

  ROBL-CRG	<b>Experiment title:</b> <b>Studies on the interaction of actinides with zirconia (ZrO<sub>2</sub>)</b>	<b>Experiment number:</b> 20-01-802
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 25.11.2018 to: 28.11.2018	<b>Date of report:</b> March 2018
<b>Shifts:</b> 9	<b>Local contact(s):</b> André Rossberg	<i>Received at ROBL:</i>
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## Report:

In this study, the interaction mechanisms of trivalent actinides with zirconia, including the uptake on the surface as well as the incorporation into the crystal structure is studied by combining x-ray powder diffraction (PXRD), laser fluorescence spectroscopic (TRLFS) and x-ray absorption spectroscopic (XAS) techniques.

The TRLFS studies of the surface speciation show a very pronounced red-shift of the luminescence emission signal of absorbed Cm<sup>3+</sup> ( $\lambda_{\text{max}} = 608.4 \text{ nm}$ ) on the zirconia surface which implies that the speciation differs from the expected case.

The PXRD studies shows that the incorporation of actinides into the lattice changes the crystal phase in dependence of the doping percentage. At high doping percentages a highly ordered  $Fm\bar{3}m$  type phase is observed in PXRD while the TRLFS however reveals a very distorted nature of the local environment of the dopant.

For the EXAFS investigations sorption samples with an  $\text{Am}^{3+}$  ion concentration of  $2 \cdot 10^{-5}$  M were prepared at varying pH. The unexpected dominance of the Zr fluorescence (Zr K-edge: 18.0 keV) even at the Am  $L_{\text{I}}$ -edge with an edge energy of 23.8 keV, however, made it impossible to extract data when measuring in fluorescence mode, due to the oversaturation of the fluorescence detector. Measurements in transmission mode were attempted but the comparably low  $\text{Am}^{3+}$  concentration didn't allow to receive good data. Further data analysis will be necessary, however, it seems likely that extractable information is limited to the first coordination shell only. This would be sufficient to compare the distance to the sorbents surface to other systems. The EXAFS samples prepared to study the local environment of incorporated trivalent ions were investigated at the Gd  $L_{\text{III}}$ -edge in fluorescence mode. Two cubic zirconia samples were prepared with a  $\text{Gd}^{3+}$  doping percentage of 18 and 30 mol% since TRLS results of the  $\text{Ce}^{3+}$  co-dopant

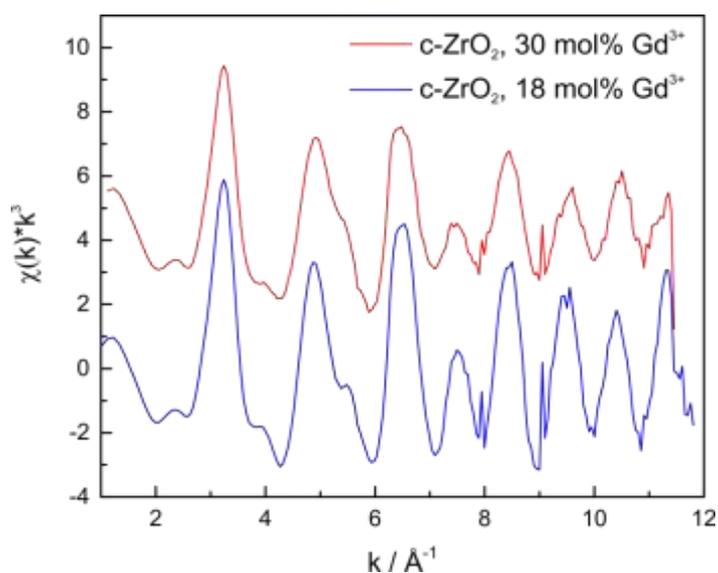


Figure 1: EXAFS oscillations of the Gd  $L_{\text{III}}$ -edge of  $\text{Gd}^{3+}$  doped c- $\text{ZrO}_2$ .

(100 ppm) in these samples imply a change in the coordination sphere at very high doping percentages. The data evaluation is still in progress, however it can be assumed when comparing the k-weighted oscillations that the close coordination around the  $\text{Gd}^{3+}$  cation is similar while the long range order seems to differ (Figure 1). At this stage it can only be speculated what the cause for that is, however it seems plausible that

the increasing amount of oxygen vacancies in the lattice or the increased distortion from the strongly oversized  $\text{Gd}^{3+}$  dopant may cause this effect. As a result from these experiments it becomes obvious that the investigation of sorption experiments will only be possible using cations with an accessible edge energy below the Zr K-edge.