

Site-selective fluorescence spectroscopy investigations of LnPO₄ xenotime ceramics for radioactive waste disposal

H. Lösch, A. Hirsch,¹ J. Holthausen,² L. Peters,¹ S. Neumeier,² N. Huittinen

¹Institute of Crystallography, RWTH Aachen University, Aachen, Germany; ²Forschungszentrum Jülich, Jülich, Germany

Europium incorporation in different LnPO₄ (Ln = Tb, Lu and Gd_{1-x}Lu_x) phases crystallizing in the xenotime structure was investigated with site-selective TRLFS, PXRD and Rietveld analyses. Based on recorded emission spectra and diffraction patterns, the formation of three different crystal systems (xenotime, anhydrite, and monazite) could be identified. Aging of the ceramic samples and a second sintering step led to an accumulation of europium in the grain boundaries and on the surface.

EXPERIMENTAL. The synthesis of the Eu³⁺-doped LnPO₄ samples was done according to a hydrothermal route described by Roncal-Herrero.^[1] Subsequent to the synthesis, site-selective TRLFS studies were conducted to investigate the incorporation of Eu³⁺ within the ceramic structure. A re-characterization of the samples using TRLFS and PXRD was performed after one year of storage under ambient conditions (25 °C, air, normal pressure). The TRLFS and PXRD analyses were followed by a second sintering step to investigate the behavior and re-distribution of the dopant within the solid matrix. This sintering step of the xenotime phases was performed at 1250 °C for 15 h. The PXRD investigation was performed on a Phillips X'Pert Pro diffractometer using a θ - θ geometry, CuK α radiation in the range 10–80° and a step size of 0.008°. The site-selective TRLFS investigations (⁷F₀→⁵D₀) were performed with a pulsed Nd:YAG pumped dye laser set-up.

RESULTS. The diffraction pattern of Eu³⁺ doped TbPO₄ indicated the formation of two different phases (Fig. 1). The major phase (87 wt-%) could be identified as a TbPO₄ in an uncommon and unexpected anhydrite-like phase with an orthorhombic structure. The minor phase (13 wt-%) belonged to the expected xenotime structure. The second sintering caused an increase of the xenotime phase to 39 wt-%. The excitation spectra of the Eu³⁺-doped TbPO₄ directly after the synthesis and after one year storage showed only one narrow signal corresponding to one Eu-species. Based on the splitting pattern of the recorded emission spectra, this species could be assigned to Eu³⁺ incorporation in the anhydrite

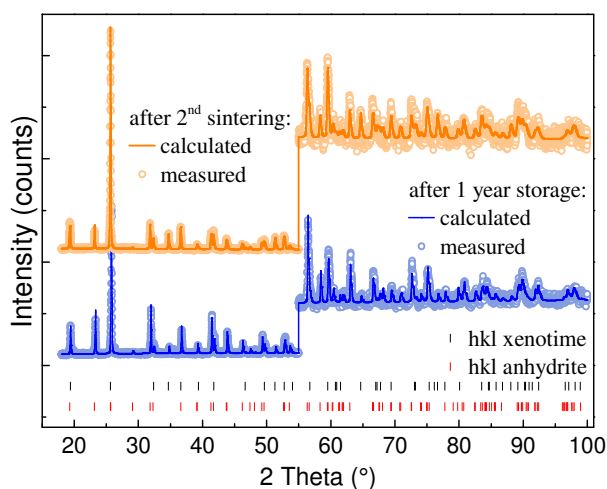


Fig. 1: PXRD patterns of Eu³⁺-doped TbPO₄ after one year storage and a second sintering.

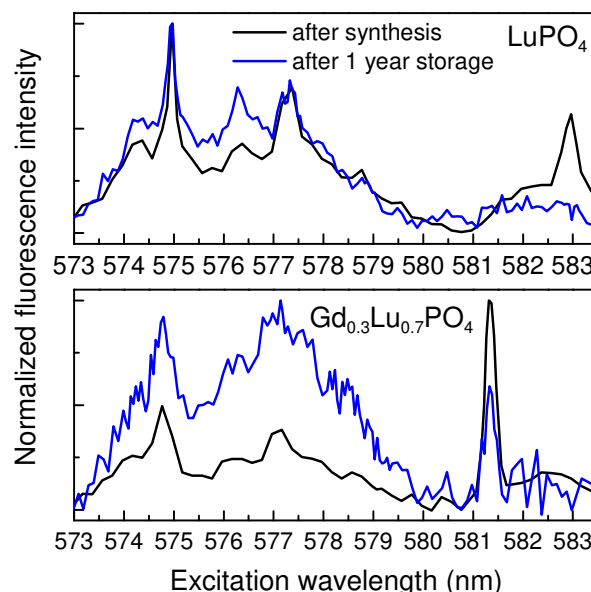


Fig. 2: Excitation spectra of LuPO₄ (above) and Gd_{0.3}Lu_{0.7}PO₄ (below) after the synthesis and after one year storage in the lab under ambient condition.

structure. After the second sintering a minor phase was identified in the TRLFS investigations, corresponding to Eu³⁺ incorporation in monazite.

In the diffraction patterns of LuPO₄ and Gd_{1-x}Lu_xPO₄ (x = 0.7, 0.5), only reflexes of a xenotime phase were observed. After the synthesis, the excitation spectra of LuPO₄ and the Gd_{1-x}Lu_xPO₄ solid solutions showed peaks at 583.0 and ~581 nm, respectively, corresponding to incorporated Eu³⁺ in the xenotime structure (Fig. 2). In addition, two minor signals in the blue shifted area around 575 and 577 nm were observed. These signals could be explained by the accumulation of europium in the grain boundaries and on the grain surfaces.^[2] After one year of storage, the signal at 583.0 nm (LuPO₄) completely vanished, while for the solid solutions, a significantly decreased intensity of the signal at 581.0 nm (Gd_{1-x}Lu_xPO₄) was observed pointing toward partitioning of Eu³⁺ from the crystal structures. The analysis of the lifetimes indicated biexponential decay after synthesis as well as after one year storage. The long lifetime suggests a full loss of the Eu³⁺ hydration sphere upon incorporation in the xenotime lattice, as it can be expected after sintering at 1450 °C. The shorter lifetime ranges from 200–850 μ s corresponding to 4.5–0.5 water molecules in the first hydration sphere of Eu, which indicates the presence of a partly hydrated Eu³⁺ species as expected for a sorbed surface species or a grain-boundary associated cation.

CONCLUSION. The results of the performed TRLFS and PXRD investigations show the formation of an anhydrite phase instead of the expected xenotime structure. It can also be seen that the storage over one year in the lab leads to a strong change of the crystal structure corresponding to partly accumulation of the Eu³⁺ in the grain boundaries and on the surface.

[1] Roncal-Herrero, T. *et al.* (2011) *Nanopart. Res.* **13**, 4049–4062.

[2] Holliday, K. *et al.* (2013) *Radiochim. Acta* **101**, 267–272.