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Supporting Information for

Atomistic modeling of La^{3+} doping segregation effect on nanocrystalline yttria-stabilized zirconia

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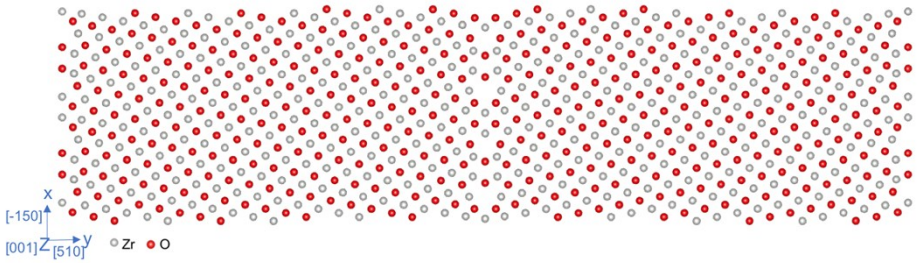
Table S1 Geometric parameter for each grain boundaries.

Structure Σn(GB plane)/tilt angle (degree)	Total number of atoms/Zr/O/dopants	Unit cell size lx/ly/lz (Å)
[001] tilt axis		
Σ13(510)/22.62	7192/2024/4720/448	26.08/104.26/30.77
Σ5(310)/36.9	5446/1532/3574/340	32.35/64.56/30.75
[110] tilt axis		
Σ11(332)/50.48	6144/1728/4032/384	24.07/102.73/28.90
Σ3(111)/70.53	6703/1886/4399/418	35.44/76.12/28.86
Σ3(112)/109.47	6703/1886/4399/418	37.54/71.49/28.90
Σ11(113)/129.52	8286/2332/5438/516	33.96/98.73/28.92
Σ9(114)/141.06	5120/1440/3360/320	21.69/97.41/28.57
Σ19(116)/153.47	7029/1978/4613/438	22.34/126.85/28.96



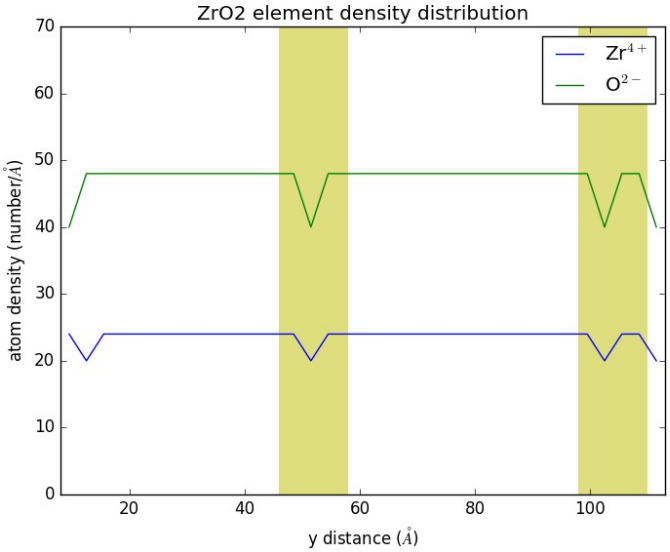


Figure S1 Energy minimized and relaxed ZrO_2 GB structure and corresponding density distribution. GB regions are marked yellow. The bin size is the same as in Figure 1.

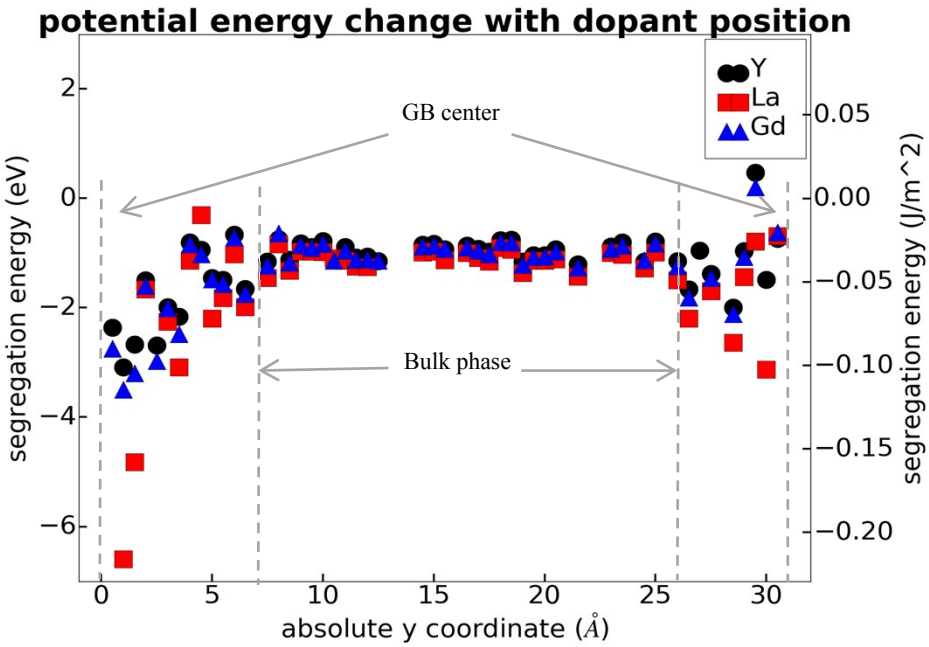


*Figure S2 Potential energy change of Σ5(310)/[001] with dopant position. Two dopants with one oxygen vacancy are introduced to ZrO_2 phase. Absolute y coordinate is the averaged y value of the 2 dopants during one doping trial, and y is the normal direction to GB plane. Total 118 trials have been made and the bin size for each point is 0.5 Å. Segregation energy in J/m² units was calculated from energy/(2*GB area), and GB area equals to lx*lz. Gd^{3+} is included for comparison.*

The segregation energy is defined as:

$$E_{seg}^{\alpha} = \left(E_{GB}^{\alpha} - E_{bulk}^{\alpha}\right) - (E_{GB} - E_{bulk})$$

Where E_{GB}^{α} and E_{GB} are the total energies of the GB structure with and without dopants, E_{bulk}^{α} and E_{bulk} are the total energies of bulk structure with and without the dopants.

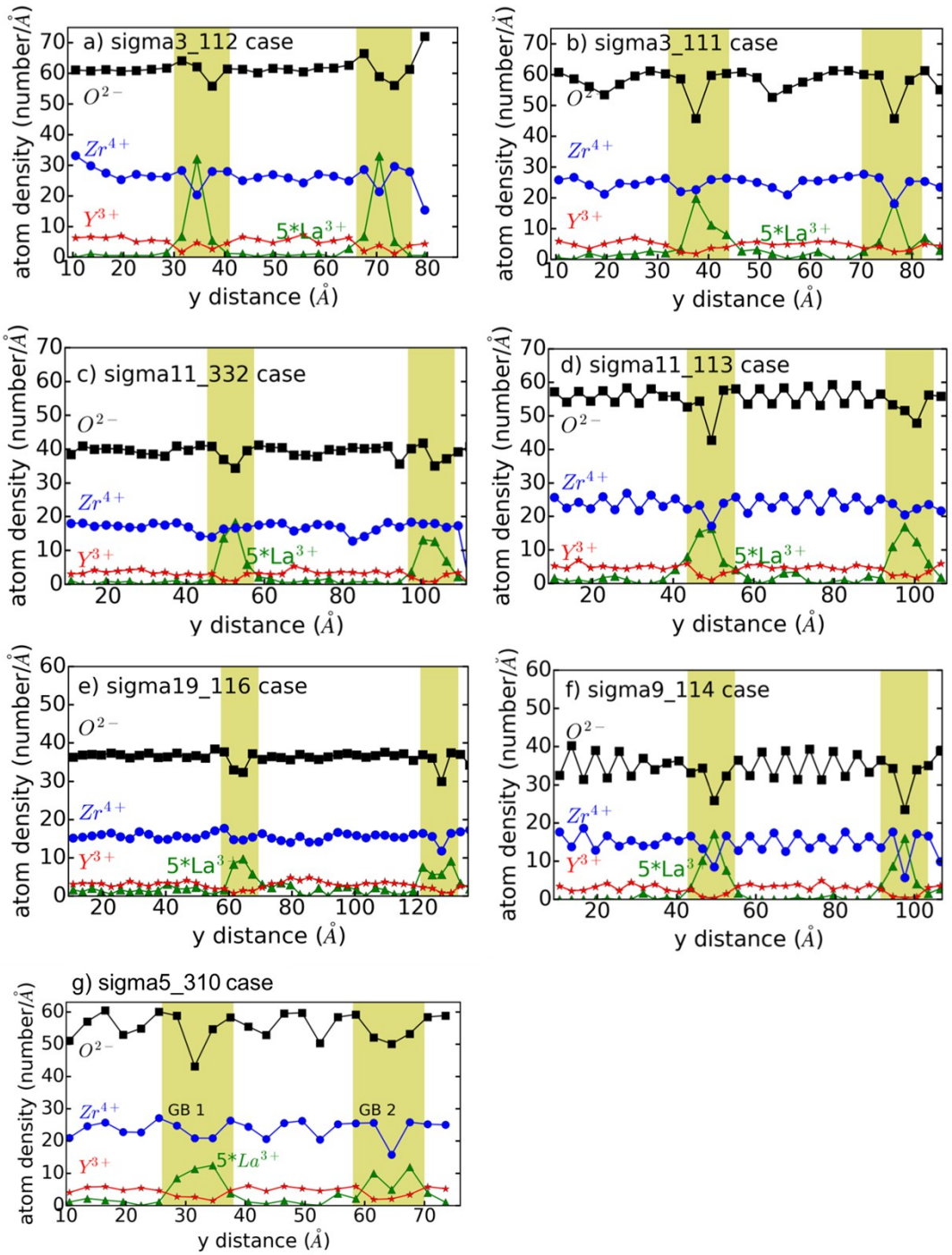


Figure S3 Density profile for different GB structures to show that La^{3+} segregation occurs in all cases. GB regions are marked yellow. The profile is averaged over 3 independent configurations, each configuration with 40 equilibrated structure snapshots uniformly sampled within 2 × 10^7 MC steps.

Table S2 Average potential energy value for each element corresponding to Figure 3 configurations

Type of ion	Potential energy, eV/atom		
	Reference 10YSZ bulk	1.5La8.5YSZ	10YSZ
Zr^{4+}	-74.66763	-74.4989	-74.45059
Y^{3+}	-41.42356	-41.3912	-41.32204
La^{3+}		-38.4308	
O^{2-}	-18.00287	-18.01102	-18.047

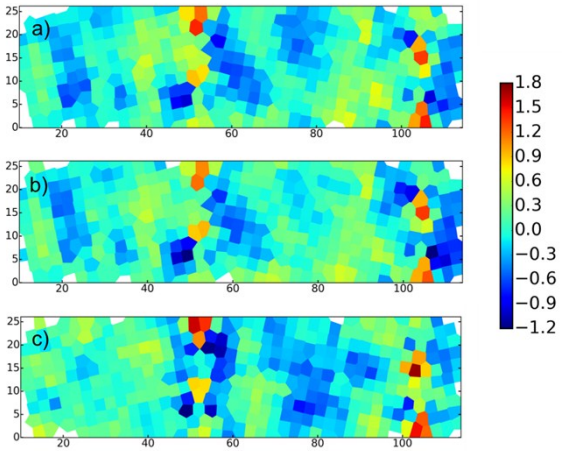


Figure S4 Anion potential energy fluctuation in 8.5Y1.5La a) configuration 1 snapshots 0 to 10 b) configuration 1 snapshots 10 to 20 c) configuration 3 snapshots 0 to 20

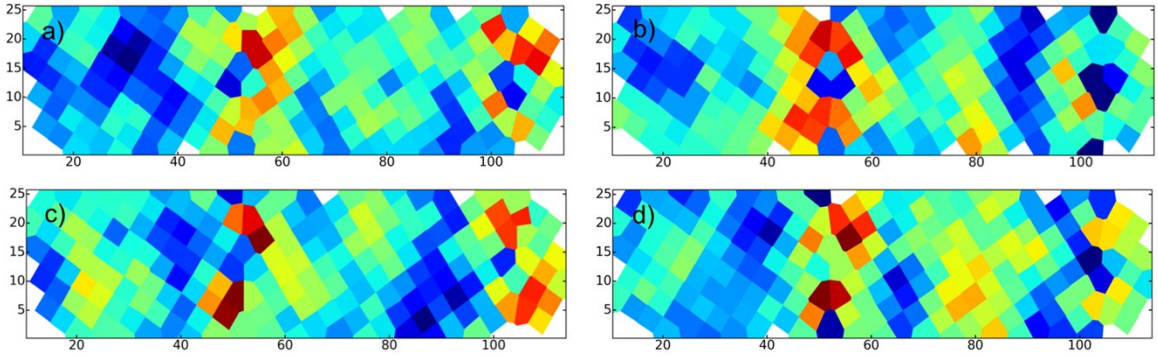


Figure S5 Cations potential energy fluctuation in a) 10YSZ configuration 1; b) 10YSZ configuration 2; c) 8.5Y1.5La configuration 1; d) 8.5Y1.5La configuration 3. The color scale bar is the same as in Figure S2.

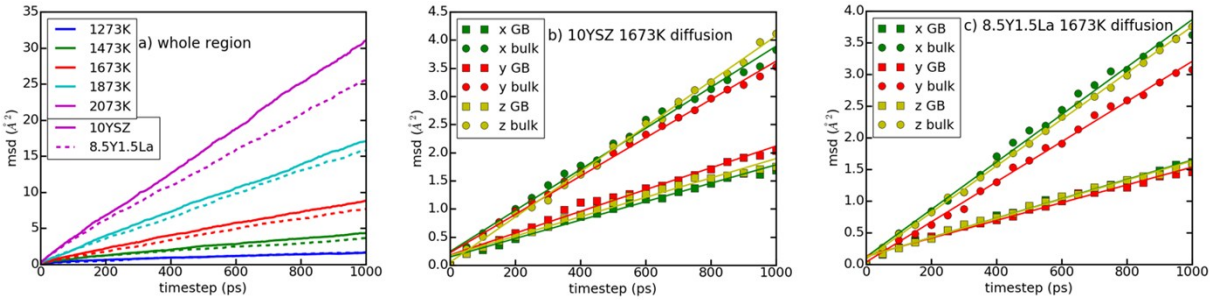


Figure S6 a) Mean square displacement of the whole structure. b) Mean square displacement decomposed to GB and bulk region, and decomposed to x, y, z axis direction: 10YSZ at 1673 K case. c) Mean square displacement decomposed to GB and bulk region, and decomposed to x, y, z axis direction: 8.5Y1.5La at 1673 K case.

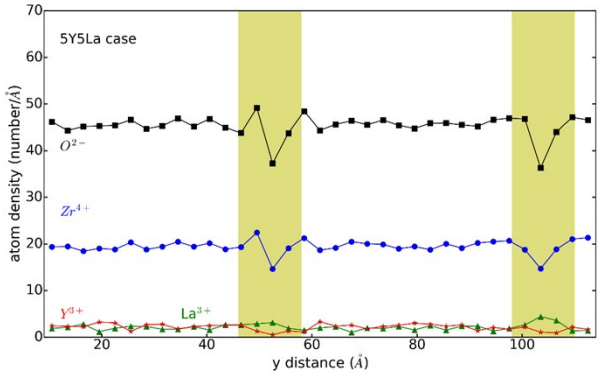


Figure S7 Density profile for 5Y5La doping case at 300 K. GB regions are marked yellow. The profile is averaged over 3 independent configurations, each configuration with 40 equilibrated structure snapshots uniformly sampled within 2×10^7 MC steps.

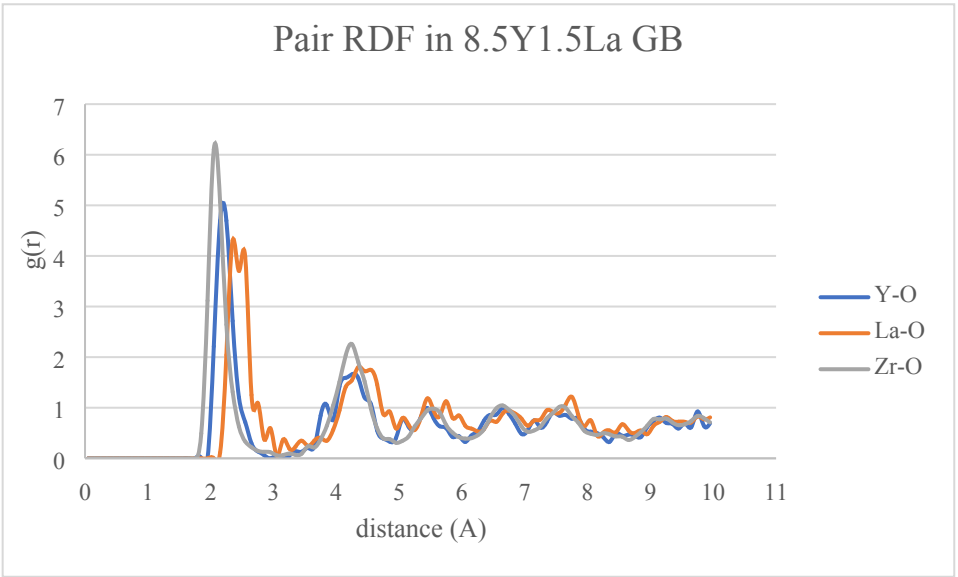


Figure S8 Radial distribution function of Y-O, La-O and Zr-O pairs at GB region. The first peak reflects the bond length of the two elements.

Figure S8 reflects the bond length of different cations with anions at GB region in 8.5Y1.5La configuration (+/- 6 Å from the GB plane), which is the distance of the first peak in RDF. Zr-O has a bond length of 2.05 Å, Y-O 2.25 Å of La-O of 2.35 Å. The RDF curve is not as smooth as in bulk phase due to the limited atom numbers considered in GB region.

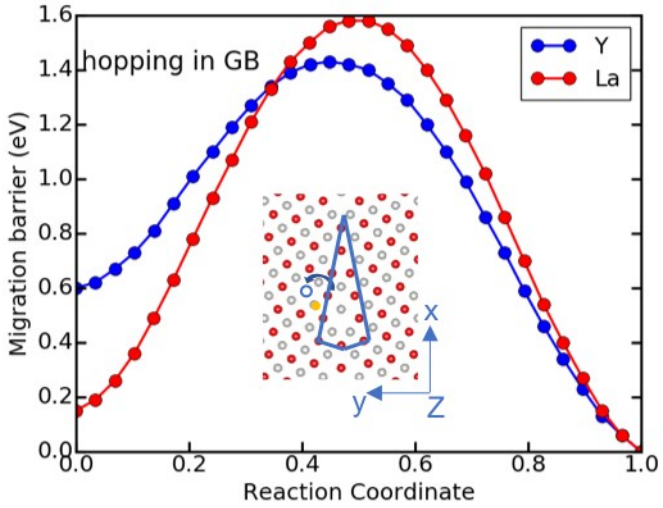


Figure S9 NEB calculation for another hopping energy barrier GB region along y axis. The inset show the oxygen vacancy and dopant positions, where blue lines mark the GB unit cell. Color representation in the insets: void blue circle: oxygen vacancy; yellow: trivalent dopant; red: O^{2-}; grey: Zr^{4+}.