Supplementary Information

Increase of the electronic conductivity in the doped *rt-nano* sample – Calculation of the corresponding SCL potential (Eq. (11))

In order to evaluate the SCL potential that is necessary to increase the electronic conductivity in the 10 mol% Gd-doped *rt-nano* sample to the value shown in Fig. 5, the bulk electronic conductivity $\sigma_{e,\infty}$ needs to be determined. This value cannot directly be obtained experimentally considering only the highly doped sample.

Therefore, starting from the electronic conductivity of a nominally pure, epitaxial CeO_2 thin film, $\sigma_{e,\infty}$ is obtained as shown below.

For the calculation, the impurity content of the nominally pure sample needs to be estimated. From the pO_2 dependence of the undoped sample (slope of about -1/5), we can conclude that – as expected – at such low temperatures (≤ 300°C) the conductivity is not entirely in the native regime but already under the partial influence of a small concentration of impurities acting as acceptor dopants*. At 280°C and pO_2 = 10^{-3} bar the (electronic) conductivity of the epitaxial nominally pure sample is $1.7 \cdot 10^{-5}$ $S \cdot m^{-1}$ while under the same conditions the conductivity of the 10 mol% Gd-doped *ht-epitaxial* sample is about three orders of magnitude higher ($1.2 \cdot 10^{-2}$ $S \cdot m^{-1}$). Therefore, the acceptor content of the nominally pure sample must be smaller than 10 mol% / 1000 = 100 ppm because otherwise already the ionic conductivity of the undoped sample would be higher than the measured value. As an ionic conductivity, which is determined by impurities, is pO_2 independent and as the nominally pure sample clearly exhibits a pO_2 dependence, the conductivity must be mainly electronic, given that the electronic mobility is much higher than the ionic one. Hence the upper limit of the impurity content must be even smaller than 100 ppm. Therefore, the impurity content is assumed to be here between 0 and 50 ppm.

This leads to an upper and lower limit of the electron concentration and therefore to an upper and lower limit of the SCL potential in the 10 mol% Gd-doped *rt-nano* sample as shown below.

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* For the electronic conductivity in pure CeO_2 a pO_2 dependence of -1/6 is expected, for an acceptor doped sample the pO_2 dependence is -1/4.

Experimental data: Undoped CeO_2 epitaxial sample

Sample:	epitaxial nominally pure CeO_2 on Al_2O_3 <0001>
	thickness L = 214 nm (TEM)
Measurement conditions:	θ = 280 °C
	$pO_2 = 10^{-3}$ bar
Conductivity data:	$\sigma_{\infty,pure} = 1.7 \cdot 10^{-5}\ \mathrm{S \cdot m^{-1}}$

Using the mobility data of Tuller and Nowick (Ref. [S1]) the bulk electron concentration of the pure sample $n_{\infty,pure}$ can be determined:

$$n_{\infty,pure} = \frac{\sigma_{\infty,pure}}{e \cdot u_e}$$

$$u_e = \frac{u_0}{T} \cdot e^{-\frac{h_n}{k_B T}} \qquad \text{with } u_0 = 390\ \frac{\mathrm{K \cdot cm^2}}{\mathrm{V \cdot s}} \text{ and } h_n = 0.40\ \mathrm{eV} \text{ (from Ref. [S1])}$$

→ $u_e = 1.6 \cdot 10^{-4}\ \mathrm{cm^2 \cdot V^{-1} \cdot s^{-1}}$ at T = 553 K

→ $n_{\infty,pure} = 6.6 \cdot 10^{15}\ \mathrm{cm^{-3}}$

Experimental data: 10 mol% Gd-doped CeO_2 rt-nano sample:

Sample: 10 mol% Gd-doped CeO_2 on SiO_2 <0001>, deposited at room temperature, thickness L = 460 nm (from TEM results of similar films), doping content: $c_{Gd'_{Ce},doped} = 2.5 \cdot 10^{21}\ \mathrm{cm}^{-3}$

Measurement conditions: $\theta = 280\,°\mathrm{C}$

$pO_2 = 10^{-5}$ bar

Conductivity data: The electronic conductivity can be obtained from the fit of the σ vs. pO_2 plot (see Fig. 5):

$$\sigma_m = \sigma^{\perp}_{V_O^{\bullet\bullet},m} + \sigma^{\parallel}_{e,m} \;=\; \sigma^{\perp}_{V_O^{\bullet\bullet},m} + \beta_L \varphi_L \left(\bar{\sigma}^{\parallel}_e\right)^* \cdot \left(\frac{pO_2}{pO_2^{\;*}}\right)^n$$

→ $\sigma^{\parallel}_{e,m} = 2.5 \cdot 10^{-6}\ \mathrm{S \cdot m^{-1}}$ (at $pO_2 = 10^{-5}$ bar)

Here $\sigma^{\parallel}_{e,m}$ is the measured effective conductivity of the electrons.

Upper limit of the SCL potential in the 10 mol% Gd-doped CeO_2 rt-nano sample

In this case one assumes the impurity (acceptor) concentration in the pure sample to be lower than the native electron concentration:

$$c_{V_O^{\bullet\bullet},\infty,pure} = \frac{n_{\infty,pure}}{2} = 3.3\cdot 10^{15}\ \text{cm}^{-3}$$

Using the mass action law of the reduction reaction in CeO_2 the lower limit of the electron concentration in the doped material can be determined:

$$pO_{2,pure}^{1/2}\cdot c_{V_O^{\bullet\bullet},\infty,pure}\cdot n_{\infty,pure}^2 = pO_{2,doped}^{1/2}\cdot c_{V_O^{\bullet\bullet},\infty,doped}\cdot n_{\infty,doped}^2$$

$$n_{\infty,doped} = \left(\frac{pO_{2,pure}}{pO_{2,doped}}\right)^{1/4}\cdot\left(2c_{V_O^{\bullet\bullet},\infty,doped}\right)^{-1/2}\cdot n_{\infty,pure}^{3/2} \qquad \left(\text{with } 2c_{V_O^{\bullet\bullet},\infty,doped} = c_{Gd_{Ce}^{/},doped} = 2.5\cdot 10^{21}\ \text{cm}^{-3}\right)$$

From this, one obtains the minimal bulk conductivity of the electrons in the doped material:

$$n_\infty = n_{\infty,doped} = 3.4\cdot 10^{13}\ \text{cm}^{-3}$$

$$\sigma_{e,\infty} = e\cdot u_e\cdot n_\infty$$

$$\sigma_{e,\infty} = 8.7\cdot 10^{-8}\ \text{S/m} \qquad (\text{with } u_e = 1.6\cdot 10^{-4}\ \text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}\text{, see above})$$

Using the bulk conductivity and the experimentally obtained effective electronic conductivity the SCL potential can be calculated. As the electronic bulk conductivity derived here is the lower limit of this variable, the resulting potential of 0.35 V represents the upper limit of the SCL potential in the doped material.

$$\frac{\sigma_{e,m}^{\parallel}}{\sigma_{e,\infty}} = \frac{2}{d\cdot e}\sqrt{\frac{\varepsilon_r\varepsilon_0 k_B T}{c_{V_O^{\bullet\bullet},\infty}}}\cdot\frac{e^{e\cdot\Delta\Phi_0/k_BT}}{\sqrt{e\Delta\Phi_0/k_BT}} \qquad \text{Eq. (11)}$$

Here *d* is the grain size (10 nm), ε_r = 26, *T* = 553 K and $c_{V_O^{\bullet\bullet},\infty} = c_{V_O^{\bullet\bullet},\infty,doped} = 1.3\cdot 10^{21}\ \text{cm}^{-3}$.

Lower limit of the SCL potential in the 10 mol% Gd-doped CeO_2 rt-nano sample

Here, one assumes the impurity (acceptor) concentration in the pure sample to be equal to 50 ppm:

$$c_{V_O^{\bullet\bullet},\infty,pure} = \frac{c_{imp.}}{2} = 6.3 \cdot 10^{17}\,\mathrm{cm}^{-3}$$

Again the mass action law is used to determine the bulk concentration of the electrons in the doped sample. In this case (under the assumption of a maximal acceptor concentration of 50 ppm in the pure sample) the upper limit of the electron concentration is obtained:

$$pO_{2,pure}^{1/2} \cdot c_{V_O^{\bullet\bullet},\infty,pure} \cdot n_{\infty,pure}^2 = pO_{2,doped}^{1/2} \cdot c_{V_O^{\bullet\bullet},\infty,doped} \cdot n_{\infty,doped}^2$$

$$n_{\infty,doped} = \left(\frac{pO_{2,pure}}{pO_{2,doped}}\right)^{1/4} \cdot \left(\frac{c_{V_O^{\bullet\bullet},\infty,pure}}{c_{V_O^{\bullet\bullet},\infty,doped}}\right)^{1/2} \cdot n_{\infty,pure}$$

Thus the resulting electron bulk conductivity represents the upper limit for the doped material.

$$n_\infty = n_{\infty,doped} = 4.7 \cdot 10^{14}\ \mathrm{cm}^{-3}$$

$$\sigma_{e,\infty} = e \cdot u_e \cdot n_\infty = 1.2 \cdot 10^{-6}\ \mathrm{S \cdot m^{-1}}$$

With this value it is then possible to determine the minimal SCL potential corresponding to the increase of the electronic conductivity; it is 0.22 V.

$$\frac{\sigma_{e,m}^{\parallel}}{\sigma_{e,\infty}} = \frac{2}{d \cdot e}\sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{c_{V_O^{\bullet\bullet},\infty}}} \cdot \frac{e^{e \cdot \Delta\Phi_0 / k_B T}}{\sqrt{e\Delta\Phi_0 / k_B T}} \qquad \text{Eq. (11)}$$

Again, d is the grain size (10 nm), $\varepsilon_r = 26$, $T = 553$ K and $c_{V_O^{\bullet\bullet},\infty} = c_{V_O^{\bullet\bullet},\infty,doped} = 1.3 \cdot 10^{21}\ \mathrm{cm}^{-3}$.

In conclusion, the SCL potential $\Delta\Phi_0$ in the doped sample ranges between 0.22 V and 0.35 V, which leads to the average value of $\Delta\Phi_0$ = 0.29 ± 0.07 V.

References

S1 H.L. Tuller, A.S. Nowick, "Defect Structure and Electrical Properties of Nonstoichiometric CeO_2 Single Crystals", *J. Electrochem. Soc.* **126** (2), 209-217 (1979).