

# Impact of dopants on diffusion in crystalline and amorphous zirconia

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## Introduction

Grain boundaries in  $ZrO_2$  may act as favourable pathways for diffusion of corrosion species (O, H)

- Impurity & alloying element segregation ( $Fe^{3+}$ ) has been observed at grain boundaries [1]
- Segregation may induce amorphisation
- Structural changes may impact diffusion

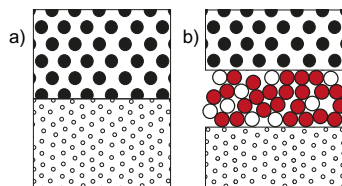
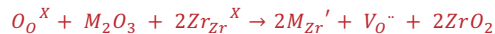


Figure 1: a) Clean to b) Nano-layer complex in a grain boundary [2]

## Method

- Undoped, 5.3 at.%, and 11 at.% doped  $ZrO_2$  investigated
- Amorphous structure generated via MD heat and quench method [3]
- Range of lanthanides used as 3+ potentials were readily available



$M = Yb, Dy, Gd, Nd, La$

- Systems equilibrated at 300K
- Temperature increases in 100K increments, NPT ensemble
- Equilibration at temperature of interest (500-900K)
- Further equilibration under NVT ensemble
- MSD calculations for 20ns

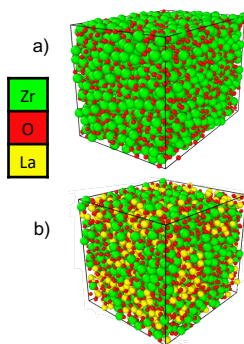


Figure 2: Amorphous a) undoped, and b) 11 at.% La doped zirconia

## Results

- Diffusivity in crystalline doped systems increases dependent on ionic radius [4]
- No considerable impact on diffusion when comparing amorphous undoped and doped
- Radial distribution function, RDF, of undoped and doped compared
- Doping affects cation-anion (Zr-O, La-O) and anion-anion (O-O) bond

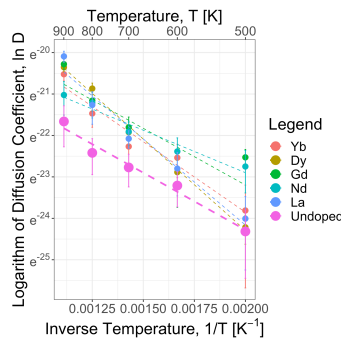


Figure 3: Oxygen diffusion in 11 at.% doped amorphous  $ZrO_2$

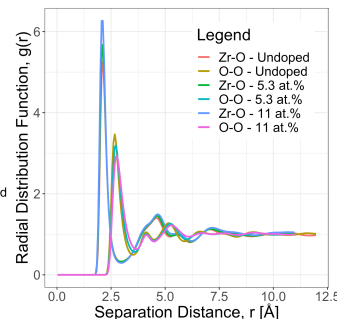


Figure 4: PRDF for undoped and La-doped  $ZrO_2$

## Conclusion

- Amorphous systems **unaffected** when doped with lanthanides, in contrast to that observed in crystalline doped systems
- Increasing dopant concentration **alters the structure**
- Investigations using relevant elements i.e. **Fe, Sn, Nb, Cr** for Zr alloys, to be conducted

## References

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- [4] M. S. Khan, et al., "Cation doping and oxygen diffusion in zirconia: A combined atomistic simulation and molecular dynamics study," *J. Mater. Chem.*, vol. 8, no. 10, pp. 2299–2307, 1998.



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