

Synthesis of thorium dioxide doped with gadolinium via a wet chemical route

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Co-promotor: Prof. Thomas Cardinaels (Radiochemical Analysis and Processes, Institute for Nuclear Materials Sciences, SCK•CEN)



I. Context of the research

Quest for new nuclear fuel

- Fissile isotopes for peaceful purposes ^{235}U , $^{239/241}\text{Pu}$ and ^{233}U .
- Existing thermal nuclear reactors burn ^{235}U , $^{239/241}\text{Pu}$ ($\eta = 0.7\%$)
- ^{233}U needs to be bred from fertile ^{232}Th



- Motivation to study the valorization of ^{232}Th :
 - Sustainability in fuel resource management (this is the main incentive also in developing Gen IV fast reactors as well).
 - Sustainability in waste management (shorter lived actinide inventory).
 - $\sigma(^{233}\text{U}) \gg \sigma(^{235}\text{U})$.
 - Already available as REE mining side product.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18						
	Atomic # Symbol Name Atomic Weight																		2					
1	1 H Hydrogen 1.00794																	2 He Helium 4.002602						
2	3 Li Lithium 6.941	4 Be Beryllium 9.012182																	7 N Nitrogen 14.0067	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797		
3	11 Na Sodium 22.98976928	12 Mg Magnesium 24.3050																	13 Al Aluminum 26.9815386	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
4	19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955912	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938045	26 Fe Iron 55.845	27 Co Cobalt 58.933195	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.63	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798						
5	37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.96	43 Tc Technetium (97.9072)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.293						
6	55 Cs Caesium 132.9054519	56 Ba Barium 137.327	57-71		72 Hf Hafnium 178.49	73 Ta Tantalum 180.94788	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.084	79 Au Gold 196.966569	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98040	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)					
7	87 Fr Francium (223)	88 Ra Radium (226)	89-103		104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Ds Darmstadtium (271)	111 Rg Roentgenium (272)	112 Cn Copernicium (285)	113 Uut Ununtrium (284)	114 Fl Flerovium (289)	115 Uup Ununpentium (288)	116 Lv Livermorium (293)	117 Uus Ununseptium (294)	118 Uuo Ununoctium (294)					

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

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57 La Lanthanum 138.90547	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92535	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9668
89 Ac Actinium (227)	90 Th Thorium 232.03806	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)



I. Context of the research

Sustainable nuclear fuel cycles

- Several alternative scenarios are being considered worldwide:
 - Fast reactors to allow Pu-multi recycling, P&T of TRU elements (Np, Pu, Am, Cm).
 - Thermal reactors using ^{233}U bred from thorium.
 - Fusion reactors?
- 
- Using ^{233}U allows the use of the existing LWR technologies* and facilities with a different and abundant fuel.
 - Thermal nuclear technology requires the fabrication of high density fuel pellets.



II. Focus of the research

Fundamental studies of physical and chemical properties

- Present study aimed at wet chemical routes amenable to remote processing, and study of fundamental properties.
 - Pellet density, sinterability, overall integrity of pellets.
 - Lattice parameter changes as a function of Gd-dopant concentration.



III. Overview:

Wet chemical synthesis and characterization

- Desired powder properties: *stable, free-flowing, highly sinterable and compactible.*

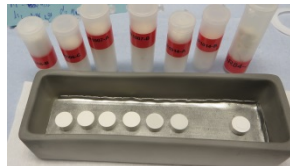
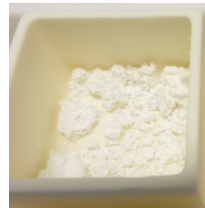
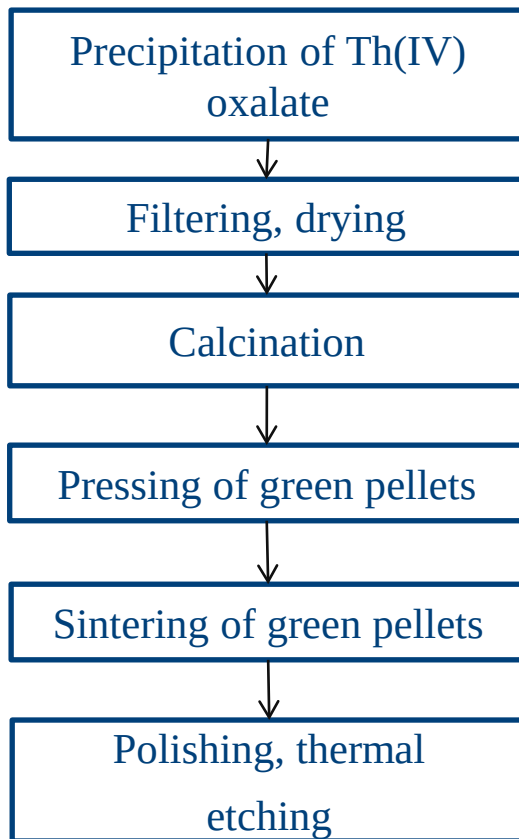
- *The precipitation reaction of the oxalate precipitation route:*





III. Overview: The oxalate precipitation route

Process steps



Characterization

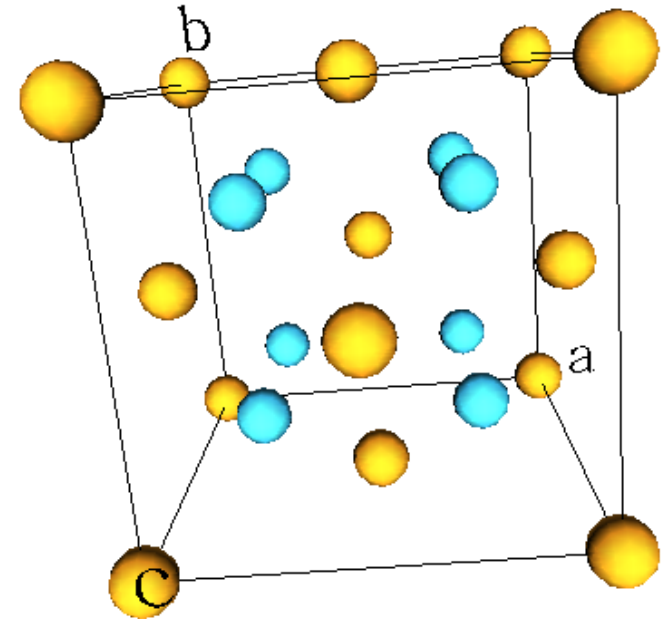
- **SEM, TG-analysis coupled to EGA-MS** on oxalate powders
- BET specific surface analysis of calcined powder, **SEM, XRD**
- Density measurement of green pellets, **dilatometry**
- Density measurement, **XRD, SEM/EDS, OM** on sintered pellets



IV. Results and discussion

Issues in focus

- Determination of change in lattice parameter as a function of Gd(III) dopant concentration.
- Studying thermal decomposition of precipitate.
- Determination of chemical homogeneity of precipitate, derived oxide and sintered pellets.

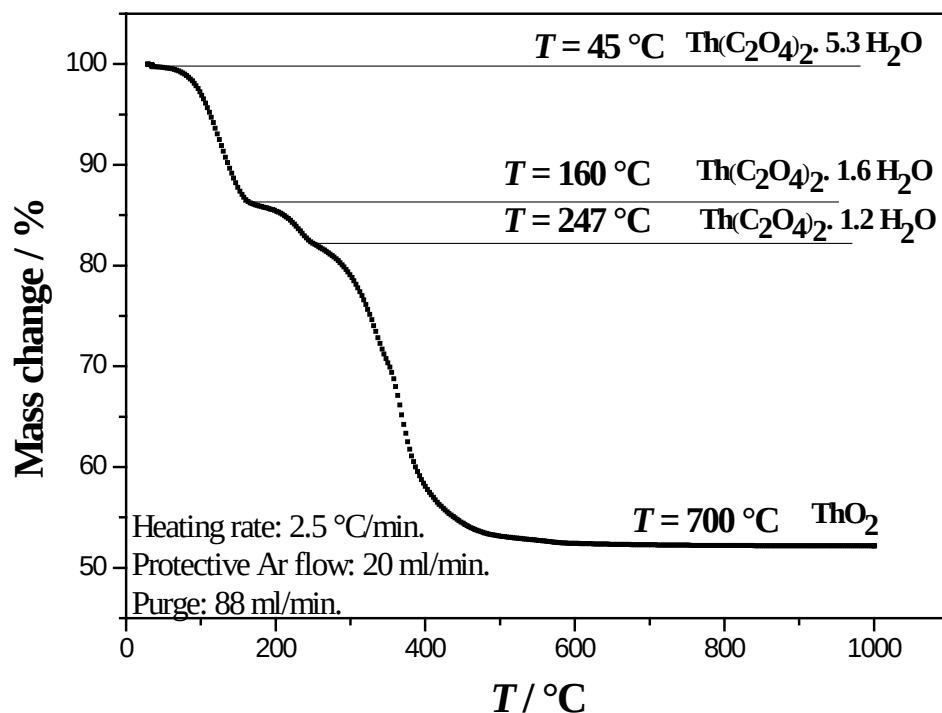




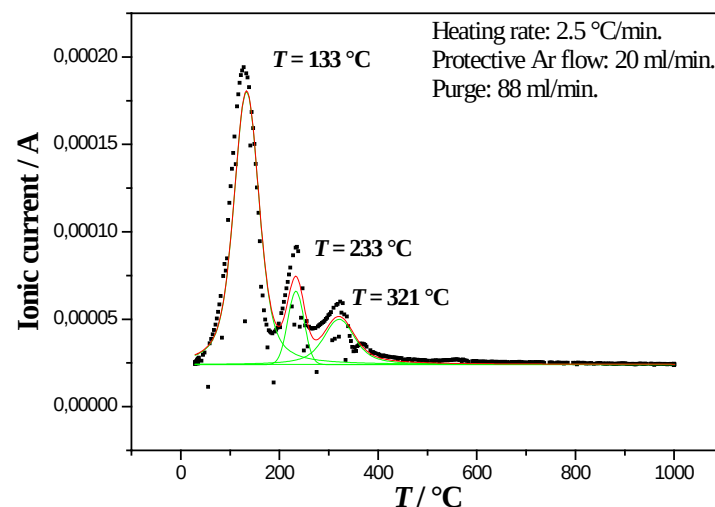
IV. Results and discussion

TG analysis and EGA-MS

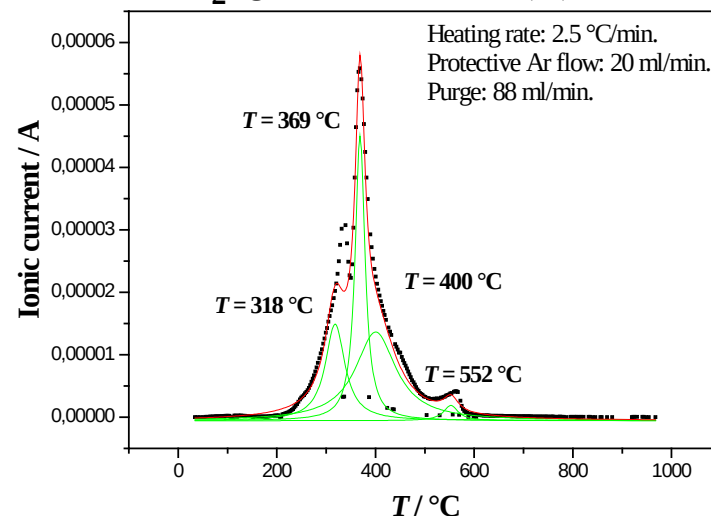
TG-curve of thorium(IV) oxalate



H_2O signal in EGA of thorium oxalate



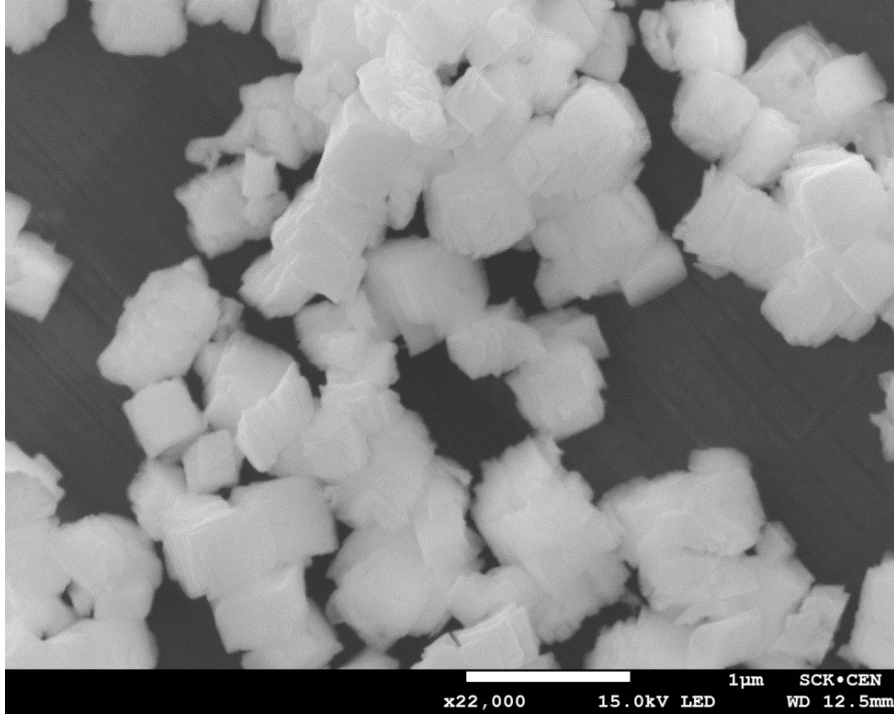
CO_2 signal in EGA of thorium(IV) oxalate



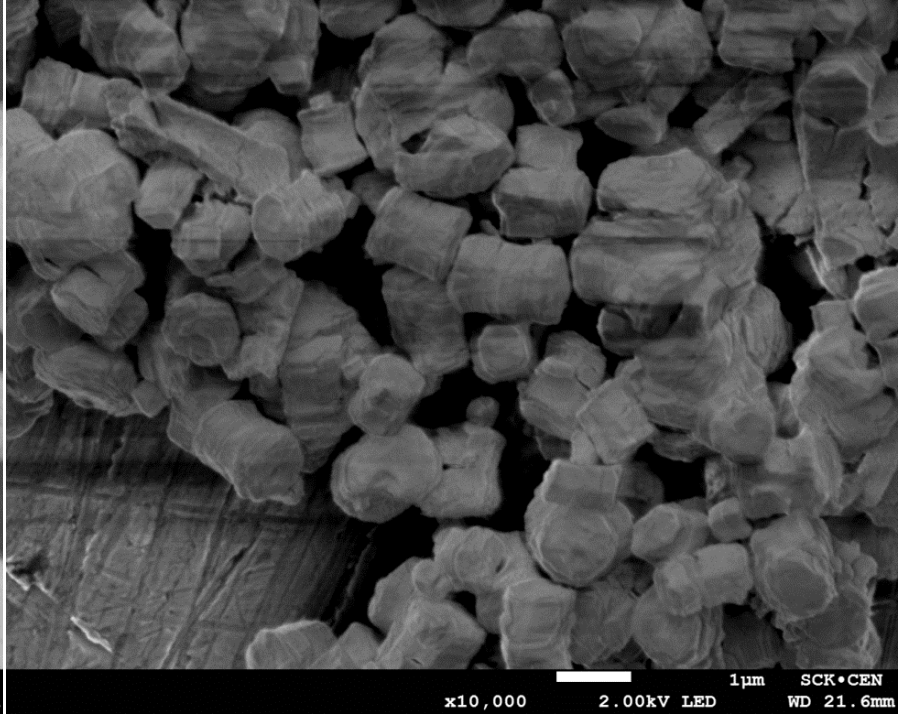


IV. Results and discussion

SEM images thoria powders



ThO_2

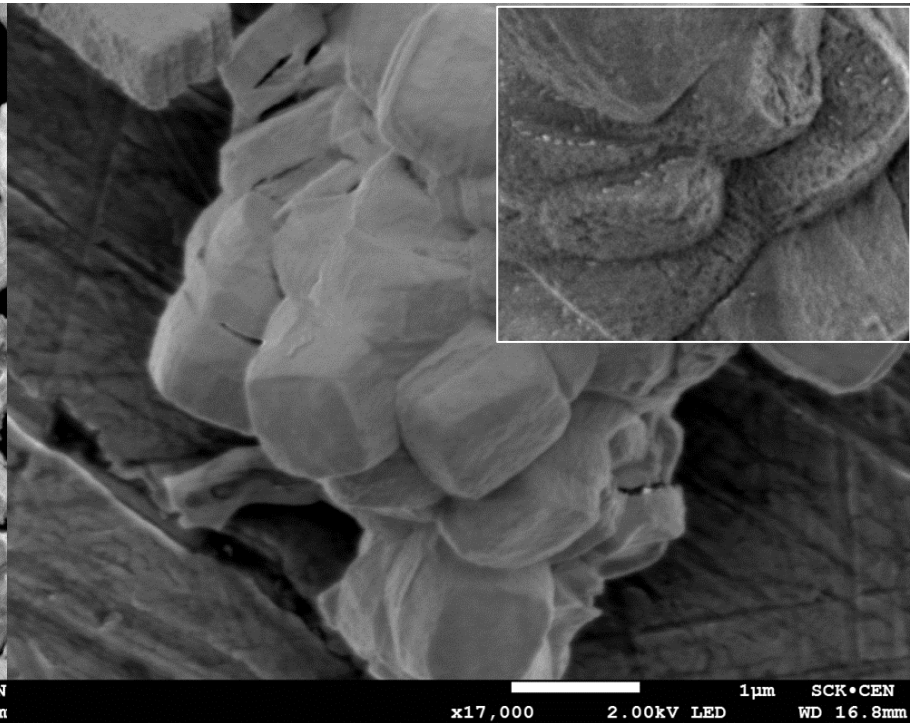
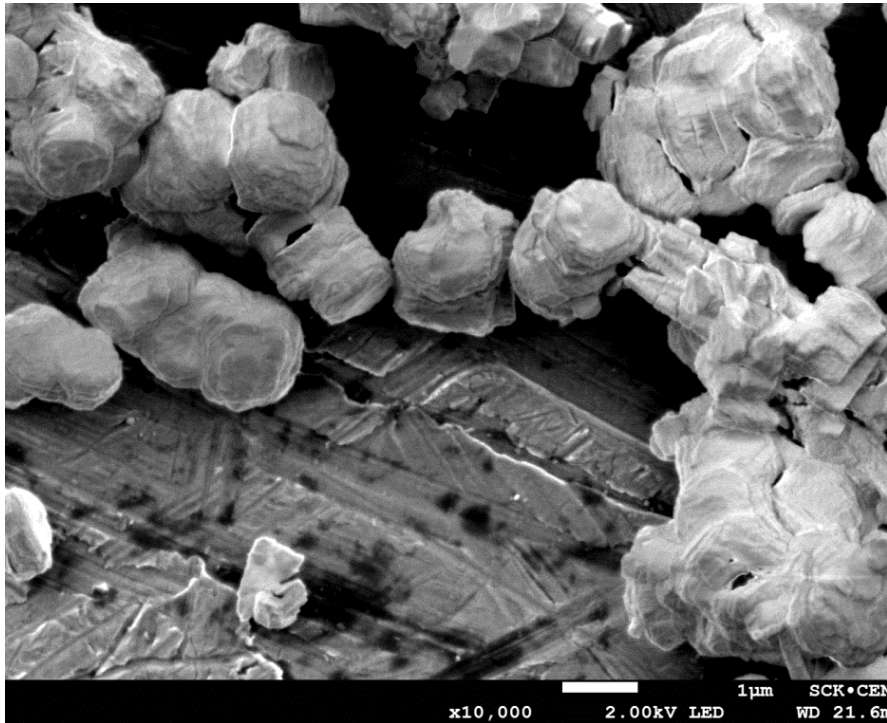


$\text{Th}_{0.95}\text{Gd}_{0.05}\text{O}_{1.975}$



IV. Results and discussion

SEM images thoria powders

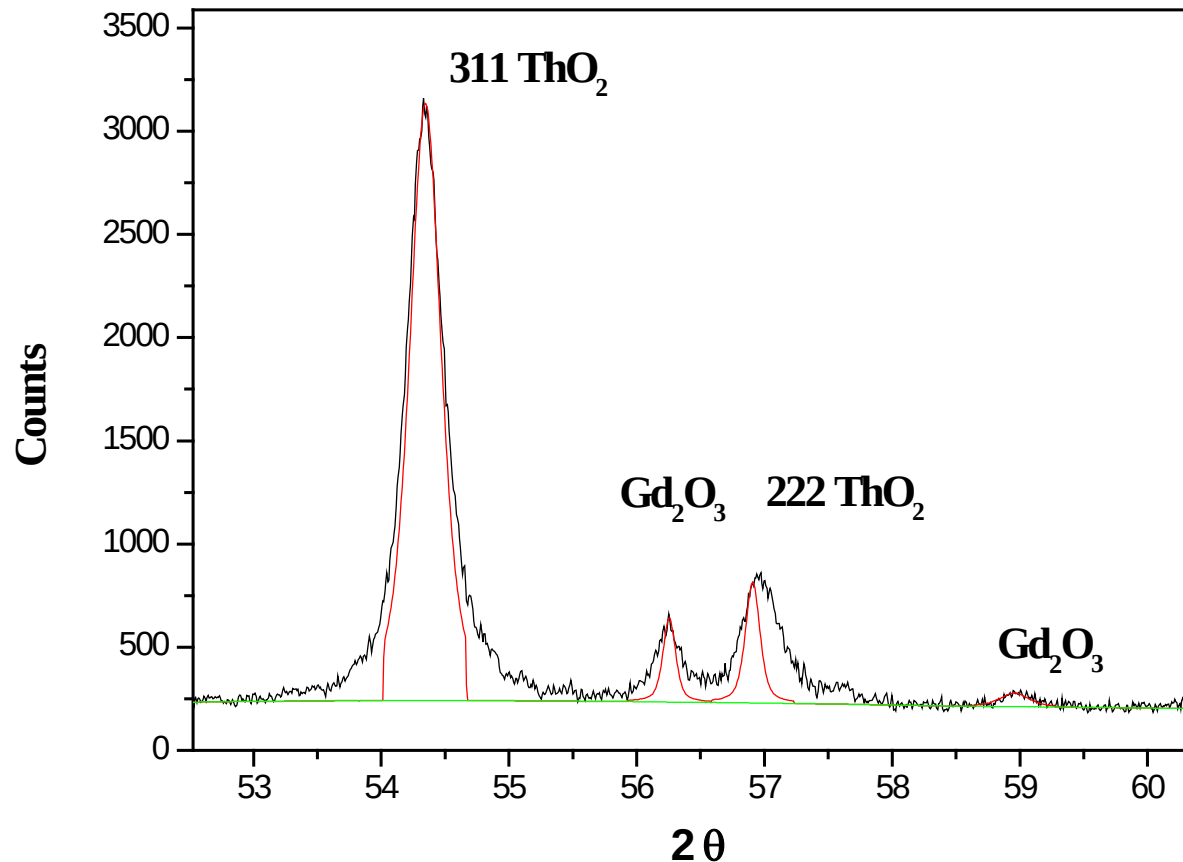




IV. Results and discussion

Powder X-ray diffraction

X-ray diffractogram of $\text{Th}_{0.70}\text{Gd}_{0.30}\text{O}_{1.85}$ powder sample
calcined at 1000 °C / 1h



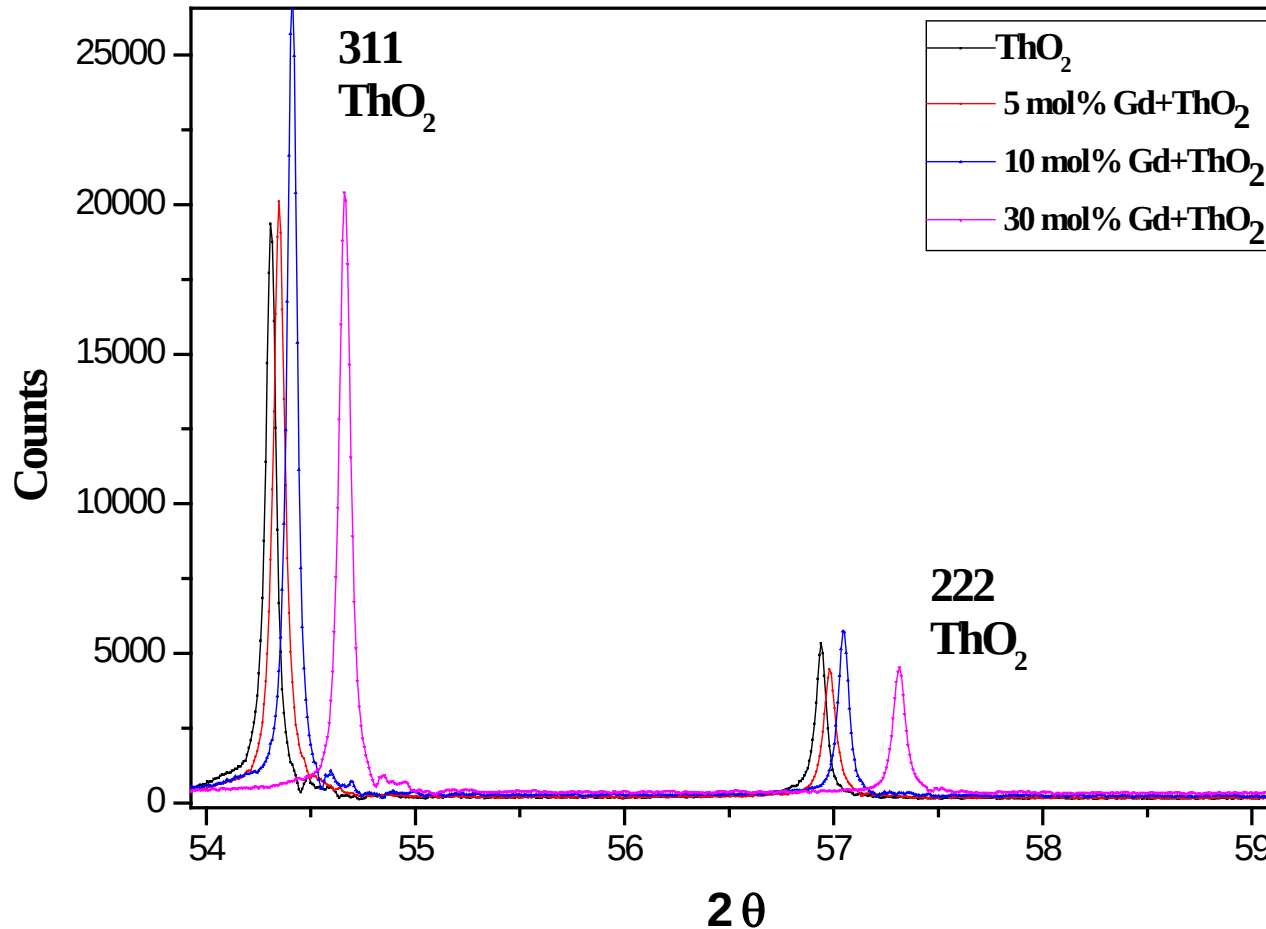
A two-phase system can be observed.



IV. Results and discussion

X-ray diffraction on sintered pellets

XRD-patterns of ThO_2 and Gd/Th oxide pellets sintered at $1750^\circ\text{C} / 8\text{ h}$



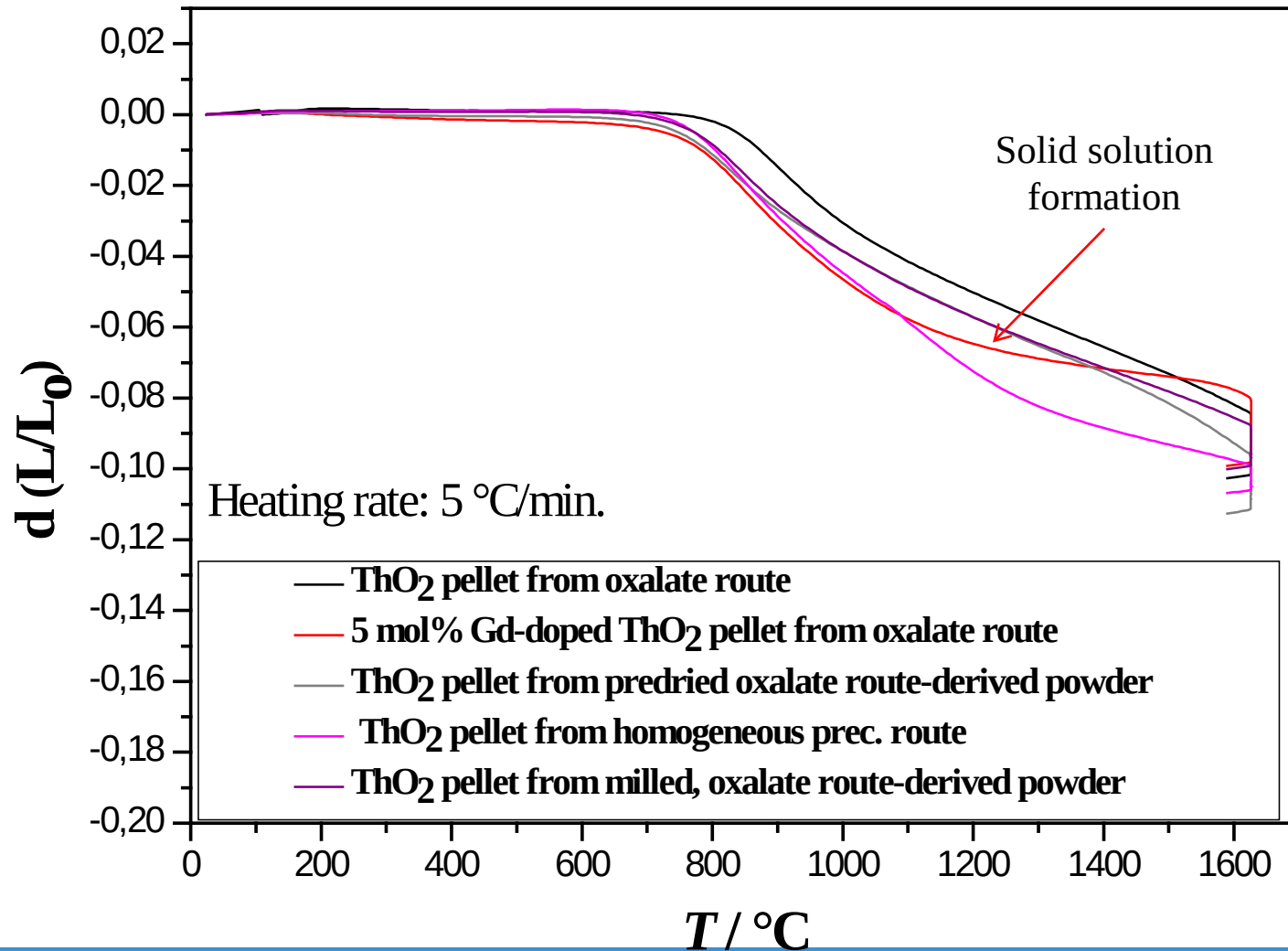
Single phase system.



IV. Results and discussion

Dilatometry studies

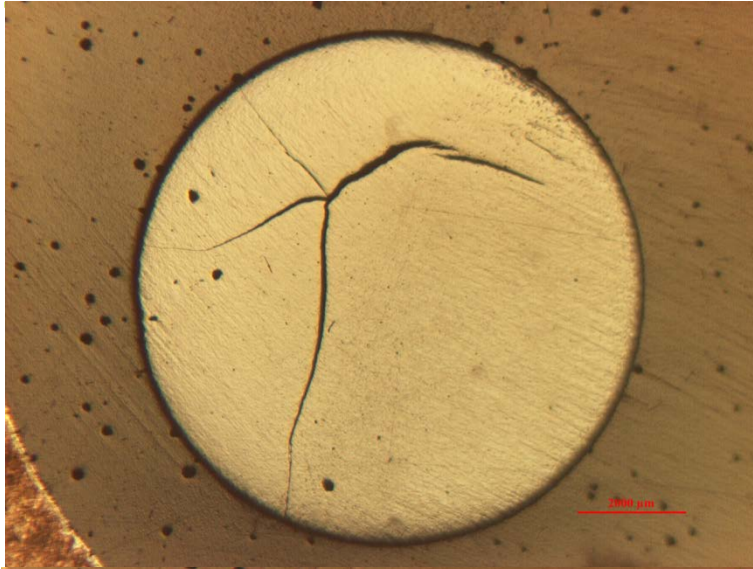
Dilatometry curves of pure thoria and Gd- doped thoria pellets





IV. Results and discussion

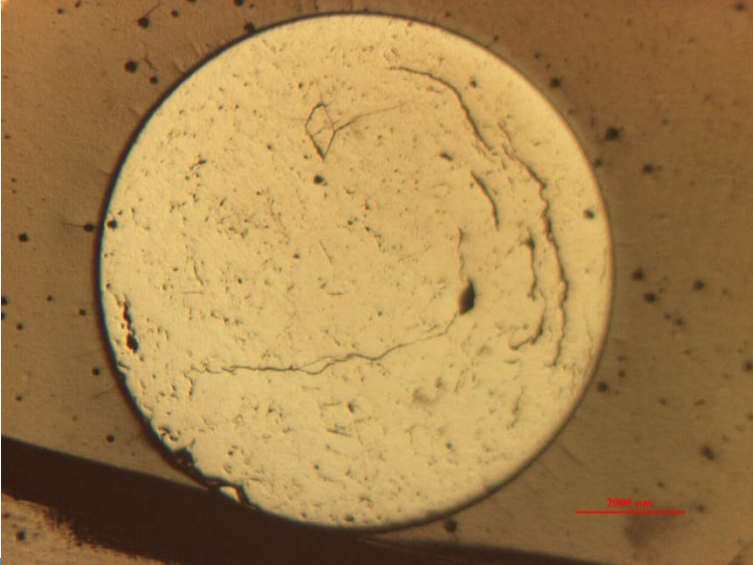
Optical microscopy of sintered pellets



Pellet ID: ThR1001-S36-A

Sintered at 1750 °C / 8 h under reducing atmosphere.

Sintered geometrical density: 92.51 % TD.



Pellet ID: ThR1003-S36-A

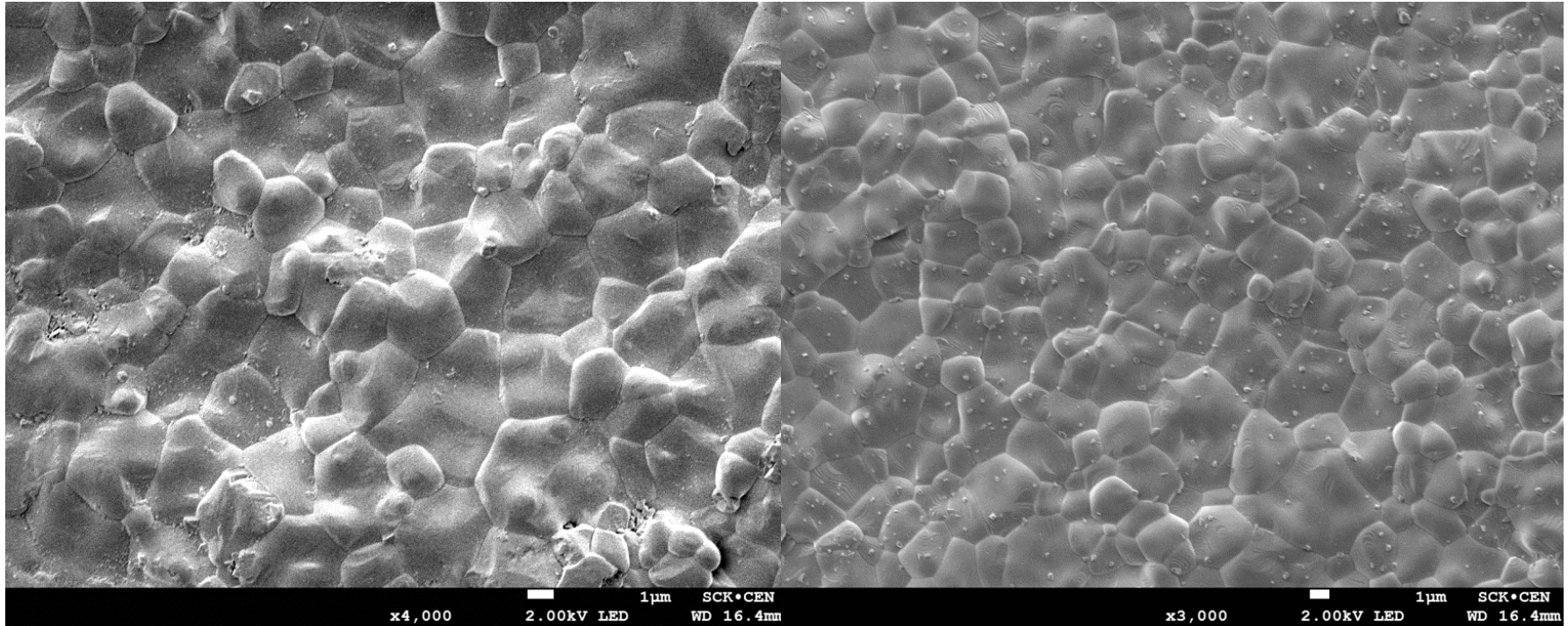
Sintered at 1750 °C / 8 h under reducing atmosphere.

Sintered geometrical density: 96.56 % TD.



IV. Results and discussion

SEM of sintered pellets

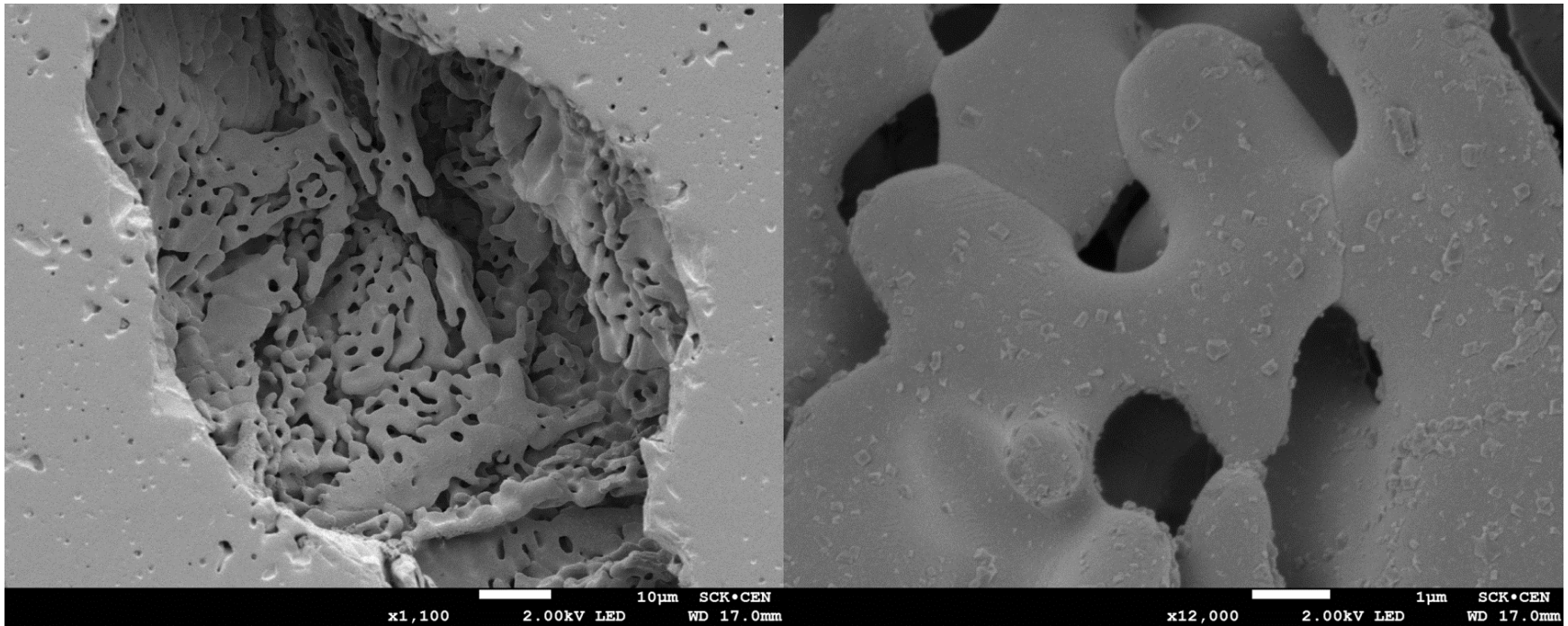


SEM images of polished and thermally etched Gd-doped pellet (10 mol% Gd)



IV. Results and discussion

SEM of sintered pellets



SEM images of polished and thermally etched Gd-doped pellet (10 mol% Gd)



V. Conclusions

1. Precipitated raw products show the presence of two phases, indicating that Gd(III) substitution for Th(IV) is only partial (simultaneous and not co-precipitation).
2. Powder samples with 5-10-30 mol% doping calcined at 1000 °C/1 h show the presence of Gd₂O₃ phase. Solid solution formation starts above 1100 °C - 1150°C.
3. In the case of all doped, sintered (1750 °C / 8h) pellets: no sign of a separate gadolinia phase → solid solution formation went into completion.
4. In the case of all sintered (1750 °C / 8 h) pellets: conditions for acceptable pellet quality were not yet determined.
5. Alternative route results:
 - Homogenous precipitation route: excellent flowability but very low sintered densities.
 - Precipitation in IL: better morphology, but incomplete calcination.



Acknowledgement

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■ *Professor Koen Binnemans*



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