Thorium fuel properties

A part of this study is the result of "Evaluation of $(Th,U)O_2$ fuel properties prepared by SPS technique with low-temperature property measurement" carried out under the Strategic Promotion Program for Basic Nuclear Research by the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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Background

Thorium oxide (ThO_2) fuel is a good candidate as a secure alternative fuel. However, the basic fuel properties data are insufficient compared to those for uranium oxide (UO_2) system.

Number of papers (by Scifinder)

- Thorium oxide + fuel + thermal conductivity : 59 hits
- Uranium oxide + fuel + thermal conductivity : 463 hits

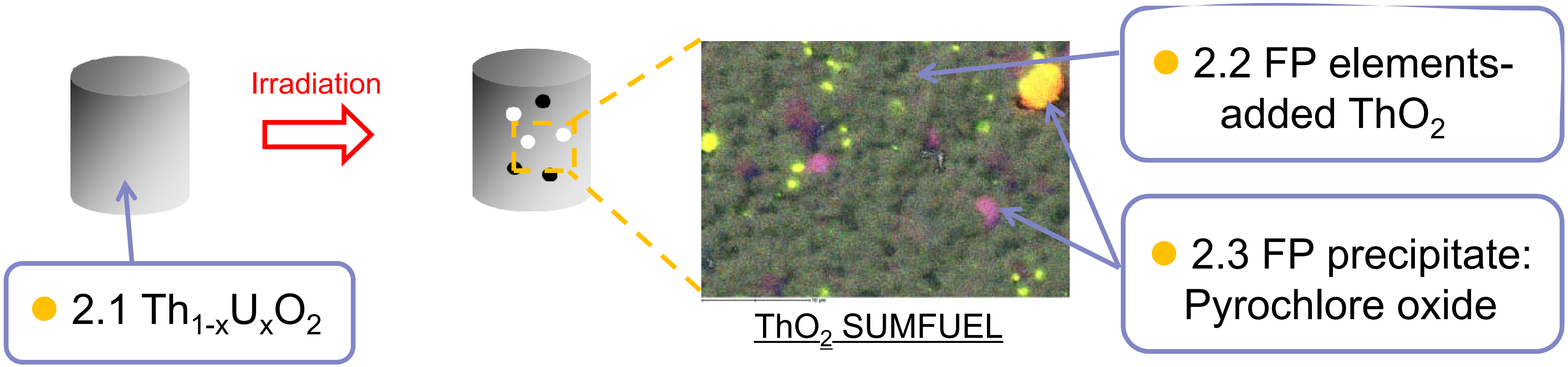
The physical properties data for ThO_2 system, including effects of the Fission Products (FPs), are needed.

In the present study, high density samples of the ThO_2 fuel system have been prepared by Spark Plasma Sintering (SPS) technique, and the thermo-mechanical properties are examined.

Content

1. Densification by Spark Plasma Sintering, SPS
   - Application of SPS for ThO_2
   - Porosity dependences of thermal conductivity and sound velocity.

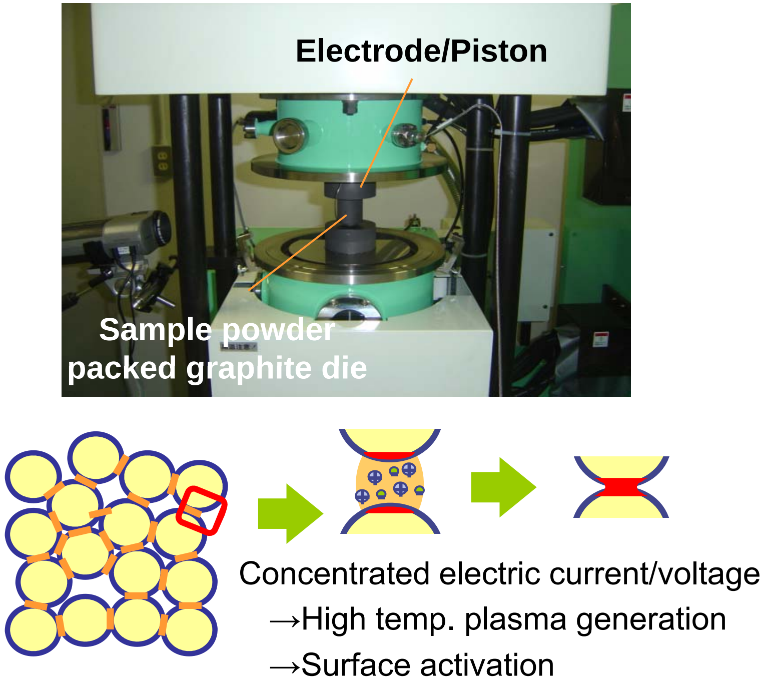
2. Thermo-mechanical properties of ThO_2 system



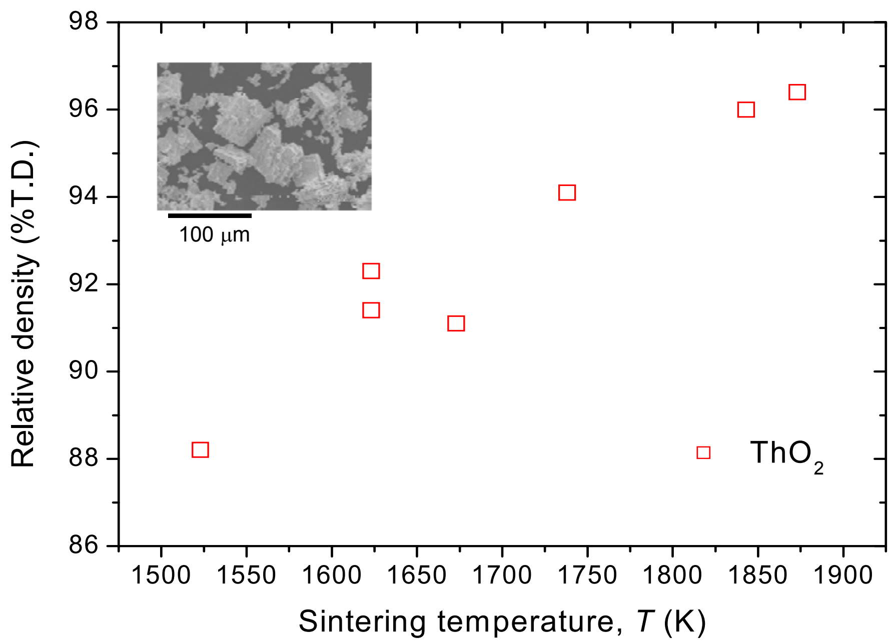
In the reactor, multiple FP elements are generated. Some of them dissolve to the ThO_2 matrix, and others form metallic or oxide precipitates. Both effects should be considered.

1. Densification by SPS

Application of Spark Plasma Sintering (SPS)



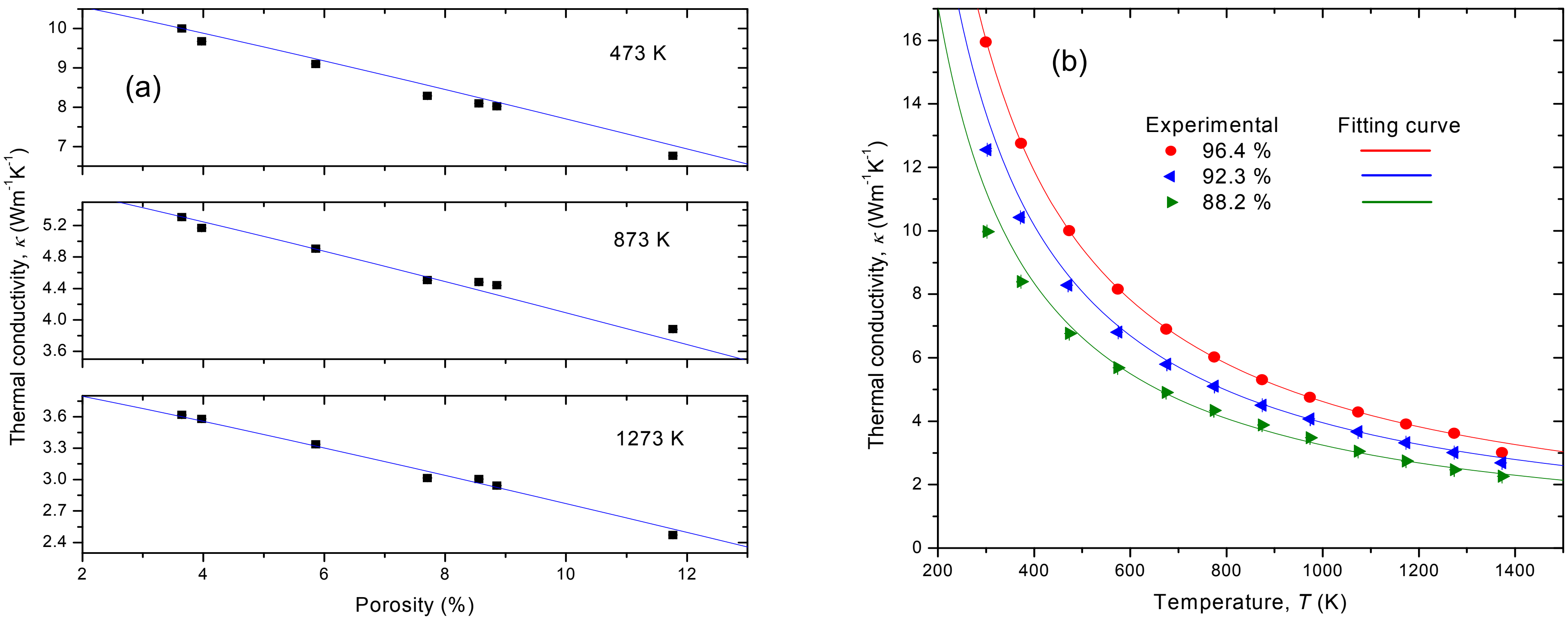
Spark Plasma Sintering.



SPS temp. vs. ThO_2 sample density.

- SPS is electric current-assisted hot-pressing. The concentrated electric current and voltage activate the powder surfaces, which promotes sintering procedure.
- SPS with only 10 minutes at 1873 K can produce >95 %TD ThO_2 samples.

Porosity dependence of thermal conductivity



(a) Porosity dependence and (b) comparison with approximation formula for thermal conductivity of ThO_2 (from 7 samples of 88 %T.D.~96 %T.D.).

$$\kappa = \kappa_{100} \cdot (1 - a \cdot P^n)$$

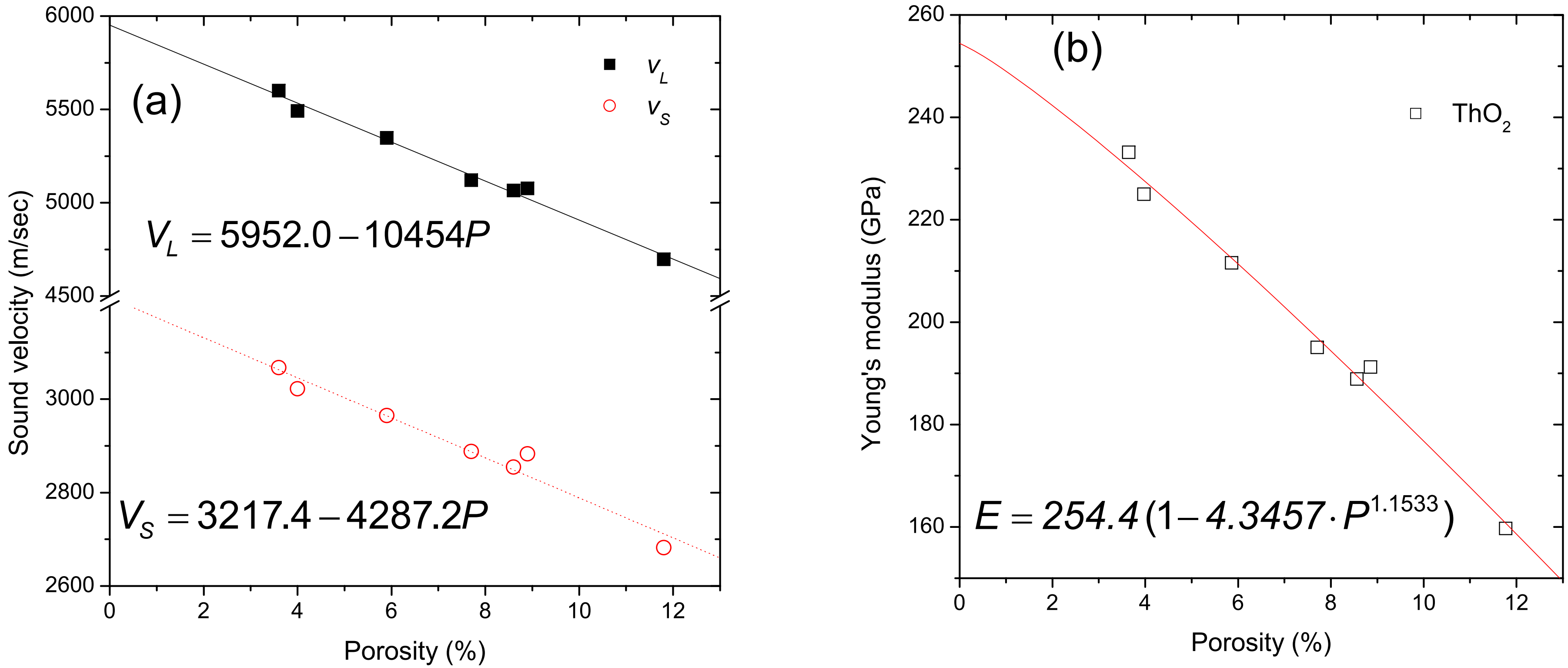
:fitting formula

$$\kappa = 6282.4T^{-1.0031} \cdot (1 - 3.8881 \cdot P^{1.0007})$$

300 K < T < 1273 K, 0 < P < 0.10

- The approximation formula corresponds the porosity and temperature dependence.

Porosity dependence of sound velocity

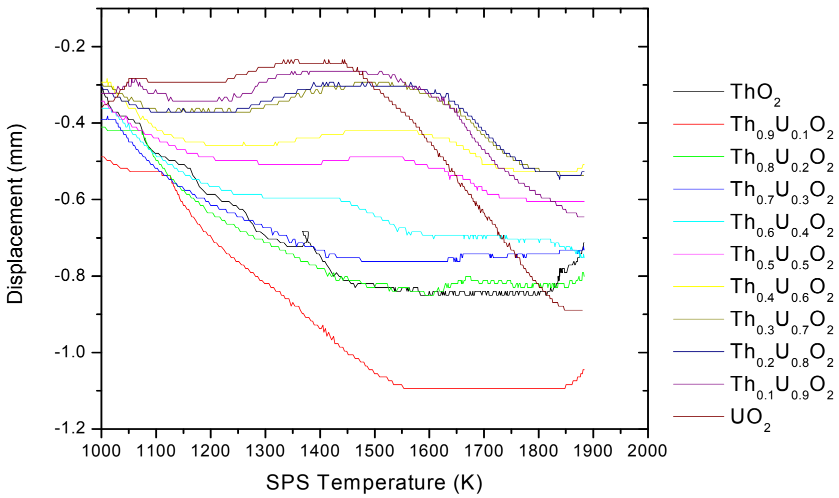


Porosity dependence of (a) longitudinal sound velocity V_L, share sound velocity V_S and (b)Young's modulus.

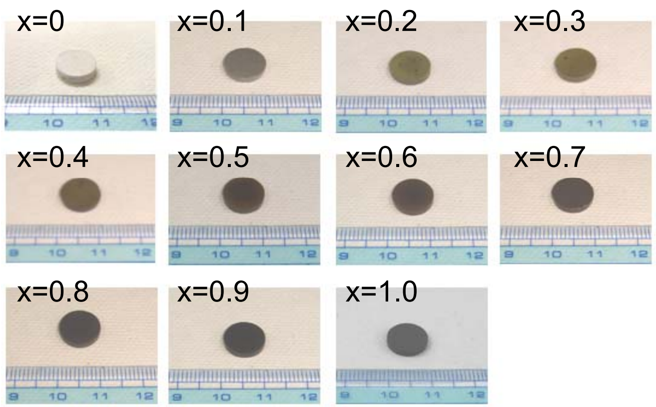
$$E = \frac{G\left(3V_L^{\ 2} - 4V_S^{\ 2}\right)}{\left(V_L^{\ 2} - V_S^{\ 2}\right)} \qquad \nu = \frac{1}{2} \cdot \frac{V_L^{\ 2} - 2V_S^{\ 2}}{V_L^{\ 2} - V_S^{\ 2}} \qquad \theta_D = \frac{h/k\,(9N/4\pi V_C)^{1/3}}{(1/v_L^{\ 2} + 2/v_L^{\ 2})^{1/3}}$$

- The porosity dependence of elastic properties can be determined from those for the sound velocity.

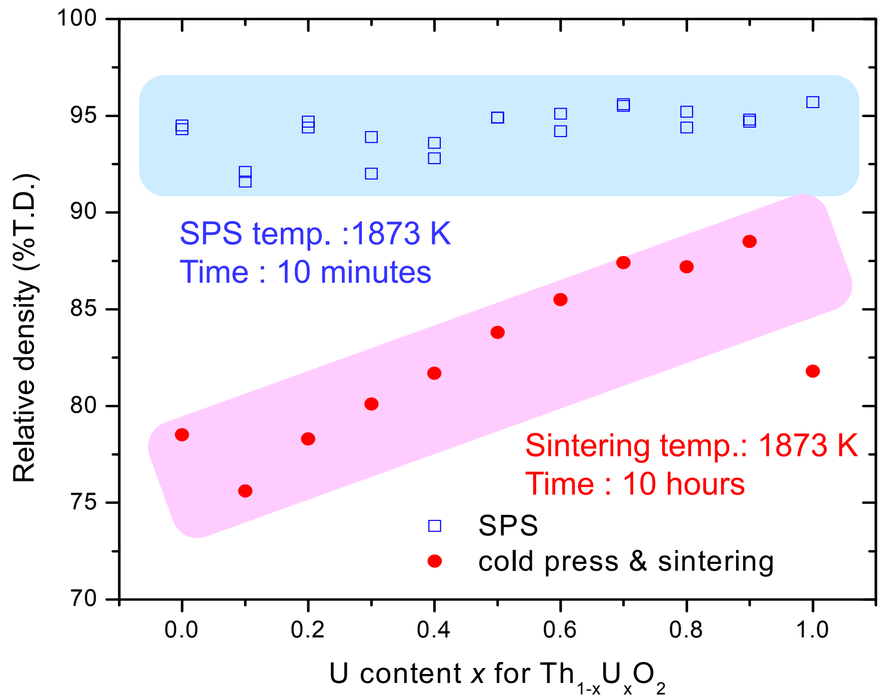
2.1 Fabrication of (Th,U)O_2



SPS temp. vs. displacement of piston.



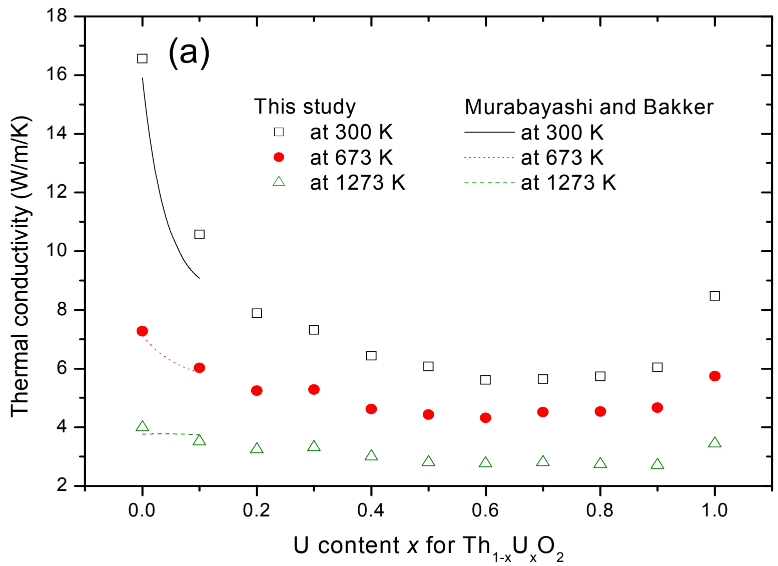
$Th_{1-x}U_xO_2$ sample appearance.

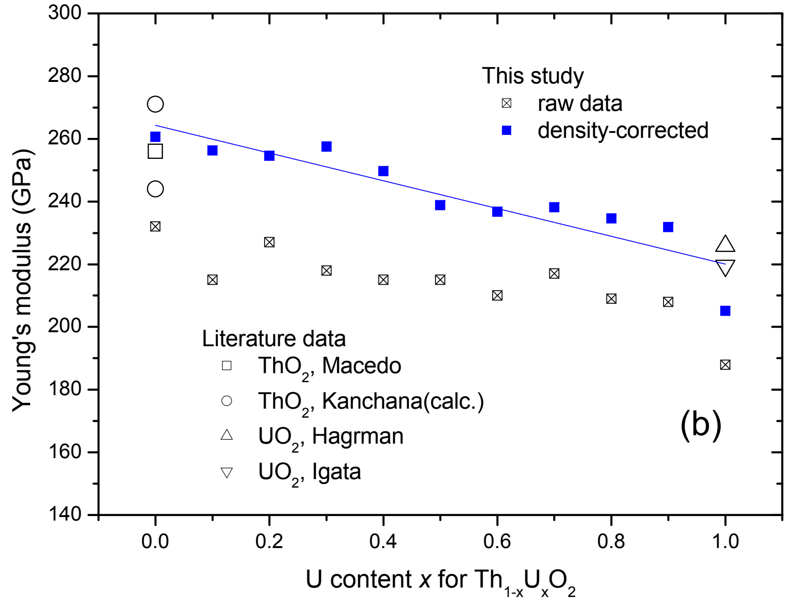


Sample density fabricated by SPS and pressureless-sintering.

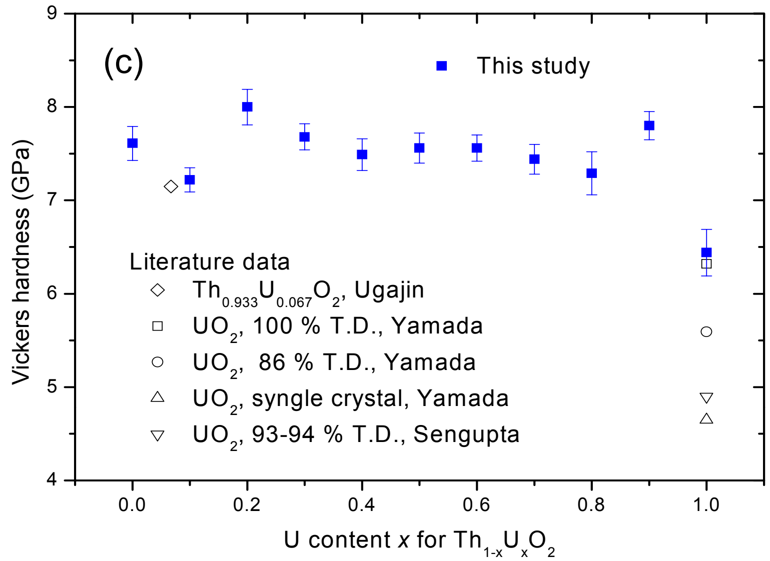
- In spite of the rapid sintering, high density pellets are obtained by SPS compared to usual pressureless sintering.

Thermo-mechanical properties of $(Th,U)O_2$





(a) Thermal conductivity, (b) Young's modulus, and (c) Vickers hardness.



- Thermo-mechanical data of $Th_{1-x}U_xO_2$ with wide range of composition x are obtained.
- $E = 264.3 - 44.3x$ for $Th_{1-x}U_xO_2$ (GPa)

2.2 FP elements added ThO_2

Typical 6 elements:

- trivalent FP : Y, La, Nd, Gd
- tetravalent FP : Ce, U

were added to ThO_2.

- $Th_{1-x}M_xO_{2-d}$ (M=Y, La, Ce, Gd, Nd, U)

Ball milling of each oxide

↓

Heat treatment at1873 K for 72 hours

↓

Ball milling for 12 hours

↓

SPS (1873 K, 10 min)

↓

Heat treatment* and measurement

*All Ce, U and Y, La, Nd, Gd are assumed to be tetravalent and trivalent.

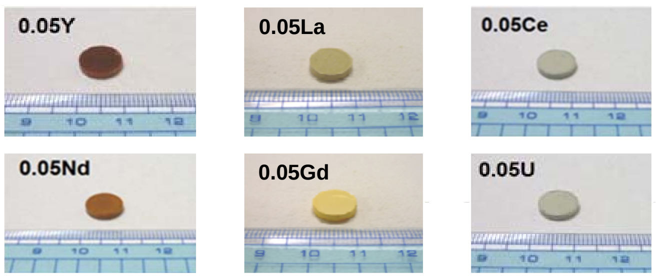
Table 2 *

Actinide and fission product inventories [a] for $(Th_{0.81}U_{0.19})O_2$ after a burnup of 21.5% FIMA in an HTGR environment

Atoms per initial 1000 atoms of Th + U

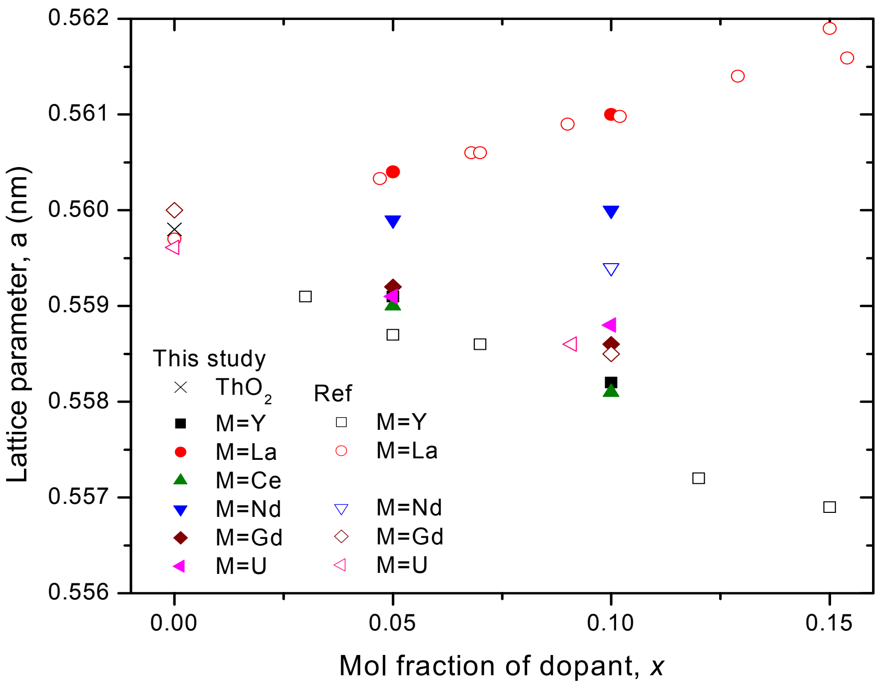
[Th] [b]	725.58	[Nd]	42.33
[U]	51.86	[Ce]	33.49
Pa	2.02	[La]	13.00
Np	3.12	[Pr]	12.70
Pu	2.42	[Y]	10.67
Am	0.12	[Sm]	5.72
		Gd	3.12
[Mo]	49.07	Eu	1.06
Tc	9.70	Pm	0.43
[Ru]	23.07		
[Rh]	1.20	[Zr]	67.44
[Pd]	7.91	[Sr]	20.12
		[Ba]	15.67

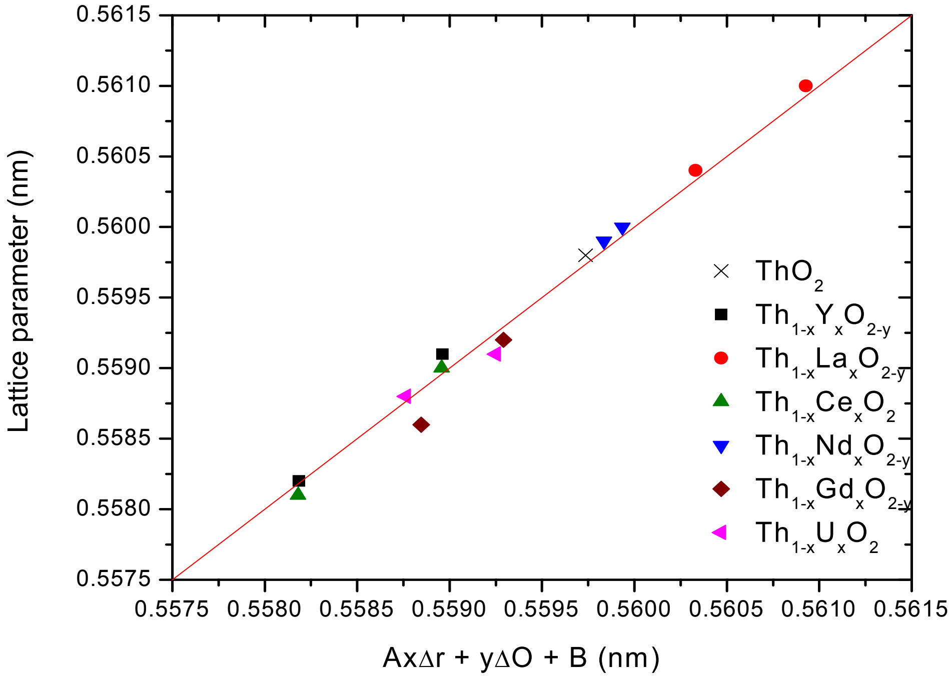
*M. Ugajin, et al., JNM, 84 (1979) 26.



Sample appearance

Lattice parameter prediction





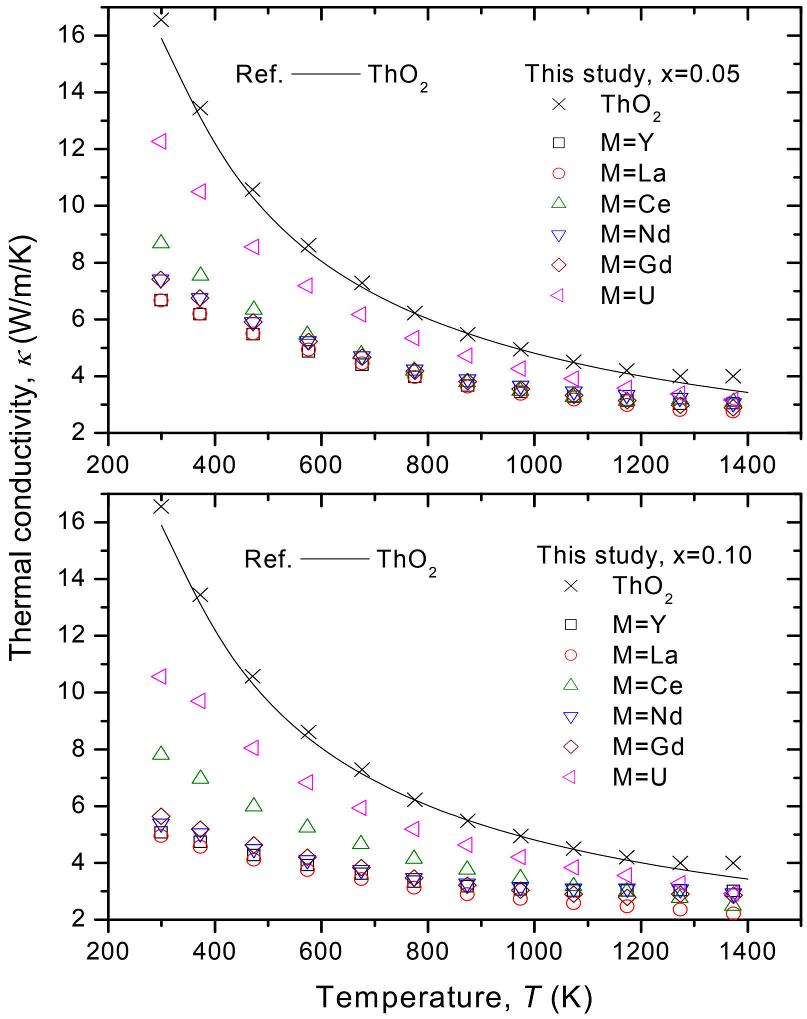
(a) Lattice parameter change and (b) the fitting

$$a = 1.9445\ \Delta r \cdot x - 0.018969\ y + 0.55974 \quad (nm)$$

for Th1-xMxO2-y, Δr : difference of Shannon's ionic radii

- Lattice parameter linearly changes with amount of FP elements.
- From the data, lattice parameter can be predicted by only using Shannon's ionic radii.

Thermal conductivity change by FP



Thermal conductivity of FP-added ThO_2

$$\kappa = \frac{k_B}{2\pi^2 v}\int_0^{k_B\theta/T} \tau_{total}\left(\frac{h\omega}{k_B T}\right)^2 \frac{\exp(h\omega/k_B T)}{[\exp(h\omega/k_B T)-1]}\omega^2 d\omega$$

Phonon's relaxation time : $\frac{1}{\tau_{total}} = \frac{1}{\tau_D} + \frac{1}{\tau_P}$, $\frac{1}{\tau_D} = A\omega^4$, $\frac{1}{\tau_P} = CT\omega^2$

Point defect scattering — Phonon-phonon scattering

$$C = \frac{k_B{}^2\theta}{2\pi^2 vhT}\cdot\frac{1}{\kappa_{ThO2}}$$

→ determined from data of pure ThO_2

$$A = \frac{\delta^3}{4\pi v^3}\sum_i x_i(1-x_i)\left[\left(\frac{\Delta M}{M}\right)^2 + \varepsilon\left(\frac{\Delta r}{r}\right)^2\right] + y\Delta O$$

Mass — Ionic radii — Oxygen defect

Determination of parameters of ε and ΔO provides thermal conductivity estimation

P. G. Klemens, Proc. Phys. Soc. (London), Vol. A68 (1955) pp. 1113.
J. Callaway, et al., Phys. Rev., Vol. 120 (1960) pp. 1149-1154.
B. Abeles, Phys. Rev., Vol. 131 (1963) pp. 1906.

Thermal conductivity prediction

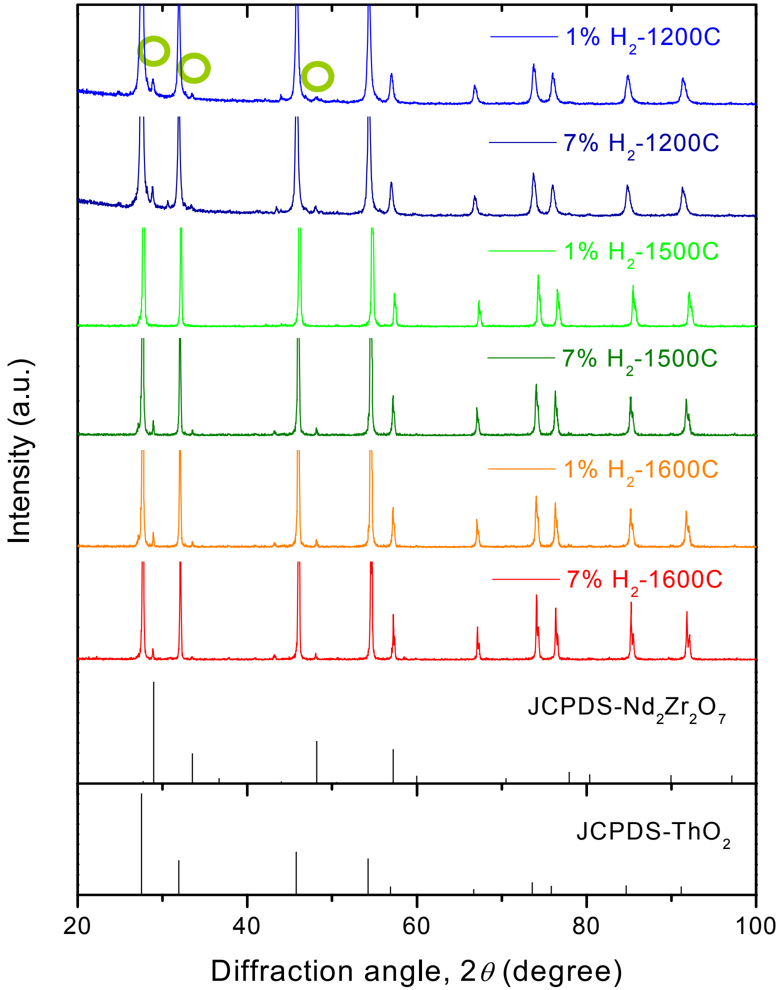
$\varepsilon = 18.3, \Delta O = 1.49$

Quantification of phonon scattering and estimated thermal conductivity κ_{est}

composition	Mass difference ($\times 10^{-2}$)	Ionic radius difference ($\times 10^{-2}$)	Oxygen defect ($\times 10^{-2}$)	A ($\times 10^{-43}$)	κ_{est} ($Wm^{-1}K^{-1}$)	κ_{exp} ($Wm^{-1}K^{-1}$)
ThO_2	-	-	-	-	-	17.8
$Th_{0.90}Y_{0.10}O_{1.95}$	7.93 (51 %)	0.295 (1.9 %)	7.45 (48 %)	44.4	5.1	5.0
$Th_{0.90}La_{0.10}O_{1.95}$	3.36 (23 %)	3.78 (26 %)	7.45 (51 %)	41.3	5.8	5.7
$Th_{0.90}Ce_{0.10}O_2$	3.27 (61 %)	2.08 (38.8 %)	-	15.1	9.2	7.8
$Th_{0.90}Nd_{0.10}O_{1.95}$	2.99 (26 %)	1.10 (9.6 %)	7.45 (65 %)	32.7	5.2	5.5
$Th_{0.90}Gd_{0.10}O_{1.95}$	2.17 (23 %)	0.00292 (0%)	7.45 (77 %)	27.2	6.7	6.1
$Th_{0.90}U_{0.10}O_2$	0.0139 (1.6 %)	0.878 (98.4 %)	-	2.53	12.8	13.3

- Thermal conductivity of ThO_2, including arbitrary amount of porosity, FP elements can be estimated from the results.

2.3 ThO_2-SIMFUEL



XRD pattern of ThO_2-SIMFUEL

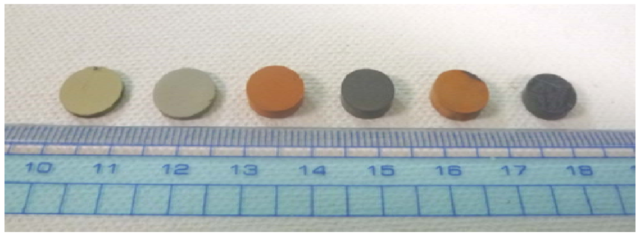
→ peaks from impurity phase were detected.

ThO_2-simfuel was prepared to estimate precipitates in ThO_2 fuel.

- FP composition: simulated APWR situation*
  - Y, (Zr), La, Ce, Nd, U
  - Sr, Ba, (Zr)
  - Mo, Ru

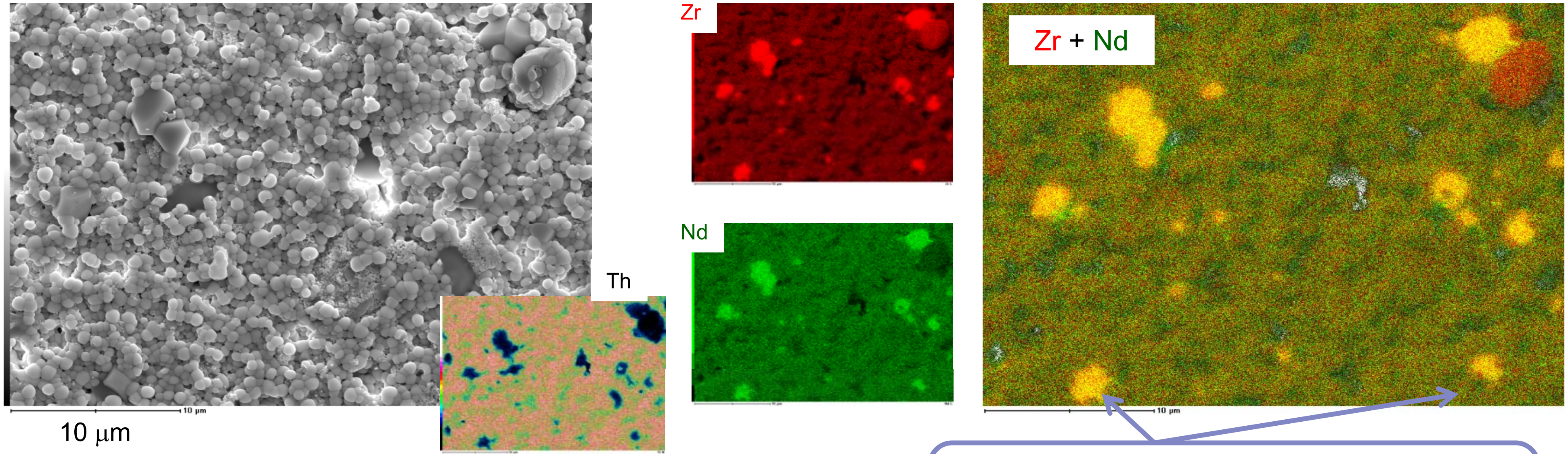
*A.N. Shirsat, et al, J. Nucl. Mater., 392 (2009) 16.

- FP amount : 20 GWd/t × 10
- Reaction temp. :1200℃, 1500℃,1600℃
- O_2 potential : -310 kJ/mol~-200 kJ/mol

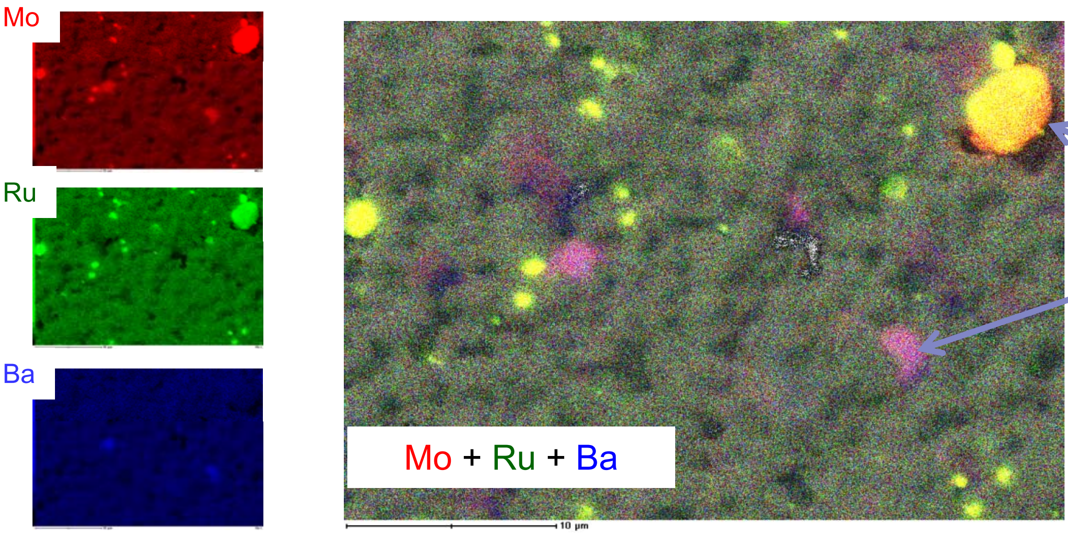


Sample appearance.
Darker samples are treated at ΔO=-310 kJ/mol.

FP precipitates in ThO_2-SIMFUEL



- Nd – Zr oxide
  → $Nd_2Zr_2O_7$ pyrochlore oxide



- Mo – Ru alloy
- Ba – Mo oxide
  → $(Sr,Ba)MoO_x$ perovskite

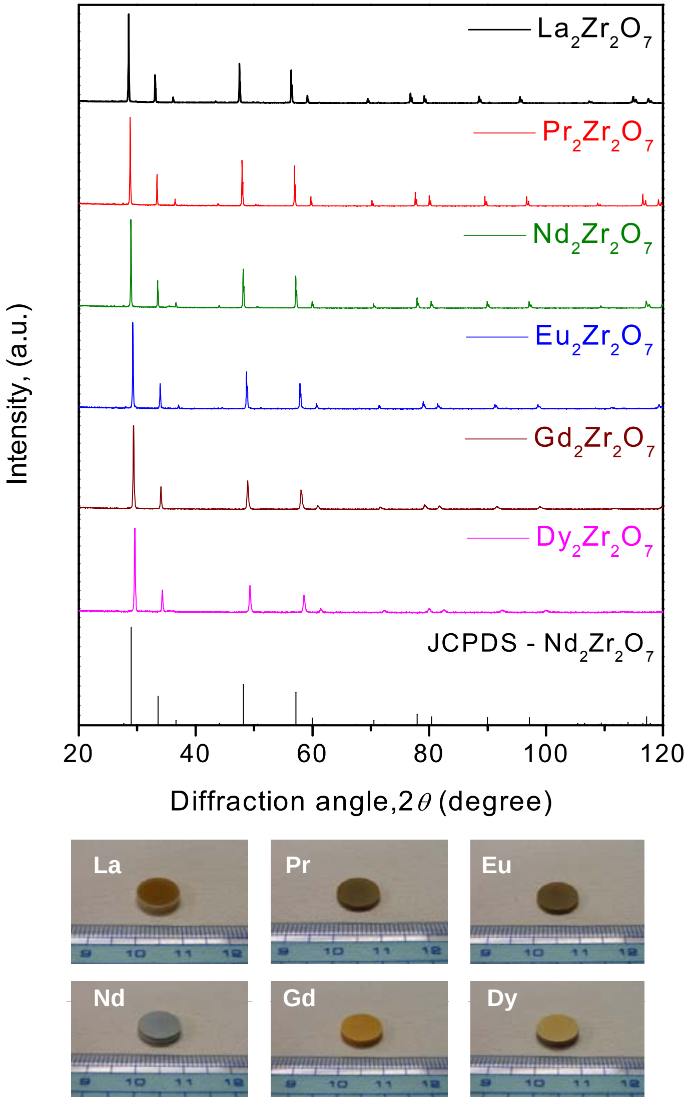
● The pyrochlore oxide, which was not precipitated in UO_2 fuel, was observed in all ThO_2-SIMFUEL.

ThO_2-SIMFUEL (treated at 1773 K with 7 %H_2 flow).

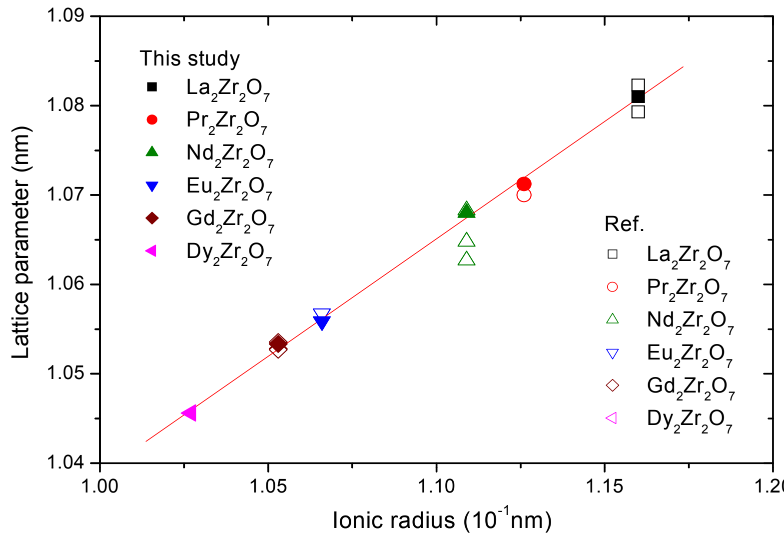
Fabrication of pyrochlore oxide

- $RE_2Zr_2O_7$ (RE=La, Pr, Eu, Nd, Gd, Dy) and $Nd_2Ce_2O_7$* were prepared by solid state reaction.
- ~94 %T.D. samples were obtained by SPS (sintered at 1773 K for 10 minutes).

*Ugajin reported that $Nd_2(Zr,Ce)_2O_7$ was observed.
M. Ugajin, K. Shiba, J. Nucl. Mater., 91 (1980) 227.

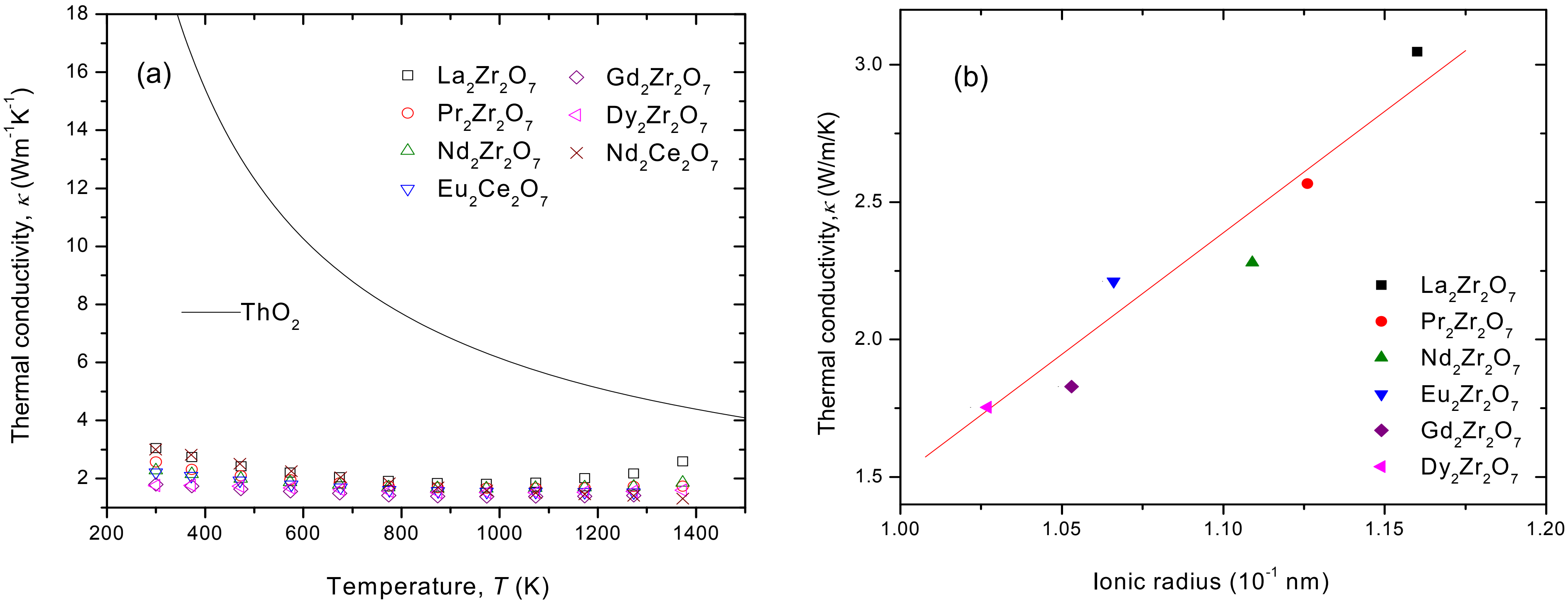


XRD pattern and appearance of $RE_2Zr_2O_7$.



Ionic radii vs. lattice parameter.

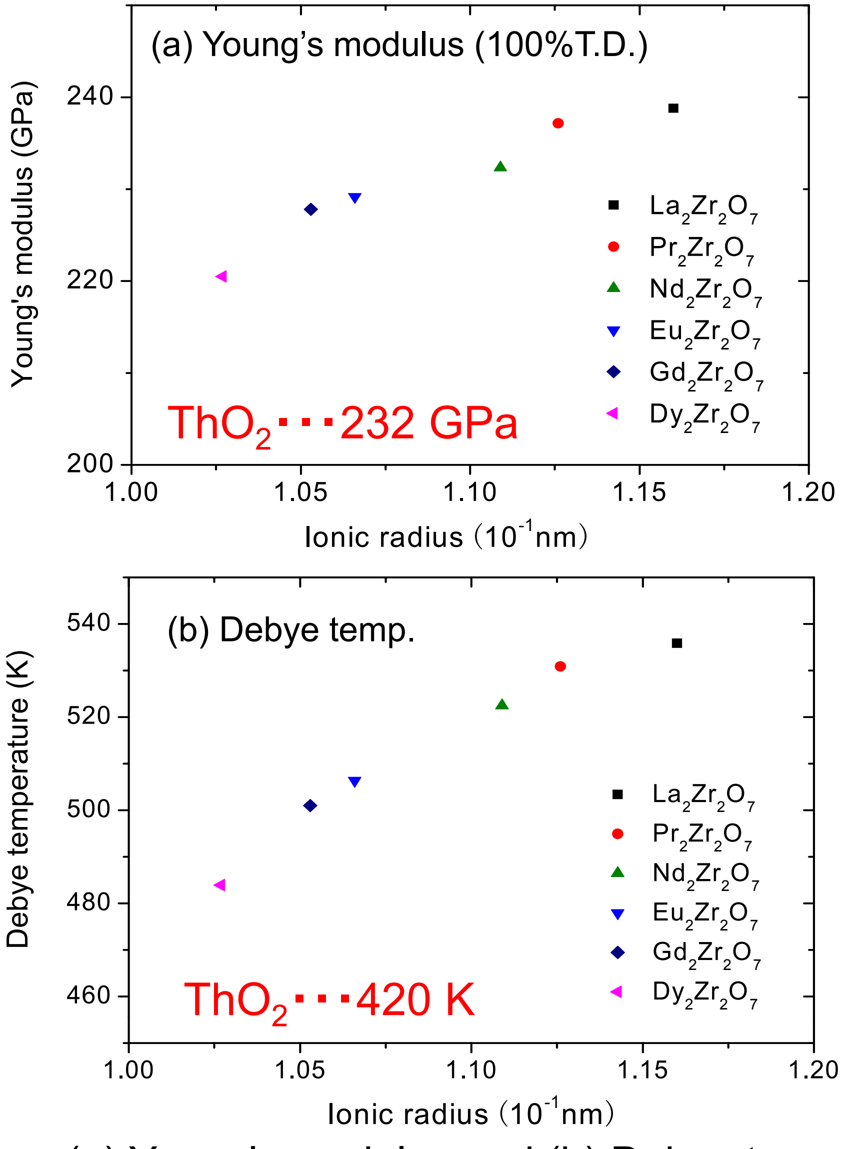
Thermal conductivity of pyrochlore oxide



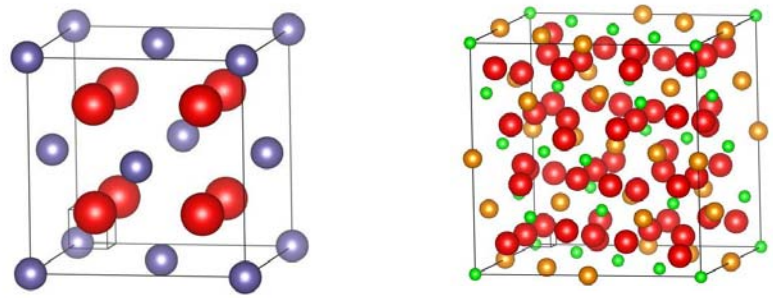
(a) Temperature dependence and (b) relation to ionic radii of RE of thermal conductivity.

- The values of thermal conductivity for pyrochlore oxide are 1~3 $Wm^{-1}K^{-1}$, significantly lower than those for ThO_2.

Comparison of properties with ThO_2



(a) Young's modulus and (b) Debye temp.



Fluorite structure (ThO_2) Pyrochlore structure ($Nd_2Zr_2O_7$)

Sample	Lattice parameter	Atom number in unit cell
ThO_2	0.5598 nm	12 (3)
$RE_2Zr_2O_7$	1.04~1.08 nm	88 (22)

Slack's thermal conductivity formula : $\kappa_L \propto \dfrac{\bar{M}\delta\theta^3}{n^{2/3}\gamma^2}$

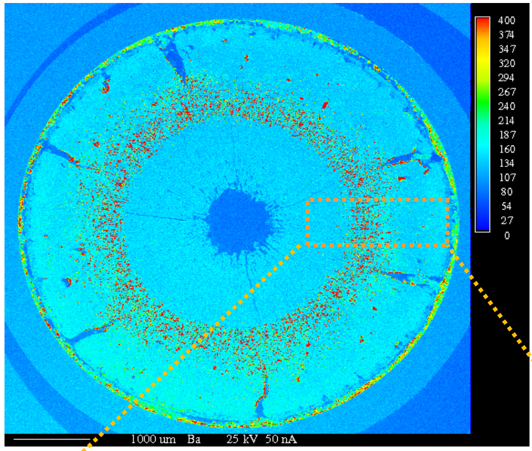
M : Mean atomic mass
δ : Mean atomic volume
θ : Debye temp.
n : atom num. in unit cell
γ : Gruneisen parameter

- Pyrochlore oxides show similar Young's modulus and Debye temp. with ThO_2.
- The low thermal conductivity attributes to the complex crystal structure.

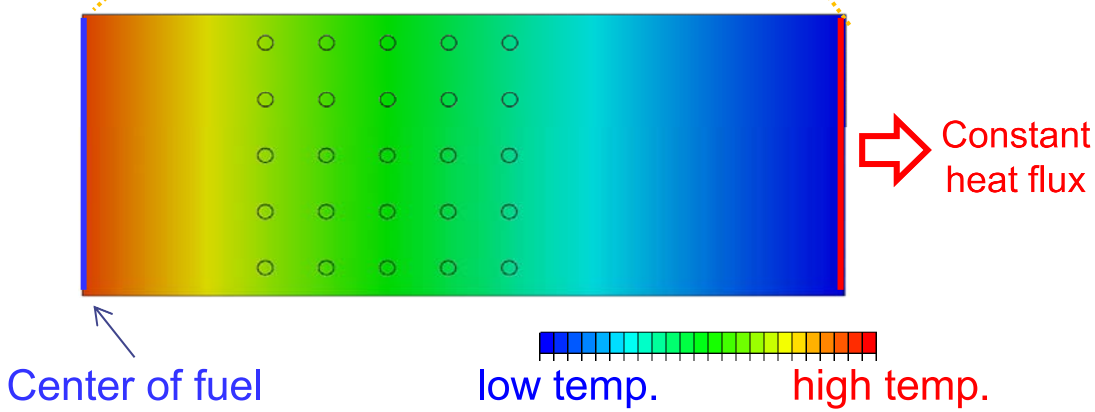
Application of FEM

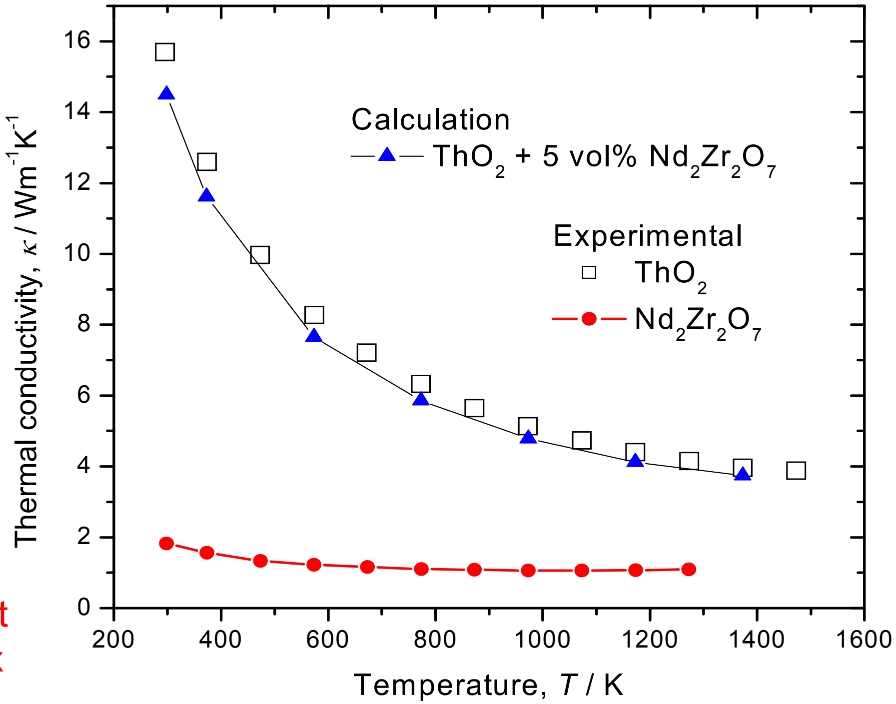
Evaluation of fuel properties : Matrix properties + Precipitate properties + Microstructure + ･･･

→ by FEM



(Example) Ba distribution in MOX fuel*





Thermal conductivity of 5 vol%$Nd_2Zr_2O_7$-including ThO_2 estimated by FEM

*K. Tanaka, et al, J. Nucl. Mater., 414 (2011) 316.

Summary

- It is confirmed that high density samples of ThO_2 based compounds and pyrochlore oxide can be obtained by SPS technique.
- Porosity dependence of thermal conductivity and sound velocity for ThO_2 is determined.
- Thermo-mechanical properties of $(Th,U)O_2$ are measured and some of them are formulated.
- FP element-dissolved ThO_2 samples are fabricated. The effects of FP element on thermal conductivity and lattice parameter are quantitatively formulated.
- As a unique precipitate in ThO_2 fuel, pyrochlore oxides are fabricated and the thermo-mechanical properties are measured. The thermal conductivity is significantly lower than that of ThO_2 due to the complex crystal structure.