Investigating the effects of dopants on the dissolution kinetics of CeO_2, an analogue for spent nuclear fuel

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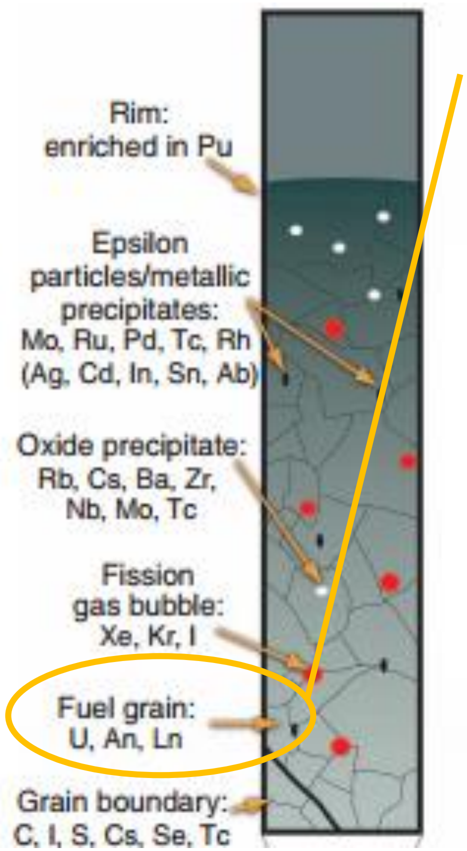
University of Sheffield

Spent Nuclear Fuel Workshop, 14-15th November 2019,Gent

Context



P. C. Burns, R. C. Ewing, R. Navrotsky, Science**, 2012**, 335, 1184-1187

Ce^{IV}/REE^{III} of interest to mimic SNF

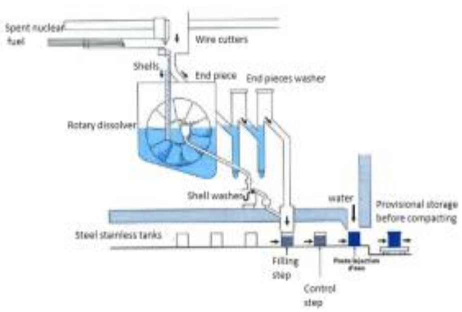
- $Ce^{IV}O_2$ crystallises in UO_2/PuO_2 structure
- Ce^{IV} ionic radius (0.97Å) close to Pu^{IV} (0.96Å)/U^{IV} (1.00Å)
- REE^{III} surrogates at Ln^{III} and MA^{III}

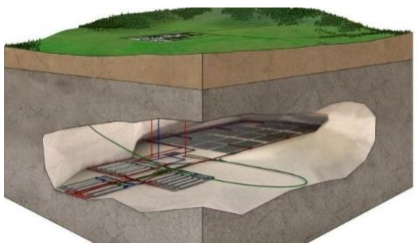
Ce^{IV}/REE^{III} of interest to future nuclear fuel

- Fuel doped with REE^{III} (modern fuel)
- RNR: incorporating MA^{III} (Np, Am, Cm) directly inside the reactor core

Ce^{IV}/REE^{III} of interest to SNF leaching

- SNF reprocessing
- Direct storage of SNF





$Ce_{1-x}REE_xO_{2-x/2}$

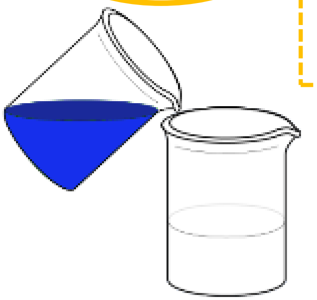
- Gd
- Nd
- Y

Observe the **impact** of the **presence** of REE on the **chemical durability** of CeO_2

Synthesis

Oxalic precipitation

$CeCl_3$ + dopants Cl

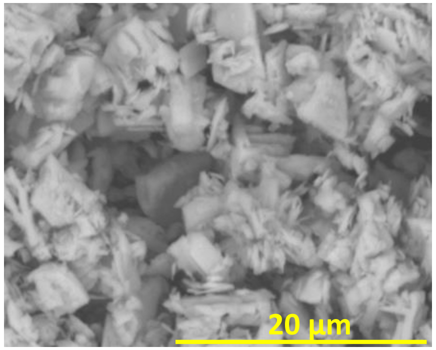


Room temperature $H_2C_2O_4$ excess

Dry at 90˚C

Washing steps (water/EtOH)

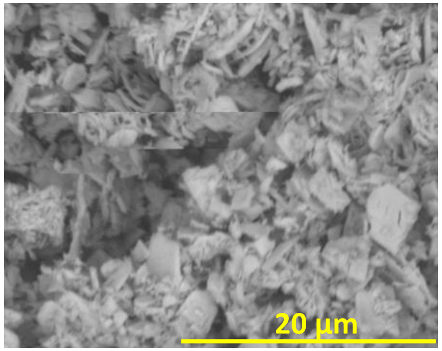
$Ce_{1-x}REE_xO_{2-x/2}$ with REE = Nd, Y, Gd and x = 0, 1, 4, 8, 15 wt%



$Ce_{0.85}Gd_{0.15}(C_2O_4)_{0.225}$

1000°C / 4 h

Air



$Ce_{0.85}Gd_{0.15}O_{1.925}$

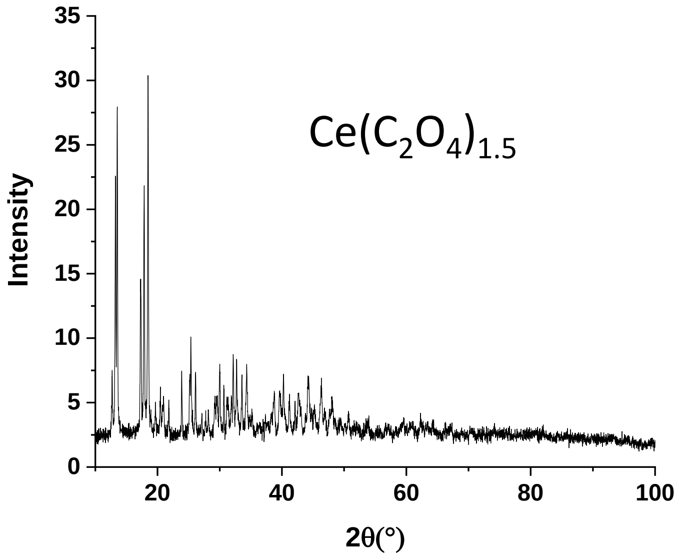
ICP-OES

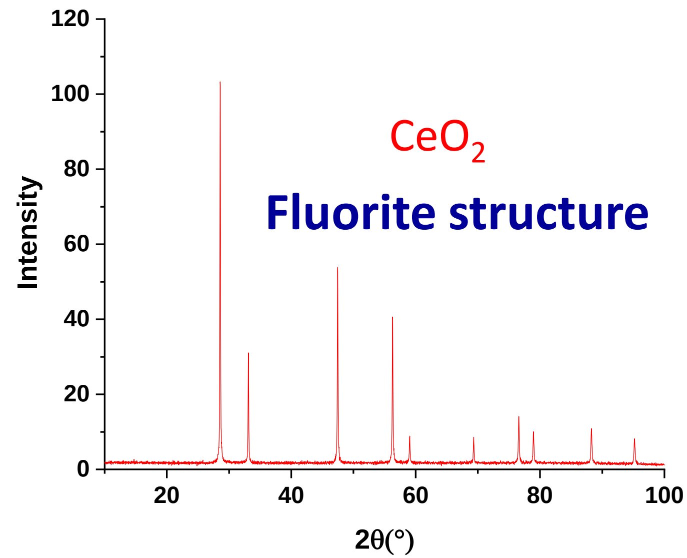
Supernatants analyses

Precipitation ratio

Ce = 99 %

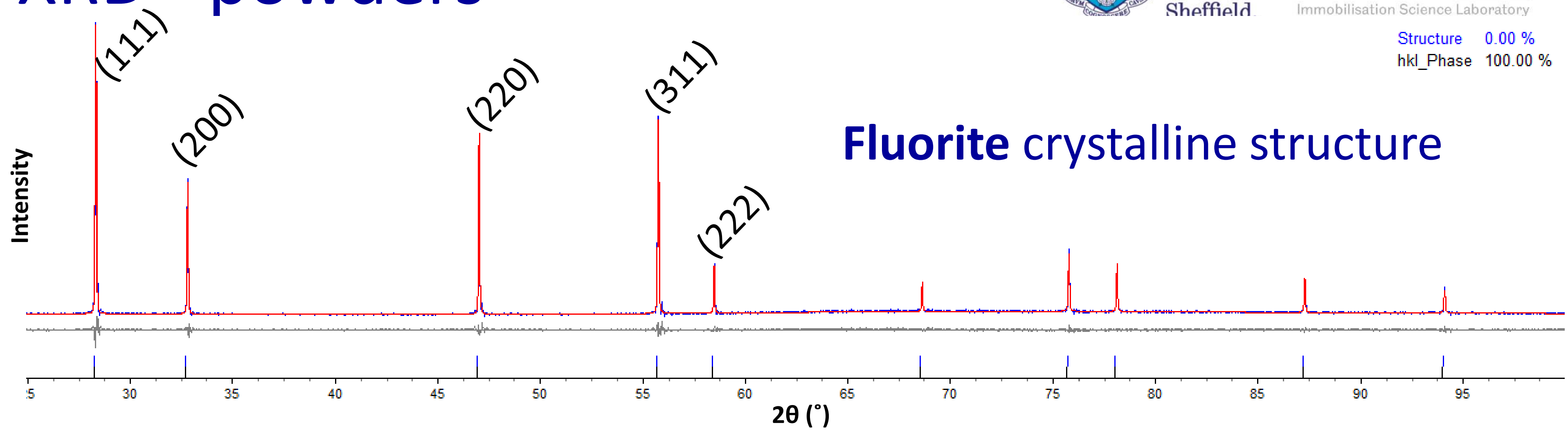
REE ≈ 98 %



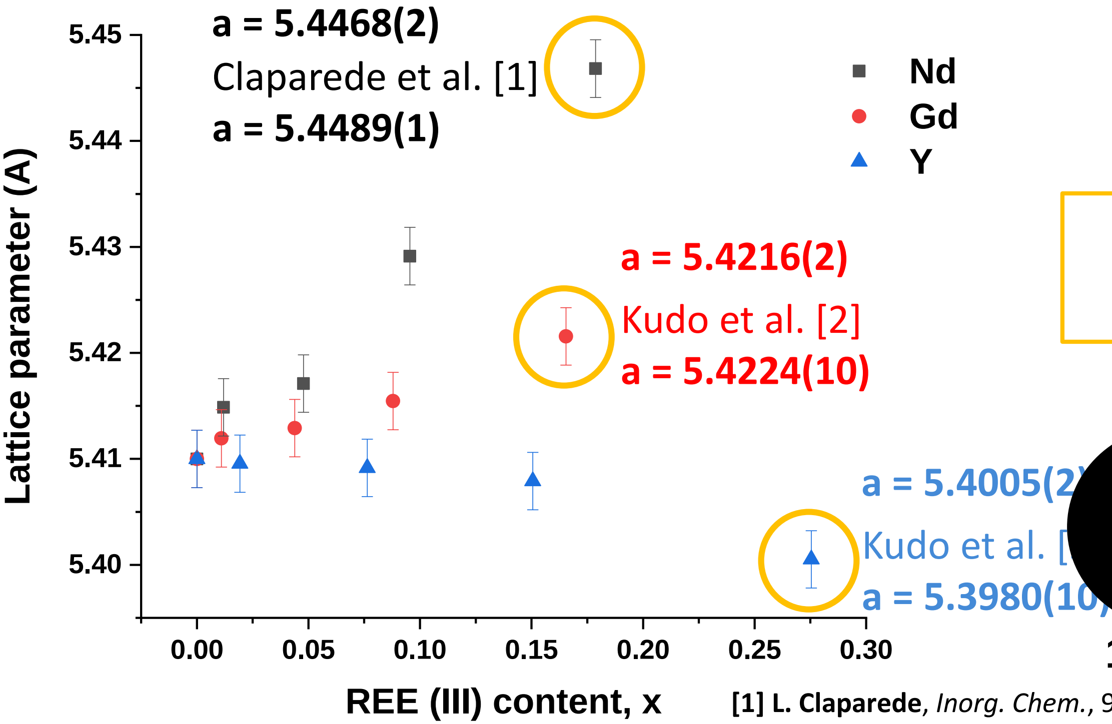


Reach expected composition

XRD - powders



Fluorite crystalline structure



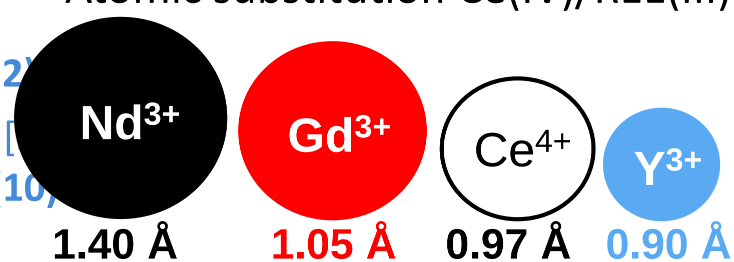
Nd: Increase of the a value

Gd: Increase of the a value

Y: Decrease of the a value

Incorporation of REE (III) in CeO_2 structure

Atomic substitution Ce(IV)/REE(III)



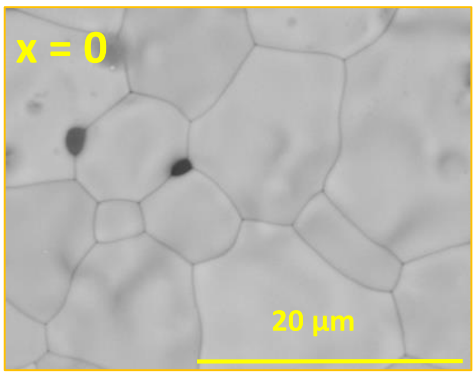
[1] **L. Claparede**, *Inorg. Chem.*, 9059–9072, **2011**

[2] **T. Kudo**, *J. Electrochem. Soc.*,142–147, **1975**

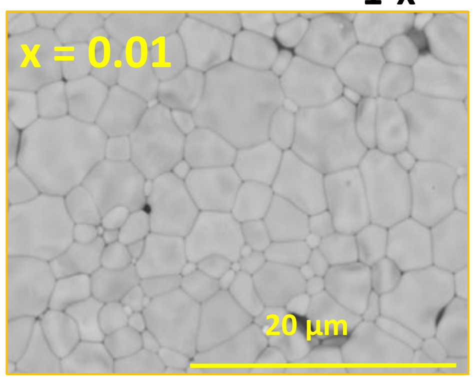
Shaping step

Oxide powder → Sieving → Pelletizing: **P = 500 MPa** → **10 mm** of diameter → Sintering: **1400°C-10h-Air**

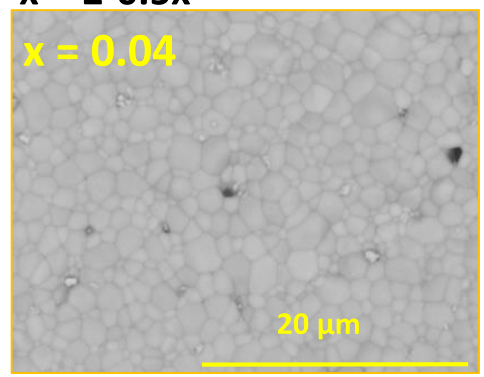
$Ce_{1-x}Gd_xO_{2-0.5x}$



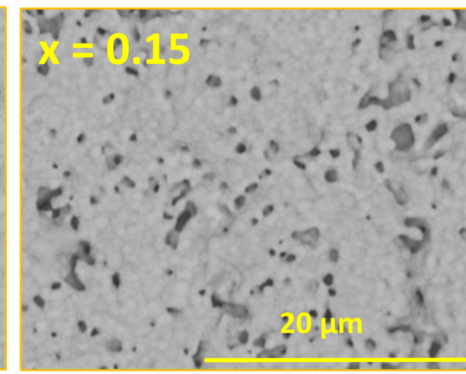
Ø = 8.7 ± 0.4 µm
d = 92 ± 2 %



Ø = 2.5 ± 0.4 µm
d = 93 ± 2 %



Ø = 1.3 ± 0.1 µm
d = 90 ± 2 %



Ø = 0.6 ± 0.1 µm
d = 85 ± 2 %

Microstructural modification with the REE incorporation rate

- Grains size decrease
- Increase of the porosity
- Pellet density decrease

→ **REE (III) enriched phases at the grain boundaries limiting the grains growth and the densification**

Dissolution

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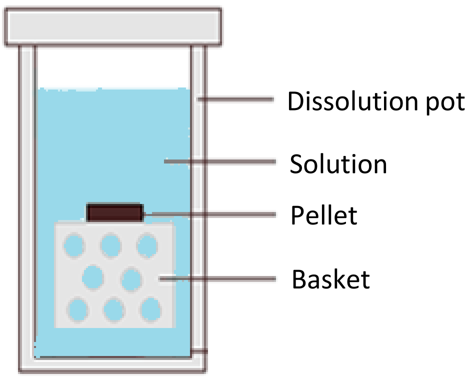
9 M HNO_3 - 60˚C

$Ce_{1-x}REE_xO_{2-x/2}$ with REE = Nd, Y, Gd and x = 0, 1, 4, 8, 15 wt.%

Static conditions



$$N_L(i) = \frac{m_i}{f_i \times S}$$

Mass (i) in solution (g)

Reactive surface (m²)

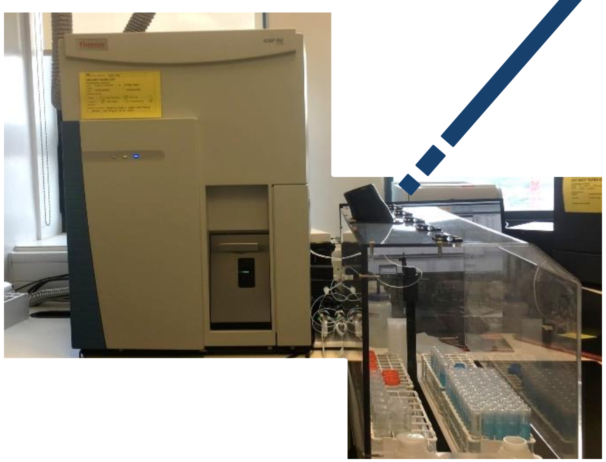
Weight fraction (i) in the solid

$$\frac{\Delta m(i)}{m_0} = \frac{m_i}{f_i \times m_0}$$

Mass (i) in solution (g)

Initial mass of the pellet (g)

Weight fraction (i) in the solid



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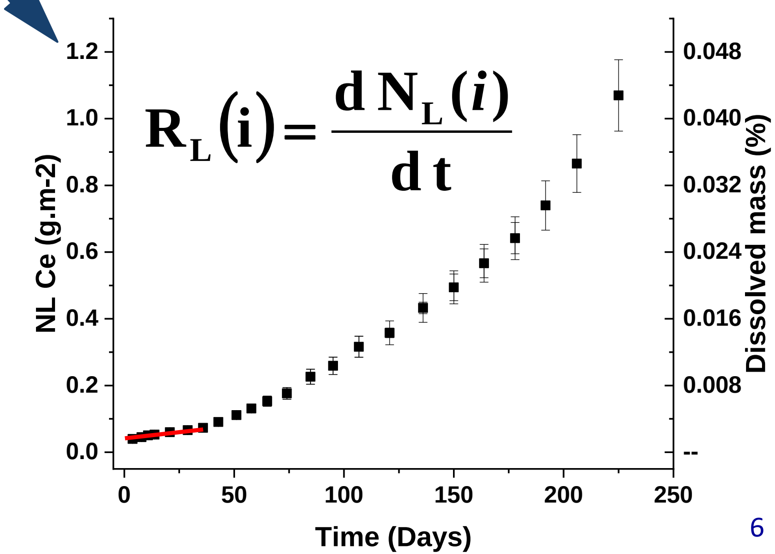
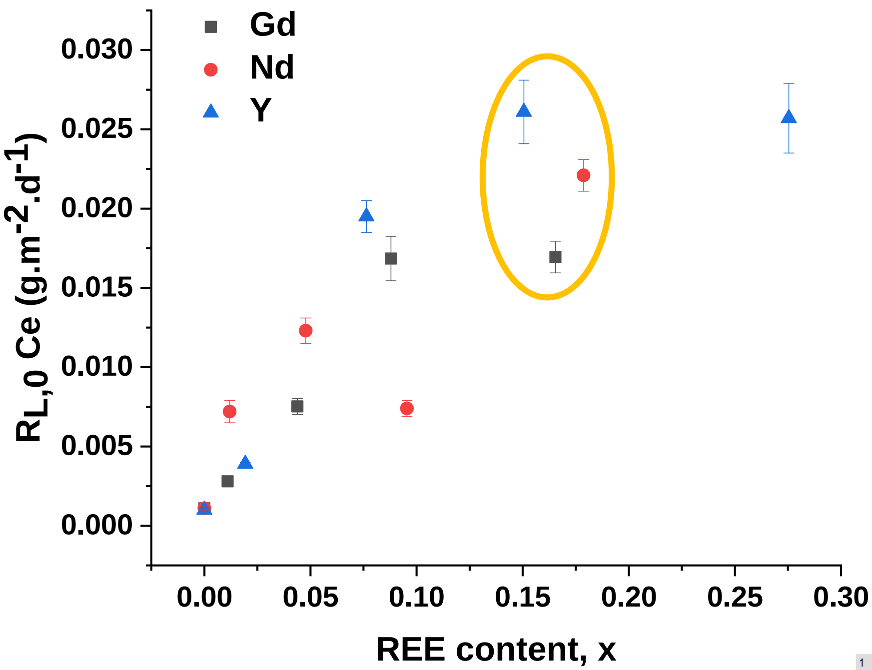


$$R_L(i) = \frac{d\,N_L(i)}{d\,t}$$

$R_L(i) \approx R_L(j)$: dissolution congruent

$R_L(i) \neq R_L(j)$: dissolution incongruent

Influence of the REE nature



$R_{L,0}$ Gd < $R_{L,0}$ Nd < $R_{L,0}$ Y

$R_{L,0}$ decrease with the REE (III) atomic weight

- ✓ Modification of the **cohesion energy** the fluorite unit cell induced by (III) impacted $R_{L,0}$
- ✓ **Heavier REE (III)**, higher the cohesion energy and **lower the $R_{L,0}$**

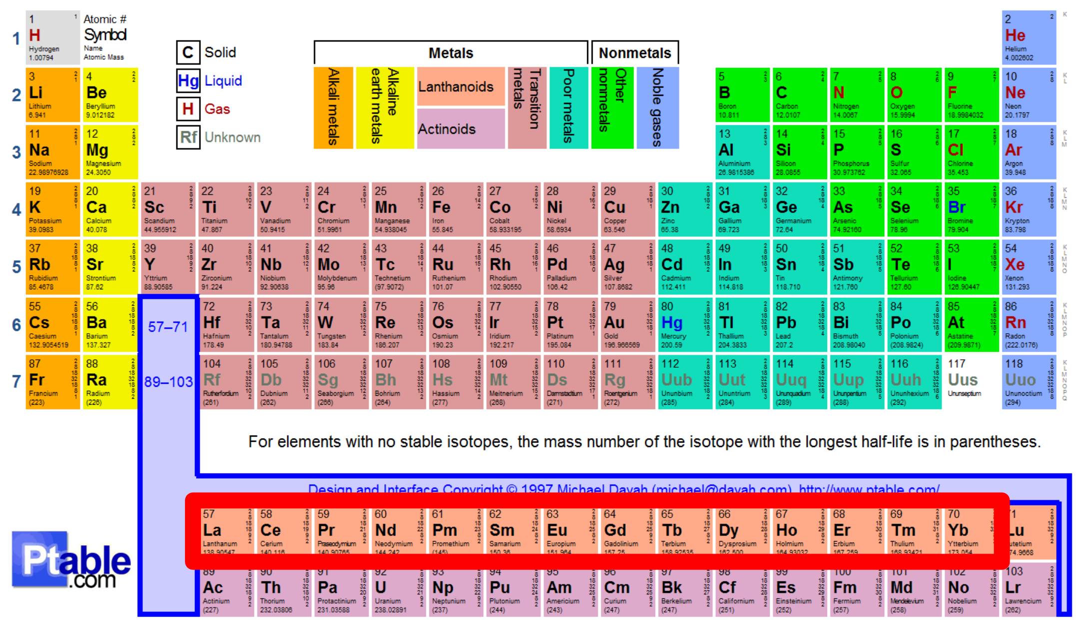
Powders

$Ce_{0.7}REE_{0.3}O_{1.85}$

4 M HNO_3 - 60˚C

Horlait *et al.*, Inorg. Chem., 3868-3878, **2012**

Ln^{III}	$R_{L,0}(Ce)$
La	$(6.6 \pm 0.7) \times 10^{-3}$
Nd	$(1.0 \pm 0.1) \times 10^{-2}$
Sm	$(4.9 \pm 0.8) \times 10^{-3}$
Gd	$(7.9 \pm 0.7) \times 10^{-3}$
Dy	$(2.5 \pm 0.2) \times 10^{-3}$
Er	$(1.6 \pm 0.2) \times 10^{-3}$
Yb	$(3.1 \pm 0.3) \times 10^{-3}$



Influence of the composition

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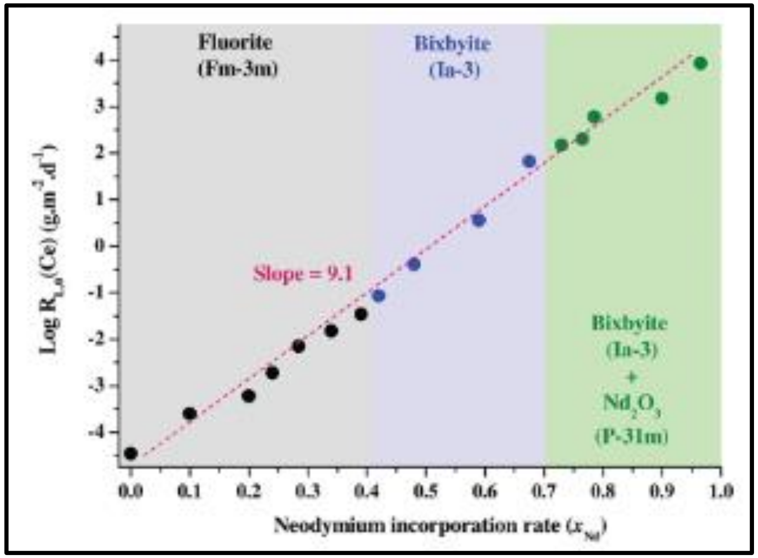
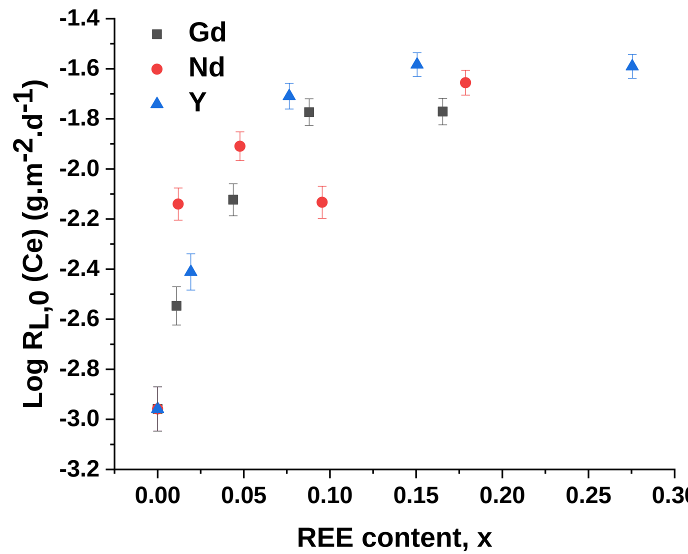
Powders
$Ce_{1-x}Nd_xO_{2-x/2}$
4 M HNO_3 - 60˚C

Pellets
$Ce_{1-x}REE_xO_{2-x/2}$
9 M HNO_3 - 60˚C

Horlait *et al.*, Inorg. Chem., 3868-3878, **2012**





x < 0.08:

- Structural defects
- Oxygen vacancies
- Ce^{3+} (higher solubility)

Increase $R_{L,0}$ Ce

4M *vs* 9M HNO_3

High x *vs* lower x

Powders *vs* pellets

Homogeneous *vs* heterogeneous

x > 0.15:

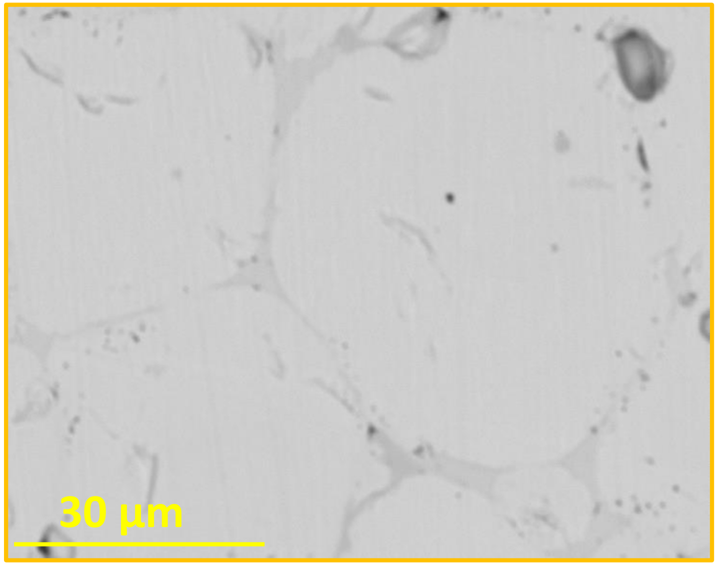
- Experimental issue?
- Presence of REE (III) enriched phases at the grain boundaries limiting the Ce matrix dissolution

Limit $R_{L,0}$ Ce

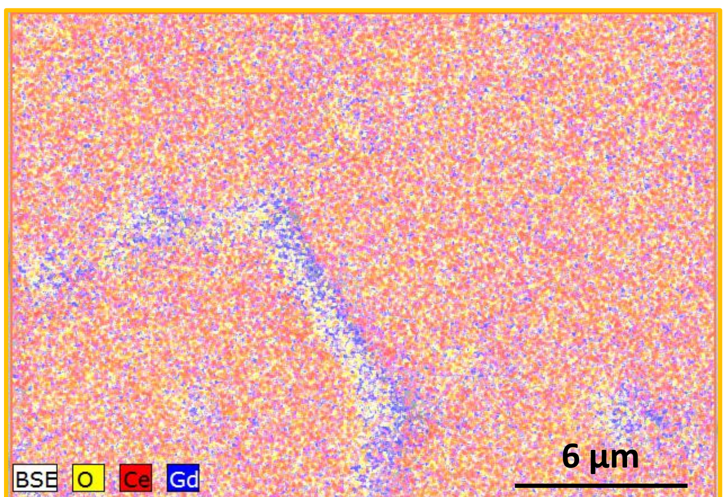
Influence of the heterogeneity

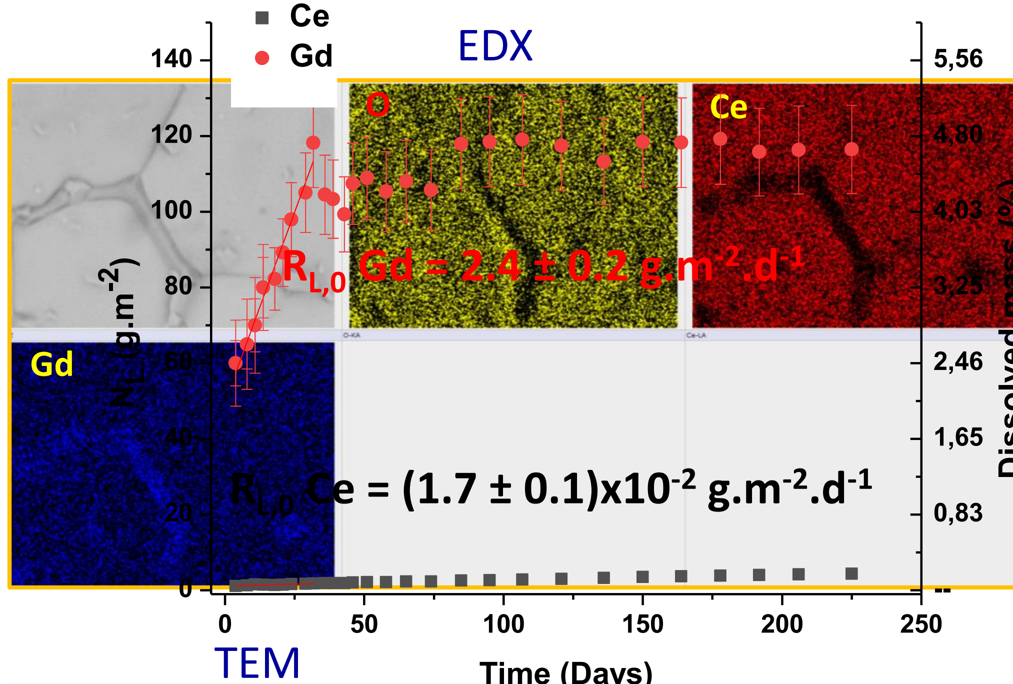
$Ce_{0.82}Gd_{0.18}O_{1.91}$

SEM

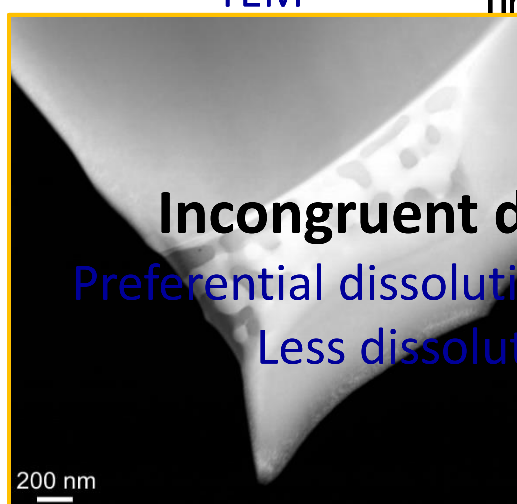


EDX





TEM



Incongruent dissolution Ce/Gd

Preferential dissolution of Gd-enriched phases

Less dissolution of Ce matrix

SEM/TEM

Confirm REE (III) enriched zone at the Grains boundaries

→ Induced by sintering step

Structural defects

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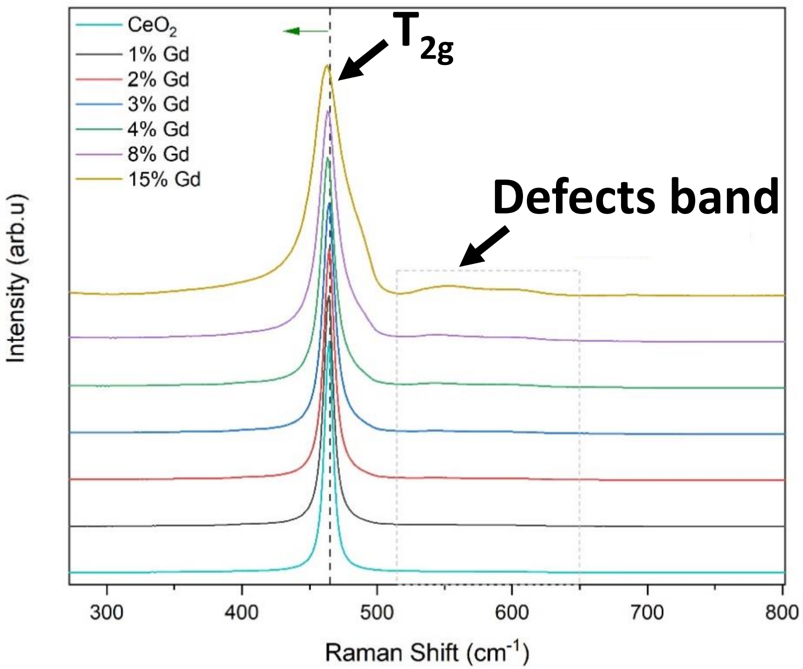


Pure CeO_2

One main peak: **T_{2g}** band (460 cm^{-1})

→ **Vibrations** of **oxygen atoms around Ce ion**

Increasing (III) doping

T_{2g} peak tends become more **asymmetric** and **Longitudinal-Optical (LO)** intensity increase

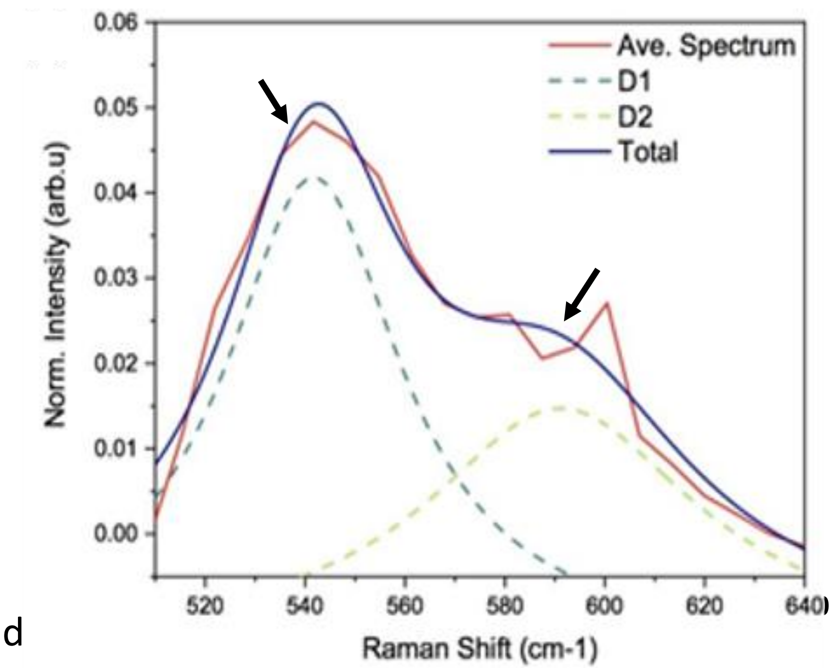
→ Indicates the presence of **crystalline defects**

Deconvolution of defects band

→ Increase of the **defects concentration** with the **REE (III) incorporation rate**

LO band is a Raman **triplet defect band** characteristics of **crystalline defect types** in the matrix structure

→ **Oxygen vacancies formation**

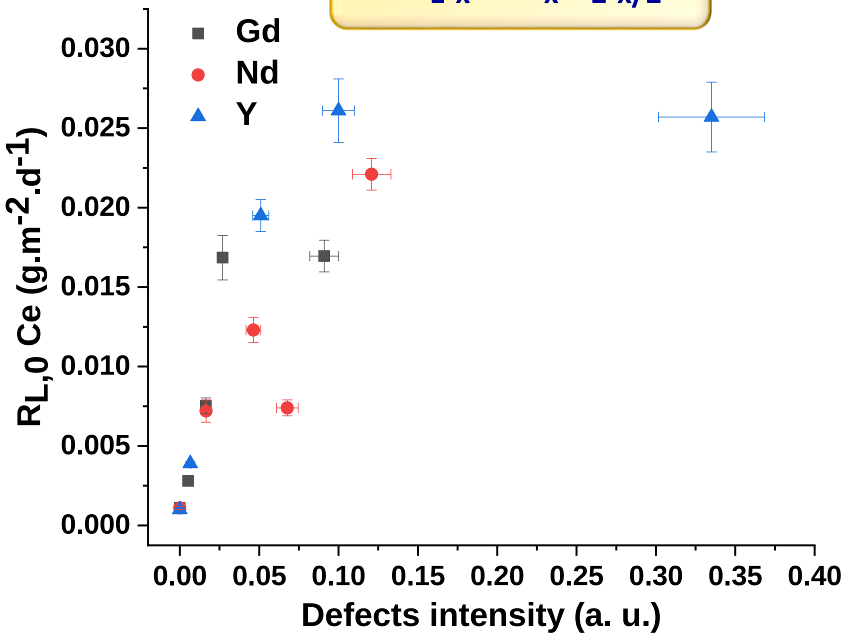


→ **Crystalline defects are generated by the (III) incorporation in CeO_2**

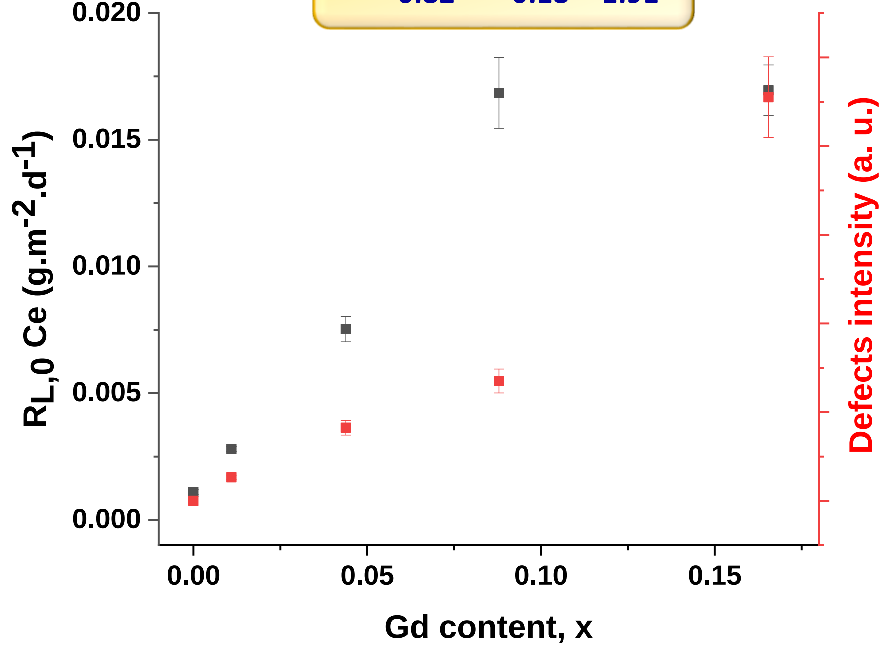
Impact of the crystalline defects on the durability?

Influence of the structural defects

$Ce_{1-x}REE_xO_{2-x/2}$



$Ce_{0.82}Gd_{0.18}O_{1.91}$



- ✓ Increase $R_{L,0}$ with defects concentration until 10 mol.%
- ✓ $R_{L,0}$ reached a plateau above 10 mol.%

More defects do not mean increase of $R_{L,0}$

- ✓ Increase of defects concentration with x
- ✓ Increase $R_{L,0}$ until 10 mol.%

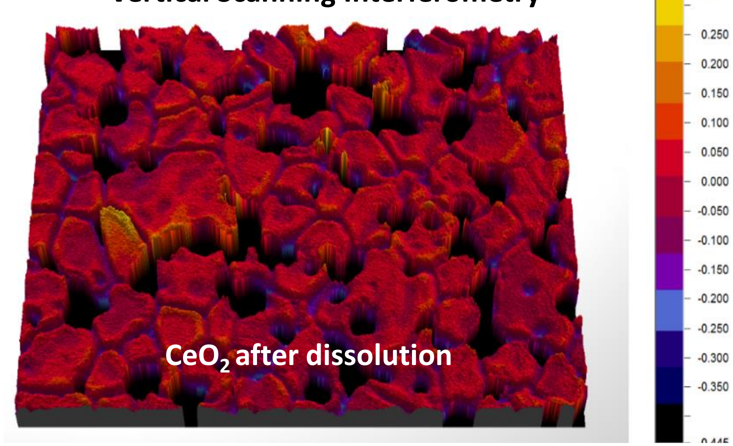
Crystalline defects not the only contribution impacting $R_{L,0}$

- Heterogeneity
- Microstructure?

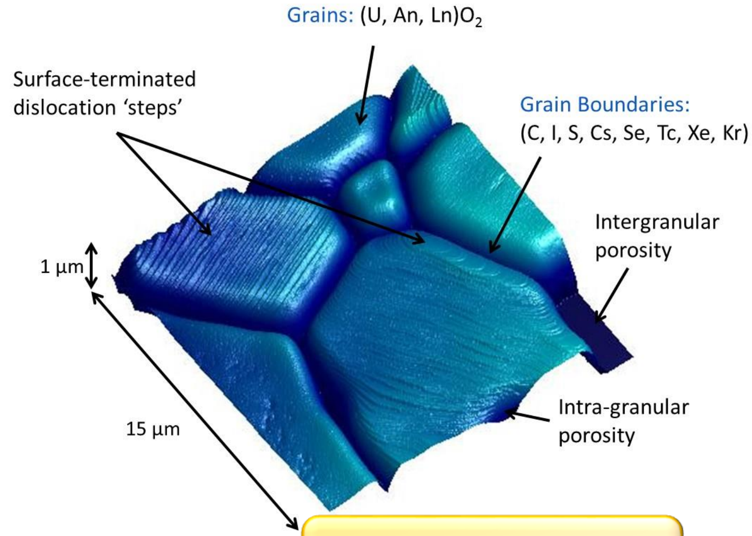
Influence of the microstructural features

- ✓ **Microstructural features** (e.g. grain boundaries, defects) can significantly **enhance the dissolution rate** of CeO_2 (×15)

Vertical Scanning Interferometry

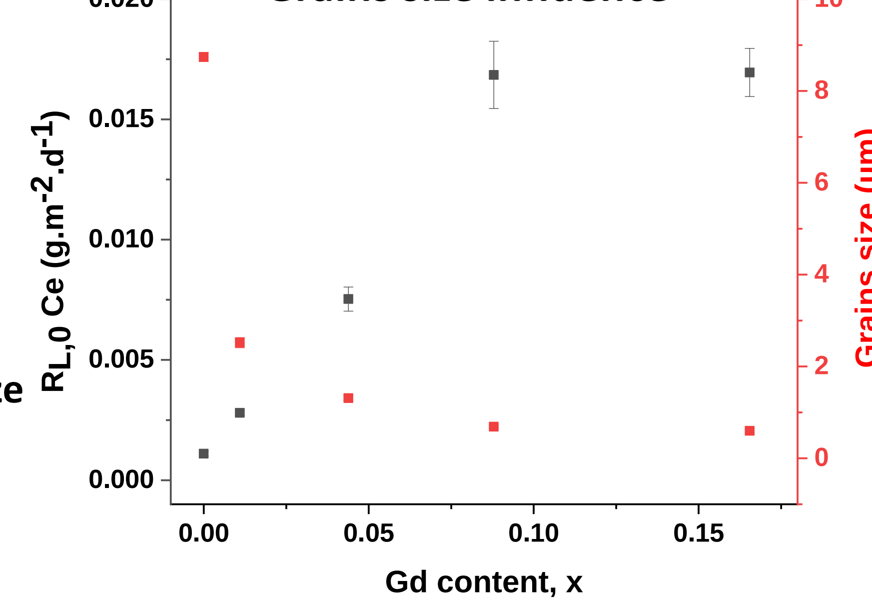


Corkhill, Applied Materials and Interfaces,12279, **2014**
Myllykylä, Corkhill, Radiochimica Acta, 565, **2015**
Corkhill, Applied Materials & Interfaces, 10562, **2016**



$Ce_{0.82}Gd_{0.18}O_{1.91}$

Grains size influence



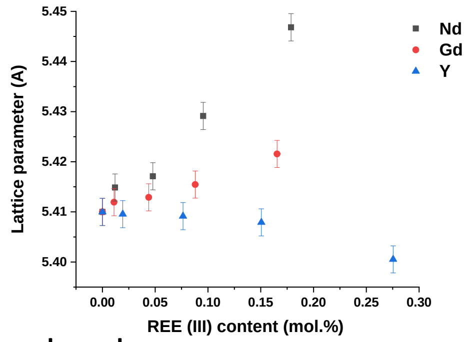
- ✓ Lower the grains size
- ✓ Higher the number of grains
- ✓ Higher the number of grain boundaries

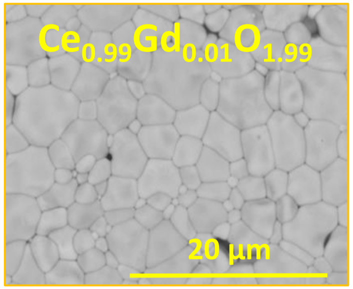
→ **$R_{L,0}$ Ce increase with lower grains size**

Grains size main contribution influencing the CeO_2 durability

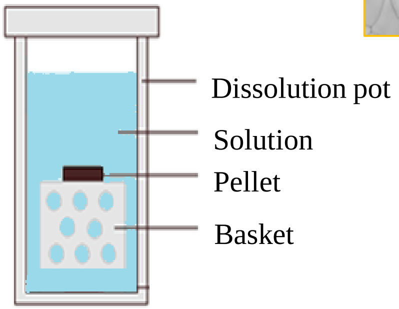
Conclusion

- ✓ **Prepare $Ce_{1-x}REE_xO_{2-x/2}$**
  - → x = 0, 1, 4, 8, 15 wt.%
  - → REE = Y, Gd, Nd
- ✓ **Oxalic precipitation**
  - → Effective precipitation
  - → Incorporation of REE in fluorite structure





- ✓ **Dense samples**
  - → Quantification of the crystalline defects
  - → Grains size determination
  - → Impact of sintering on heterogeneity

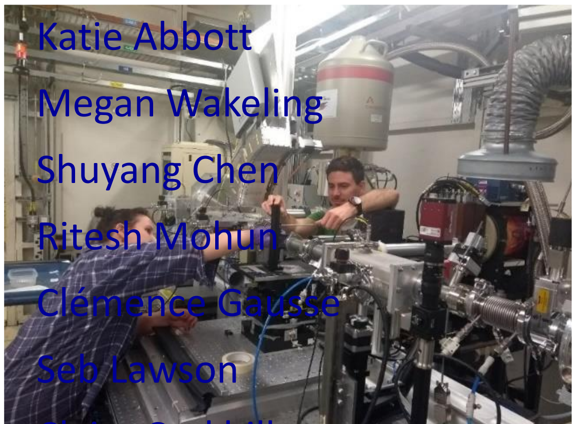


- ✓ **Heterogeneity**
  - → x < 0.08: $R_{L,0}$ increased
  - → x > 0.08: agglomerates limit $R_{L,0}$ Ce matrix
  - → Non-congruente dissolution Ce/REE
- ✓ **Influence of crystalline defects**
  - → Role on $R_{L,0}$
  - → Not the main contribution
- ✓ **Influence of grains size**
  - → $R_{L,0}$ increase with lower grains size
  - → Microstructure and heterogeneity main contributions

Further work

- ✓ **MET/EPMA**
  - → REE location
  - → GB composition
  - → REE oxidation state
- ✓ **SEM**
  - → Preferential dissolution area

Acknowledgements



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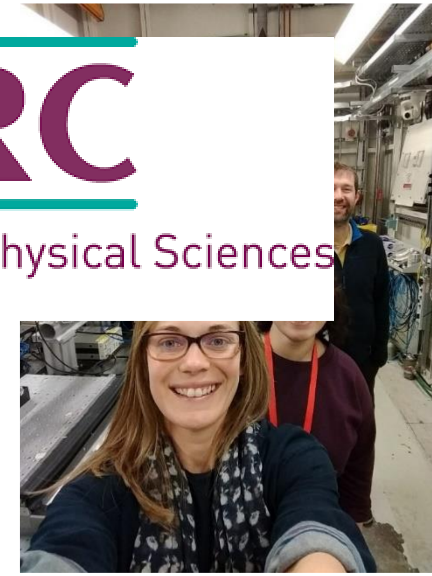

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