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| Experiment title: Resolving the oxidation state of cerium in Ce-doped LaPO ₄ monazites | Experiment number: A20-1-843 |
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Names and affiliations of applicants (* indicates experimentalists):

Nina Huittinen and Sara Gilson / Institute of Resource Ecology, Helmholtz-Zentrum Dresden-Rossendorf

Theresa Lender* and Lars Peters / Institute of Crystallography, RWTH Aachen University

Gabriel Murphy / Institute of Energy and Climate Research (IEK-6), Forschungszentrum Jülich GmbH

Julien Marquardt* / Institut für Geowissenschaften, Goethe-Universität Frankfurt

Report:

In this work, the oxidation state of cerium in a series of Ca(+2) or Sr(+2) and Ce(+4) co-doped LaPO₄ and GdPO₄ monazites subjected to different syntheses procedures was investigated using high-energy resolution fluorescence detection X-ray absorption spectroscopy (HERFD-XAS) at the Ce L₃-edge. Prior to the XANES measurements, different synthesis procedures to obtain pure phase Ca/Sr(+2)Ce(+4) co-doped monazites had been tested and optimized, followed by diffraction studies (XRD) and elemental mapping (EPMA) of the resulting solids. In Figure 1 (left and middle), selected lattice parameters from the diffraction studies of Ca(+2)Ce(+4) co-doped LaPO₄ monazites synthesized via solid state synthesis (left) and coprecipitation (middle) have been compiled.

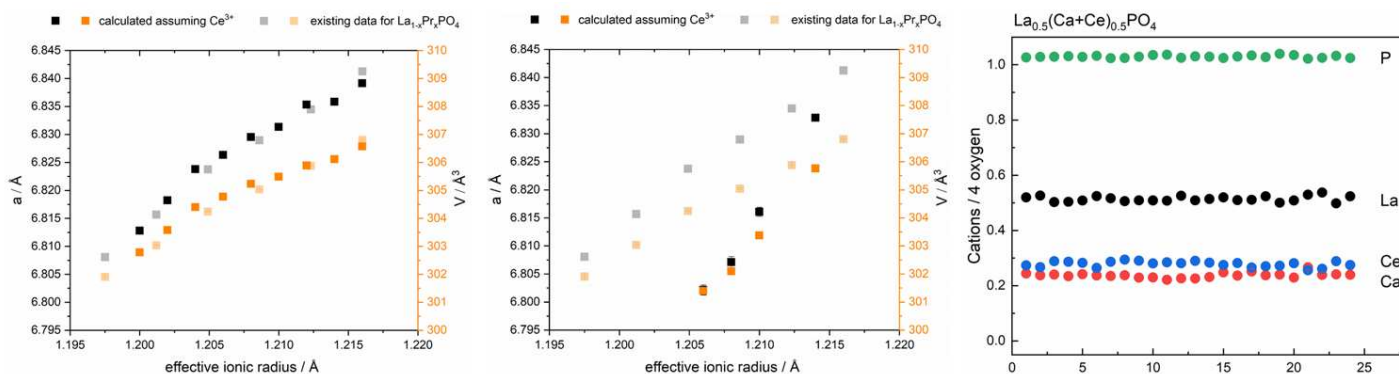


Figure 1: Selected lattice parameters from the diffraction studies of Ca(+2)Ce(+4) co-doped LaPO₄ monazites synthesized via solid state synthesis (left) and coprecipitation (middle). EPMA mapping of La_{0.5}(Ca+Ce)_{0.5}PO₄ monazite (right).

The results indicate, that solid state synthesis produces Ce(+3)-doped LaPO₄ without Ca incorporation. In contrast, the coprecipitation route yields solid phases that are clearly different from calculated Ce(+3)-doped LaPO₄, implying successful synthesis of Ce(+4)Ca(+2)-doped LaPO₄. Moreover, the elemental mapping via EMPA (Figure 1, right) of a selected monazite composition following coprecipitation synthesis, shows the expected Ca+Ce and La contents for a pure phase Ce(+4)Ca(+2)-doped LaPO₄ monazite.

XANES measurements were performed at the Ce L₃-edge on powder samples of both solid solutions with various levels of doping as well as on doped LaPO₄ single crystals. Surprisingly, in all samples cerium is mainly present in trivalent form. Powders of the GdPO₄ – Ca_{0.5}Ce_{0.5}PO₄ solid solution contain slightly larger amounts of tetravalent cerium than the solid solution containing lanthanum. The highest percentage of Ce(+4) in any of the measured samples was 27.6 %, more specifically, this was recorded from the powder sample of the composition Gd_{0.5}(Sr,Ce)_{0.5}PO₄. In general the best ratio of Ce(+4)/Ce(+3) was found in powder samples with an intermediate degree of doping (see figure 2 left and middle). With the combined results from the EPMA analyses and the XANES data, the charge imbalance from incorporation of Ca/Sr(+2)+Ce(+3), rather than Ce(+4), must be compensated by the formation of oxygen vacancies.

Ce(+4) levels in the single crystals were expectedly lower than in the powders given the high temperatures necessary for single crystal growth that facilitate cerium reduction. Low levels of approximately 5 % Ce(+4) were found in highly doped crystals with the compositions La_{0.1}(Sr,Ce)_{0.9}PO₄ and La_{0.3}(Sr,Ce)_{0.7}PO₄ while the pre-edge region of intermediate crystals was congruent with the Ce(+3) standard.

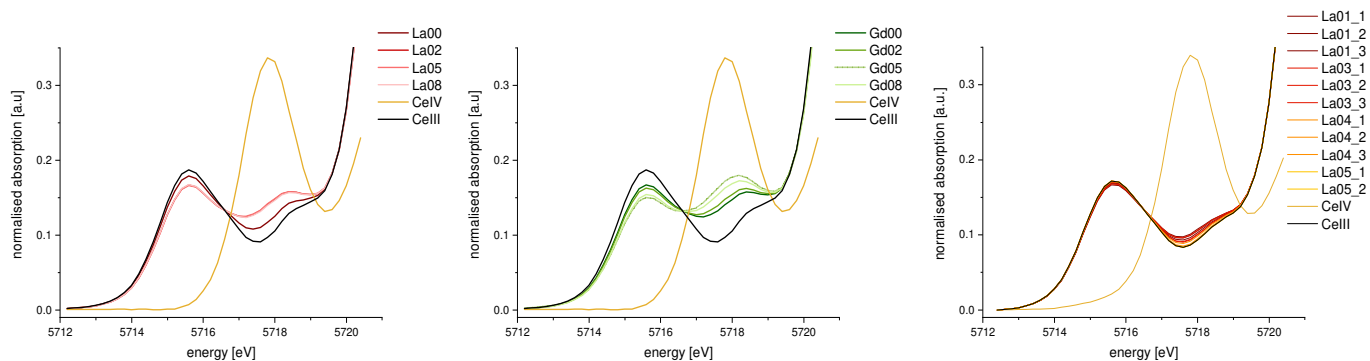


Figure 2: Ce L₃ pre-edge region of Ca(+2)Ce(+4) co-doped LaPO₄ (left) and GdPO₄ powders (middle) as well as doped LaPO₄ single crystals (right). Standards of Ce(+3) and Ce(+4) are given for comparison.

For further analysis of the reduction of cerium in co-doped powders during the coprecipitation synthesis – especially during the temperature induced phase transition from rhabdophane to monazite – a proposal for in-situ XANES measurements has been submitted.