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Nuclear Waste Management IEK-6
Institute of Energy and Climate Research

JÜLICH FORSCHUNGSZENTRUM

Structural incorporation of Cm^{3+} and Pu^{3+} in phosphate ceramics with monazite structure

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Motivation

At the present time borosilicate (or phosphate) glasses is the generally accepted first generation waste form

But with the increasing demand for the immobilization of large quantities of HLW, there is a strong incentive to reconsider ceramic (single or poly-phase) as waste forms

⇒ higher chemical durability

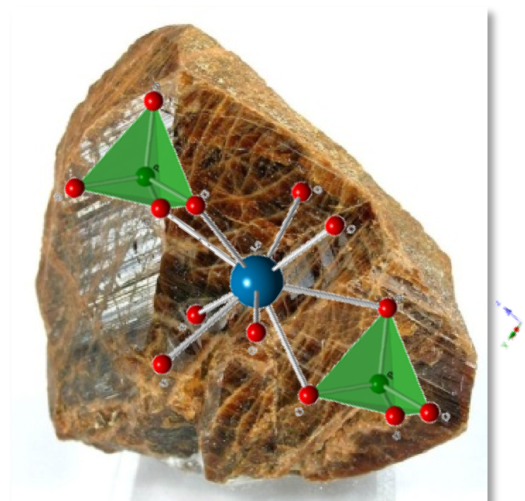
⇒ aqueous durability

⇒ high waste loading

⇒ radiation tolerance

⇒ volume swelling

⇒ existence of natural analogues



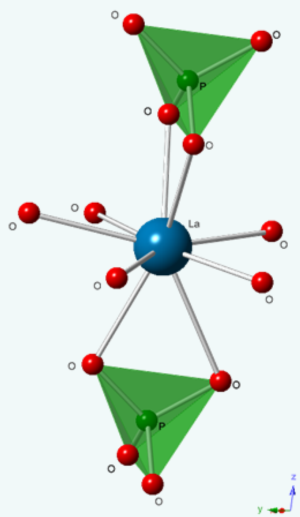
Introduction to REE-Phosphates

lanthanum	cerium	praseodymium	neodymium	promethium	samarium	europium	gadolinium	terbium	dysprosium	holmium	erbium	thulium	ytterbium	lutetium
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
138.91	140.12	140.91	144.24	[145]	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
					plutonium	americium	curium							
					94	95	96							
					Pu	Am	Cm							
					[244]	[243]	[247]							

$LaPO_4$ – $GdPO_4$

9-fold coordinated monazite structure

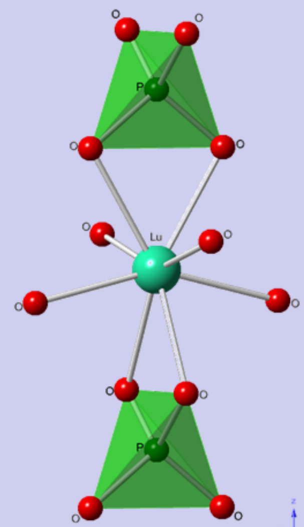
Monoclinic symmetry (C_1)



$TbPO_4$ – $LuPO_4$

8-fold coordinated xenotime structure

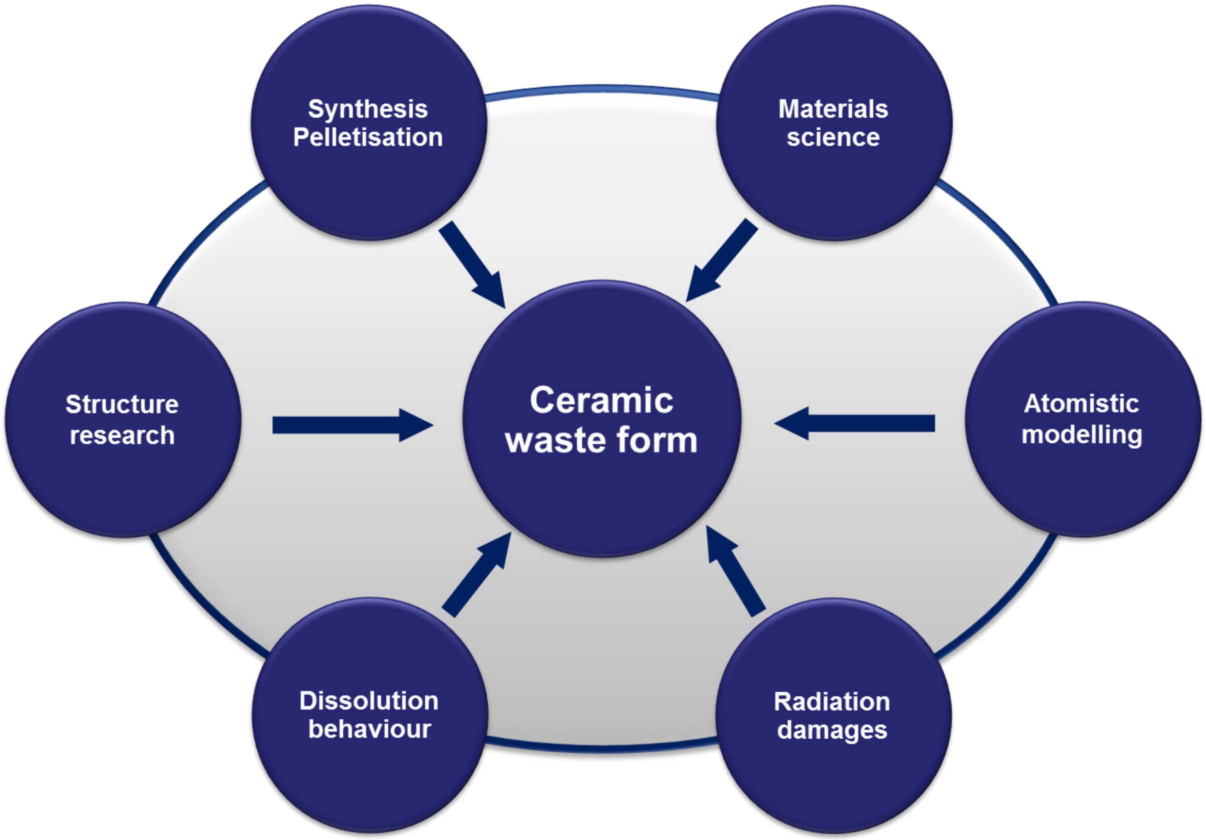
Tetragonal symmetry (D_{4h})



Y.X. Ni et al. (1995) *Am. Mineral*. 80 (**1995**) 21-26; R.D. Shannon (1976) *Acta Cryst*. A32 (**1976**) 751–767; David&Vokhmin *New J. Chem.* 27 (**2003**) 1627–1632.

N. Dacheux et al. *Am. Mineral.* 98 (**2013**) 833; S. Neumeier Radchim. Acta (**2017**) https://doi.org/10.1515/ract-2017-2819

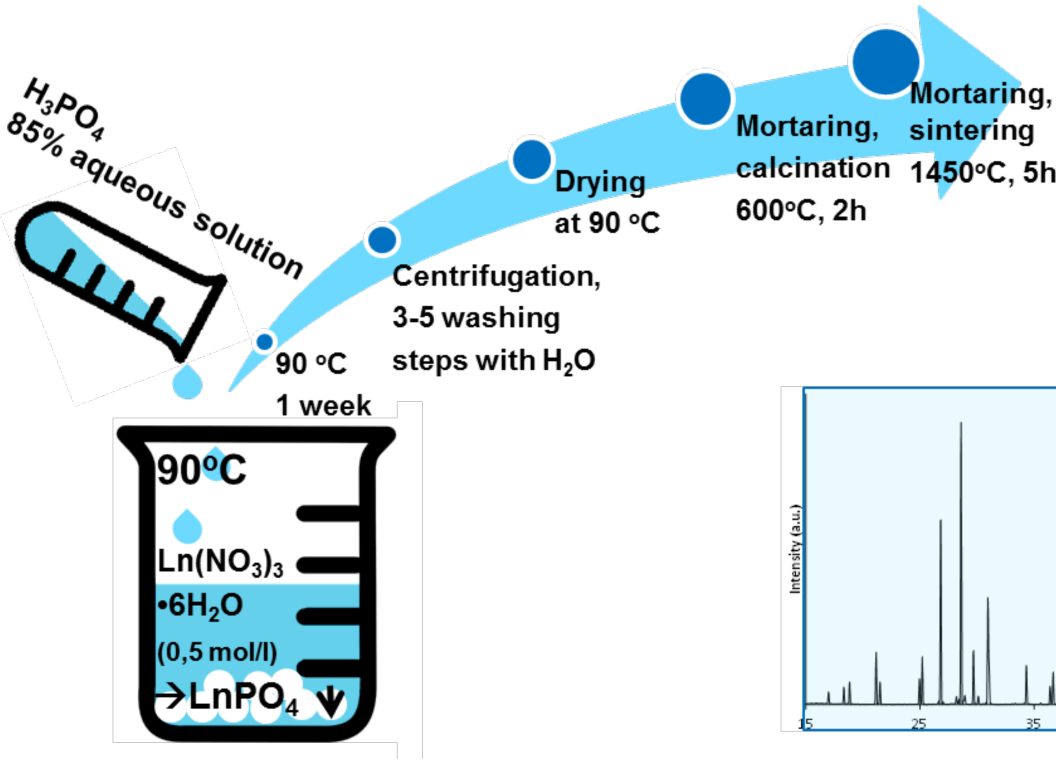
Methodology to study ceramic waste forms

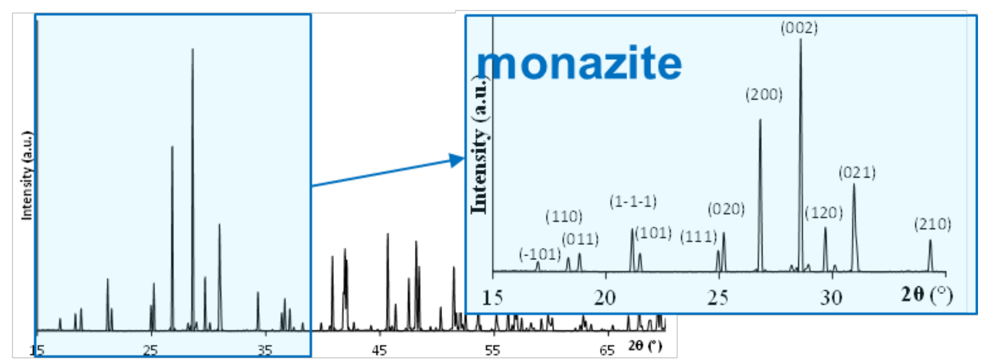


<u>Main questions:</u>

- How *An* can be incorporated into the crystal structure of ceramic waste form?
- Where do the *An* sit after incorporation and how does the chemical environment look like?
- How do the *An* behave in the long-term under repository relevant conditions?

Precipitation of $LnPO_4$





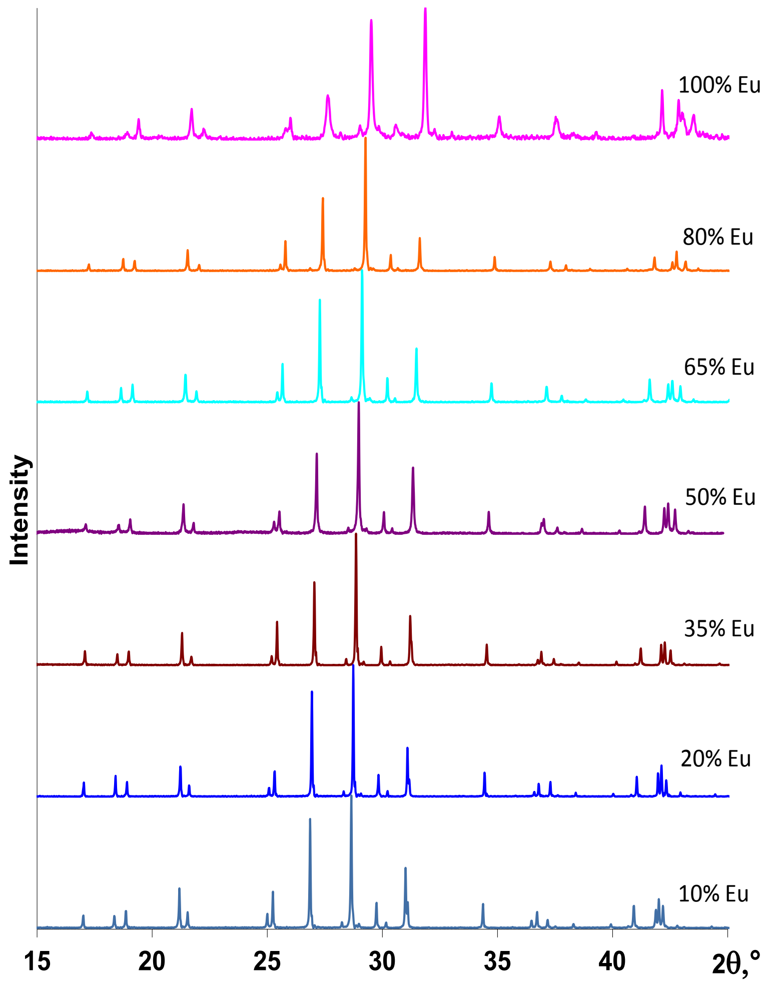
Samples synthesized:

Pure *Ln*PO_4 endmembers

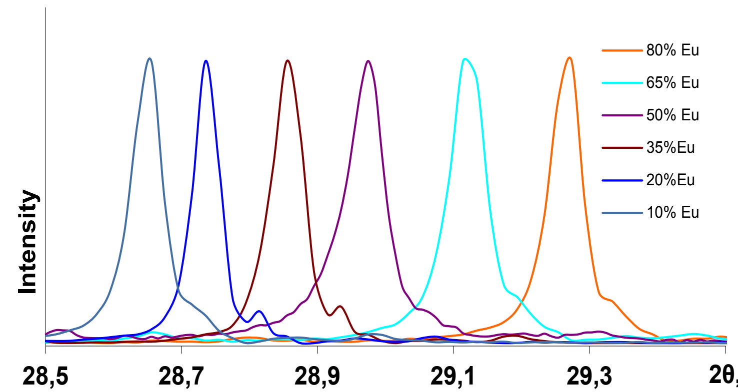
Mixed phases of $La_{1-x}Ln_xPO_4$ (*Ln* = Eu, Gd; monazite solid solution)

Y. Arinicheva et al. Prog. Nucl. Energy 72 (**2014**) 144-148. S. Neumeier et al. Prog. Nucl. Energy 92 (**2016**) 298-305.

Vegard's law for (La,Eu)PO_4 solid solutions

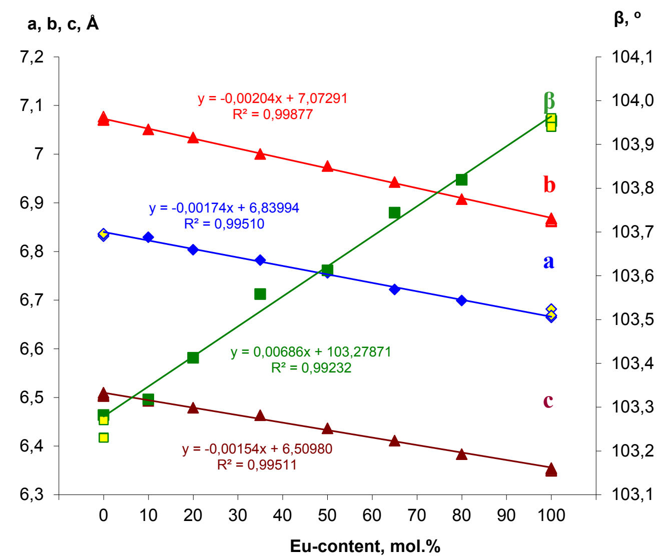


XRD patterns of (La,Eu)PO_4 solid solution series



Magnification of 120-reflexes:

- 2Θ shift in dependence of Eu-content

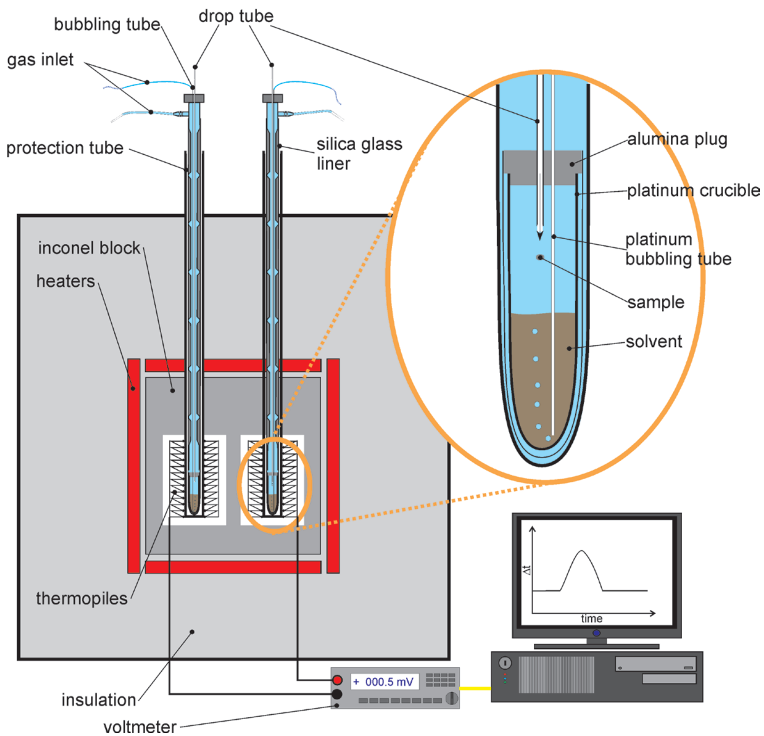


Lattice parameter in dependence of Eu-content

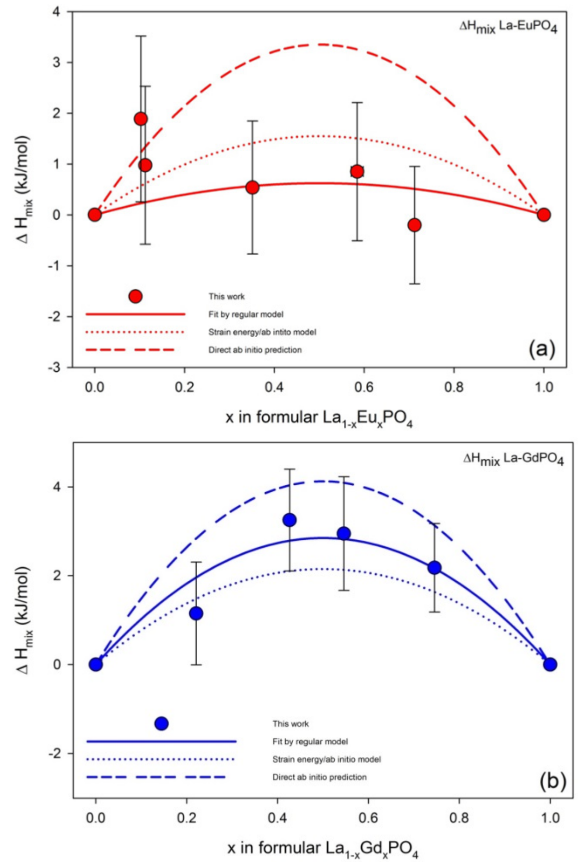
Y. Arinicheva et al. Prog. Nucl. Energy 72 (**2014**) 144-148. S. Neumeier et al. Prog. Nucl. Energy 92 (**2016**) 298-305.

Thermochemistry of $La_{1-x}Ln_xPO_4$ solid solutions (Ln = Eu, Gd)

Drop solution calorimetry @ UC Davis



Modified after Navrotsky 2014



- Single phase $La_{1-x}(Eu,Gd)_xPO_4$ solid solutions are thermodynamically stable
- Excess properties due to lattice strain
- **More details during poster session, Philip Kegler**

S. Neumeier J. Chem. Thermodyn. 105 (**2017**) 396-403.

Questions to be solved using TRLFS

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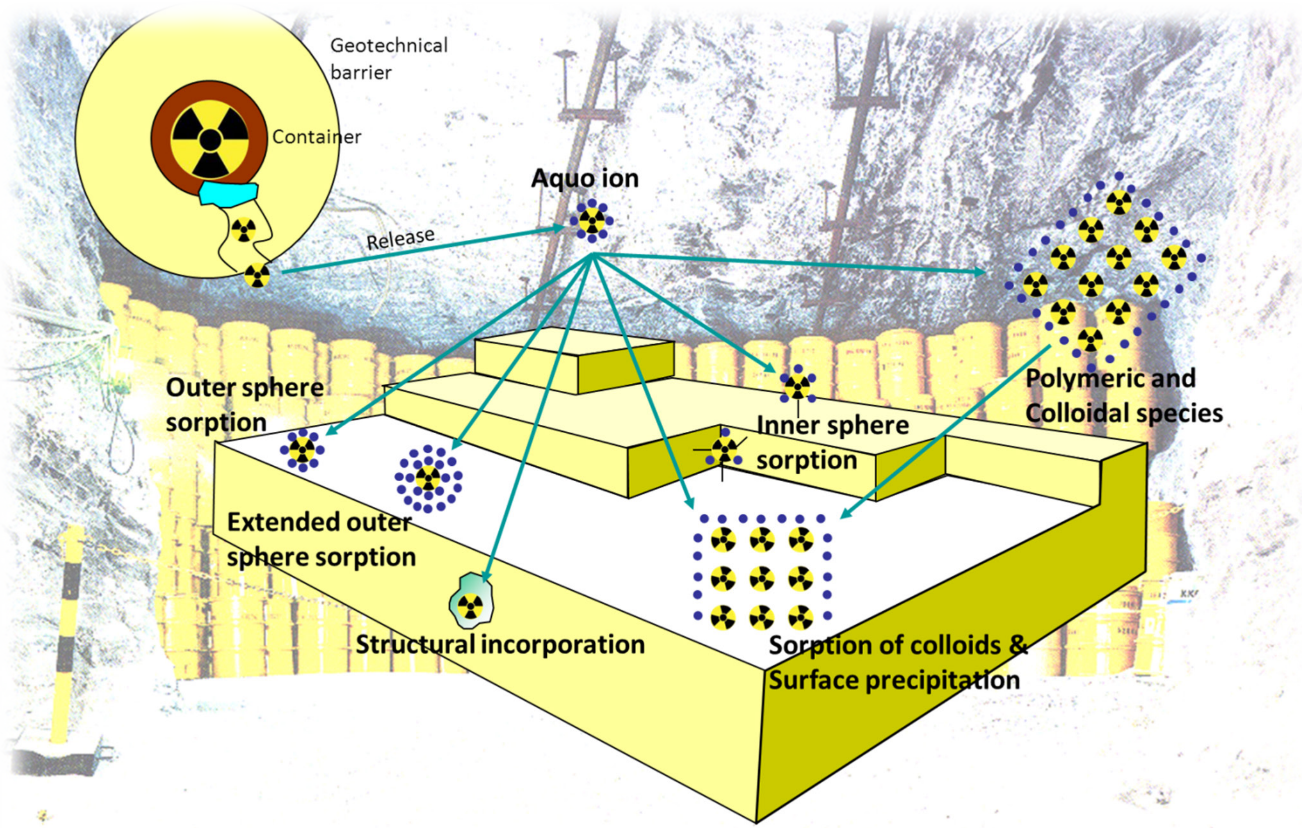
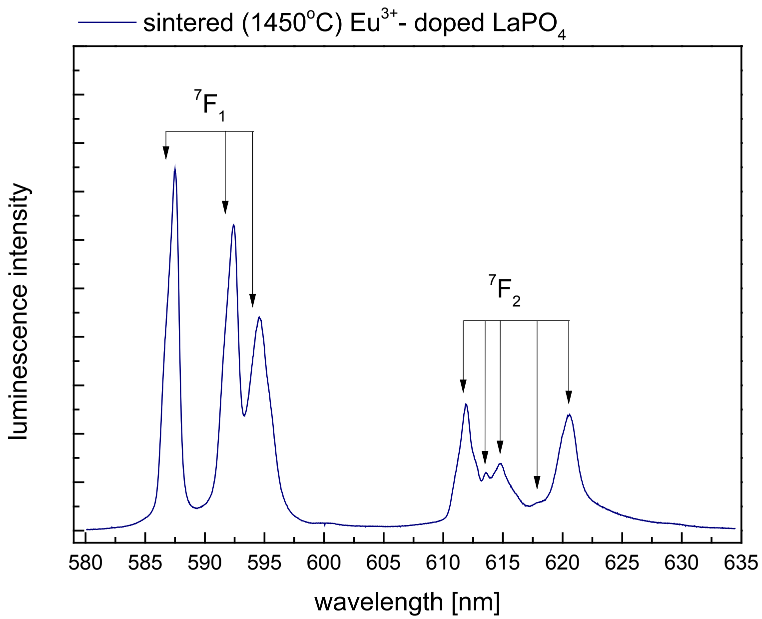
- Non-destructive, extremely sensitive method
- Solving reaction mechanisms at solid/water interfaces which are essentially needed for any reliable long-term safety prognosis of nuclear waste repositories

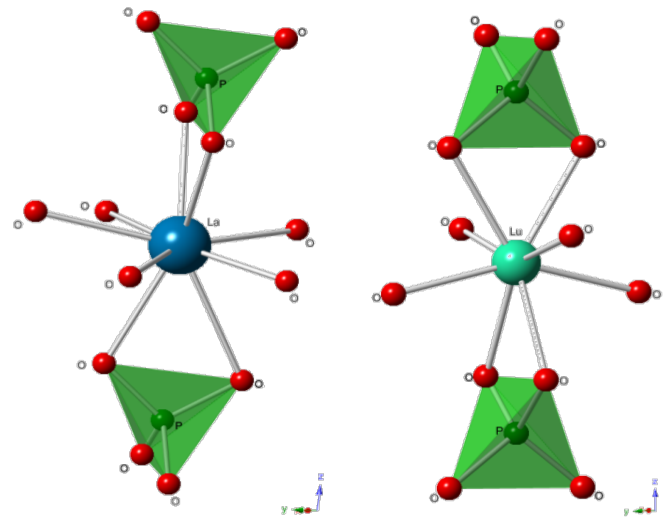


By courtesy of Dr. M. Schmidt, HZDR

TRLFS - Emission spectra

- Symmetry splitting pattern of e.g. $^7F_1$ and $^7F_2$ bands





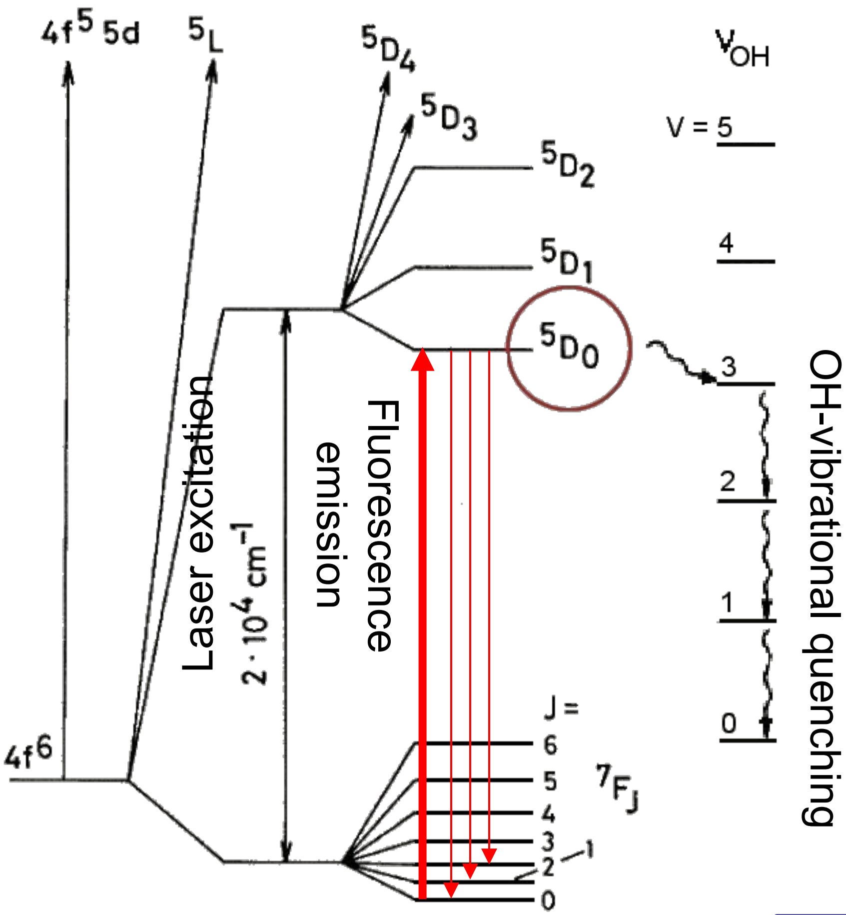
Monoclinic (C_1) Tetragonal (D_{4h})

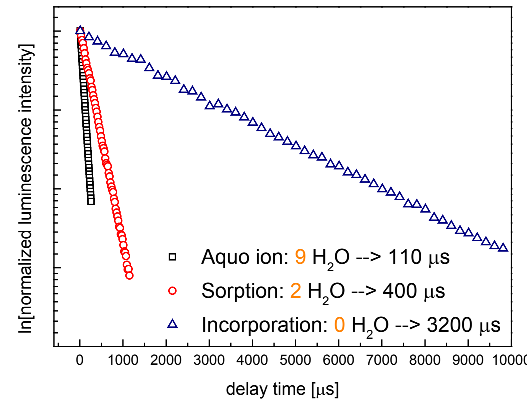
Symmetry	Site symmetry	No. of Stark levels vs. quantum number J						
		J = 0	1	2	3	4	5	6
Cubic	T, T_d, T_h, O, O_h	1	1	2	3	4	4	6
Hexagonal	C_{3h}, D_{3h}, C_6, C_{6h}, C_{6v}, D_6, D_{6h}	1	2	3	5	6	7	9
5-fold	D_5, C_5, C_{5h}, C_{5v}, D_{5h}	1	2	3	4	5	7	8
Tetragonal	C_4, S_4, C_{4h}, C_{4v}, D_4, D_{2d}, D_{4h}	1	2	4	5	7	8	10
Trigonal	C_3, S_6, C_{3v}, D_3, D_{3d}	1	2	3	5	6	7	9
Low	C_1, S_2, C_s, C_2, C_{2h}, C_{2v}, D_2, D_{2h}	1	3	5	7	9	11	13

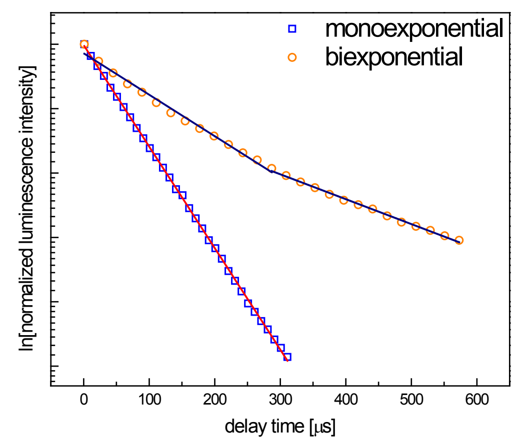
Table from: Bünzli and Choppin (Eds.) (1989) Elsevier Science B.V., Amsterdam.

TRLFS - Lifetimes

- Hydration state, number of species (mono vs. multiexponential decay)



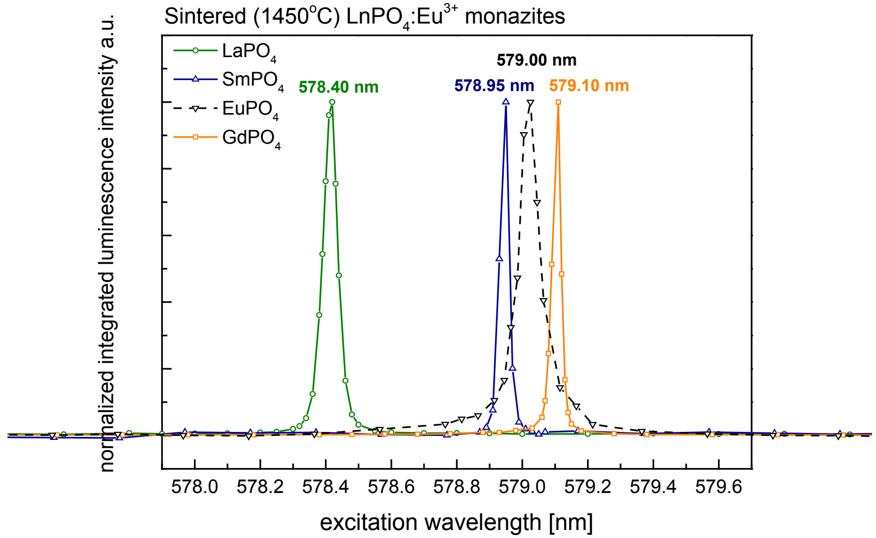


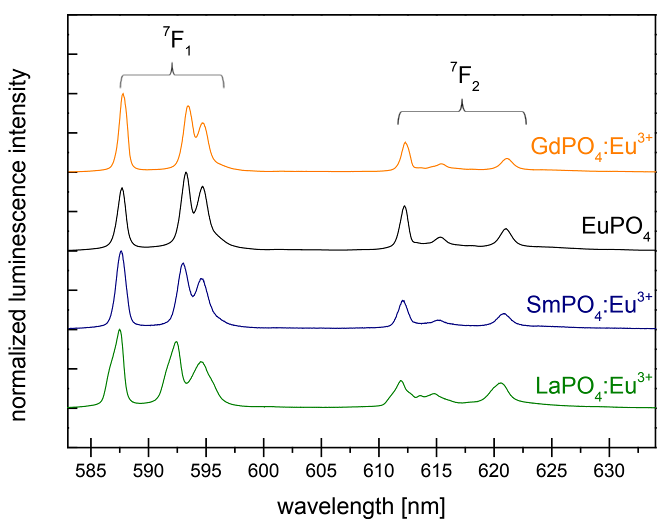


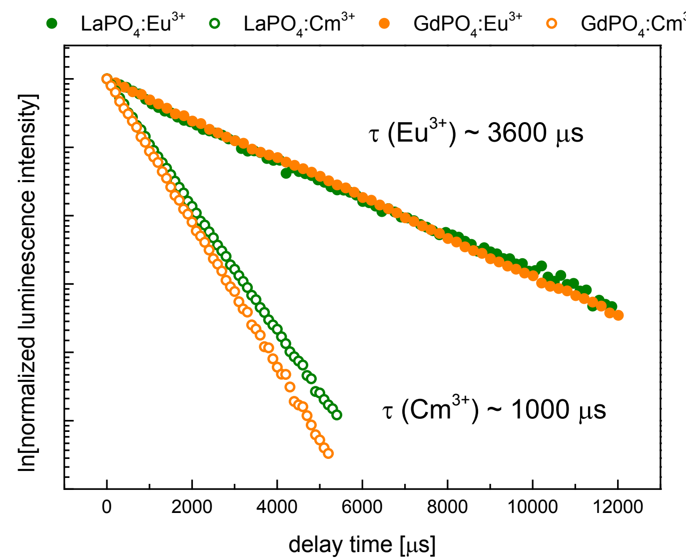
$$Eu^{3+}: n(H_2O) = 1.07 \times \tau^{-1}(ms) - 0.62$$

If τ is 580 us → 1.07/0.58 ms – 0.62 = 1.2 H_2O

Eu^{3+} incorporation in *Ln*PO_4 monazites

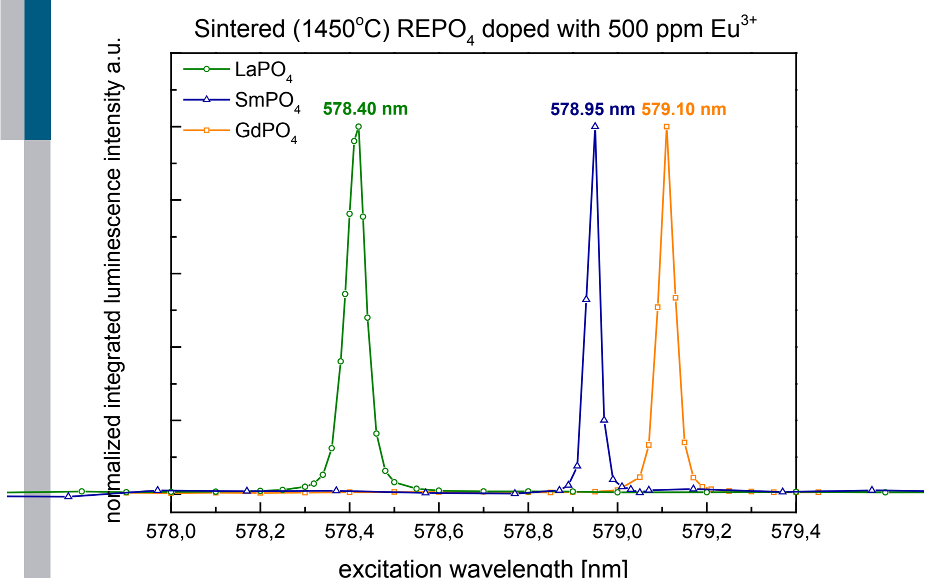


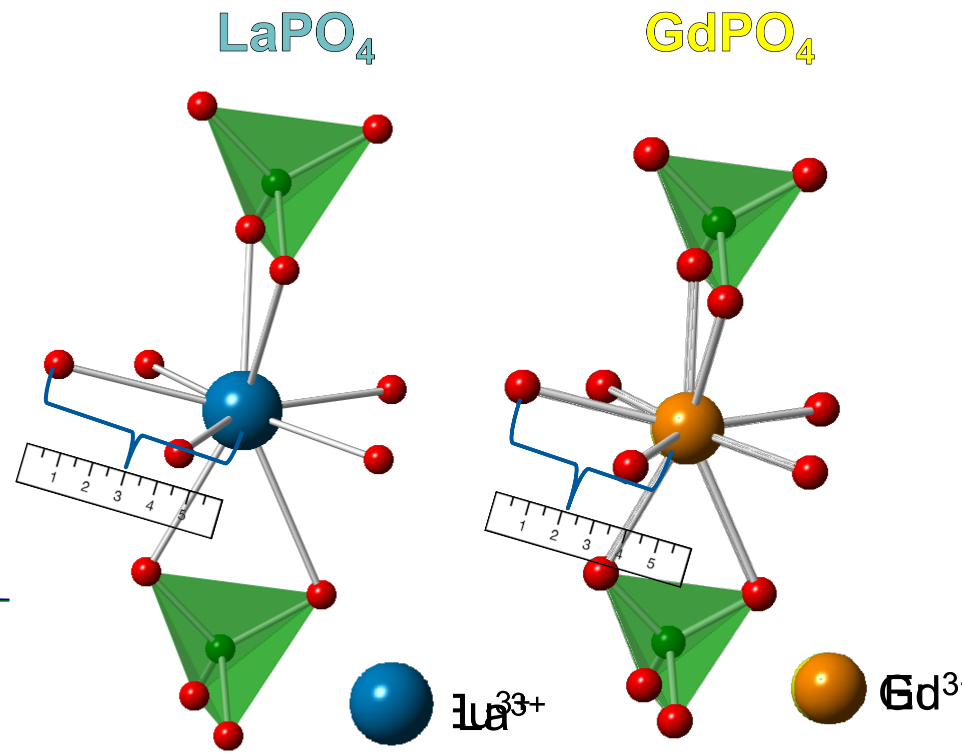




N. Huittinen et al. *J. Coll. Interf. Sci.* 483 (**2016**) 139–145.

Site-selective TRLFS studies of Eu^{3+} incorporation in $LnPO_4$

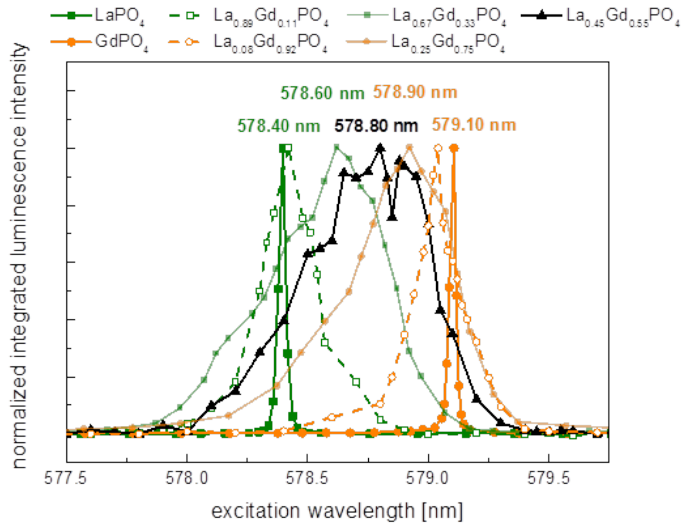


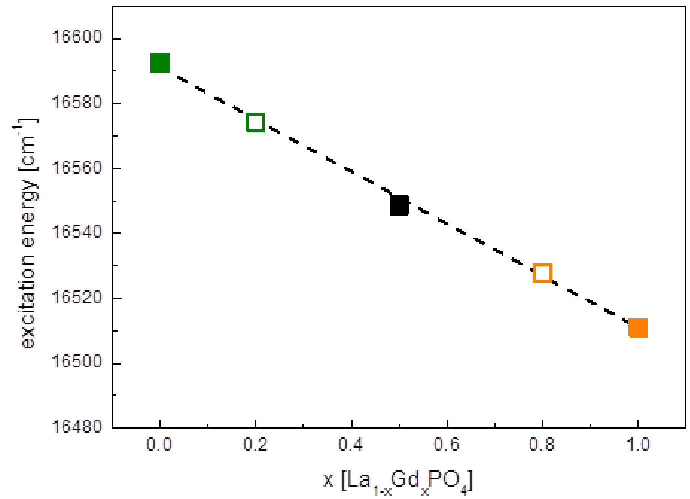


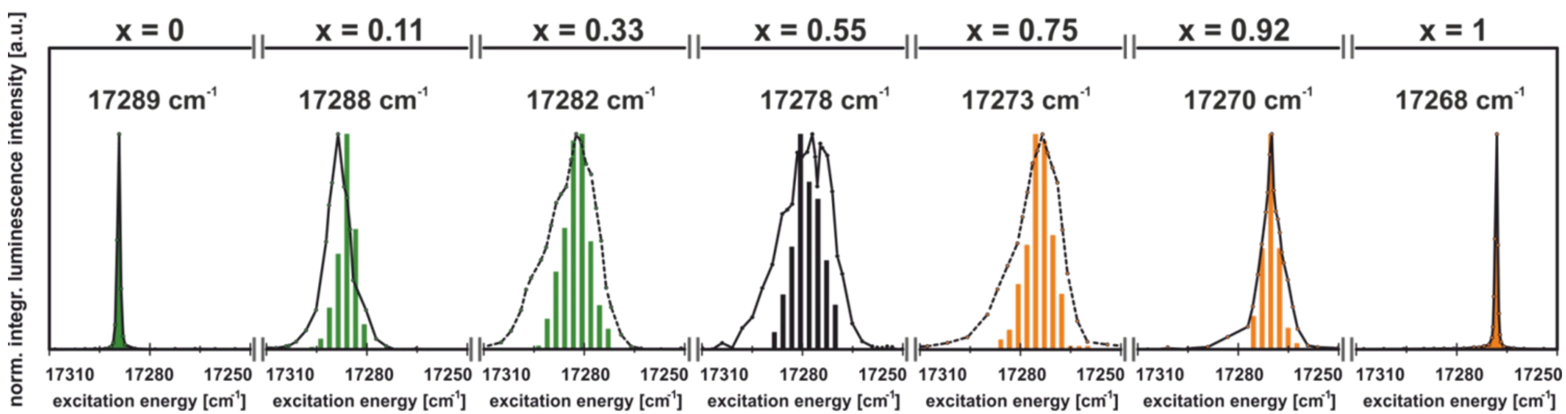
- ➢ Eu^{3+} substitution into the $REPO_4$ matrix
- ➢ excitation peak redshifted in comparison to $LaPO_4$
- ➢ stronger ligand field effect in $GdPO_4$

N. Huittinen et al. *J. Coll. Interf. Sci.* 483 (**2016**) 139–145.

Eu^{3+} and Cm^{3+} incorporation in *Ln*PO_4 monazites







- Cm^{3+} substitution into the $REPO_4$ solid solution matrix confirm homogeneity
- $REPO_4$ solid solutions result in a local disordering of the crystal structure due to bond length distribution (contribution to lattice strain)

N. Huittinen et al. *J. Nucl. Mater.* 486 (**2017**) 148-157. N. Huittinen et al. **in preparation**

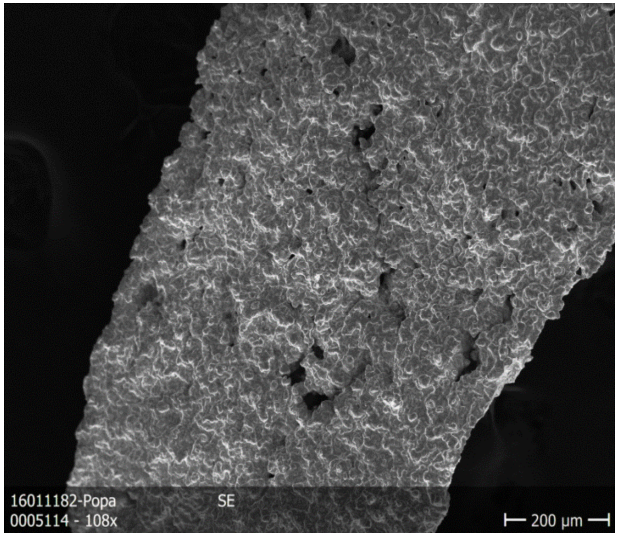
Solid state formation reaction of $La_{1-x}Pu_xPO_4$

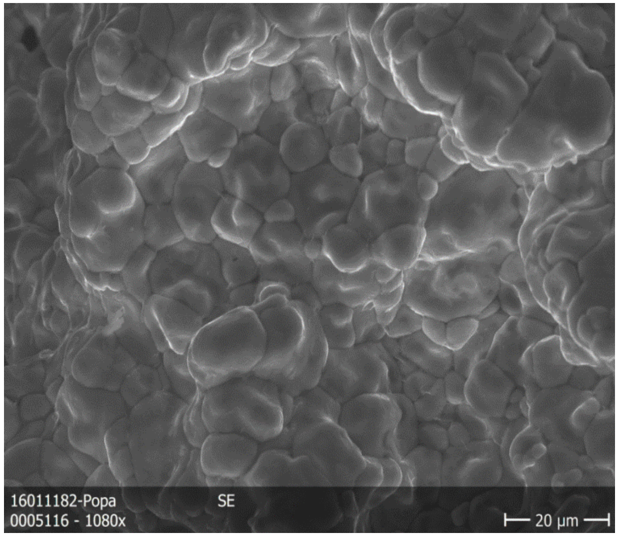
$(1-x)La_2O_3 + 2xPu^{IV}O_2 + 2(NH_4)_2HPO_4 \rightarrow 2La_{1-x}Pu_x{}^{III}PO_4 + 4NH_3\uparrow + 3H_2O + \frac{1}{2}xO_2\uparrow$

(10% molar excess)

$Pu^{IV}O_2 + 2\,(NH_4)_2HPO_4 \rightarrow Pu^{IV}P_2O_7 + 4\,NH_3 + 3\,H_2O$

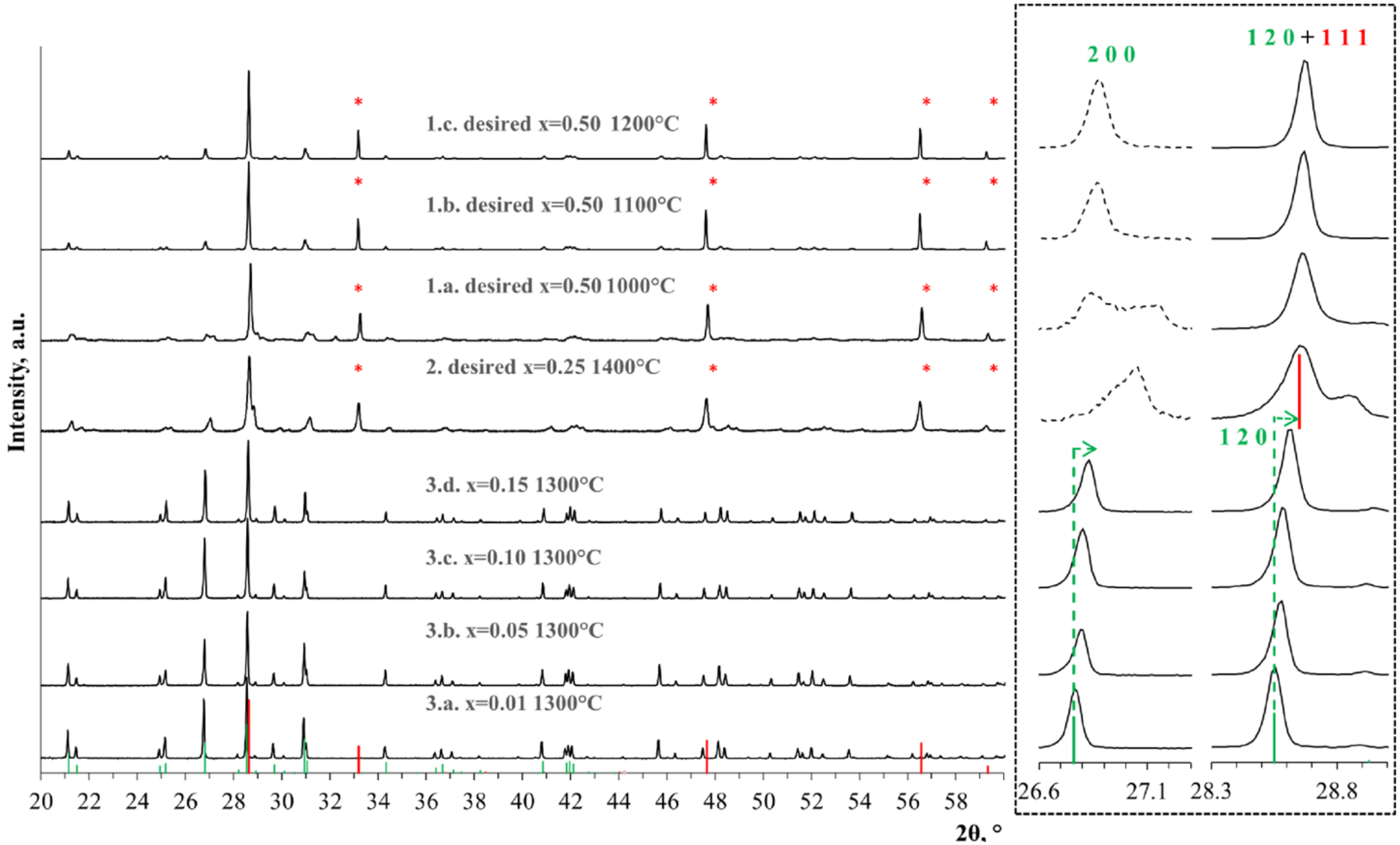
$4\,Pu^{IV}P_2O_7 \rightarrow 4\,Pu^{III}PO_4 + P_4O_{10} + O_2$





Y. Arinicheva et al. *J. Nucl. Mater.* 493 (**2017**) 404-411.

Characterization of $La_{(1-x)}Pu_xPO_4$
XRD

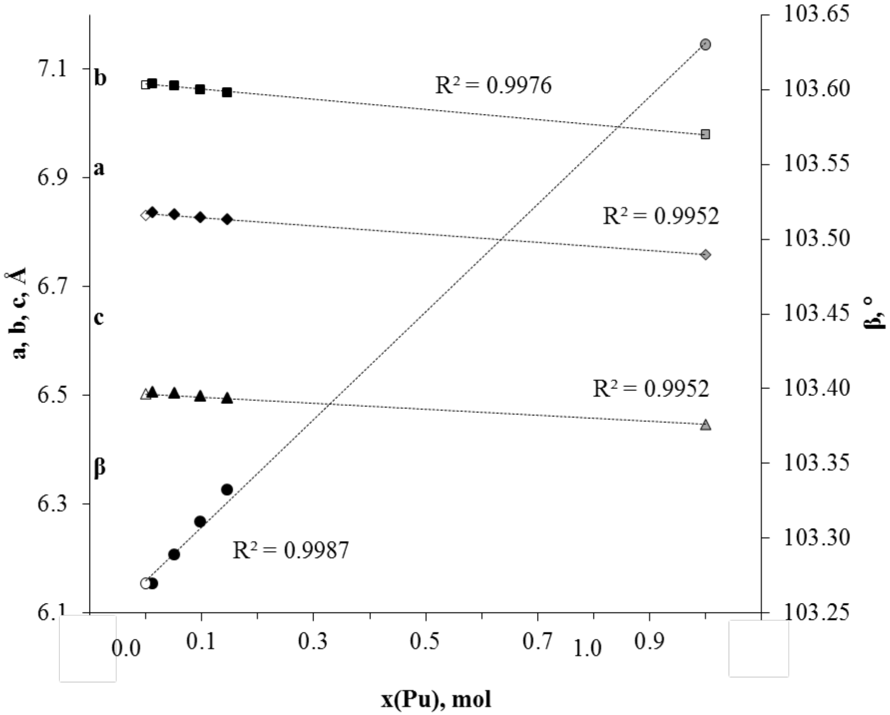


- Formation of single phase $La_{1-x}Pu_xPO_4$ solid solution up to x = 0.15
- PuO_2 residues point to incomplete reaction, decomposition (Pu_2O_3) can be excluded

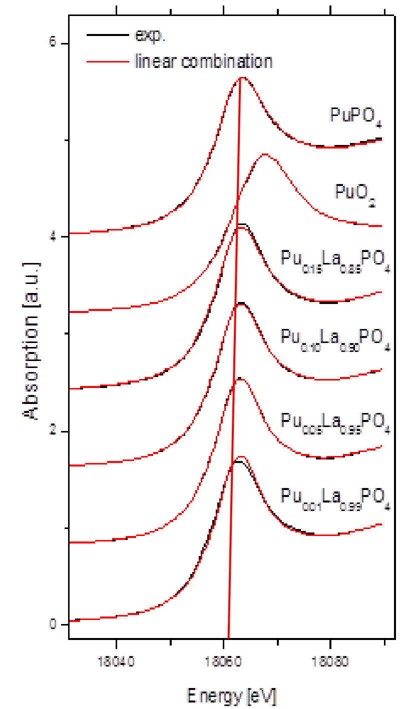
Y. Arinicheva et al. *J. Nucl. Mater.* **493** (2017) 404-411
R. Jardin et al. *J. Nucl. Mater.* **378** (2008) 167-171; O. Beneš et al. *J. Nucl. Mater.* **418** (2011) 182-185

Characterization of $La_{(1-x)}Pu_xPO_4$
XRD, XANES

Lattice parameter (XRD)



Oxidation state (XANES)



- Formation of single phase $La_{1-x}Pu_xPO_4$ solid solution up to x=0.15
- Pu is incorporated in oxidation state of +III

Y. Arinicheva et al. *J. Nucl. Mater.* 493 (**2017**) 404-411.
K. Popa et al. *J. Solid State Chem.* 230 (**2015**) 169-174.

Conclusion

- Homogeneous and thermodynamically stable regular monazite-type solid solutions are accessible by wet chemistry methods (precipitation)
  - ➢ Host matrix can be designed consisting of a main matrix element, e.g. La^{3+} and a neutrom poison, e.g. Gd^{3+}
- Trivalent actinides such as Cm^{3+} are homogeneously incorporated on monazite lattice sites after sintering
- Pu is incorporated in oxidation state +III
- Monazite structure stabilizes the incorporation of Pu in oxidation state +III
  - ➢ Points to the stability of monazite-type waste form
- Single phase monazite-type $La_{1-x}Pu_xPO_4$ x~0.15 solid solutions are accessible by conventional solid state method starting from PuO_2
  - ➢ Reasonable loading for a waste form
  - ➢ Dissolution of hardly soluble PuO_2 can be prevented
  - ➢ However, loading might be increased by optimization of sythesis method (precipitation)
- La increases the thermal stability of $PuPO_4$ (supresses decomposition)

➢ **Monazite-type lanthanide phosphates are suitable host phases to incorporate trivalent actinides**

Acknowledgements

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