Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Molecular Dynamics Study of Oxygen-ion Diffusion in Yttria-Stabilized Zirconia Grain Boundaries

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Table S1. *Parameters for potential (Eq. (1)) used in this study.*[1,2]

Ion pair	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eVÅ^6)
O^{2-}—O^{2-}	9547.96	0.2192	32
Zr^{4+}—O^{2-}	1502.11	0.3477	5.1
Y^{3+}—O^{2-}	1766.4	0.33849	19.43

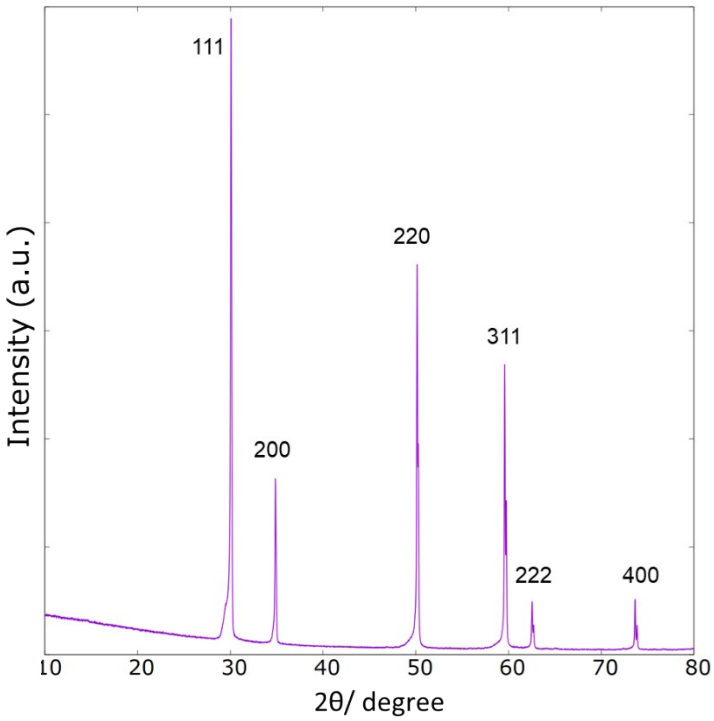

Figure S1. XRD patterns of the synthesized 8YSZ polycrystalline pellet.

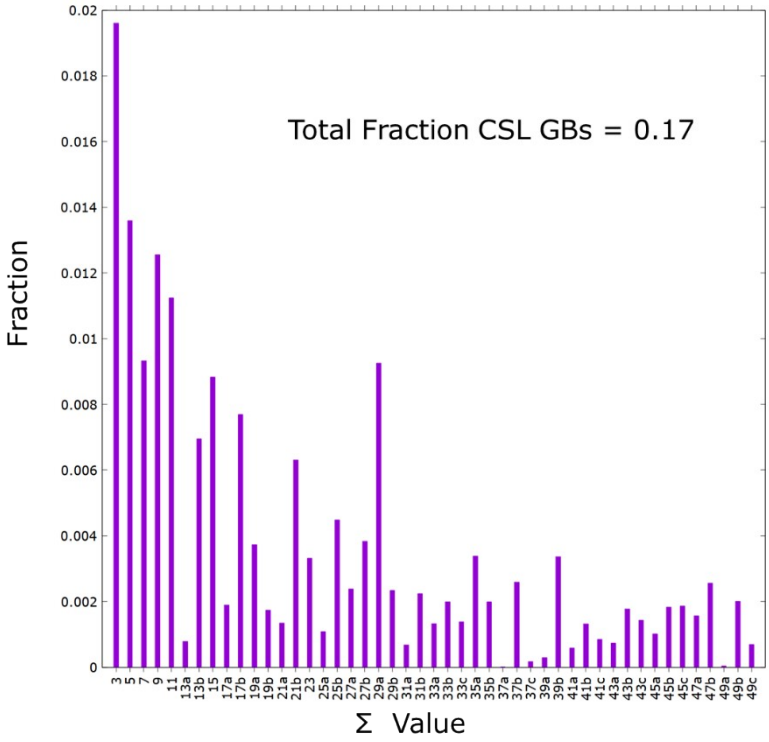

***Figure S2**. CSL distribution for the 8YSZ sample.*

Σ5 GB was built analogously to mixed GB. To obtain the similar size and number of atoms, (310) and (-310) surfaces of ZrO_2 cubic fluorite each with 70 layers thickness were considered. Both surfaces were aligned parallel with 7Å distance between them, zero orientation angle no strain, and lowest possible number of atoms (420). Then, the model was repeated seven times along the x-axis and four times along y-axis, resulting in two grains with 5880 atoms (3920 Zr and 7840 O) each. Depending on the desired dopant concentration (4,8,11 or 14YSZ), Zr^{4+} ions were substituted with Y^{3+}, creating the corresponding oxygen vacancies to maintain the system neutrality. The initial models were then used to generate realistic GB structure via Amorphization and recrystallization (A&R) technique as described in the main article. The resulting structure (**Fig. S3 (c)**) agreed in all cases visually with what have been reported elsewhere for Σ5.[3–5]

S1

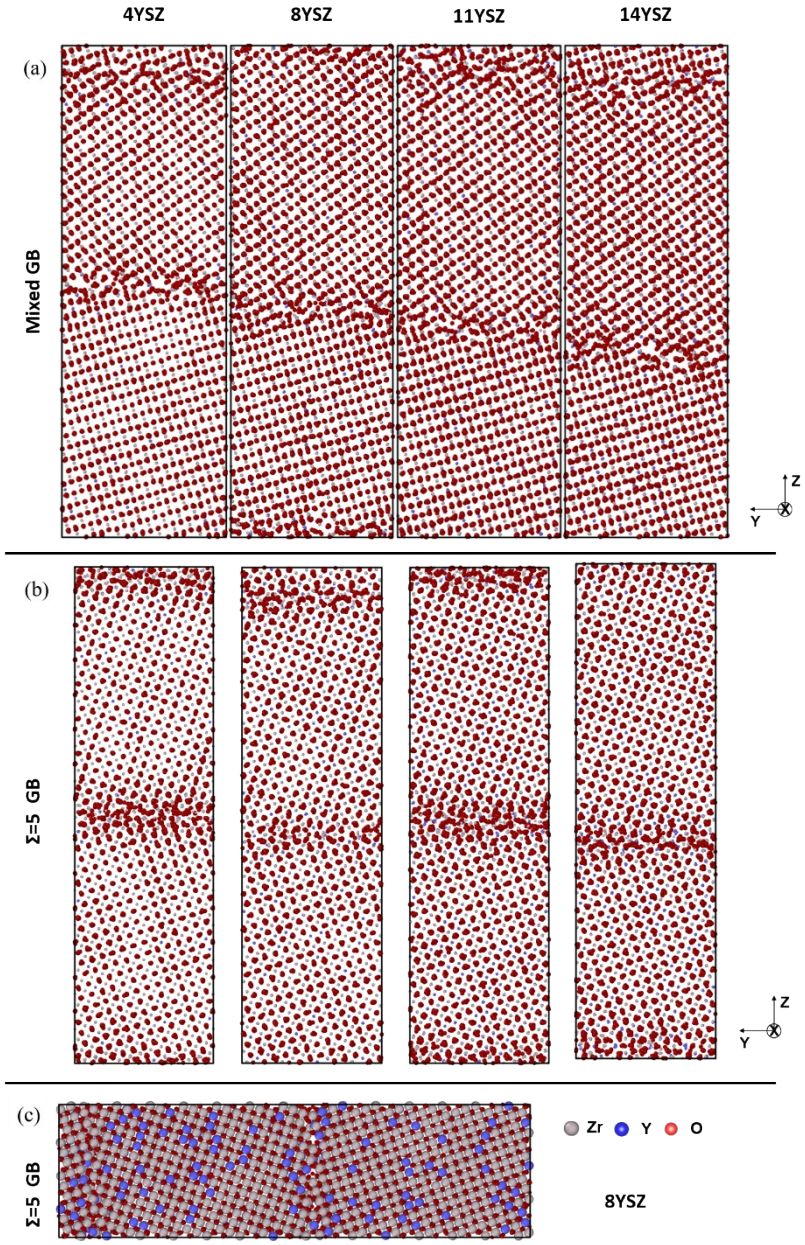

Figure S3. *Recrystallized structure of 4,8,11, and 14 YSZ grain boundary systems, (a) mixed GB; (b) Σ5 GB; (c) represents 8YSZ Σ5 GB with normal cations sizes.* O^{2-}, Zr^{4+} *and* Y^{3+} *are represented by red, blue and grey colors, respectively.*

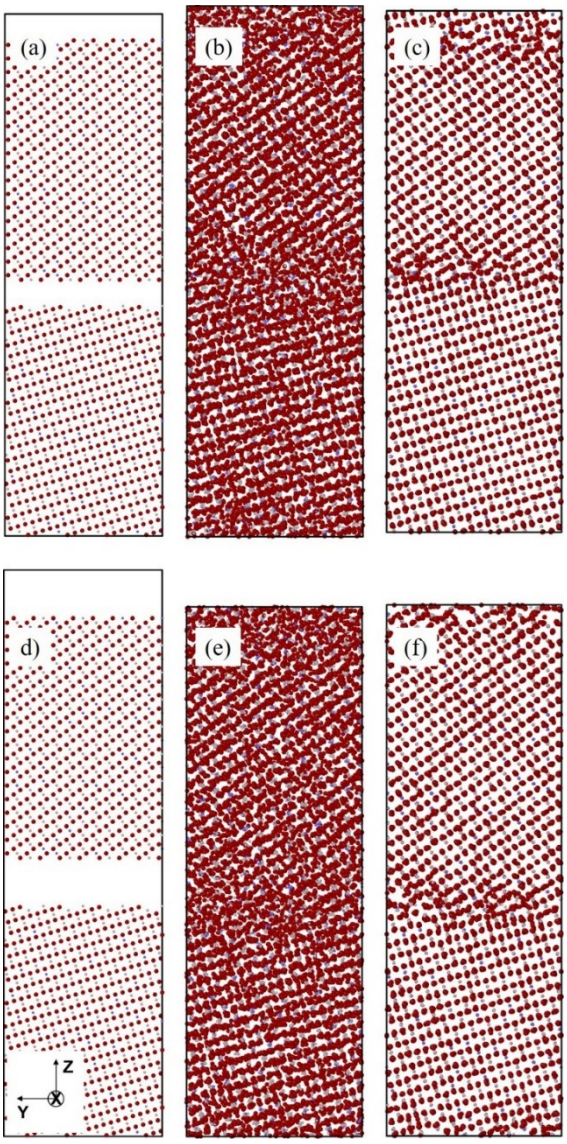

Figure S4. *(a)&(d) initial structure (with 5 and 10 Å void between the two grain respectively), (b)&(e) amorphized structures, and (c)&(f) recrystallized structure of YSZ grain boundary system.* O^{2-}, Zr^{4+} *and* Y^{3+} *are represented by red, blue and grey spheres, respectively.*

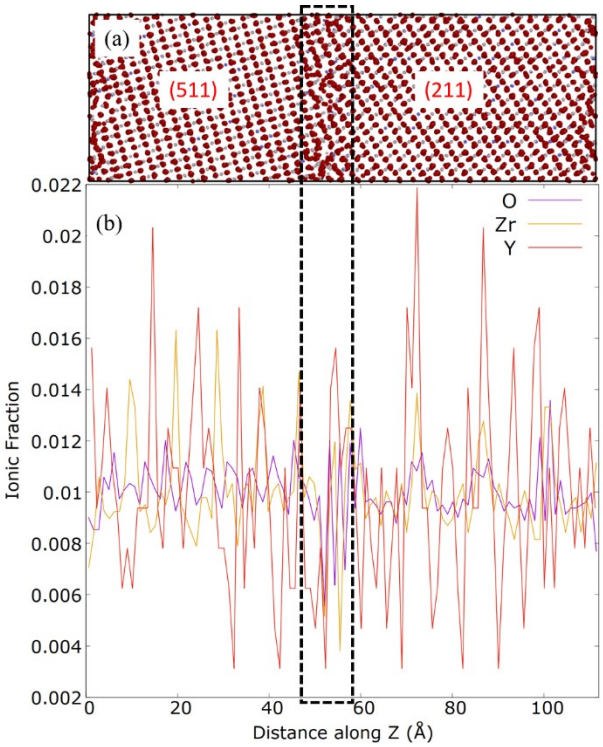

Figure S5. (a) 8YSZ GB system. O^{2-}, Zr^{4+} and Y^{3+} are represented by red, blue and grey spheres, respectively. (b) normalized ionic count as a function of distance perpendicular to the GB core. The dotted box in (a) and (b) represent the GB core.

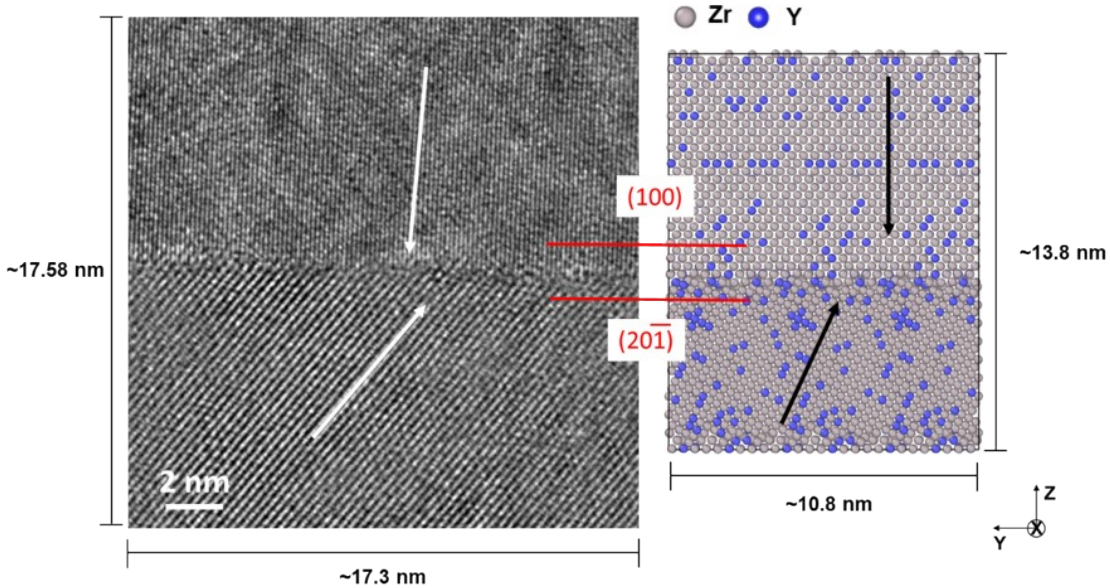

Figure S6. *TEM image of a mixed GB formed by (20-1) and (100) orientated grains, with a misorientation angle of 26.6º (left) and the computational model representing the same mixed GB, prepared by amorphization and recrystallization method (right).*

Three other GBs of 8YSZ were built analogously to the previous ones. The size of each structure slightly change due to the CSL algorithm used by Quantum-ATK package to create the interface:
a) Mx GB (20-1)(100) contains 10744 atoms (7072 O, 3128 Zr and 544 Y) in a cell volume of 30.01 x 33.42 x 127.88 Å.
b) Σ13 GB contains 12780 atoms (8412 O, 3720 Zr and 648 Y) in a cell volume of 36.3 x 39.45 x 108.56 Å.

c) Σ11 contains 12359 atoms (8135 O, 3598 Zr and 626 Y) in a cell volume of 29.2 x 36.26 x 138.86 Å.

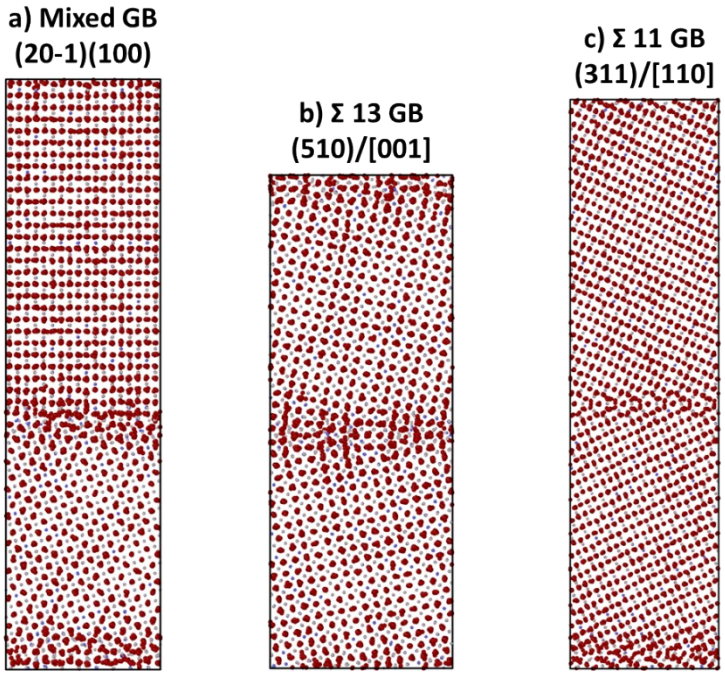

Figure S7*. Recrystallized structure of 8 YSZ grain boundary systems, (a) mixed GB (20-1)(100); (b) Σ13 GB; and c) Σ11 GB. O^{2}, Zr^{4+} and $Y^{3+}$are represented by red, blue and grey colors, respectively.*

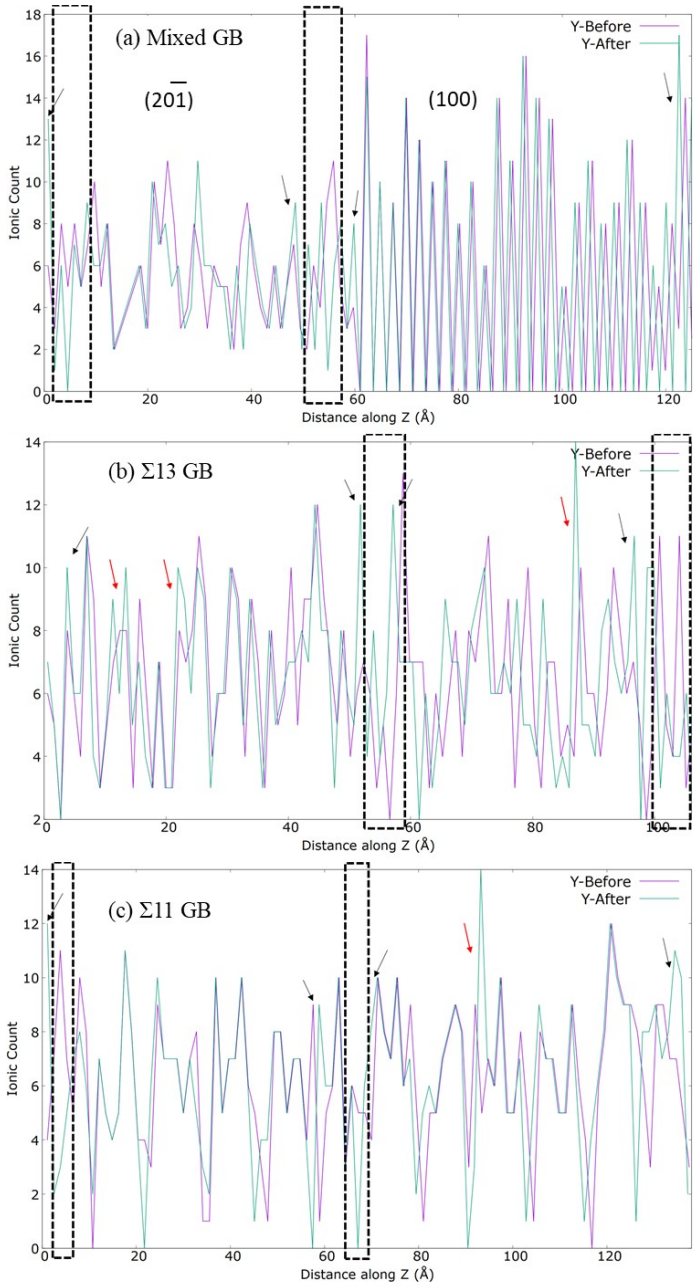

Figure S8. Calculated Y-ion count along z direction for (a) 8YSZ GB (20-1)(100) system. (b) 8YSZ Σ13 GB system. (c) 8YSZ Σ11 GB system The dotted box in (a) and (b) represent the GB cores.

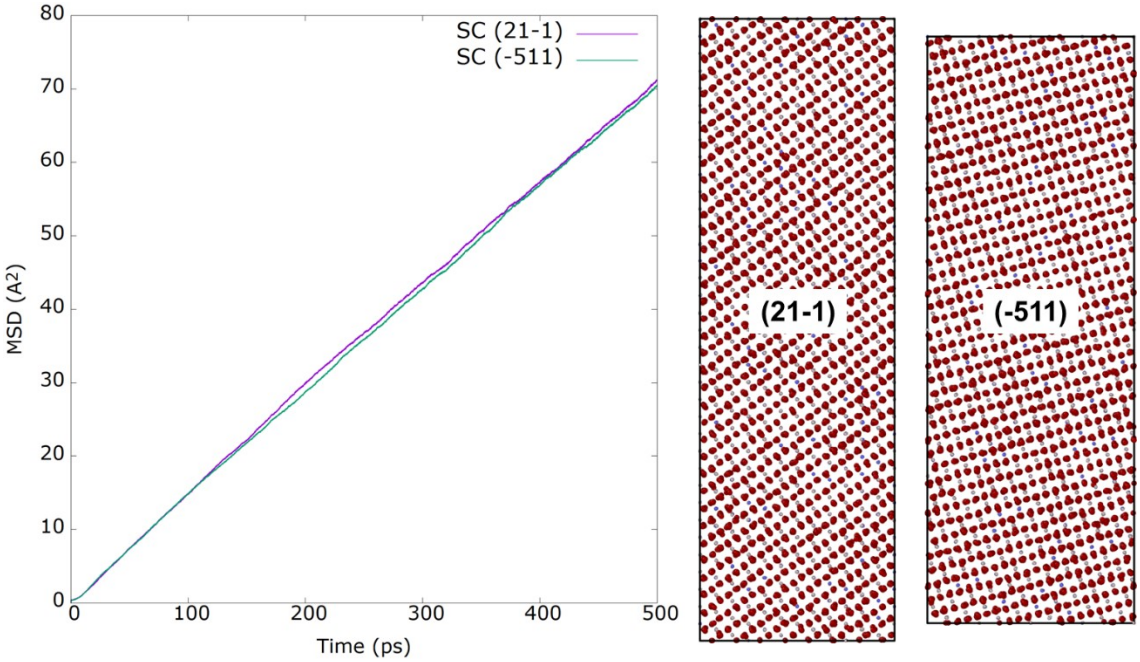

Figure S9. *Mean square displacements of oxygen atoms at 2300 K for Single Crystal (21-1) and Single Crystal (-511) systems.*

Table S2*. Percentage of cations found with a coordination number < 8 for different Y_2O_3 doping concentration at grain boundary and grain interior regions.*

	CN	Cations % in 4YSZ	Cations % in 8YSZ	Cations % in 11YSZ	Cations % in 14YSZ
GB	7	6.41	7.75	9.12	5.88
	6	5.09	6.55	7.20	7.11
	5	0.74	0.95	1.02	1.18
	4	0.02	0.02	0.02	0.07
Grain (21-1)	7	9.77	19.88	22.92	29.35
	6	0.16	1.34	1.44	4.51
	5	0.00	0.00	0.00	0.05
	4	0.00	0.00	0.00	0.00
Grain (-511)	7	9.38	12.08	17.62	20.32
	6	0.35	0.49	1.06	1.62
	5	0.00	0.00	0.00	0.00
	4	0.00	0.00	0.00	0.00
Total	7	25.56	39.72	49.65	55.56
	6	5.60	8.38	9.70	13.24
	5	0.74	0.95	1.02	1.23
	4	0.02	0.02	0.02	0.07

References

1. Minervini, L., Zacate, M. O. & Grimes, R. W. Defect cluster formation in M2O3-doped CeO2. *Solid State Ionics* **116**, 339–349 (1999).

2. Minervini, L., Grimes, R. W. & Sickafus, K. E. Disorder in pyrochlore oxides. *J. Am. Ceram. Soc.* **83**, 1873–1878 (2000).

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4. González-Romero, R. L., Meléndez, J. J., Gómez-García, D., Cumbrera, F. L. & Domínguez-Rodríguez, A. A Molecular Dynamics study of grain boundaries in YSZ: Structure, energetics and diffusion of oxygen. *Solid State Ionics* **219**, 1–10 (2012).

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