	Experiment title: Elucidating the electronic structure of Cm^{3+} in Gd_2O_3 and ZrO_2	**Experiment number**: MI-1386

Beamline: BM20	**Date of experiment**: from: 22.06.2021 to: 25.06.2021	**Date of report**: 27.09.2022
Shifts: 9	**Local contact(s)**: Kristina Kvashnina and Elena Bazarkina	*Received at ESRF:*

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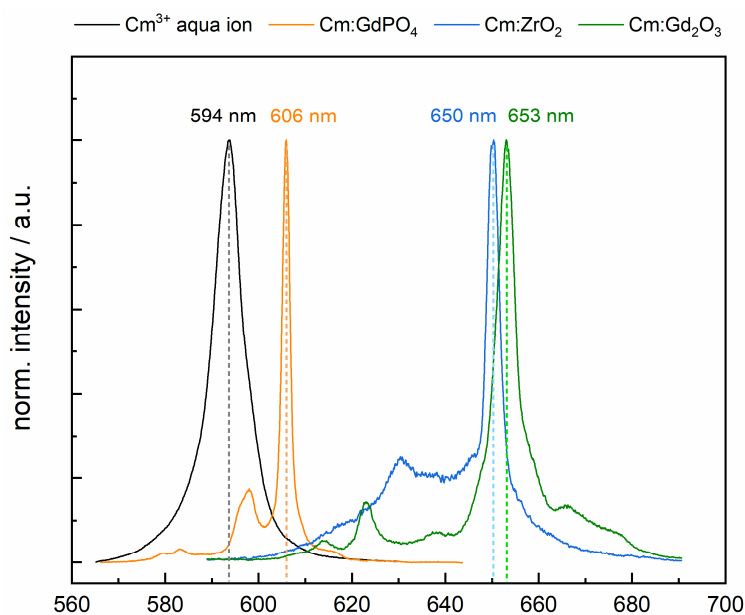
Report:

Figure 1: Emission spectra of the Cm^{3+} aqua ion and Cm^{3+}-doped crystalline solid phases containing 50 ppm Cm.

In the present work, three oxide materials, namely monoclinic (m) ZrO_2, cubic (c) Gd:ZrO_2, and c-Gd_2O_3 doped with 50-300 ppm of the minor actinide Cm^{3+}, were investigated using HERFD–XANES. The aim of the study was to elucidate the origin of an unusually strong perturbation of the electronic levels of Cm^{3+} in these host materials as determined by luminescence spectroscopy. Such perturbation may arise from *e.g.* an unusually short Cm–O bond in the host phases or from a covalent character of the Cm–O bond [1]. For comparison, a solid sample of $GdPO_4$ containing 50 ppm Cm was measured as a representative for an almost ionic (non-covalent) solid phase, showing a very low crystal field splitting of the incorporated Cm^{3+} ion (of similar magnitude to the Cm^{3+} aqua ion), Figure 1.

To date, there are no HERFD-XANES data for curium at the M_4 or M_5 edges, and an important aspect of the study was to optimize and test the experimetnal set-up at the BM20. Typically, the M_4 edge of actinide lements is measured (not M_5) as the transition probability as well as the resolution are greater. Unfortunately, Cm M_4 is not accessible with the Johann-type spectrometer as no analyzers exists for the Cm M_4 energy range. Thus, the M_5 edge was probed instead. The first effort in recording Cm M_5 edge data in high resolution at a distance of 1 m was not successful. No Cm was visible in this measurement geometry at the energy of approximately 3950 eV. At the Cm L_3 edge (18970 eV) the efficiency of the spectrometer is not optimal, and no Cm signal could be detected at a distance of 1 m. Moving the spectrometer to 0.5 m increased the signal intensity in the monoclinic ZrO_2 sample. However, the background from Zr was so high (due to edge overalp, as the Zr K-edge is just below the Cm L_3-edge), implying that at these low concentrations, Cm cannot be measured in Zr-containing systems.

Instead, Cm signal could be collected from the Zr-free samples, namely the cubic phase Gd_2O_3 (assuming strong covalent contribution in the sample) and the ionic $GdPO_4$ monazite. In additon, Gd L_3-edge data were collected from the same samples. The XANES data are shown in Figure 2.
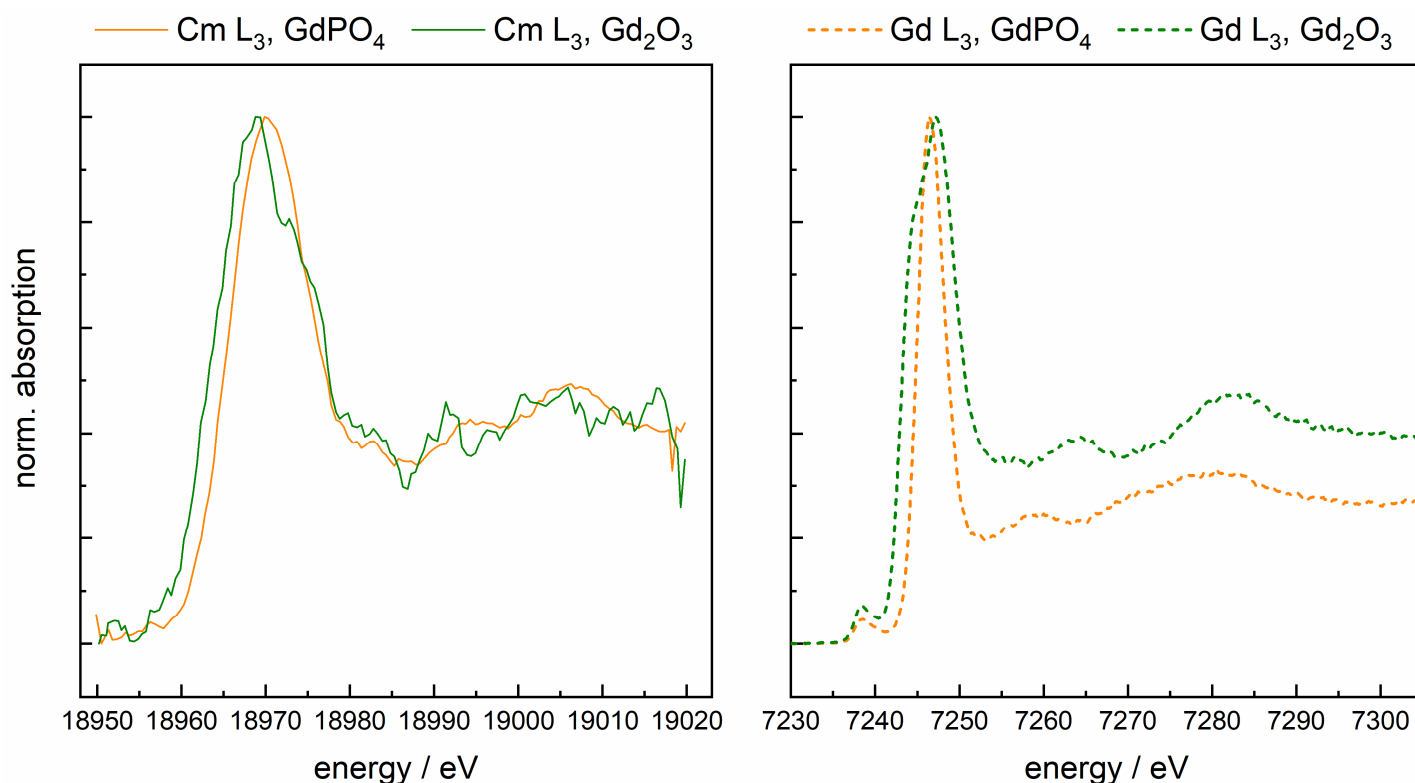

Figure 2. Cm L_3-edge data (left) and Gd L_3 edge data (right) collected for Gd_2O_3 and $GdPO_4$ with 50 ppm Cm doping.

The Gd L_3-edge data show clear differences between the two samples. There are two peaks at the main edge transition for Gd_2O3 and a single peak for $GdPO_4$. This is due to the crystal field splitting of the Gd 5d states in the particular local environment. The assumption is, that the broadening of the Cm L_3-data for Gd_2O_3 in comparison to the $GdPO_4$ and the clear splitting, which is similar to the Gd L_3 data, has the same origin. The 6d states of Cm in the Gd_2O_3 matrix split in the same way as in Gd 5d states in the oxide structure.

To resolve the origin of the splitting electronic structure calculations are planned. Further measurements on samples with higher Cm doping would also be necessary, to probe the Cm environment in the Zr-containing phases and to confirm the observations in the current study. Further, a higher Cm concentration may allow for measurements at the M_5 edge, and this way gain access to the 5f electrons in the system. Only then, a direct comparison of the luminescence and XANES data can be made.

References
[1] M. Eibl (2020) Ph.D. thesis, TU Dresden, Germany