouin zone center of about 4 eV. Analyzing the temperature dependence of the mullite resistivity up to 1400 °C, Chaudhuri et al. (1999) stated that mullite behaves like a non-metallic electrical conductor because its conductivity rises faster at low temperature but slows down at high temperature. Finally, Rommerskirchen et al. (1994) claimed that the mullite conductivity is predominantly ionic in the temperature range 1400 °C - 1600 °C.

As far as we know this is the first study performed on the electrical conductivity of mullite single crystals at high temperatures (up to 1400 °C) and also the first time that electrical conductivity of mullite is measured using impedance spectroscopy. The analysis of frequency dependence using impedance spectroscopy provides information about the dc-conductivity and can also give information on the nature of charge carriers in the samples.
EXPERIMENTAL

Sample preparation

Mullite single crystals of about 2:1-composition (2Al$_2$O$_3$·SiO$_2$) were grown by P. Reiche (Institute of Crystal Growth, IKZ Berlin, Germany). The starting materials were highly pure Al$_2$O$_3$ (77.3 wt.%) and SiO$_2$ (22.7 wt.%) powders which were homogeneously mixed and subsequently melted. Colorless single crystals of high optical quality with dimensions up to 80 mm in length and 20 mm in diameter were obtained employing the Czochralski method (for details see Guse and Mateika, 1974). According to infrared spectroscopic analysis the mullite single crystal is anhydrous (Rüschert et al., 2002). Plane parallel single crystal discs being about 1 mm thick and with about 1 cm$^2$ surface were cut perpendicular to [100], [010] and [001] from one single crystal, and were subsequently polished.

Electrical conductivity

Impedance spectra were recorded on the samples using a Solartorn SI 1260 spectrometer in the frequency range 1 Hz to 1 MHz and in the temperature range 550 °C - 1400 °C under air. The electrodes were platinum foils held in contact with the surface sample by a weak mechanical pressure controlled by a spring system and transmitted to the sample using an alumina rod. The sample was placed in the central zone of a vertical tubular furnace where the temperature is uniform. The temperature of the sample was measured using a Pt/Pt-10%Rh thermocouple located near the sample with an uncertainty of ± 20 °C.

Electrical conductivity data of oxides at high temperatures (T > 1000°C) are rather scarce and generally inaccurate. For example, for α-alumina, the magnitude of conductivity determined by different authors varies by up to 4 orders of magnitude (Will, 1992). The difference between the results may be due to impurities and/or to different experimental
conditions and procedures. The crucial point when measuring the conductivity is the choice of
the electrode metal and configuration. At low temperature \( T < 800^{\circ}\text{C} \), electrodes obtained by
sputtering or painting the surface of the sample using Pt, Au or Ag metals generally give good
and accurate results. Unfortunately, this method is not applicable at higher temperatures
because of the disconnection of metal from the surface sample especially for single crystals
where the surface is generally polished. Öijerholm et al (2006) studied the influence of
different electrode configurations on the electrical conductivity of \( \alpha \)-alumina ceramics and
single crystals versus temperature. They concluded that above 700 °C, the spring-loaded Pt
foil electrodes give accurate results and can be used for their simplicity. However, below 700
°C the surface conduction can have a significant influence on the measured conductivity for
highly resistive oxides and the use of the so-called guarded electrodes (Macdonald, 1987)
may be necessary to prevent such influence.

We used spring-loaded and unguarded electrodes in the temperature range 550 °C to
1400 °C. The sample was heated from room temperature up to 1400 °C using a rapid heating
rate (400 °C/h), and then the temperature was held two hours at 1400 °C in order to obtain the
maximum surface contact by sticking of the electrodes on the sample surface. The data
acquisition did not show any increase of the electrical conductivity \( \sigma \) during the plateau at
1400 °C indicating the good contact electrodes/sample even before reaching 1400 °C. After
slow cooling (120 °C/h) data were recorded by sweeping the frequency from 1 Hz to 1 MHz
each 5 minutes. A second heating/cooling cycle was performed on each sample and showed a
very good reproducibility of the conductivity results. Only data measured during decreasing
the temperature are presented and discussed in this paper. In order to check the contact quality
at low temperatures \( T < 700^{\circ}\text{C} \), we used the standard method by sputtering Pt on both faces
of the sample after the second cycle at high temperature. The comparison of the results
between the two methods (Pt foils and sputtering Pt) show no significant difference
suggesting that, on cooling the sample, stable electrode-sample contact is reached after the previous annealing at 1400 °C.

RESULTS

Frequency dependence of the electrical conductivity

In order to study the frequency dependence of the electrical conductivity of the single crystals, we used the Cole-Cole (or Nyquist) representation where we plot the opposite of the imaginary part of the complex impedance (-Z") versus its real part (Z'). Two common behaviors against temperature were observed (Figure 2):

1. At high temperatures (T > 900 °C), the plot consists of a semicircular arc at high frequencies (left part) and a spike at low frequencies (right part) the length of which increases with temperature. The left side arc is due to the dielectric relaxation process, while the spike is due to the well-known electrode polarization effects and is characteristic of ionic conductors (Grandjean 2006, Macdonald, 1987). The intersection of the curve with the real axis (Z"=0) gives the DC-resistance $R_{DC}$ which is related to the static conductivity $\sigma_{DC}$ by the relationship (Macdonald, 1987):

$$\sigma_{DC} = \frac{e}{S} \cdot \frac{1}{R_{DC}}$$

(1)

where $e$ is the thickness of the sample and $S$ is the electrode surface area.

2. At low temperatures (T < 900 °C), the left side arc still exists but the spike is replaced by a flat curve corresponding to Z"=0. For these low temperatures and high insulator materials, this flat curve cannot represent the electrode polarization effects. This purely resistive behavior should be a signature of an electronic conductivity. Such behavior has been observed for example in RuO$_2$-glass composites by Simonnet et al. (2004) who proved the mixed ionic and electronic character of the conductivity in their samples using DC-electrical measurements in the time domain. Unfortunately, this technique was not applicable in the case
of our highly resistive samples where the signal versus time was in the order of the magnitude
of noise due to the very low value of the DC-current generated in the sample. As we will see
in the next section, the value of the activation energy for \( T < 900 \, ^\circ\text{C} \) is also in favor of mixed
ionic and electronic conductors.

The circular arc (left side) can be fitted using an RC parallel circuit (Macdonald, 1987) which
gives \( R = 3 \times 10^6 \, \Omega, C = 7 \times 10^{-12} \, \text{F} \) for \( T = 800 \, ^\circ\text{C} \) and \( R = 1.6 \times 10^8 \, \Omega, C = 2.2 \times 10^{-9} \, \text{F} \) for \( T = 1300
\, ^\circ\text{C} \) (Figure 2a and 2b). Using the same fit on the data reported by Chiekh et al (2001) on a
single crystal (ZrO\(_2\)+9.5% mol Y\(_2\)O\(_3\)) at 300 \, ^\circ\text{C} \) we found \( R = 1.7 \times 10^5 \, \Omega \) and \( C = 5.2 \times 10^{-11} \, \text{F} \).
The comparison of the resistive part of the two samples shows that the mullite crystal is a
better insulator than the yttria doped zirconia one.

**Temperature dependence of electrical conductivity**

Analyzing the frequency dependence of the electrical conductivity allowed us to
determine the total DC-electrical conductivity \( \sigma(T) = \sigma_{\text{DC}}(T) \) as a function of temperature. At
high temperatures (\( T > 900^\circ\text{C} \)), the conductivity \( \sigma(T) \) is predominantly ionic and at low
temperatures (\( T < 900^\circ\text{C} \)), there is most probably an electronic contribution to the DC-
conductivity. However, due to the highly resistive character of our samples, we were not able
to separate each contribution (ionic and electronic) and its evolution with temperature.

Figure 3 shows the evolution of the DC-conductivity versus \( 10^4/T \) for the different
orientations of the mullite single crystal sample. Applying the propagation of error formula
(Ku, 1966) to equation 1:

\[
\frac{\Delta \sigma}{\sigma} = \frac{\Delta e}{e} + \frac{\Delta S}{S} + \frac{\Delta R}{R}
\]

we estimate the error of the conductivity \( \sigma \) to \( \pm 5 \% \) at the highest temperature (\( T = 1400 \, ^\circ\text{C} \)).

At lower temperatures, however, the uncertainty of \( R \) increases because of the use of
unguarded electrodes (Öijerholm et al., 2006). The estimated error bars of the conductivity $\sigma$
are shown in Figure 3 only on the [001] orientation for some selected temperatures for clarity.

The first important observation is that in the investigated temperature interval from 550 °C to
1400 °C the conductivity lies between about $10^{-9} \Omega^{-1} \text{cm}^{-1}$ and $10^{-5} \Omega^{-1} \text{cm}^{-1}$. This means that
mullite single crystal is an electrical insulator material even at high temperature ($\sigma \approx 1.3 \times 10^{-5}
\Omega^{-1} \text{cm}^{-1}$ at 1400°C). We also notice that the conductivity curve exhibits the same global trend
for the three crystallographic directions with a change in the slope between $T \approx 850$ °C and $T
\approx 950$ °C depending on the crystal orientation. In the low temperature range (LTR) the slope is
lower than in the high temperature range (HTR).

In order to describe the evolution of the electrical conductivity with temperature $T$ and to
compare our results with previous ones, we used the “original” Arrhenius equation,

$$\sigma(T) = \sigma_0 \exp \left( \frac{-E_a}{kT} \right)$$

(3)

where $k$ is the Boltzmann constant, $E_a$ is the activation energy associated with the transport
mechanism and $\sigma_0$ is a pre-exponential factor. The obtained values of $E_a$ and $\sigma_0$ for the three
crystallographic orientations are summarized in Table 1. The rather low value of the activation
energy ($\approx 0.64$ eV) observed in the LTR supports the assumption of a mixed ionic and
electronic conductivity we already suggested by analyzing the frequency dependence of
electrical conductivity, whereas the high value in the HTR is consistent with an ionic
conductivity driven by oxygen ions associated to vacancies (see discussion).

DISCUSSION

Our experimental results clearly indicate that the electrical conductivity of mullite single
crystal is controlled by two processes with different activation energies (Table 1). Below
about 800 °C the conductivity is dominated by electronic contributions with the highest
conductivity along [010] and with $\sigma_{[010]} > \sigma_{[100]} > \sigma_{[001]}$ ($\sigma_{\text{av}} \approx 5.4 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$, average

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conductivity at 550 °C). Above about 800 °C ionic conductivity becomes more and more
important, particularly along the [001] direction, which eventually leads to an anisotropic
electrical conductivity characterized by \( \sigma([001]) > \sigma([100]) = \sigma([010]) \). For example, at about
1400 °C the observed values are \( \sigma_{[001]} = 1.31(7) \cdot 10^{-5} \Omega^{-1} \text{cm}^{-1} \), \( \sigma_{[100]} = 1.01(5) \cdot 10^{-5} \Omega^{-1} \text{cm}^{-1} \)
and \( \sigma_{[010]} = 0.98(5) \cdot 10^{-5} \Omega^{-1} \text{cm}^{-1} \) (\( \sigma_v \approx 1.1 \cdot 10^{-5} \Omega^{-1} \text{cm}^{-1} \), average conductivity at 1400 °C).
The changing anisotropy of the electrical conductivity of mullite in the low and high
temperature region can be clearly seen in Figure 4 where typical representation surfaces of the
longitudinal electrical conductivity are shown. From the phenomenological point of view
electrical conductivity can be considered a second rank tensor \( \{ \sigma_{ij} \} \) in first approximation.

Following this, the longitudinal conductivity \( \sigma(u) \) along an arbitrary direction \( u = u_i e_i \) \( |u| = 1 \), \( e_i \) are the axes of the Cartesian reference system, i.e. \( e_1//a \), \( e_2//b \) and \( e_3//c \) in the case of
orthorhombic mullite) is given by \( \sigma(u) = \sum u_i u_j \sigma_{ij} \) (Einsteins sum convention applies).

Apart from the relatively low onset temperature of about 800 °C, the development of
ionic conductivity with temperature fits well to the picture of a glass-like transition derived
from anomalies observed in the temperature evolutions of heat capacity (Hildmann and
Schneider, 2004), thermal expansion (Schreuer et al., 2006, Schneider et al., 2008), and elastic
constants (Schreuer et al. 2006) for example. According to Schneider et al. (2008) the
distribution of defects, namely the oxygen vacancies required for charge compensation and
the triclusters (cf. Figure 1), is in a frozen-in state at low temperatures. At high temperatures
hopping of oxygen atoms, bridging tetrahedral double chains (O(C) oxygen atoms) towards
neighboring oxygen vacancies are possible. Gradual activation of this site-exchange processes
leads to a glass-like static ↔ dynamic transition. According to this model, the onset of oxygen
ion mobility and the correlated oxygen ion conductivity is associated with the observed
discontinuous changes of the slopes of \( \sigma(10^4/T) \). Because hopping of oxygen atoms can occur
more easily between O(C) atoms and neighboring O(C) vacancies parallel to the c-axis than
perpendicular to it, the anomaly in the \( \sigma \) versus \( 10^4/T \) curve occurs at lower temperatures (850
± 20 °C along [001] and at higher temperatures for directions within the (001) plane (890 ±
20 °C along [100] and 950 ± 20 °C along [010]). However, the small anisotropy of
conductivities parallel and perpendicular to the crystallographic e-axis shows that oxygen
hoppings have only a limited influence. This agrees well with the observation that oxygen
diffusion in mullite displays no significant anisotropy (Fielitz et al. 2001a,b). The broad
variation of the glass tranformation temperature ranging between about 850 °C derived from
electrical conductivity and up to about 1200 °C from calorimetric experiments cannot be
explained so far. It is not clear whether the different frequency regimes, and time and lengths
scales of the experiments can account for the large spread.

The little impact of oxygen hoppings along to the crystallographic e-axis on the
electrical conductivity can be explained by the complexity of site-exchange processes. The
entering of an oxygen into a neighboring vacancy eliminates this vacancy by forming a new
tetrahedral T-O(C)-T (T = Al³⁺, Si⁴⁺) bridge. This goes along with a migration of the TS*
tricluster cations adjacent to the former O(C) oxygen vacancy to newly formed TS sites².
Simultaneously a new vacancy at the originally occupied O(C) site is produced (see Schneider
et al. 2008, Figure 24). The latter requires a migration of the two tetrahedral TS atoms
adjacent to the originally occupied O(C) atoms to the newly formed tetrahedral TS* tricluster
sites. These structural rearrangements are much more sluggish than are simple O(C) hoppings
and thus control the velocity of the whole process. The complex structural processes
associated with these hoppings explain (i) the relative high values of activation energy in the
high temperature conductivity region of mullite (≈ 1.6 eV) compared to that of Y₂O₃-doped
ZrO₂ single crystal (≈ 0.82 eV) as reported by Filal et al. (1995) (note that in the paper of Filal
et al., 1995, the value of activation energy is given as 0.90 eV because the authors considered
a modified Arrhenius-type equation), and (ii) why the oxygen ionic conductivity in mullite is
much lower than that of effective oxygen ion conductors like CaO- or Y₂O₃-doped ZrO₂ (σ ≈
10⁻⁶ Ω⁻¹ cm⁻¹ for mullite instead of σ ≈ 10⁻¹ Ω⁻¹ cm⁻¹ for 3%Y₂O₃-doped ZrO₂, both values for
1100°C, see Figure 5). Furthermore, the complex structural processes of oxygen mobility
make the high oxygen ionic conductivities beyond 1400°C as published by Rommerskirchen
et al. (1994) rather unlikely. On the other hand due to the contribution of ionic conductivity
the overall conductivity of mullite is higher than it is in high temperature insulators like α-
alumina (at 1100 °C \(\sigma(\text{mullite}) \approx 10^{-6} \ \Omega^{-1}\text{cm}^{-1}\) instead of \(\sigma(\alpha-\text{alumina}) \approx 10^{-10} \ \Omega^{-1}\text{cm}^{-1}\), Figure
5).

The mean electrical conductivity of mullite single crystals in the low temperature
region displays a similar temperature-dependent behavior with comparable activation energies
as that obtained by Chaudhury et al. (1999) from polycrystalline mullite ceramics, although
the latter is significantly higher (Figure 6). The difference between both data sets is explained
by the contribution of grain boundary effects to the overall conductivity in the case of
ceramics caused by an enrichment of defects and impurities at the grain boundaries. In the
high temperature region the difference between single crystal and polycrystalline ceramic data
is continuously reduced with temperature and becomes almost zero at about 1400 °C (Figure
6). One reason of it may be the number of oxygen vacancies which are required for oxygen
ionic conductivity. This number is higher in Al-rich 2/1-mullite single crystals (\(x = 0.4\),
corresponding to 2 oxygen vacancies per 5 unit cells) than in 3/2-mullite polycrystalline
ceramics (\(x = 0.25\), corresponding to 1 oxygen vacancy per 4 unit cells). The influence of
grain boundaries probably is less important, since the free paths of ions and electrons between
collisions is less than about 150 Å (see Kingery et al. 1975).
REFERENCES CITED


FIGURE CAPTIONS

Figure 1. Crystal structure of mullite in comparison to that of sillimanite in projections parallel [001] (above) and parallel [100] (below). The structure plots of mullite give a schematic and simplified view of the oxygen vacancies and the tetrahedral triclusters (see the text).

Figure 2. Cole-Cole (or Nyquist) plots for the crystal [001] at two temperatures (a) $T = 800 ^\circ C$ and (b) $T = 1300 ^\circ C$. $Z'$ and $Z''$ represent the real and the imaginary parts of the complex impedance, respectively. Scatters represent the experimental points and solid lines the fit of the circular arc (left side) using an RC parallel circuit (see text).

Figure 3. Arrhenius plot of the DC conductivity for the three mullite single crystals. Solid lines represent the fit of the experimental points using equation 2 (see text).

Figure 4. Representation surfaces of longitudinal electrical conductivity of mullite single crystal at 550 $^\circ C$ (left) and 1400 $^\circ C$ (right). Units of axes are $10^8 \Omega^{-1} \text{cm}^{-1}$ and $10^6 \Omega^{-1} \text{cm}^{-1}$, respectively.

Figure 5. Comparison of the electrical conductivity of the single crystals: mullite [001] (this work), pure alumina [001] (Will et al., 1992) and 3% $\text{Y_2O_3}$-doped $\text{ZrO_2}$ (Filal et al., 1995).

Figure 6. Comparison between the mean electrical conductivity of the three orientations of our mullite single crystals and the conductivity of the mullite ceramic reported by Chaudhury et al. (1999).
Table 1

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<td>$E_a$ (eV)</td>
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<td>1.64 ± 0.04</td>
<td>0.64 ± 0.12</td>
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<td>log($\sigma_0$)</td>
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<td>0.01 ± 0.05</td>
<td>-4.45 ± 0.26</td>
<td>-0.13 ± 0.05</td>
<td>-4.25 ± 0.26</td>
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Table 1. Activation energy ($E_a$) and pre-exponential factor (log($\sigma_0$)) values for the electrical conductivity along to [001], [100] and [010] of mullite in low temperature region (LTR) and in high temperature one (HTR).
Figure 1. Crystal structure of mullite in comparison to that of sillimanite in projections parallel [001] (above) and parallel [100] (below). The structure plots of mullite give a schematic and simplified view of the oxygen vacancies and the tetrahedral triclusters (see the text).
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Figure 4. Representation surfaces of longitudinal electrical conductivity of mullite single crystal at 550 °C (left) and 1400 °C (right). Units of axes are $10^{-9} \Omega^{-1} \text{cm}^{-1}$ and $10^{-6} \Omega^{-1} \text{cm}^{-1}$, respectively.
Figure 5.

Figure 5. Comparison of the electrical conductivity of the single crystals: mullite [001] (this work), pure alumina [001] (Will et al. 1992) and 3%Y2O3-doped ZrO2 (Filal et al. 1995).
**Figure 6.** Comparison between the mean electrical conductivity of the three orientations of our mullite single crystals and the conductivity of the mullite ceramic reported by Chaudhury et al (1999).