ESRF	**Experiment title:** Pr and Ce doped La2O2CO3 as materials for CO2 gas sensors – insight into mechanistic aspects of unique f-electrons configuration	**Experiment number**: MA2617
Beamline: ID26	**Date of experiment**: from: 29.04.2015 to: 05.05.2015	**Date of report**: 02-03-2017
Shifts: 18	**Local contact(s)**: Kristina Kvashnina	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

1) A part of the results have been already published. This articles was highlighted as ACS Editors choice.

O. Hirsch, C. Willa, K. Kvashnina, **D. Koziej**,
Hard X-ray Photon-in Photon-out Spectroscopy as a Probe of the Temperature-Induced Delocalization of Electrons in Nanoscale Semiconductors
Chem. Mater. 29 2017, 29, 1461 10.1021/acs.chemmater.6b05218

Abstract
Hard X-ray photon-in photon-out spectroscopy has so far mainly been applied to investigate fundamental physical phenomena in superconductors and chemical reactivity of bioinorganic, photocatalytic, and catalytic materials. Here, we show, with the example of Pr_6O_{11} nanoparticles, an n-type semiconductor, how high-energy resolution fluorescence detected (HERFD) X-ray absorption near edge structure (XANES) can be used to track the changes of partially filled f-bands. We observe a reversible variation of the spectral features related to the tetravalent Pr ions upon heating and cooling, whereas structural and chemical transformations can be excluded. We assign these changes to the occupancy of the O 2p–Pr 4f band and show that they directly relate to changes in the electrical conductance. Our results demonstrate how HERFD-XANES can be used to particularly study in situ the electronic properties of f-electrons in a semiconductor and how this method can be further extended to other classes of semiconducting nanomaterials

2) We are currently finalizing the manuscript related to rare earth doping.
Data evaluation, FEFF analysis and calculation based on the multiplet theory have been accomplished. Additionally the Rietfeld refinment and HR-TEM analysis have been already performed.

The incorporation of dopants into a host matrix is worth an investigation with two major questions: a) On which position within the crystal lattice does the dopant go? b) What are its the implications on the electronic properties i.e. what is the oxidation state of the dopant?

Our main findings from HERFD XAS are:

- Measurements at the La edge show no changes upon Pr doping (Figure 1, left)
- Pr is incorporated into $La(OH)_3$ in the oxidation state of +3
- The coordination of Pr in $Pr:La(OH)_3$ and $Pr:La_2O_2CO_3$ changes with the doping concentration, visible trough a changing pre-edge feature (Figure 1, right)
- Partial oxidation of Pr upon heating, but no oxide phase observed (Figure 1, right)
- We were able to follow the phase transformation of 1% and 10% doping at the Pr and at the La edge. The results are consistent with *ex situ* experiments

Our main findings from vtc XES are:

- Measurements at the La edge show no changes upon Pr doping (Figure 2, left)
- Vtc XES Pr: $La_2O_2CO_3$ excited at the resonant energy of Pr^{4+} shows no band gap/states within the band gap. This is consistent with conductivity measurements which showed an increased overall conductivity of the doped oxycarbonate compared to the pure one. (Figure 2, right)

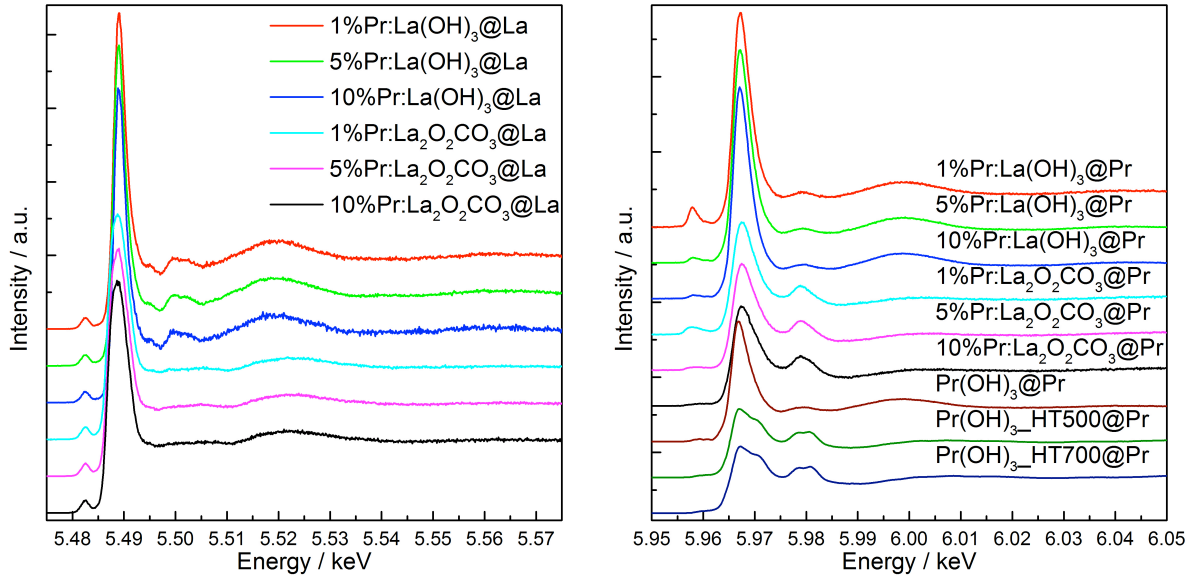

Figure 1. HERFD XAS of $Pr:La(OH)_3$ and Pr: $La_2O_2CO_3$ with various dopant concentrations measured at the La edge (left) and at the Pr edge (right).

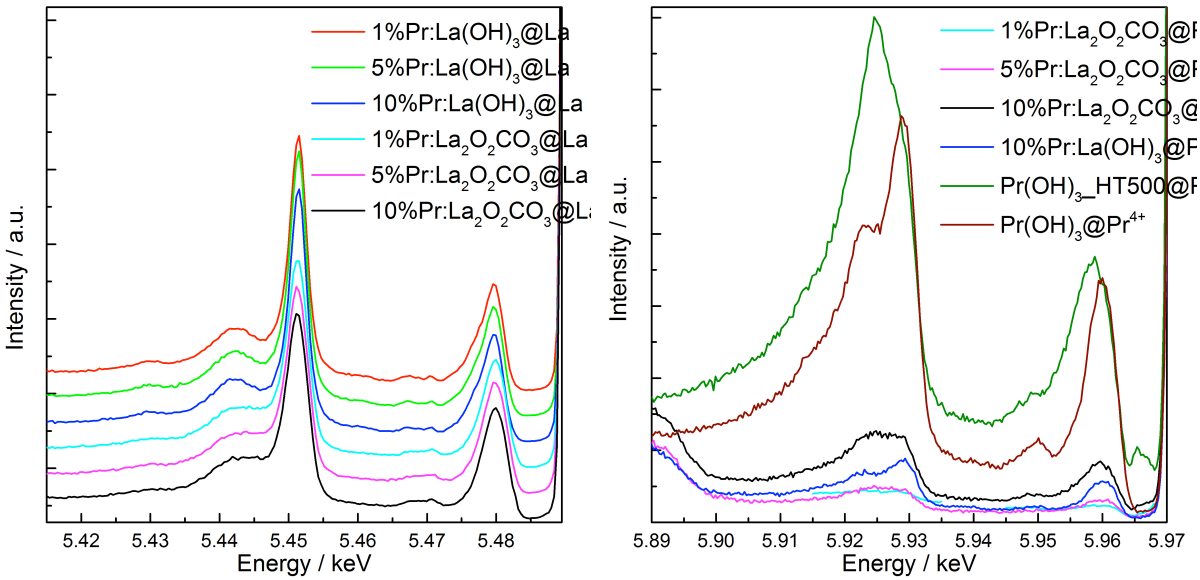

Figure 2. Vtc XES of $Pr:La(OH)_3$ and Pr: $La_2O_2CO_3$ with various dopant concentrations resonantly excited at the La^{3+} position (left) and at the Pr^{4+} position (right).