Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information

A combined DFT+U and Monte Carlo study on rare earth doped ceria

Steffen Grieshammer,* Benjamin Grope, Julius Koettgen and Manfred Martin*

S.1. Time dependence in Kinetic Monte Carlo simulations

The dependence of the mean displacement <x> of all oxygen ions in the electric field during the KMC simulations on the simulation time t was checked. A linear dependence between <x> and t was found as expected. A typical example is shown in Fig. S1.

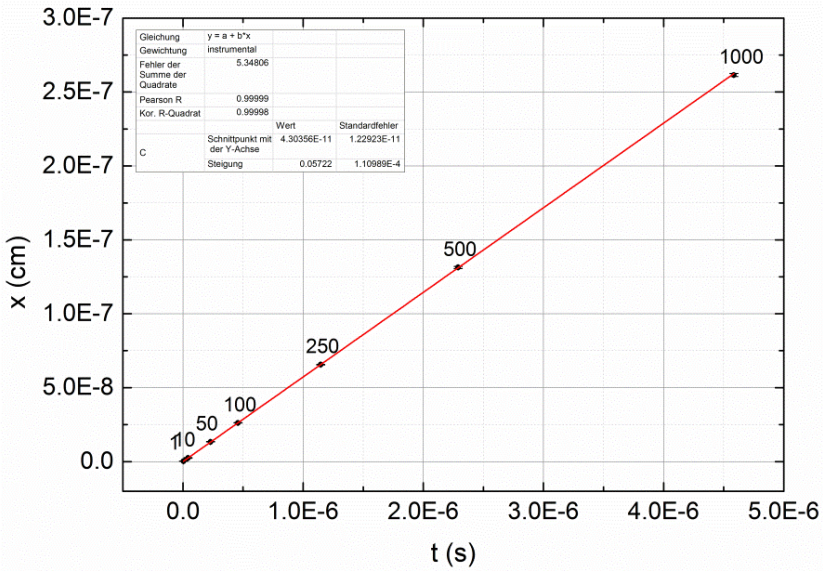

Fig. S1 Dependence of the mean displacement <x> of all oxygen ions as a function of the KMC simulation time t. The numbers denote the MCS/particle in a lattice containing 16x16x16 unit cells, an intermediate dopant concentration of x=0.16 and a temperature of 800K. The electric field energy w_{el} was chosen to be $w_{el} = 0.1 \cdot k_B T$, with *T* being the absolute temperature and k_B the Boltzmann constant.

S.2. Phase seperation in Sc_2O_3–doped CeO_2

Sc^{3+} ions show a much larger association energy with oxygen vacancies (-0.75 eV) than the other investigated rare earth ions. Therefore, lattices obtained from Metropolis Monte Carlo simulations show a strong clustering of oxygen vacancies and scandium ions (Fig. S2), suggesting phase separation into Sc_2O_3 and CeO_2. This result is of course only a qualitative result since pure Sc_2O_3 (C-type) exhibits another crystal structure than CeO_2 (fluorite) which was not considered in the MMC simulation. Nevertheless, the observation of phase separation agrees with the fact that Sc_2O_3 has a low solubility in ceria.

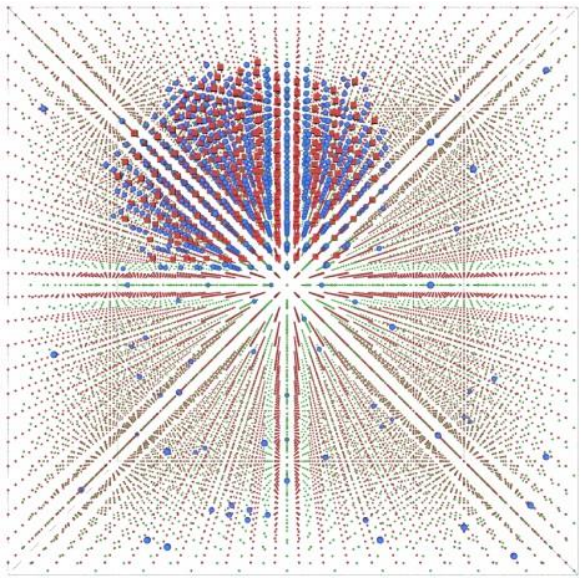

Fig. S2 Simulated ion and vacancy distribution in $Ce_{0.9}Sc_{0.1}O_{1.95}$ in a 12x12x12 simulation cell. Oxygen ions (red) and cerium ions (green) are depicted by small symbols while scandium ions (blue) and oxygen vacancies (red boxes) are shown by large symbols. The strong clustering of Sc and V and the small concentration of Sc within the surrounding CeO_2 matrix indicates phase separation.

S.3. Influence of the different association energies on the coordination numbers

The Metropolis Monte Carlo simulations require three types of association energies (RE-RE, V-V and RE-V) to reproduce experimental values. Exclusion of one of the interactions leads to a significant deviation from experiment resulting in exaggerated clustering (without RE-RE or V-V interaction) or a random distribution (without RE-V interaction). This is shown in Fig. S3.

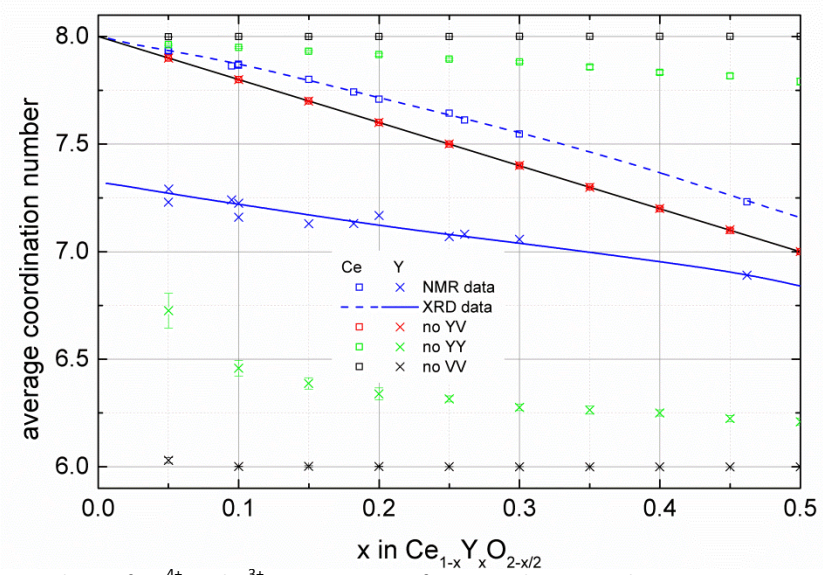

Fig. S3 Coordination numbers of Ce^{4+} and Y^{3+} in $Ce_{1-x}Y_xO_{2-x/2}$ from simulations without Y-V interaction (red), without Y-Y interaction (green) or without V-V interaction (black). Experimental values from NMR measurements (blue symbols) as well as from XRD fitting (blue lines) are given. The CN for both cations in a random distribution is drawn as a black line. The exclusion of one particular interactions leads to a strong deviation from the experimental data.

S.4. Y-Y pairs for larger distances

In the DEG lattice at 1000 K the number of Y-Y pairs increases compared to the other lattices suggesting the formation of larger clusters of yttrium ions and oxygen vacancies.

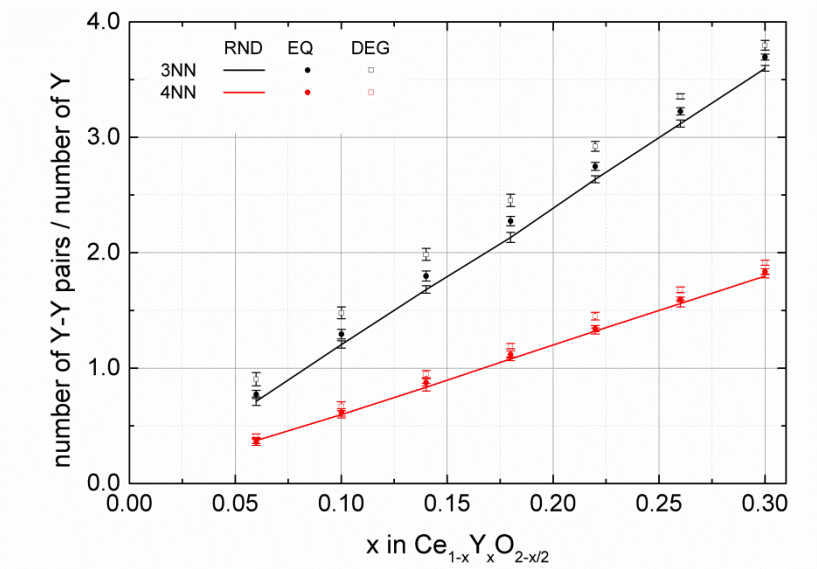

Fig. S4 Number of Y-Y pairs in 3NN (black) and 4NN (red) positions for lattices RND (lines), EQ (circles) and DEG (squares) at 1000 K in $Ce_{1-x}Y_xO_{2-x/2}$.

S.5. Jump attempts through migration edges for the lattices RND, EQ and DEG

The number of jump attempts through Ce-Ce edges decreases from 1000 K (Fig. S5) to 700 K (Fig. S6) for all lattices although the number of different migration edges does not change much for the RND and EQ lattices. This behaviour can be explained by the smaller mobility of oxygen vacancies at lower temperature. At 700 K the oxygen vacancies are more often in the vicinity of yttrium ions due to the attractive interaction.

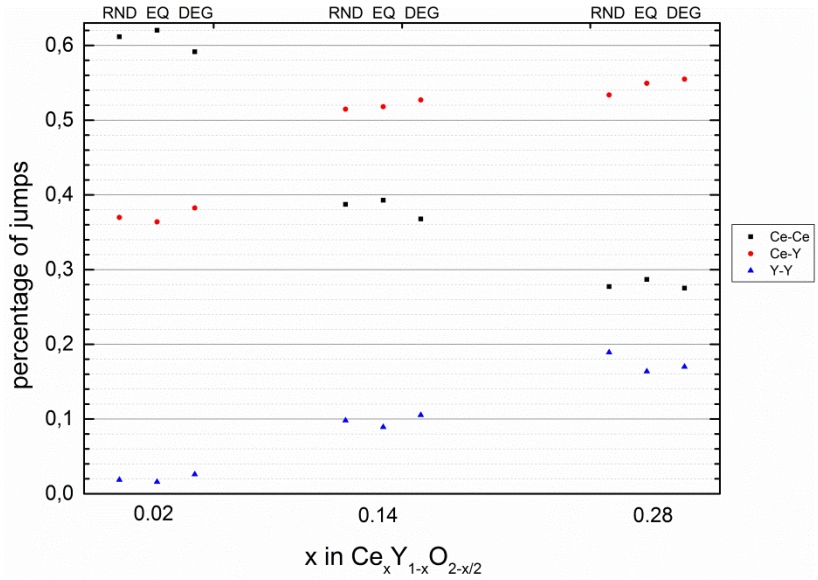

Fig. S5 Percentage of jump attempts through a Ce-Ce edge (black), a Ce-Y edge (red) and a Y-Y edge (blue) at 1000 K for all lattices and three yttrium fractions.

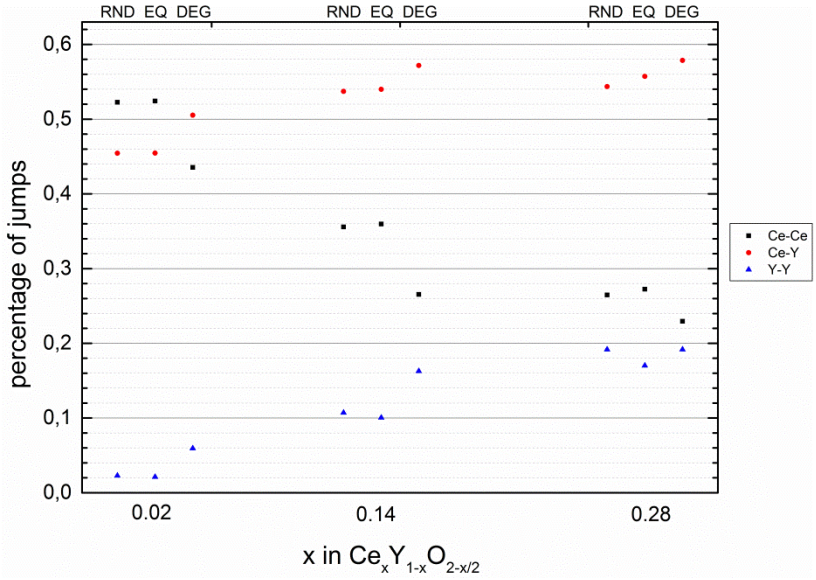

Fig. S6 Percentage of jump attempts through a Ce-Ce edge (black), a Ce-Y edge (red) and a Y-Y edge (blue) at 700 K for all lattices and three yttrium fractions.

S.6. Y-Y and Y-V pairs at 700 K

The drop in oxygen ion conductivity in the DEG lattice at 700 K compared to the RND and EQ lattices can be attributed to the increase of Y-Y and Y-V pairs leading to an increase in blocking and trapping. The number of Y-Y pairs in the DEG lattice at 700 K is shown in Fig. S7. The number of 2NN to 4NN Y-Y pairs is increased compared to the RND and EQ lattice suggesting larger areas with a high fraction of yttrium ions.

The number of Y-V pairs is shown in Fig. S8 (1000 K) and Fig. S9 (700 K) for EQ and DEG lattices. The number of Y-V pairs in the DEG lattice is higher than in the EQ lattice especially for 700 K. This suggests a strong clustering of oxygen vacancies and yttrium ions at 700 K in the DEG lattice.

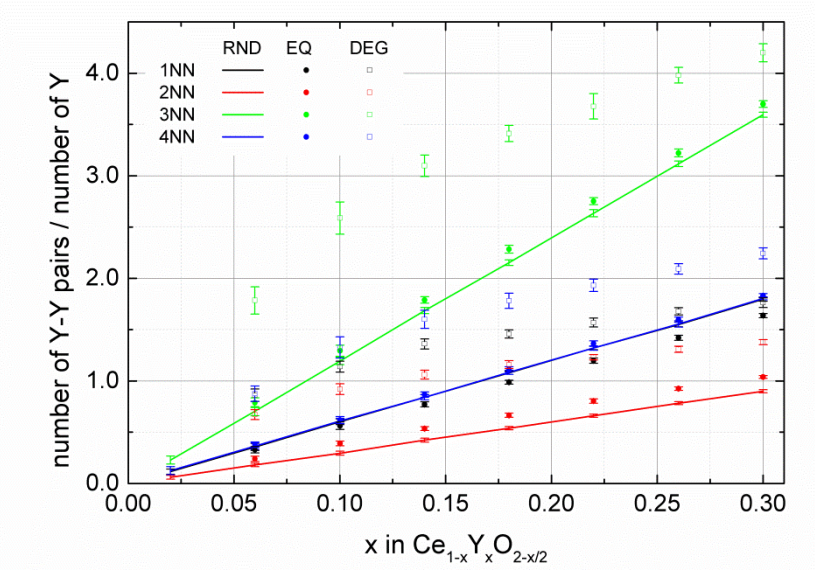

Fig. S7 Number of Y-Y pairs in 1NN (black), 2NN (red), 3NN (green) and 4NN (blue) positions for lattices RND (lines), EQ (circles) and DEG (squares) at 700 K in $Ce_{1-x}Y_xO_{2-x/2}$.

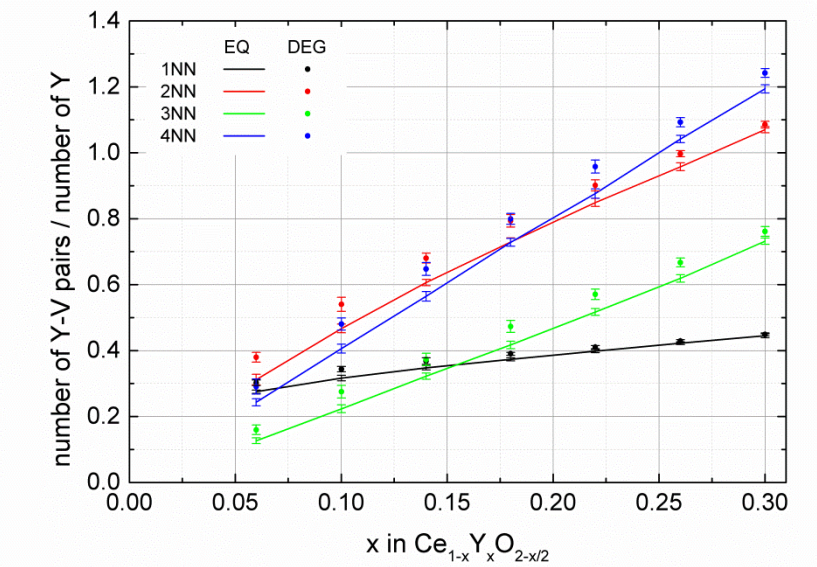

Fig. S8 Number of Y-V pairs in 1NN (black), 2NN (red), 3NN (green) and 4NN (blue) positions for lattices EQ (lines) and DEG (squares) at 1000 K in $Ce_{1-x}Y_xO_{2-x/2}$.

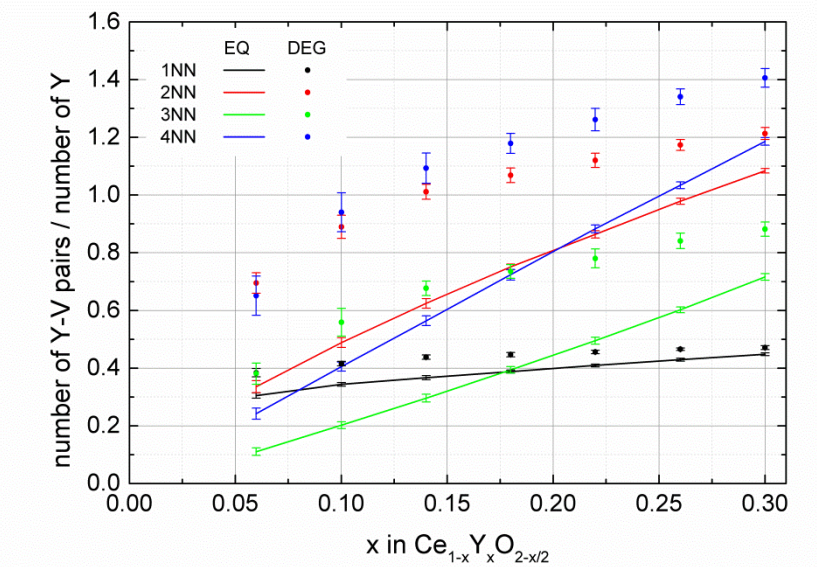

Fig. S9 Number of Y-V pairs in 1NN (black), 2NN (red), 3NN (green) and 4NN (blue) positions for lattices EQ (lines) and DEG (squares) at 700 K in $Ce_{1-x}Y_xO_{2-x/2}$.

S.7. Configurations of oxygen vacancies at 700 K

Every oxygen vacancy has four cation sites in nearest neighbour position. Thus the number of yttrium ions in 1NN position can vary between 0 and 4. For the DEG lattice at 700 K the formation of vacancies with two yttrium ions in 1NN is favoured (Fig. S10) also in comparison with the EQ lattice. These configurations favour the formation of percolation paths with adjacent Ce-Y edges.

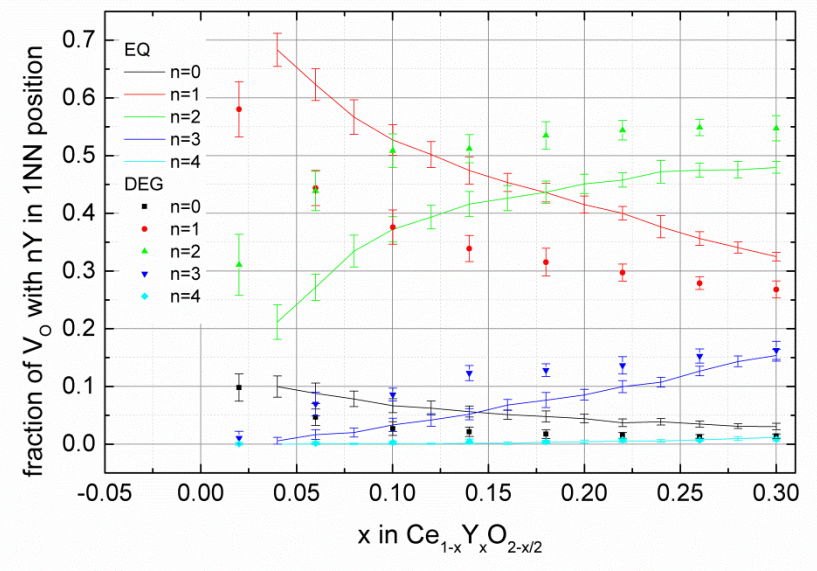

Fig. S10 Fraction of oxygen vacancies with n (0≤n≤4) yttrium ions in nearest neighbour position in $Ce_{1-x}Y_xO_{2-x/2}$ for lattices EQ (lines) and DEG (symbols) at 700 K. At high yttrium fractions most oxygen vacancies have two yttrium ions in nearest neighbour position. For the DEG lattice this trend is more distinct.