

## Evaluation of surrogate-models for the incorporation of tetravalent actinides in monazite- and zircon-type phases for long-term disposal

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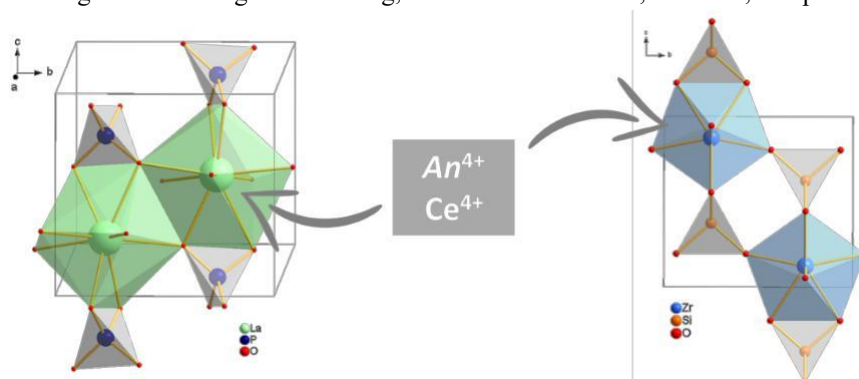
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The idea of immobilizing radionuclides in crystalline host materials was put forward 70 years ago [1]. Since then, continuous research has been conducted on a wide variety of crystalline materials that are considered as possible host matrices. However, many challenges remain, owing, *e. g.*, to the complex chemistry of nuclear waste streams and the exceptionally high requirements regarding physical and chemical long-term stability.

Monazite ( $LnPO_4$ ,  $Ln = La-Gd$ ) has long been considered as one of the most promising crystalline host materials for long-term storage of radionuclides, especially actinides. The main reasons for this are its chemical flexibility, its excellent aqueous durability and its low recrystallization temperature, which allows for rapid self-healing of radiation induced damages [2, 3]. It has been shown that monazites can accommodate large amounts of trivalent actinides within its crystal structure [3]. However, the incorporation of tetravalent dopants *via* coupled substitution with divalent cations has proven challenging [4, 5], even though natural monazite is known to contain significant amounts of Th and U (combined up to 27 wt-%) [6]. The incorporation of tetravalent cations into the zircon-type structure ( $ZrSiO_4$ ) was found to be less challenging, probably due to the tetravalent oxidation state of zirconium. A zircon-type structure called Xenotime is also formed by  $LnPO_4$  with  $Ln = Tb-Lu$ . Similar to monazite, this phase exhibits high resistance against leaching, its radiation tolerance, however, is reported to be much lower [7].



**Figure 1.** Monazite (left) and zircon (right) can accommodate tetravalent actinides in their crystal structures.

To facilitate assessments with respect to selection criteria such as chemical flexibility, radiation resistance and aqueous durability, efforts are made to identify inactive surrogate-models. The use of cerium as a surrogate for tetravalent actinides will be discussed for monazite- and zircon-type phases based on the solid solutions  $La_{1-x}(Ca,Ce)_xPO_4$  and  $Zr_{1-x}Ce_xSiO_4$ . These were extensively studied using powder and single crystal XRD, electron imaging techniques including EPMA, SEM and TEM, spectroscopic measurements including Raman, TRLFS, EXAFS and in-situ XAS experiments.

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