Structural studies on rhabdophane-monazite phase tranformation in $La_{1-x}Ln_xPO_4$ (Ln=Eu, Gd)

Y. ARINICHEVA [1*], N. CLAVIER [2], N. HUITTINEN[3], A. BUKAEMSKY[1], S. NEUMEIER [1], T. STUMPF[3], N. DACHEUX[2], D. BOSBACH[1]

[1] Institute of Energy and Climate Research (IEK-6), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany (*correspondence: y.arinicheva@fz-juelich.de)

[2] Marcoule Institute for Separative Chemistry, UMR 5257 CEA/CNRS/UM2/ENSCM Site de Marcoule – Bât. 426, BP 17171, 30207 Bagnols / Cèze cedex, France

[3] Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany

Phosphate ceramics with monazite structure ($LnPO_4$, Ln = La – Gd) are promising materials as potential nuclear waste forms for the conditioning of special nuclear waste streams (separated plutonium from civilian or military sources unsuitable for further use) due to their outstanding properties, such as chemical durability and radiation damages resistance.. The rhabdophane phases are low temperature precursors for synthesis of monazites and can also be neo-formed as secondary phases upon dissolution of monazites. Rhabdophane has been considered to crystallize in the hexagonal lattice [1]. A recent re-examination of the system revealed two distinct monoclinic rhabdophane structures of hydrated and dehydrated compounds [2].

In the present work TG-DSC, HT-XRD, HT-PND, HT-Raman and TRLFS measurements were performed on La,Eu/Gd-phosphates to study structural evolution by dehydration of rhabdophane and the rhabdophane to monazite phase transition. The obtained data shows the transition from hydrated to dehydrated rhabdophane between 200 and 300ºC, and from dehydrated rhabdophane to monazite between 700 and 850°C. TRLFS-measurements of the Eu-doped lanthanum phosphate with hydrated rhabdophane structure yield fully split emission spectra and biexponential decay curves of the luminescence lifetimes indicating the presence of at least two Eu^{3+} species with low symmetry. Dehydration of rhabdophane causes the appearance of an additional ν_1 band in the Raman spectra, pointing on the presence of two phosphate tetrahedra with different P-O bond lengths.

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