Mitglied der Helmholtz-Gemeinschaft

ASGARD

JÜLICH FORSCHUNGSZENTRUM

ASGARD 5th Project Meeting

July 1st – July 3th 2014 (Lancaster, England)

Progress Report of Beneficiary No 5: Jülich

Domain 2:

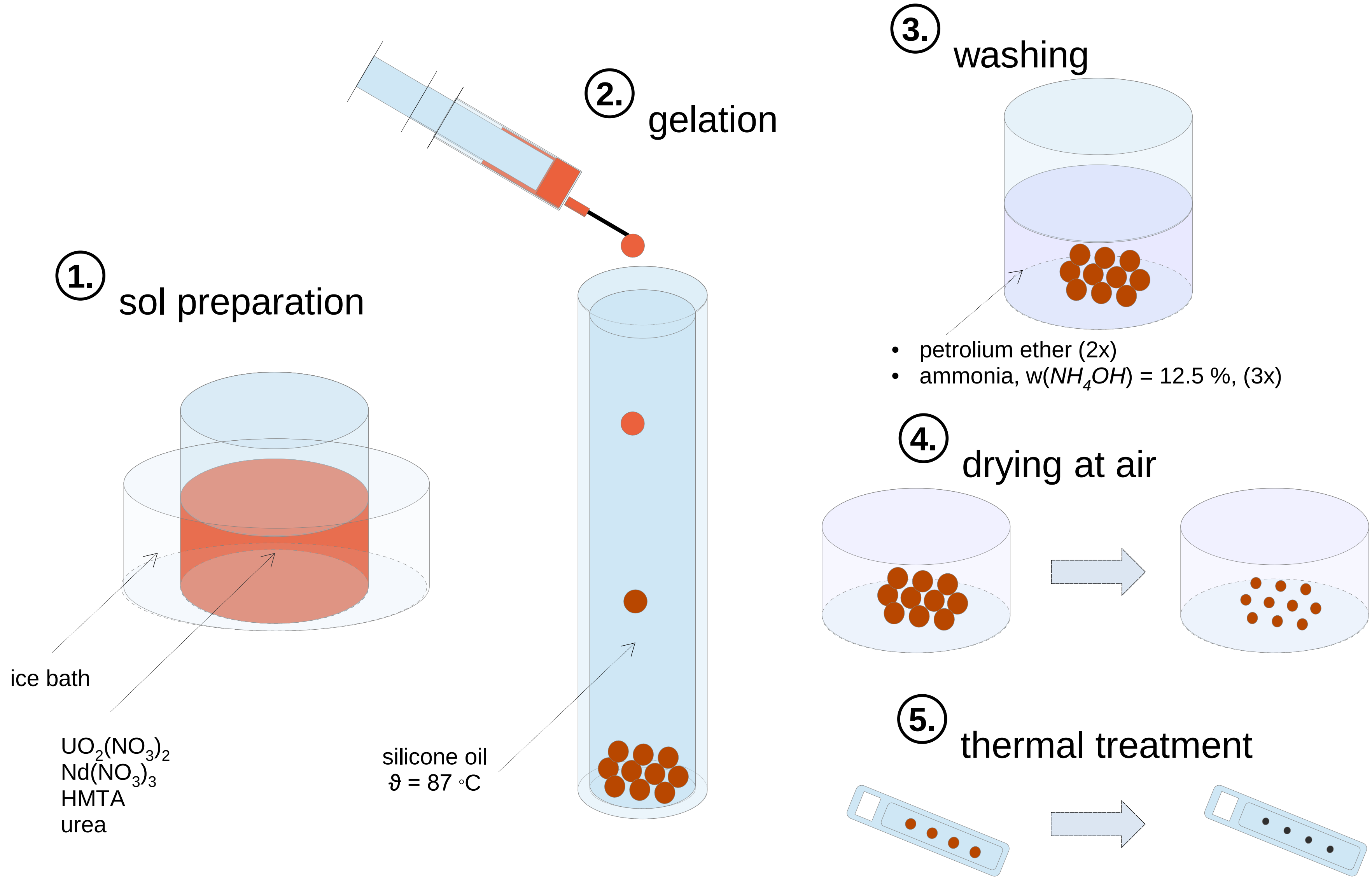
WP 2.1 Inert Matrix Fuels
WP 2.3 Conversion from solution to oxide pre-cursors
Task 2.3.1 Co-conversion by sol-gel routes
Task 2.3.2 Co-conversion by impregnation of solid matrixes

Christian Schreinemachers, Ronald Middendorp, Elena Ebert, Andrey A. Bukaemskiy, Stefan Neumeier, Giuseppe Modolo

Institut für Energie- und Klimaforschung (IEK-6)
– Nukleare Entsorgung und Reaktorsicherheit

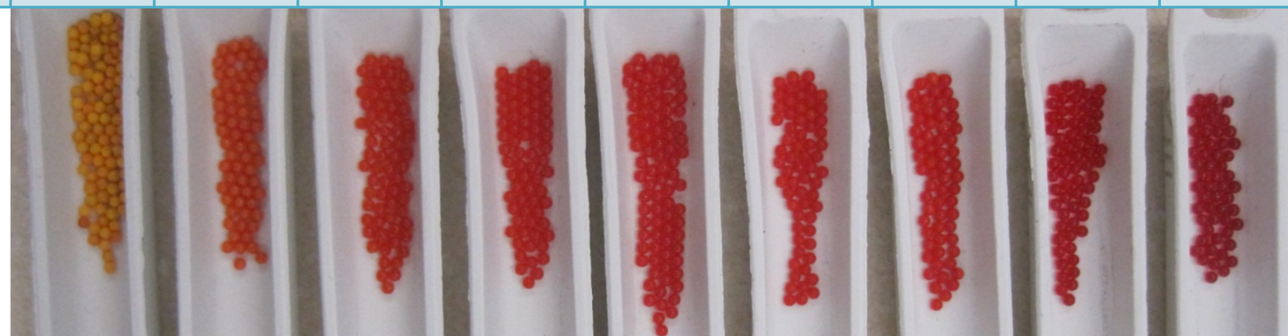
Co-conversion by sol-gel routes

Particles fabrication by internal gelation



Introduction

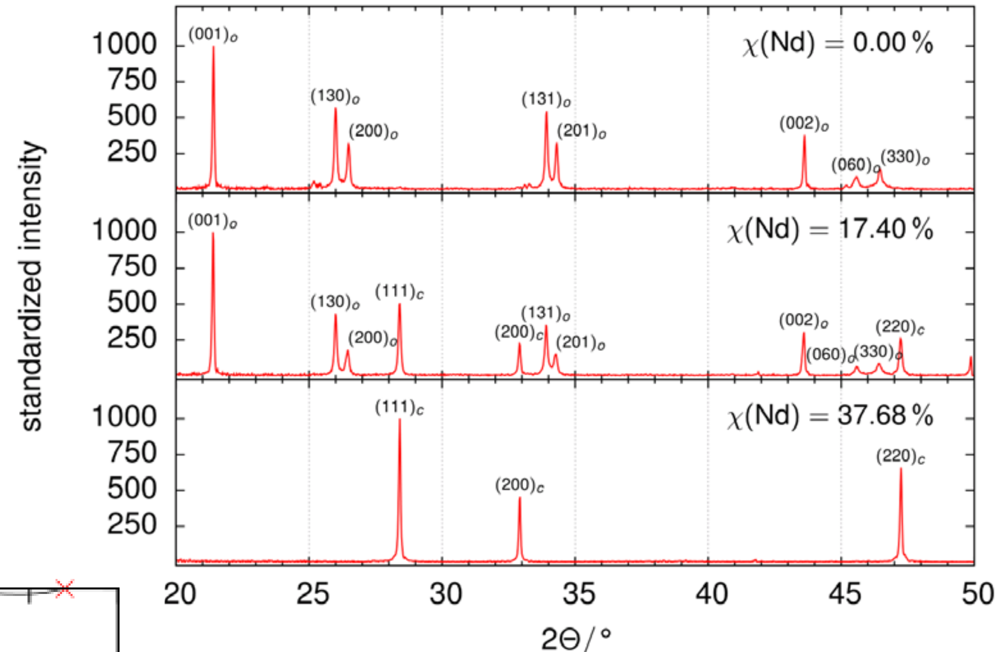
Particle characterization

$\chi(\mathrm{Nd})_{\mathrm{ICP\text{-}MS}}$	%	0	5.80	11.99	17.40	22.62	27.59	33.49	37.68	42.63
$c(\mathrm{U+Nd})_{\mathrm{sol}}$	mol/L	2.50	2.60	2.62	2.56	2.58	2.60	2.62	2.65	2.67
										
$\bar{\mathrm{m}}(\mathrm{particle})$	mg		5.38	5.23	4.96	5.24	4.83	5.00	5.34	5.55
$\bar{\mathrm{d}}(\mathrm{particle})$	mm		1.35	1.35	1.33	1.38	1.34	1.35	1.38	1.41
$\bar{\rho}(\mathrm{particle})$	$\mathrm{g/cm^3}$		4.15	4.04	3.99	3.85	3.87	3.86	3.85	3.81

$$\chi(\mathrm{Nd}) = \frac{n(\mathrm{Nd})}{n(\mathrm{Nd+U})} \qquad R(\mathrm{urea}) = \frac{n(\mathrm{urea})}{n(M^{n+})} = 1.80 \qquad R(\mathrm{HMTA}) = \frac{n(\mathrm{HMTA})}{n(M^{n+})} = 1.35$$

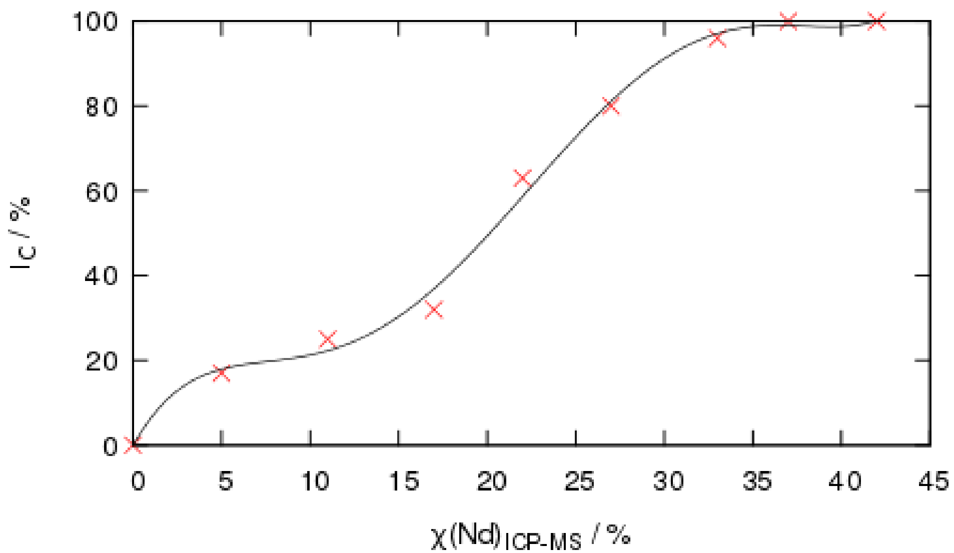
Characterization of U/Nd microspheres

XRD analyses of particles treated in air



Presence of orthorhombic and cubic crystal lattice structure

$$I_C = \frac{I(111)_C}{I(111)_O + I(001)_C}, \quad I_O = \frac{I(001)_O}{I(001)_O + I(111)_C}$$

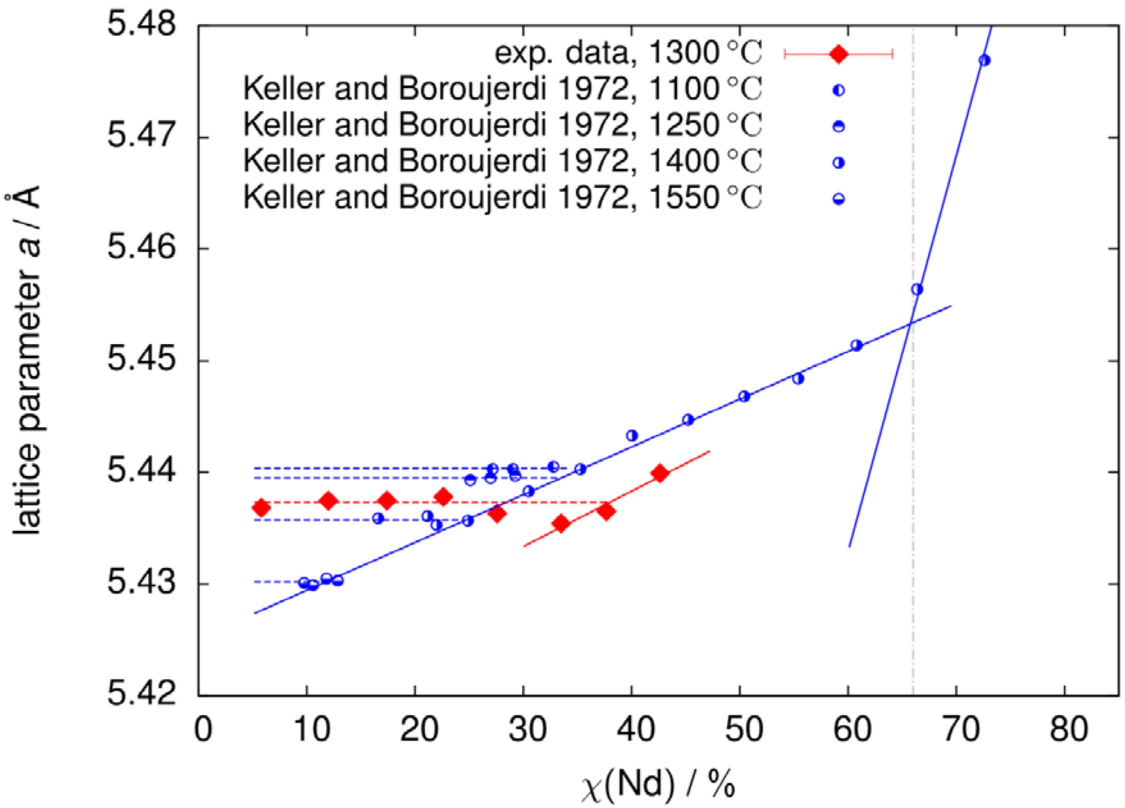


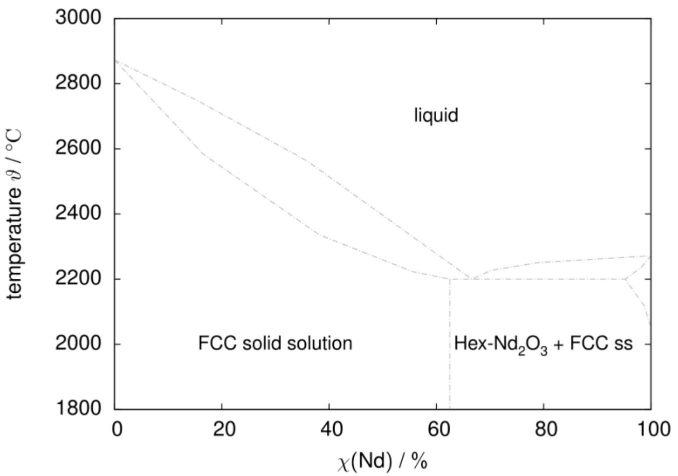
Lattice parameter determination:

1. Gaussian function → 2θ
2. Bragg's law → a_i
3. Nelson & Riley method → a

Characterization of U/Nd microspheres

XRD analyses of particles treated in air





- Constant a for mixed phase region (5.4374 Å)
- Linear increase for single phases

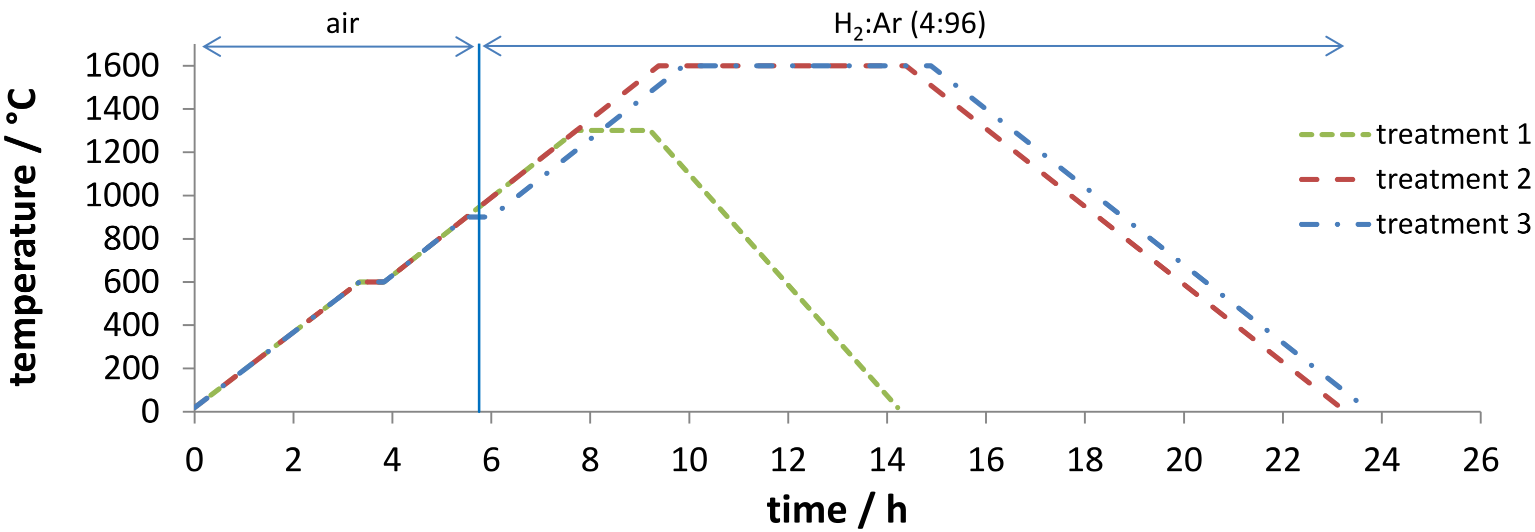
Vegard's rule

$$a_{AB} = a_A(1 - \chi_B) + a_B\chi_B$$

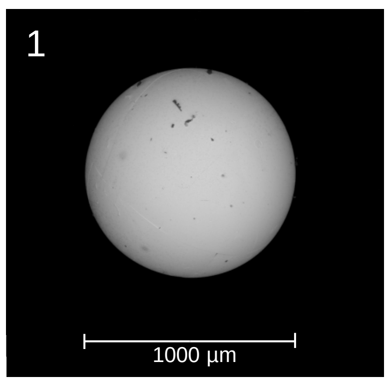
Keller, C. and A. Boroujerdi (1972). "Phasengleichgewichte in den Systemen UO_2–UO_3–$NdO_{1.5}$ und $NpO_2 + xNdO_{1.5}$". In: Journal of Inorganic and Nuclear Chemistry 34, pp. 1187–1193.

Thermal treatment of microspheres

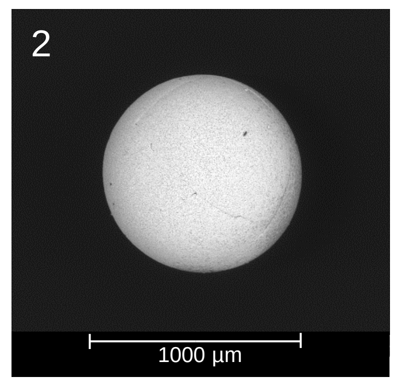
Optimization of sintering conditions



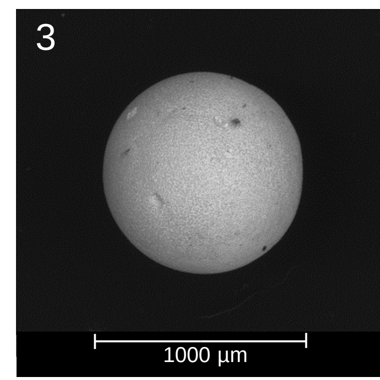
***χ*(Nd) = 42.63 %**



$\bar{m}$ = 4.17 mg
$\bar{d}$ = 919.1 µm
$\bar{\rho}$ = 10.25 g/cm³



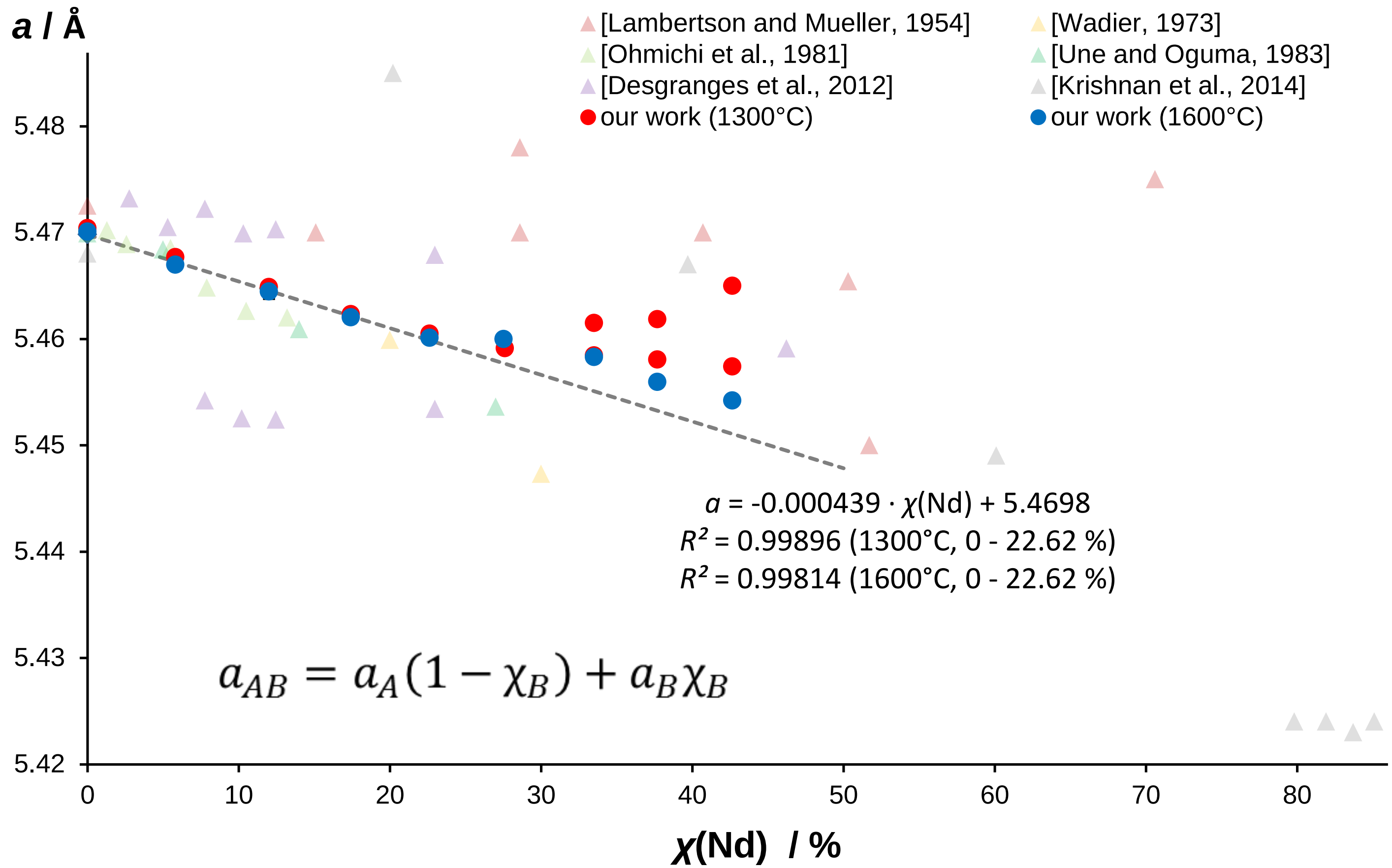
$\bar{m}$ = 3.96 mg
$\bar{d}$ = 899.7 µm
$\bar{\rho}$ = 10.13 g/cm³



$\bar{m}$ = 3.96 mg
$\bar{d}$ = 922.3 µm
$\bar{\rho}$ = 9.56 g/cm³

Thermal treatment of microspheres

XRD analyses - comparison with literature data



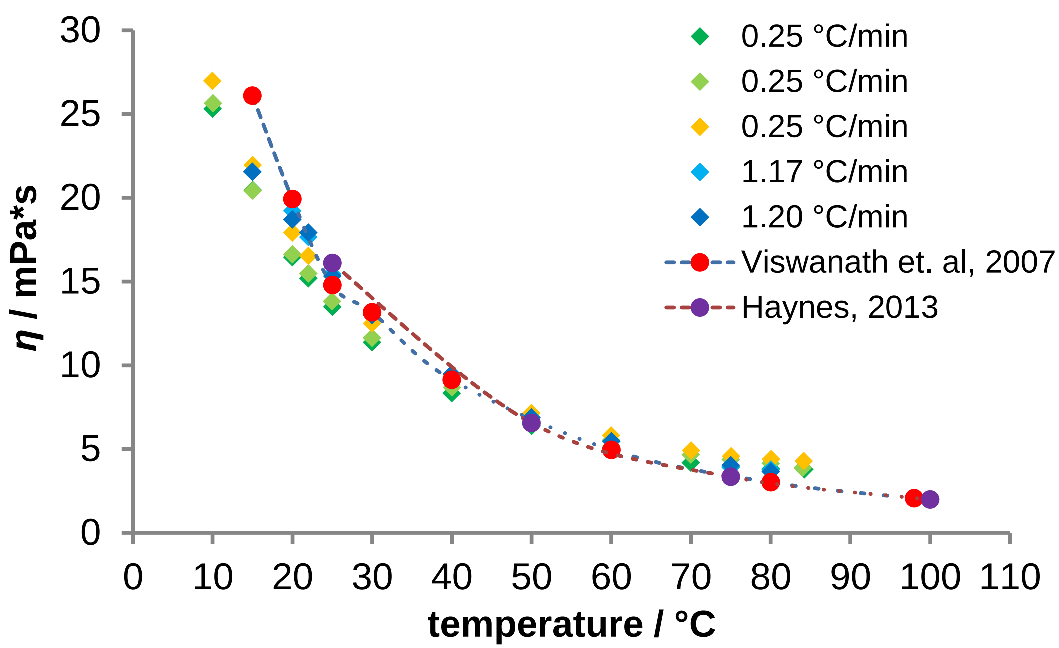
→ lattice formation depends on synthesis route

Sintering time not sufficient => increase of plateau to 10 h

Determination of gelation temperature

Viscosity measurements

- Measurements with given geometry
  V = 9 mL (Ethylenglycol)
- Verification with self-made geometry
  V = 2 mL (Ethylenglycol)



Determination of gelation temperature

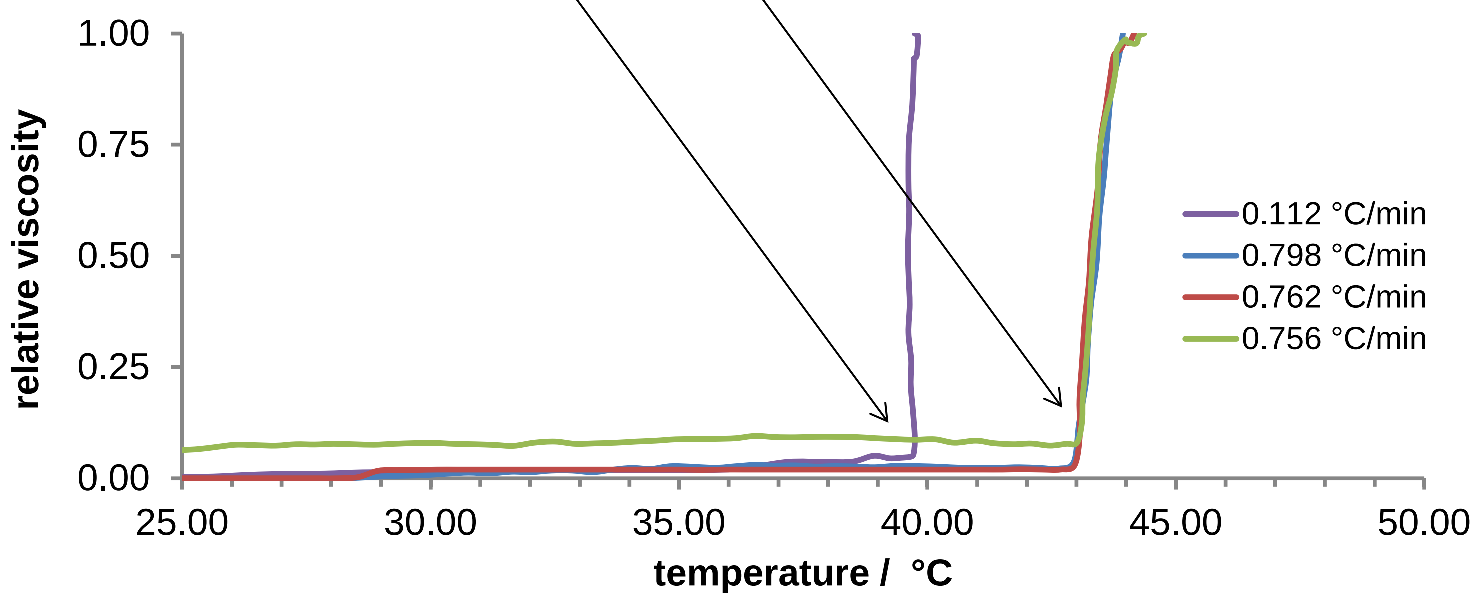
Viscosity measurements

- Zr/Y/Ce (76:14:10); $R_{HMTA} = 0.56$, $R_{urea} = 0.75$
  - influence of the heating rate
  - the reproducibility of the system

$\bar{\vartheta}_{gelation} = 43.55 \pm 0.14\ °C$

$\vartheta_{gelation} = 39.73\ °C$

Calculation of 1st derivation to determine $\vartheta_{gelation}$



c.schreinemachers@fz-juelich.de

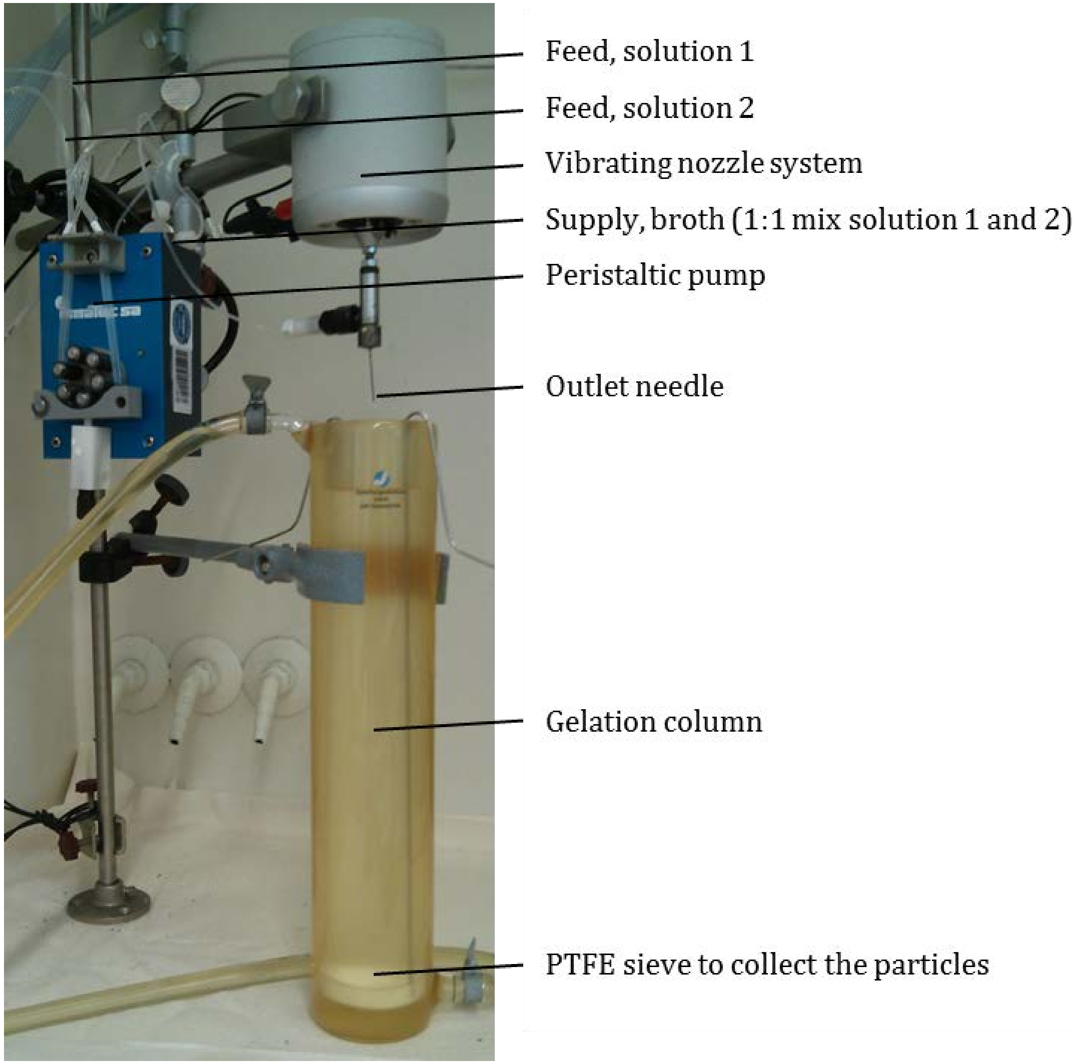
The vibrating nozzle system

Change of synthesis strategy: 2 feed solutions

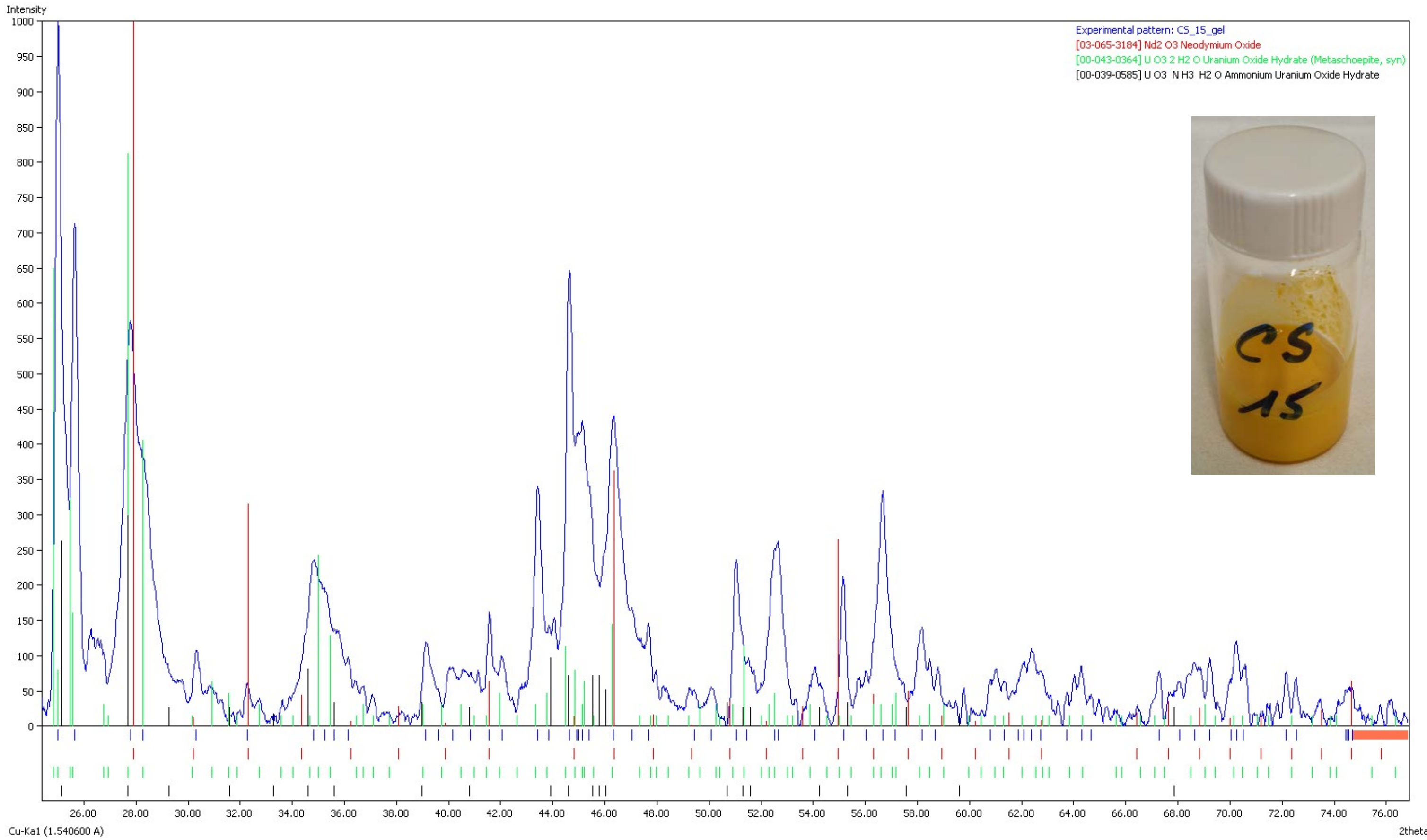
System modification: Replacement of syringe pump by peristaltic pump.

Batch experiments with χ(Nd) = 40 %.

→ precipitation



The vibrating nozzle system



Precipitation *(XRD)*: $UO_3NH_3 \cdot H_2O$; $UO_3 \cdot 2\ H_2O$; Nd_2O_3

→ suspension transformed into a gel

Outlook

- Characterization of the precursor solution: Influence of the U/Nd ratio on the gelation system by potentiometric titrations.
- Characterization of the sol: Determination of pH-values (initial and during process, time dependent).
- Temperature depending viscosity measurements to determine the gelation temperature of the sol.
- Preparation of a large amount of particles of each composition by the use of the “vibrating nozzle” system.
- Thermal treatment with increased sintering time of existing particles.

Acknowledgment

- Jakob Dellen (XRD)
- Alexander Poll (viscosimetry)
- Fabian Sadowski (ICP-MS)

European Atomic Energy Community's 7^{th} Framework Programme (FP7 2007-2011) - grant agreement No. 295825.

Thank you for your attention!