

Eu³⁺ incorporation into xenotime LnPO₄: the effect of local distortion on long term stability

MORITZ SCHMIDT¹, HENRY LÖSCH¹, ANTJE HIRSCH²,
JACQUELINE HOLTHAUSEN³, LARS PETERS², BIN XIAO¹,
STEFAN NEUMEIER³, AND NINA HUITTINEN¹

¹Helmholtz-Zentrum Dresden-Rossendorf, Institute of
Resource Ecology, Dresden, Germany

²Institut für Kristallographie, RWTH Aachen University,
Aachen, Germany

³Forschungszentrum Jülich, Institute of Energy and Climate
Research, Nuclear Waste Management and Reactor
Safety (IEK-6), Jülich, Germany

Ceramic matrices are considered for the immobilization of specific nuclear waste streams. Recently, our group has studied the suitability of orthophosphates with monazite structure for this purpose, and found generally good exchangeability between host and guest cation and a corresponding high stability of the materials. Nonetheless, it was evident that both bulk structure and the local coordination environment of the guest cation need to be studied in order to assess the structural strain in the ceramic material on the molecular level.

Here, we present an in-depth study of the incorporation of Eu³⁺ as a luminescent homologue for the trivalent actinides, such as Am³⁺, into xenotime orthophosphates. We combine XRD with laser-induced luminescence spectroscopy (TRLFS) as a method to probe the local structure, to understand the impact of the substitution process.

Polarization-dependent TRLFS studies with single crystalline materials show that Eu³⁺ occupies identical lattice sites in Tb, Y, Ho, Er, and YbPO₄. The site has a distinct lower symmetry than the crystallographic cation lattice site, indicating local distortion. In LuPO₄, the material with the smallest host cation, this distortion is no longer viable and Eu³⁺ occupies a less distorted site with similar geometry to the crystallographic lattice site. The very small site enforces a strong overlap of ligand and metal orbitals, inducing strong spectral shifts as well as coupling to lattice phonons.^[1]

Characterization of polycrystalline materials reveals a more complex mineralogy, including an anhydrite-type phase and monazite in addition to xenotime. Eu³⁺ distribution indicates a clear aversion for the xenotime lattice when other phases are present. In the absence of other phases, Eu³⁺ is incorporated into xenotime initially, but long term studies reveal a complex unmixing process^[2].

[1] Xiao, B. et al., (2018), *Chem Eur J.*, 24, 13368-77.

[2] Lösch, H. et al., (2019), *Front. Chem.*, 7, 94.