



	Experiment title: Determination of cation disorder in pyrochlore ceramics by resonant scattering of synchrotron X-rays	Experiment number: CH-2038
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Report:

Introduction

Ceramics with the pyrochlore ($A_2B_2O_6X$) structure are widely regarded as good candidates for the immobilisation of actinides (U, Pu, Am, Np) from high level nuclear waste (HLW). The presence of α -emitting radionuclides in natural pyrochlore minerals that are hundreds of millions of years old has been documented, showing the resilience of this structure to intrinsic radiation damage.

Recently, zirconate pyrochlores have received a lot of attention. Such pyrochlores are not common in nature, but synthetic compositions have been demonstrated to have a very high resistance to radiation damage.

When considering a candidate ceramic for the immobilisation of radionuclides, it is crucial to have a good understanding of where in the crystalline structure the active nuclei will be incorporated. Whether an active nucleus resides on a lattice site or interstitial position, and how it partitions across the various available sites will profoundly affect the response of the structure to radiation, as well as the timescale of retention of active nuclei within the crystalline matrix, when it is exposed to groundwater in a repository environment. Ce (IV) can be implemented as a non-radioactive analogue of Pu (IV) (ionic radii: 0.97 Å and 0.96 Å respectively), thus removing the complications associated with working with radioactive nuclei. A 10% waste loading is typically employed. If Ce is added to a 3+/4+ pyrochlore such as $Nd_2Zr_2O_7$, it is necessary to balance the additional 4+ charge by, for example, placing an equal proportion of a 3+ cation on the pyrochlore B site. This 3+ cation must be sufficiently small, so as not to migrate preferentially to the A site. Suitable candidates for zirconate pyrochlore (ionic radius of 6 coordinate $Zr^{4+} = 0.72$ Å) are Sc^{3+} (0.745 Å), Fe^{3+} (0.645 Å) and In^{3+} (0.8 Å). Because of its large size, Ce might be expected to be incorporated onto the pyrochlore A site, but if

Ce is found to reside preferentially on the B site instead (because of its 4+ oxidation state), the retention of waste actinides within the structure over time may vary considerably. The literature suggests that that position of Ce or Pu cations within the pyrochlore structure varies, depending on the other elements making up the composition.

Information the disorder of four elements across the two cation sites in pyrochlore cannot be obtained by Rietveld refinement of a single (e.g. neutron) powder diffraction pattern alone. Resonant scattering using synchrotron X-rays should yield this information.

Experimental results

Oxides with nominal composition $\text{Nd}_{1.8}\text{Ce}_{0.2}\text{Zr}_{1.8}\text{M}_{0.2}\text{O}_7$, where $\text{M} = \text{Sc}, \text{Fe}, \text{In}$ were fabricated using a mixed-metal-oxide method. In all cases, a pyrochlore phase was observed by powder X-ray and TOF neutron diffraction.

The resonant X-ray powder diffraction experiments on the Sc-, Fe- and In- bearing samples were planned to determine the occupancies of up to four elements on each of the two cation sites. Due to the allocated time and the necessity of changing the setup for every edge, only two samples (In and Sc) were selected to examine up to three different edges within this experiment. In particular, the Ce and In edges were explored in the In sample and the Ce, In and Zr edges in the Sc sample. In addition, offedge patterns were collected in both cases. Some experimental results for the Sc sample are showed in the figure 1.

The anomalous scattering factors for the different edges were obtained *in situ* by means of the fluorescence energy scans and the software *Chooch*. The f' and f'' values are used to determine the structure using the Rietveld method, but refining the occupancies of the Ce and M sites in this case. This work is currently in progress.

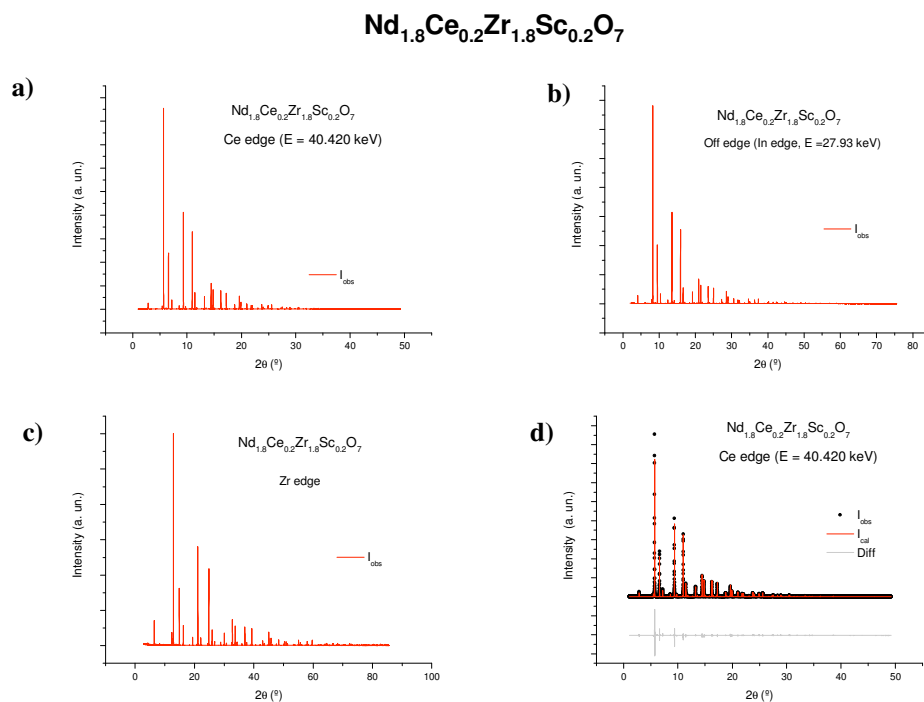


Figure 1 Experimental results on the $\text{Nd}_{1.8}\text{Ce}_{0.2}\text{Zr}_{1.8}\text{Sc}_{0.2}\text{O}_7$ compound at different energies (different edges): a) Ce edge ($E=40.42$ keV), b) Offedge ($E=27.93$ keV) and c) Zr edge. The best Rietveld refinement in the Ce edge before considering anomalous scattering factors is showed in d).

Apart from the structural information gained by means of the Rietveld refinement in both samples, additional information is to be obtained from the analysis of the absorption spectra around the edge (EXAFS signal). The absorption spectra, although initially obtained for determining the f'' and f''' values, were extended up to the maximum possible energy in order to perform qualitative EXAFS analysis. In this sense energies up to 41.2 keV could be reached during the Ce edge scanning with an acceptable noise-signal ratio. The following XAS spectra were collected: Ce and Zr edges in Sc sample and Ce and In edges in In sample. Some relevant absorption spectra together with the extracted EXAFS signal and the corresponding Fourier transforms are shown in figure 2.

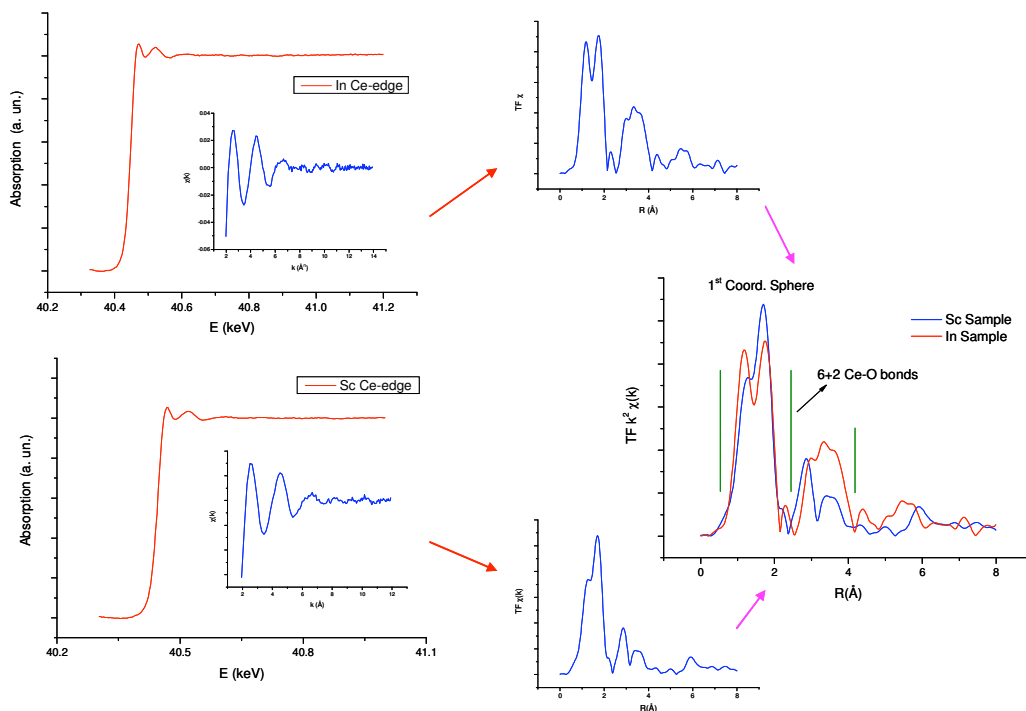


Figure 2 XAS spectra of the $Nd_{1.8}Ce_{0.2}Zr_{1.8}Sc_{0.2}O_7$ and $Nd_{1.8}Ce_{0.2}Zr_{1.8}In_{0.2}O_7$ compounds at the Ce-edge. Note that ,beyond the first shell, the Fourier transforms of the EXAFS signal show abrupt differences in the second coordination sphere (between 2.5 and 4.5 Å) related to the variable Ce neighbourhood.

Preliminary diffraction results agree with structural information (Ce-O bond distances) from the EXAFS analysis in our samples. Moreover, additional information about the different site occupancies is expected from the work in progress. In this sense, this analysis is delicate since special attention must be paid to the background subtraction for obtaining the EXAFS signal. On the other hand, some qualitative information can be derived from these spectra at this stage, just considering the difference in the intensities of the second coordination sphere. These differences are directly related to the variable Ce environment in both samples. In particular, the three contributions under the second coordination sphere correspond to the Ce-Nd and Ce-Zr bonds at 3.76 Å. In addition, some multiple scattering contributions in the 3.90 Å - 3.94 Å range are overlapped to these signals, so the analysis is again quite delicate, even considering the important intensity difference between both, In and Sc samples, in this region. Nevertheless, a detailed analysis is currently being performed, and the definitive results will be ready in the near future.