# The oxygen ion conductivity of Lu doped ceria

Julius Koettgen,<sup>1,2,3,4,\*</sup> Gerald Dück,<sup>1</sup> and Manfred Martin<sup>1,5,6,2,†</sup>

<sup>1</sup>Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, 52056 Aachen, Germany

<sup>2</sup>JARA-HPC, Forschungszentrum Jülich and RWTH Aachen University, Germany

<sup>3</sup>Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

<sup>4</sup>Department of Materials Science and Engineering,

University of California, Berkeley, California 94720, United States

<sup>5</sup>Helmholtz-Institut Münster (IEK-12), Forschungszentrum Jülich GmbH, Corrensstr. 46, 48149 Münster, Germany

<sup>6</sup> JARA-Energy, Forschungszentrum Jülich and RWTH Aachen University, Germany

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The oxygen ion conductivity of polycrystalline samples of Lu doped ceria is studied using impedance spectroscopy. Lutetium doped ceria is of particular interest as Lu has a similar ionic radius as the host cation Ce. The change of the ionic conductivity as a function of the Lu dopant fraction is investigated in detail revealing a similar behavior as Sm doped ceria that has one of the highest ionic conductivity in ternary cerium oxides. In comparison with simulations, the experimental dependence of the conductivity on the dopant fraction reveals that migration barriers for oxygen vacancy jumps around Lu ions are slightly higher than for jumps in pure ceria. The absolute conductivity is small due to the strong trapping of oxygen vacancies near Lu dopants.

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### I. INTRODUCTION

Materials with high ionic conductivity are essential for applications including Solid Oxide Fuel Cells and Solid Oxide Electrolyzer Cells for energy conversion and storage,<sup>1,2</sup> oxygen membranes and catalysis.<sup>3–6</sup> Ceria (CeO<sub>2</sub>) doped with rare-earth oxides (RE<sub>2</sub>O<sub>3</sub>) can exhibit high oxygen ion conductivity. Doping with lower valent oxides leads to oxygen vacancies, as shown in Eq. 1 in Kröger-Vink notation, which significantly increase the ionic conductivity.<sup>7</sup>

$$\operatorname{RE}_{2}\operatorname{O}_{3} \longrightarrow 2\operatorname{RE}_{\operatorname{Ce}}^{'} + 3\operatorname{O}_{\operatorname{O}}^{\times} + \operatorname{V}_{\operatorname{O}}^{\bullet\bullet} \tag{1}$$

Oxygen vacancies lead to ionic conductivity as oxygen ions can jump to a vacant lattice site (hopping mechanism). For the oxygen ion conductivity, jumps of oxygen ions or vacancies occur mainly between adjacent tetrahedral oxygen sites in (100) direction<sup>8</sup> with the experimental jump distance of about l = 2.7 Å given by half of the unit cell length at room temperature.<sup>7</sup> Along the migration pathway, the migrating oxygen ion passes between two adjacent cations, which form a migration edge as shown in Fig. 1.<sup>9–11</sup>

In the last 50 years, doped ceria has been investigated in experiments,<sup>12–16</sup> analytical models,<sup>17–19</sup> semiempirical,<sup>20,21</sup> and *ab initio* calculations.<sup>11,22,23</sup> The focus was on the search for dopants that lead to the highest ionic conductivity. For the detailed understanding of the underlying mechanism, which determines the magnitude of the oxygen ion conductivity as a function of the dopant concentration, we will focus in this work on Lutetium as dopant.

Lu doped ceria is of particular interest as the dopant  $Lu^{3+}$  has a similar ionic radius as the host cation  $Ce^{4+}$ .<sup>24</sup> As a result, migration barriers for oxygen vacancy jumps around Lu ions (Ce-Lu edge in Fig. 1, 0.45 eV) are similar to the migration barriers in pure ceria (0.47 eV)as shown in *ab initio* calculations.<sup>9–11</sup> Jumps through the edge formed by two adjacent Lu ions (Lu-Lu edge in Fig. 1, 0.64 eV)<sup>11</sup> have a larger migration barrier but these edges appear only rarely for dopant fractions x < 0.3 in  $\widetilde{\operatorname{Ce}}_{1-x} \operatorname{Lu}_x \operatorname{O}_{2-x/2}$ .<sup>11</sup> Therefore, migration energy barriers in Lu doped ceria are mainly determined by the Lu-V association between the migrating oxygen vacancies and Lu dopants as well as the V-V repulsion between oxygen vacancies. Thus, lutetium is the ideal candidate to unravel the interplay of the oxygen vacancy creation by doping as shown in Eq. 1 and the Lu-V association determining the ionic conductivity. Lu doped ceria is rarely investigated due to its low ionic conductivity. Only for a few dopant fractions the bulk $^{16,25}$  and total conductivity<sup>26</sup> have been measured. However, solubilities above x > 0.25 are reported.<sup>27–29</sup> Therefore, Lu doped ceria is investigated in this work using impedance spectroscopy and a fine-grained spacing of the dopant fraction  $(0.025 \leq \Delta x \leq 0.05)$ . The results are compared with Sm doped ceria. One of the highest conductivity for a ternary cerium oxide has been reported for Sm doped ceria.

The paper has the following structure: The experimental setup are described in section II. In section III, results for the ionic conductivity in Lu doped ceria are shown. Finally, a short summary is given in section IV.

#### II. EXPERIMENTAL DETAILS

Polycrystalline samples of the composition  $Ce_{1-x}Lu_xO_{2-x/2}$  were prepared according to the sol-gel method.<sup>30</sup> Cerium (III) nitrate hexahydrate  $(Ce(NO_3)_3 \cdot 6H_2O, 99.9\%$  Chempur), lutetium (III) nitrate hydrate (Lu(NO<sub>3</sub>)<sub>3</sub>  $\cdot y$  H<sub>2</sub>O, 99.9%, Chempur) and citric acid (VWR International, 2.5 equivalent) were dissolved in water, where y was determined by oxidation and gravimetric analysis. During mixing for several hours at 50 °C, the sol-gel transformation occurred. The temperature was raised to 120–150 °C leading to foaming. The foam was dried for three hours at 350 °C and treated for four hours at 1000 °C with a heating and cooling rate of 5 °C/min. The powder was milled and uniaxially pressed to pellets with 10 mm diameter using a force of 25 kN for 25 min. The pellets were sintered in air at 1400 °C for 24 hours with a heating and cooling rate of 200 °C/hour.

Scanning electron microscope measurements (LEO 1450VP, Carl Zeiss, Oberkochen, Germany) show that grain sizes are similar for the variously doped ceria (about 1  $\mu$ m, see Fig. 2). Only for Ce<sub>0.85</sub>Lu<sub>0.15</sub>O<sub>1.925</sub> and Ce<sub>0.8</sub>Lu<sub>0.2</sub>O<sub>1.9</sub> smaller grain sizes were found (0.5±0.1  $\mu$ m). The compositions were successfully verified using energy dispersive X-ray spectroscopy (Oxford INCA, Oxford Instruments, Abingdon, UK). Using X-ray diffraction measurements ( $\theta/\theta$ -diffractometer, STOE & Cie GmbH, Darmstadt, Germany with secondary monochromator),<sup>31</sup> the phase purity was successfully investigated (Fig. 3) and successfully compared with lattice parameters reported earlier (Figs. 4 and 5).<sup>27-29</sup>

Samples were covered and contacted with platinum paste and wire for impedance spectroscopy measurements. Samples were equilibrated at 1000 °C for 3 hours with a heating rate of 0.5 °C/min and cooling rate of 0.9 °C/min. Impedance spectroscopy measurements were performed in air using a Solatron 1260 (Schlumberger) and a 2-point geometry (e.g., Fig. 6). The impedance was measured for frequencies between  $(0.07 - 10^7)$  Hz. Between (0.07 - 20) Hz, measurements were repeated five times and averaged. The impedance measurements were repeated for every composition with multiple samples and the reproducibility for few temperatures was verified. Ceria can be reduced under oxygen-poor con-



Figure 1: Migration edge configurations in lutetium doped ceria. Ce-Ce edge (a), Ce-Lu edge (b) and Lu-Lu edge (c). Lutetium ions (blue spheres), oxygen ions (red spheres) and vacancies (red boxes), and cerium ions (green).<sup>9</sup> - Reproduced by permission of the PCCP Owner Societies



Figure 2: Scanning electron micrographs of  $\operatorname{Ce}_{1-x}\operatorname{Lu}_x\operatorname{O}_{2-x/2}$  and  $\operatorname{Ce}_{1-x}\operatorname{Sm}_x\operatorname{O}_{2-x/2}$  as a reference. Tonal values are adapted.



Figure 3: Rietveld refined X-ray diffractometer measurement of Ce<sub>0.9</sub>Lu<sub>0.1</sub>O<sub>1.95</sub>. Measurement (black), calculation (red), difference (observed-calculated; lower box) and Bragg positions (marked with a line).

ditions leading to the formation of polarons and oxygen vacancies.<sup>32,33</sup> Therefore, measurements are restricted to oxidizing conditions. Here, the ionic conductivity is significantly larger than the electronic conductivity, which can be neglected.

Bulk, grain boundary and electrode contributions were identified in the Nyquist plot with decreasing frequency according to the corresponding capacitances in agreement with literature (Fig. 6).<sup>34,36–41</sup> The capacitance of the bulk domain is in the range of tens of picofarads  $(10^{-11} \text{ F})$ , which is consistent with the geometric capacitance of the samples according to literature. The capacitance of the grain boundary domain is in the range of tens of nanofarads  $(10^{-8} \text{ F})$ .<sup>13,34,35</sup> Rarely all contributions can be measured at the same time due to the limited frequency range in the experiment. The bulk oxygen ion conductivity could be measured between (81 - 368) °C, grain boundary conductivities could be measured between (173 - 681) °C. Beyond that, interferences caused by other electric fields and overlapping semicircles appear. Therefore, in this work, every semicircle is fitted individually using the equivalent circuit model  $R_1 + Q_2/R_2$ with the resistance  $R_2$  and a constant phase element



Figure 4: X-ray diffractograms of  $Ce_{1-x}Lu_xO_{2-x/2}$ .



Figure 5: Lattice parameter a of  $Ce_{1-x}Lu_xO_{2-x/2}$  in comparison with literature.<sup>27–29</sup>



Figure 6: Impedance spectrum of Ce<sub>0.8</sub>Lu<sub>0.2</sub>O<sub>1.9</sub> at 368 °C. The a) Nyquist plot and b) real Z' and imaginary part Z'' of the impedance as a function of the frequency f is shown. Bulk (1), grain boundary (2) and electrode (3) semicircles are identified in agreement with literature.<sup>13,34,35</sup>



Figure 7: The applied equivalent circuit model  $R_1 + Q_2/R_2$ .



Figure 8: Arrhenius behavior of the bulk conductivity in  $\operatorname{Ce}_{1-x}\operatorname{Lu}_x\operatorname{O}_{2-x/2}$ . Compared to results by Omar *et*  $al.^{16,25}$ 

 $Q_2$  of the semicircle with  $R_1 = 0$  for the bulk domain (Fig. 7).<sup>42</sup> Impedance measurements were analyzed using EC-Lab (BioLogic). Fitting semicircles individually can lead to an overestimation of the resistance as found for several measurements: For the fit of individual semicircles, the resistance was overestimated below 5% for the bulk domain and below 10% for the grain boundary domain. For dopant fractions above x = 0.1, grain boundary and electrode semicircles overlap leading to a large error on the grain boundary conductivity.

The ionic conductivity is calculated according to

$$\sigma_i = \frac{l}{R_i \cdot A} \tag{2}$$

for the bulk and grain boundary domain, respectively, where  $R_i$  is the resistance according to the equivalent circuit, l the thickness of the sample and A the surface area. The sample dimensions are chosen identically for bulk and grain boundary domains. Errors arise due to the equivalent circuit fit, the thickness of the sample ( $\pm 0.02 \text{ mm}$ ) and the diameter of the pellets. The resulting error on the conductivity (and stoichiometry) is mostly smaller than the symbol sizes in the corresponding figures. The prefactor of conductivity, the attempt frequency and the activation enthalpy are determined from an Arrhenius plot according to an earlier work.<sup>11</sup>

According to the serial brick layer model, the total resistivity is the sum of the macroscopic resistivities of bulk and grain boundary domains,  $R_{\text{total}} = R_{\text{bulk}} + R_{\text{gb}}$ .<sup>43–46</sup>



Figure 9: Arrhenius behavior of the macroscopic grain boundary (left) and total conductivity (right) in  $\operatorname{Ce}_{1-x}\operatorname{Lu}_x\operatorname{O}_{2-x/2}$  in comparison with literature.<sup>26</sup>



Figure 10: Bulk oxygen ion conductivities of Lu doped ceria. Lines are a guide to the eye only.

Therefore the total conductivity

$$\sigma_{\rm total} = \frac{l/A}{R_{\rm bulk} + R_{\rm gb}} \tag{3}$$

is always dominated by the higher resistivity or the lower conductivity according to

$$\sigma_{\rm total} = \frac{\sigma_{\rm bulk} \cdot \sigma_{\rm gb}}{\sigma_{\rm bulk} + \sigma_{\rm gb}}.$$
(4)

## III. RESULTS AND DISCUSSION

Bulk conductivities (discussed in the first paragraph), macroscopic grain boundary conductivities and total conductivities of Lu doped ceria (discussed in the second paragraph) follow the Arrhenius behavior as demonstrated in Figs. 8 and 9. Figures 10 and 11 show the conductivities as a function of the dopant fraction. The pre-exponential factor and activation enthalpy are shown in Fig. 12.

The bulk conductivity is enhanced with increasing dopant fraction to a maximum at about x = 0.075 be-

low 250 °C or x = 0.1 above 250 °C. For higher dopant fractions, the bulk conductivity decreases. The behavior of the conductivity as a function of the dopant fraction is similar to Sm doped ceria, which has one of the highest ionic conductivities for a ternary cerium oxide, though the conductivity is smaller by 1–2 orders of magnitude.<sup>42,47</sup> Other rare-earth doped ceria show similar dopant fractions leading to the highest bulk ionic conductivity, e.g. Yb,<sup>15</sup> Y,<sup>13,15,48,49</sup> and Gd doped ceria,<sup>50,51</sup> while for larger dopants also maxima at smaller dopant fractions are reported, e.g. La doped ceria.<sup>15</sup> A small shift of the dopant fraction of the maximum in conductivity with temperature can be found: For higher temperatures, the maximum in conductivity appears at higher dopant fractions. A similar shift of the dopant fraction of the maximum in conductivity was found for other rare-earth doped ceria in experiments and simulations.<sup>11,42</sup> The higher thermal energy enhances the probability for oxygen vacancies to exit the association radius of the dopant ions (trapping). Furthermore, the probability of jumps around dopants is enhanced that have a larger migration energy (blocking).<sup>9,11,52–54</sup> Therefore, the maximum of the simulated ionic conductivity is shifted to larger dopant fractions. The activation enthalpy for the bulk domain gains in value with increasing dopant fraction (Fig. 12) and is significantly higher than in Sm doped<sup>42</sup> and other rare-earth doped ceria,<sup>11</sup> which is expected due to the low experimental conductivity as well as the strong association of Lu dopants and oxygen vacancies found in empirical<sup>55</sup> and *ab initio* calculations.<sup>11,56</sup> Density functional theory calculations predict the energy difference between a Lu dopant and an oxygen vacancy in nearest neighborhood and next nearest neighborhood to be 0.37 eV.<sup>11</sup> The experimental attempt frequency derived from the measured pre-exponential factor shows a similar dependence on the dopant fraction (Fig. 12) and has the same order of magnitude compared to Sm doped ceria. As apparent from the Arrhenius equation, a low activation enthalpy is more important than a high experimental attempt frequency for a high conductivity. The bulk con-



Figure 11: Macroscopic grain boundary oxygen ion conductivities (left) and total conductivities (right) of Lu doped ceria. Lines are a guide to the eye only.



Figure 12: Experimental attempt frequency derived from the measured pre-exponential factor (left) and activation enthalpy (right) of the conductivity of Lu doped ceria according to impedance experiments. Lines are a guide to the eye only.

ductivity and activation enthalpy for  $Ce_{0.9}Lu_{0.1}O_{1.95}$  are in agreement with measurements by Omar *et al.*<sup>16,25</sup>

The grain boundary conductivity (Figs. 9 and 11) exhibits a maximum in conductivity at dopant fraction x = 0.1 for all measured temperatures similar to Sm doped ceria.<sup>42</sup> At higher dopant fractions, the conductivity passes through a minimum at about x = 0.15 and increases again leading to the highest conductivities at x = 0.25 above 330 °C for all dopant fractions. In Sm doped ceria, the minimum in conductivity was already detected at x = 0.125 while above x = 0.15 the conductivity decreases again. However, the determination of the impedance of Sm doped ceria may be imprecise as the separation of the grain boundary and the electrode semicircle is challenging for dopant fractions above x > 0.1 as reported in our earlier work.<sup>42</sup> The grain boundary conductivity is more than one order of magnitude smaller than the bulk conductivity with exception of  $Ce_{0.75}Lu_{0.25}O_{1.875}$ , where bulk and grain boundary conductivity are similar. The grain boundary conductivity is 1–2 orders of magnitude smaller than in Sm doped ceria. The activation enthalpy of the grain boundary conductivity decreases up to a dopant fraction of x = 0.1 significantly and increases slightly for higher dopant fractions. This correlates with the maximum in grain boundary conductivity. The grain boundary activation enthalpy is higher than in Sm doped ceria. Surprisingly, the experimental attempt frequency derived from the measured pre-exponential factor de-, in- and again decreases with increasing dopant fraction and therefore deviates from the behavior of the activation enthalpy. The total conductivity is nearly identical to the grain boundary conductivity except for a lower conductivity for  $Ce_{0.75}Lu_{0.25}O_{1.875}$ . The total conductivity and its activation enthalpy for  $Ce_{0.8}Lu_{0.2}O_{1.9}$  are in agreement with measurements by Balazs and Glass.  $^{26}$ 

Finally, a comparison of the experimental bulk conductivity with simulations is particularly insightful.<sup>11,57</sup>

The dependence of the conductivity on the dopant fraction is similar for Lu and Sm doped ceria in experiments with a conductivity maximum at about x = 0.1.<sup>42</sup> However, Kinetic Monte Carlo simulations for Lu doped ceria falsely predict a conductivity maximum at higher dopant fractions.<sup>11</sup> In the simulation, migration energies from density functional theory calculations are applied, which suggest that the Ce-Lu edge migration energy (cp. Fig. 1) is slightly smaller than the Ce-Ce edge migration energy. as discussed in detail in our earlier publication.<sup>11</sup> Selectively deactivating energy contributions in the underlying migration energy model in the simulation shows that the dopant fraction leading to the maximum in conductivity is determined by the Ce-RE edge migration energy (blocking). For example, the dopant Yb shows a significantly lower dopant fraction of the maximum in conductivity compared to Lu. The dopants  $Yb^{3+}$  and  $Lu^{3+}$  have similar ionic radii,<sup>24</sup> similar Lu-Lu edge and Yb-Yb edge migration energies, as well as comparable association energies with oxygen vacancies (trapping). The significantly lower Yb dopant fraction of the conductivity maximum is therefore a result of the Ce-Yb edge migration energy that is higher than the Ce-Ce edge migration energy. As a result, the Ce-Lu edge migration energy must be larger than the Ce-Ce edge migration energy to reproduce the experimental results. In summary, the experimental dependence of the conductivity on the dopant fraction reveals that migration barriers for oxygen vacancy jumps around Lu ions are higher than for jumps in pure ceria.

The difference in the absolute oxygen ion conductivity values of Lu-doped and Sm-doped ceria can be explained as follows: In Sm doped ceria, oxygen vacancy jumps away from (towards) dopants are increased (decreased) by 0.04 eV. In Lu doped ceria, oxygen vacancy jumps away from (towards) dopants are increased (decreased) by 0.18 eV. As a result, oxygen vacancy are trapped near Lu dopants while they can easily jump around Sm dopants. This trapping decreases the absolute oxygen ion conductivity values of Lu-doped compared to Sm-doped ceria.

In this work, the oxygen ion conductivity of Lu doped ceria was investigated by means of impedance spectroscopy measurements, which allow the separation of bulk and grain boundary contributions to the ionic conductivity. The dependence of the conductivity on the dopant fraction is similar in Lu and Sm doped ceria both exhibiting a conductivity maximum as a function of the dopant fraction at about x = 0.1. However, in Ludoped ceria, the conductivity is about two orders of magnitude smaller than in Sm-doped ceria that has one of the highest ionic conductivities for a ternary cerium oxide. In comparison with simulations, the experimental dependence of the conductivity on the dopant fraction reveals that migration barriers for oxygen vacancy jumps around Lu ions are slightly higher than for jumps in pure ceria. The low conductivity for Lu doped ceria results from a high activation enthalpy caused by the strong trapping of oxygen vacancies near Lu dopants. The dopant fraction of the maximum in conductivity shifts with temperature. Higher thermal energies enhance the probability for oxygen vacancies to exit the association radius of the dopant ions (trapping). Furthermore, the probability of jumps around dopants with a larger migration energy (blocking) is increased. This results in a shift of the maximum of the ionic conductivity to larger dopant fractions.

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- julius.koettgen@rwth-aachen.de
- martin@rwth-aachen.de
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