HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF ROBL-CRG	**Experiment title:** Investigation of $Th_xZr_{(1-x)}SiO_4$ and $U_xZr_{(1-x)}SiO_4$ Solid Solutions: colloid formation and solid state characteristics	**Experiment number**: 20-01-745
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Names and affiliations of applicants (* indicates experimentalists): Sabrina Labs*, Stephan Weiss*, Christoph Hennig*		

Report:

Commercially used fuel rods use zircalloy claddings of with high-purity zirconium as a first barrier. Zirconium will therefore be present in a deep geological repository for spent nuclear fuel. On the other hand zircon, $ZrSiO_4$, has been under investigation as a potential waste matrix for high-level radioactive wastes. Additionally, the formation of $U_xZr_{(1-x)}SiO_4$ in the so called Chernobyl lavas has been postulated [1]. While data on Pu doped $ZrSiO_4$ exists [2], data on other $ZrSiO_4$ – $An(IV)SiO_4$ solid solutions is scarce. Examining the mixing properties of the zircon-type orthosilicates such as $USiO_4$, $ThSiO_4$, $ZrSiO_4$ and $HfSiO_4$ can help to understand tendencies of thermodynamic properties in these systems and to deduce values, which are otherwise hard to obtain.

Complete solid solutions between $USiO_4$ and $ThSiO_4$ have been shown to be possible [3-5] and lattice parameters in the $U_xTh_{(1-x)}SiO_4$ system exhibit behavior according to Vegard's Law. $Zr_xHf_{(1-x)}SiO_4$ solid solutions have also been described in detail recently [6] and exhibit a negative excess volume of mixing, indicator for non-ideal mixing behavior. To the best of our knowledge neither has the successful synthesis of $U_xZr_{(1-x)}SiO_4$ solid solutions nor that of

$Th_xZr_{(1-x)}SiO_4$ been reported so far. First principle calculations by Ferriss et al. [7] suggest that there is a miscibility gap between $USiO_4$ and $ZrSiO_4$ and $ThSiO_4$ and $ZrSiO_4$ (calculated for 500 K and 1000 K). For the $HfSiO_4$ and $ZrSiO_4$ system their paper proposes near ideal mixing with a weak tendency for phase separation. The latter was later confirmed by Cota et al [6].

Stoichiometric solid $Th_xZr_{(1-x)}SiO_4$ and $U_xZr_{(1-x)}SiO_4$ samples were prepared from sol-gel synthesis through a hydrothermal procedure with the aim to obtain well defined material for XRD characterization and subsequent experiments. The $Th_xZr_{(1-x)}SiO_4$ (x=0.1, 0.2,…,0.9) solid solution series as well as $ZrSiO_4$ was successfully synthesized and characterized prior to measurement by XRD, IR, and Raman. The aim of the present study is to investigate $U_xZr_{(1-x)}SiO_4$ and $Th_xZr_{(1-x)}SiO_4$ solid solutions regarding their mixing behavior. Refinement of the lattice parameters showed that the $Th_xZr_{(1-x)}SiO_4$ solid solutions follow Vegard's rule but contain a positive deviation in excess volume of mixing. It is notable, that especially a = b lattice parameters contribute to this effect, while the c lattice parameter behaves nearly ideal. Spectroscopic data from IR measurements show that the ν_2 and ν_4-modes, associated to the SiO_4^{4-} tetrahedron shift towards smaller wavenumbers with increasing mole fraction *x*. The Raman study of these solid solutions shows the same effect for most modes: a linear decrease of the wavenumber with increasing *x*. EXAFS was used to investigate the local structure. The near-order structure in $Th_xZr_{(1-x)}SiO_4$ was investigated by using the Zr K-edge and Th L_3-edge. The Th L_3 edge was used to determine Th-Zr and Th-Th distances and the Zr K edge was used to determine Zr-Th and Zr-Zr distances. XANES edge-step was used to determine the mole fraction *x*. The obtained values are confirmed by SEM-EDS analysis. It appears that the $ThSiO_4$ – $ZrSiO_4$ system forms a complete solid solution, which show deviations from Vegards law. Results received from bulk material show significant structural differences related to colloidal samples [8].

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