ESRF	**Experiment title:** Immobilization of Th(IV) in Yttrium Stabilized Tetragonal and Cubic Zirconia Ceramics	**Experiment number**: 20-01-823
Beamline: BM20 ROBL	**Date of experiment**: from: 04/06/2021 to: 07/06/2021	**Date of report**: 13/09/2021
Shifts: 9	**Local contact(s)**: C. Hennig	*Received at ESRF:*

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Report:

During the 20-01-823 experiment high resolution synchrotron powder diffraction data on tetragonal and cubic Th-incorporated Yttrium Stabilized Zirconia (YSZ) have been collected. For the tetragonal $Zr_xY_{0.11}Th_yO_{2-z}$ and $Zr_xY_{0.14}Th_yO_{2-z}$ series maximum Th intake was found to be ~ 10 at.%, as concluded from the corresponding expansion of the unit cell volume as a function of % Th (Fig. 1, left). In addition, precipitation of ThO_2 was observed for the sample with 12 at. % Th concentration.

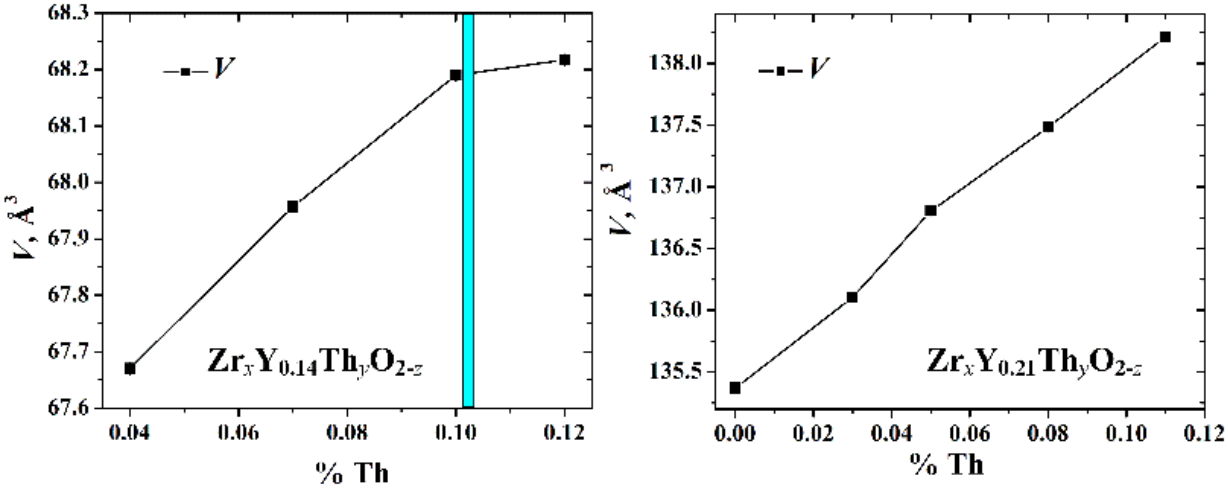

Fig. 1. Evolution of the unit-cell volumes in tetragonal $Zr_xY_{0.14}Th_yO_{2-z}$ (left) and cubic $Zr_xY_{0.21}Th_yO_{2-z}$ (right).

Introduction of Th atoms into the YSZ system was found to induce flattening of the ZrO8 polyhedra. This behaviour is explained by the larger ionic radius of Th^{4+} compared to Ce^{4+} (1.19 vs. 0.98 Å, respectively, in 8-fold coordination). Thus, insertion of Th atoms introduces additional volume in the unit cell allowing for the coordinating oxygen atoms to arrange in a more symmetrical way with more equilibrated Zr-O distances. Accordingly, the higher Th at. % content may be expected to be favoured by higher (cubic) symmetry. Indeed,

cubic $Zr_xY_{0.21}Th_yO_{2-z}$ system featured intake of Th up to at least 11 at.%, as concluded from the corresponding expansion of the unit cell volume (Fig. 1, right). Investigations in the cubic YSZ system for higher Th content are planned in the upcoming 20-01-830 experiment.

Phases with higher Th at.% are expected to be identified. Subsequent studies on their stabilities (as a function of temperature, pressure and irradiation) will allow to conclude if these materials are suitable as host matrices for radioactive elements in nuclear waste repositories.