

  ROBL-CRG	Experiment title: Structural incorporation of Cm ³⁺ in La _{1-x} Gd _x PO ₄ (x = 0, 0.2, 0.5, 0.8, 1) monazites	Experiment number: 20-01-771
Beamline: BM 20	Date of experiment: from: 24.02.2016 to: 26.02.2016	Date of report:
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Report:

In the present work, the structural incorporation of the minor actinide Cm³⁺ in a series of synthetic La_{1-x}Gd_xPO₄ (x = 0, 0.2, 0.5, 0.8, 1) monazite ceramics has been studied by combining two spectroscopic methods, time-resolved laser fluorescence spectroscopy (TRLFS) and extended X-ray absorption fine structure (EXAFS).

Our laser spectroscopic studies indicate the presence of only one, very well-defined, crystalline environment for the incorporated Cm³⁺ cation in the La and Gd monazite end-members. The situation changes when examining the solid solution compositions (La_{0.8}Gd_{0.2}PO₄, La_{0.5}Gd_{0.5}PO₄, and La_{0.2}Gd_{0.8}PO₄), where the recorded luminescence data indicate a decrease of the short-range order in these solid solutions. The laser-spectroscopic studies were complemented with Cm³⁺ L₃ edge XAFS investigations. Due to the very low Cm³⁺ doping of 50 ppm in the solid matrix requiring very long XAFS data collection times, only the Cm³⁺-doped LaPO₄, La_{0.5}Gd_{0.5}PO₄, and GdPO₄

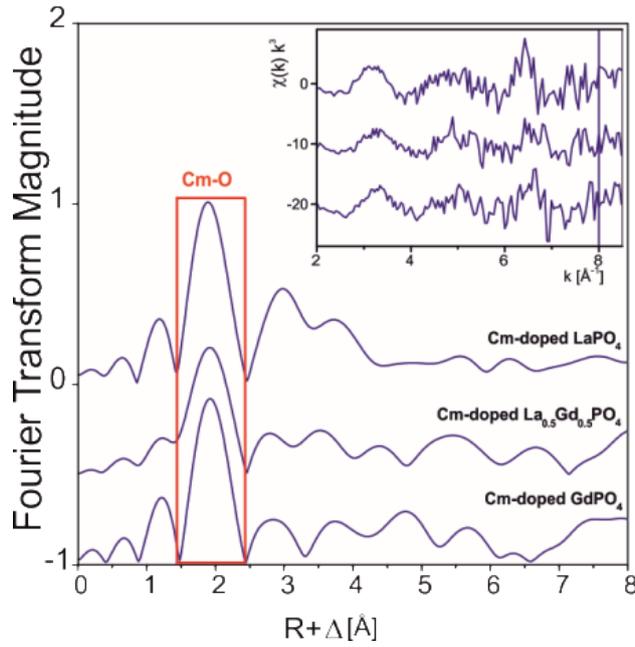


Fig. 1. Cm L₃-edge XAFS spectra of the Cm-doped monazite ceramics.

compositions were measured. The fitting of the first coordination shell of our Cm L₃ XAFS data (Fig. 1) for LaPO₄, La_{0.5}Gd_{0.5}PO₄, and GdPO₄, indicate a contraction of the Cm···O distance when going from the larger LaPO₄ monazite toward GdPO₄ (Table 1). The fitting results also show that the Debye-Waller (DW, σ^2) factor substantially decreases from 0.0090 Å² in LaPO₄ to 0.0063 Å² in GdPO₄, while an increase is observed for the solid-solution composition (0.012 Å²).

The differences in the DW factors between the monazite end-members indicate a larger disorder in the larger LaPO₄ host, presumably do to the larger mismatch of host and dopant radii causing a larger distortion of the monazite crystal lattice around the trivalent dopant ($\Delta r_{\text{La-Cm}} = 7 \text{ \AA}$) in comparison to GdPO₄ ($\Delta r_{\text{Gd-Cm}} = -3.9 \text{ \AA}$). The large DW factor obtained for La_{0.5}Gd_{0.5}PO₄ in comparison to the monazite end-members is in concordance with the laser spectroscopic data, showing an increasing disordering of the monazite crystal structure for the solid solution composition. These results are in very good agreement with already published data for Eu³⁺ incorporation in monazite solid solutions¹, where the disordering of the crystal structure in the solid solution compositions could be assigned to broadened distribution of Eu···O bond distances in these solids.

Table 1. Cm-L_{III} EXAFS fit results of the Cm-doped phosphate phases (fit range 1.5 – 8.5 Å⁻¹).

Sample	Path	CN	R [Å]	σ^2 [Å ²]	ΔE_0 [eV]	S_0^2	χ_{res} [%]
LaPO ₄	Cm-O	9	2.46	0.0090	7.3	0.80	19.2
La _{0.5} Gd _{0.5} PO ₄	Cm-O	9	2.43	0.0120	8.8	0.57	12.6
GdPO ₄	Cm-O	9	2.42	0.0063	8.8	0.50	16.5

¹N. Huittinen et al. (2017) J. Nucl. Mater. 486, 148–157