



	Experiment title: Elucidating the crystal structure of Zr(IV)-bearing phases with trivalent and tetravalent dopants	Experiment number: A20-1-824
Beamline: BM20	Date of experiment: from: 29.10.2021 to: 31.10.2021	Date of report: 27.09.2022 <i>Received at ESRF:</i>
Shifts: 9	Local contact(s): Volodymyr Svitlyk and Christoph Hennig	
Names and affiliations of applicants (* indicates experimentalists): Nina Huittinen and Volodymyr Svitlyk* / Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf		

Report:

Parts of the results from this beamtime enabled the completion of a Master's thesis by M.Sc. Lucas Opitz [1]. The report summarizes the main results, with focus on the diffraction data, from his thesis.

This work deals with the possible incorporation mechanism of representatives of the trivalent lanthanides and actinides into zirconium(IV)oxide (ZrO_2 , zirconia) to elucidate whether or not this material is capable of acting as a retention barrier to prevent the environment from contamination. Zirconia is formed during reactor operation as a result of corrosion of the fuel rod cladding. When the whole fuel rod assembly is disposed of, this zirconia layer is the first retention barrier for released radionuclides.

The work has focused on understanding the association of trivalent metal ions with the monoclinic ZrO_2 structure during crystallization in aqueous solution. Experiments were performed mainly at 80 °C to account for the conditions in the near field of heat generating spent nuclear fuel. This also means that reducing conditions are expected, so that especially the minor actinides are present in the +3 oxidation state. Solution conditions were varied in terms of pH, ionic strength, and metal ion concentration. In addition to the experiments under aqueous conditions, the incorporation of lanthanides in the monoclinic ZrO_2 phase following calcination at high temperatures of 1500 °C was investigated. Experiments were done using two different sample rows. On the one hand Gd^{3+} and Eu^{3+} co-doped ZrO_2 with a trace amount of Eu^{3+} (100 ppm) and varying amounts of Gd^{3+} were synthesized. Eu^{3+} was used in luminescence spectroscopic investigations, while Gd^{3+} allowed for electron paramagnetic resonance (EPR) studies at room temperature. On the other hand, Ce^{4+} samples co-doped with 1000 ppm Eu^{3+} were synthesized, as up to 10 mol% Ce^{4+} can be

incorporated into the monoclinic ZrO_2 structure without modifying the phase composition. In this sample row the large Ce^{4+} cation (in comparison to Zr^{4+}) was used to facilitate the incorporation of Eu^{3+} into the monoclinic crystal structure. In all experiments, powder X-ray diffraction (PXRD) was used to study the phase composition of the Ln/An-containing ZrO_2 solids. Further, the crystallite sizes could be determined from the PXRD data. TEM-EDX was additionally performed to visualize structural changes and the morphology of the samples as well as the distribution of the incorporated species to localize possible accumulations within the solid structure.

The phase composition of all synthetic solid phases, i.e. the Eu^{3+} doped and $\text{Gd}^{3+}/\text{Eu}^{3+}$ co-doped ZrO_2 solids as well as the Ln_2O_3 phases were analyzed with PXRD. The diffraction data of the samples show clear phase transformation with increasing Gd doping, Figure 1

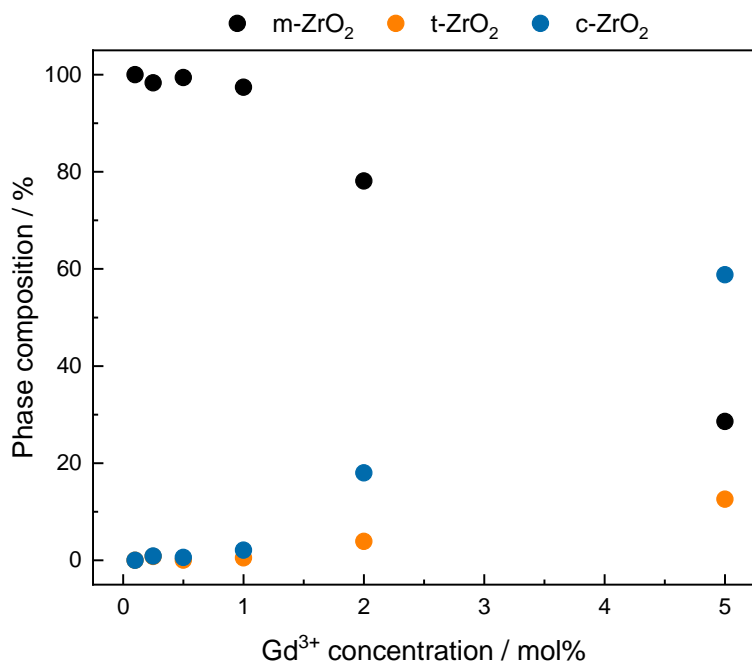


Figure 1: Phase composition of Gd^{3+} -doped ZrO_2 samples with 100 ppm Eu^{3+} co-doping.

For samples containing less than 1 mol% Gd^{3+} , the crystal structure is almost fully monoclinic. The amount of the monoclinic phase decreases systematically with further increase of the subvalent dopant, and at 5 mol% Gd, the cubic structure becomes the main phase with approximately 60% abundance. The Gd occupancy was determined for the two samples with highest Gd^{3+} concentration, i.e. 2 mol% and 5 mol%. In both cases, no Gd could be found in the monoclinic phase, while a Gd occupancy of 11-12 mol% was derived for the stabilized phase. This is a first indication for a preferred incorporation of the subvalent dopant into the higher symmetry phases. Finally, as for the Ce-containing samples, the crystallite sizes could be calculated for the Gd-doped ZrO_2 samples. The monoclinic crystallite size decreases with increasing Gd^{3+} concentration. The overall crystallite size is smaller than for the $\text{Ce}^{4+}/\text{Eu}^{3+}:\text{ZrO}_2$ samples, which is likely an effect of the oxygen vacancies in the structure and the larger size of the dopant (100 pm Gd^{3+} vs. 92 pm Ce^{4+} , in CN 7).

References

[1] Lucas Opitz – Interactions of Ln (Ce, Eu, Gd) and Cm with $\text{ZrO}(\text{OH})_2$ and their incorporation into m- ZrO_2 , Master's thesis, Technische Universität Dresden, 12/2021.