The Rossendorf Beamline at ESR

Experiment Report Form

The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL). This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the HZDR. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.

Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the reference number of the proposal / experiment to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as ”Times” or ”Arial” , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

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ROBL-CRG	**Experiment title:** Systematic XAS study on Pu containing mixed phosphate solid solutions	**Experiment number**: 20-01 777
Beamline: BM 20	**Date of experiment**: from: 12 May 2016 to: 16 May 2016	**Date of report**:
Shifts: 12	**Local contact(s)**: Dr. André Rossberg	*Received at ROBL:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Monazite ceramics are promising materials as potential nuclear waste forms for the conditioning of Pu and minor actinides due to such properties as high loading, high chemical stability and irradiation resistance [1].

Four $L_{(1-x)}Pu_xPO_4$ (x = 0.01, 0.05, 0.1, 0.15) solid solutions were synthesized by solid state reaction in inert atmosphere and characterized thoroughly by XRD and SEM/EDX to be homogeneous and single phase monazite solid solutions. $Pu^{IV}O_2$ and $Pu^{III}PO_4$ from the work [2] were used as reference materials. The powders were diluted with boron nitride powder and pressed into pellets and encapsulated in a double sealed confinement. The XAS measurements of the Pu L_{III} edge and La L_{III} edge were collected at RT in fluorescence mode at 18057 eV and 5483 eV, respectively.

The XANES spectra (Fig. 1, left) of the solid solutions compared to the reference material ($Pu^{IV}O_2$ and $Pu^{III}PO_4$) clearly confirm that Pu^{III} is incorporated in the solid solutions as observed by Popa et al. for pure $PuPO_4$ [2].

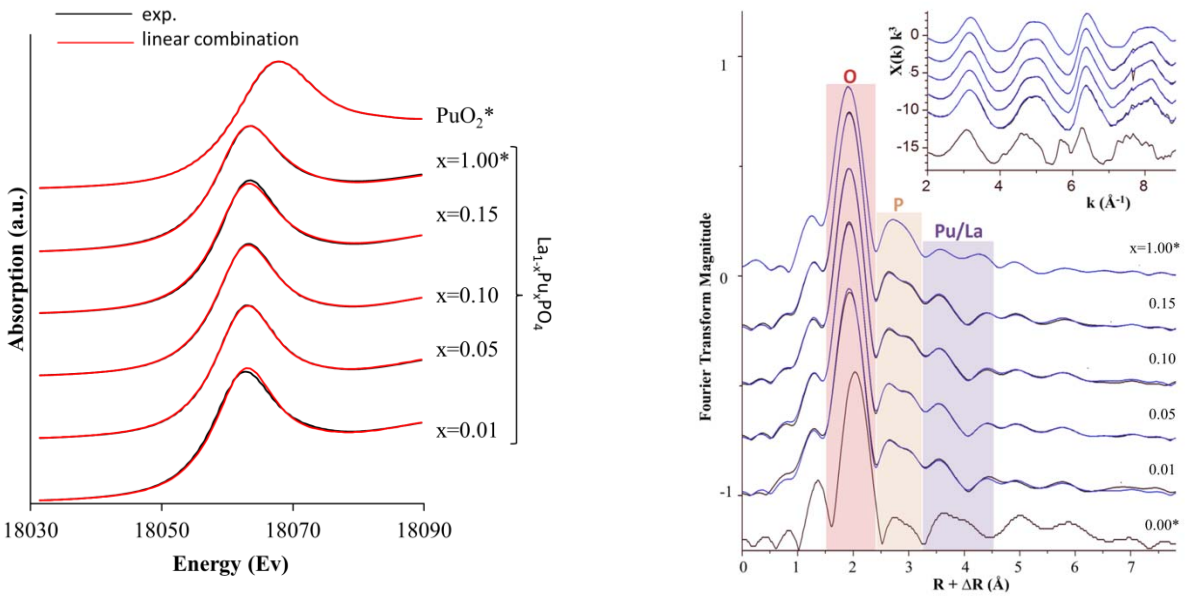

Figure 1: XAS spectra of $La_{1-x}Pu_xPO_4$ solid solutions as well as reference spectra.

From a combination of XRD and XAS data it can be concluded that the incorporation of PuIII on the defined lattice sites of the monazite structure is adjusted by the local environment of LaPO4, while local environment of Pu remains $PuPO_4$-like for the entire solid solution range. It was demostrated that the fabrication of a monazite-type ceramic containing a 10-15% Pu is feasible by conventional solid state synthesis method.

The results are accepted for publication at *J. Nucl. Mater.*.

Table 1. EXAFS shell fit results of Pu-doped La-monazites in comparison to $PuPO_4$ and $LaPO_4$ (Pu-L_{III} and La-L_{III} spectra, respectively).

Sample	Path	CN	R [Å]	σ^2 [Å^2]	ΔE_0 [eV]	S_0^2	χ_{res} [%]
$PuPO_4$	Pu-O	9	2.47	0.0103	9.9	0.70	7.4
(T)	Pu-P	3	3.21	0.0117			
	Pu-P	4	3.74	0.0105			
	Pu-Pu	3	4.07	0.0061			
	Pu-Pu	3	4.24	0.0057			
$La_{0.85}Pu_{0.15}PO_4$	Pu-O	9	2.48	0.0094	9.2	0.77	6.3
(T)	Pu-P	3	3.20	0.0122			
	Pu-P	4	3.75	0.0083			
	Pu-Pu	3	4.10	0.0014			
	Pu-La	3	4.33	0.0010			
$La_{0.90}Pu_{0.10}PO_4$	Pu-O	9	2.48	0.0098	8.9	0.79	6.3
(T)	Pu-P	3	3.20	0.0125			
	Pu-P	4	3.74	0.0085			
	Pu-Pu	3	4.05	0.0016			
	Pu-La	3	4.32	0.0010			
$La_{0.95}Pu_{0.05}PO_4$	Pu-O	9	2.48	0.0094	8.8	0.78	6.6
(T)	Pu-P	3	3.20	0.0130			
	Pu-P	4	3.74	0.0082			
	Pu-Pu	3	4.06	0.0014			
	Pu-La	3	4.33	0.0010			
$La_{0.99}Pu_{0.01}PO_4$	Pu-O	9	2.48	0.0100	9.2	0.74	7.6
(F)	Pu-P	3	3.20	0.0112			
	Pu-P	4	3.74	0.0083			
	Pu-Pu	3	4.06	0.0012			
	Pu-La	3	4.33	0.0010			
$LaPO_4$	La-O	9	2.53	0.0106	10.2	0.63	13.8
(F)	La-P	3	3.31	0.0205[c]			
	La-P	4	3.73	0.0205[c]			
	La-La	3	4.08	0.0082[c]			
	La-La	3	4.38	0.0082[c]			
$LaPO_4$	La-O	9	2.56				
(XRD)[6]	La-P	3	3.32				
	La-P	4	3.76				
	La-La	3	4.11				
	La-La	3	4.32				

References:

[1] Ewing, R.C.; Wang, L.M.: Phosphates as nuclear waste forms. *Rev. Miner. Geochem.* **2002**, *48*, 673 – 699.

[2] Popa, K.; Raison, P. E.; Martel, L.; Martin, P.M.; Prieur, D.: Solari, P. L.; Bouëxière, D.; Konings, R.J.M.; Somers, J.: Structural investigations of Pu^{III} phosphate by X-ray diffraction, MAS-NMR and XANES spectroscopy. *J. Solid State Chem.* **2015**, *230*, 169 – 174.