Pyrochlore – a promising host phase for actinide immobilisation

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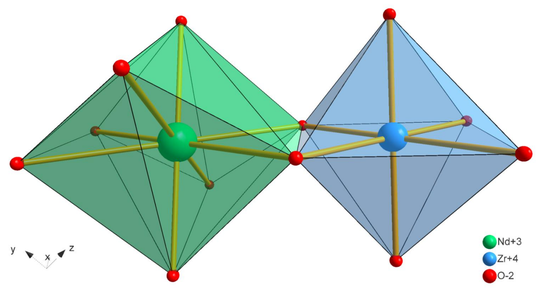


Coordination polyhedra in the pyrochlore crystal structure:
- Eightfold coordination of A^{3+} cation by a scalenohedron.
- Sixfold coordination of B^{4+} cation by a trigonal anti-prism.

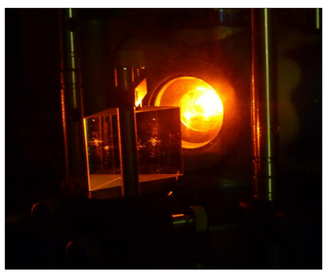
Background: Zirconate based pyrochlores ($A_2B_2X_6Y$) seem to be very promising materials as high-level nuclear waste forms for the MA (Np, Am, Cm) and plutonium. They exhibit high aqueous durability and a high radiation resistance. Radiation damages are expected to cause an order to disorder transition[1], i.e. a transformation of the pyrochlore structure to the defect fluorite structure is expected.

Objectives:
- Identification of structural sites of Ln^{3+}/An^{3+} within the crystal structures.
- Distinction between the species of the defect fluorite and the pyrochlore crystal structure by TRLFS.
- Synthesis of pyrochlores with Pu as major component.

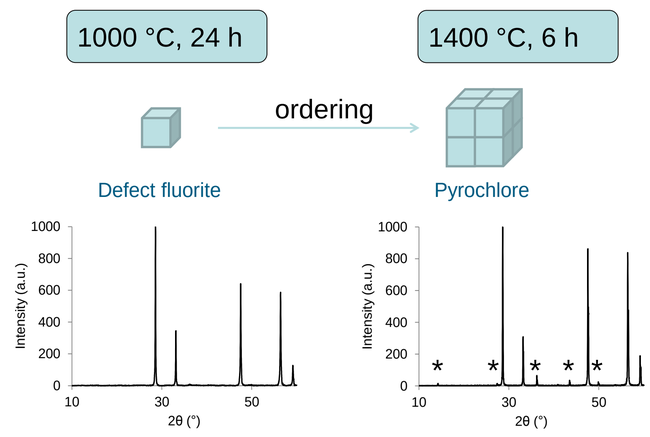
TRLFS studies on $La_2Zr_2O_7$

- Insight into the structural environment of MA within the pyrochlore and defect fluorite crystal structure.
- Samples were doped with 1000 ppm Eu and 2 ppm ^{248}Cm respectively.
- TRLFS: pulsed (20 Hz) XeCl-excimer laser (Lambda Physics, EMG, 308 nm) pumped dye laser (Lambda Scanmate).

- UV excitation: QUI.
  Direct excitation:
  Rhodamine 6G → Eu.
  Rhodamine B → Cm.

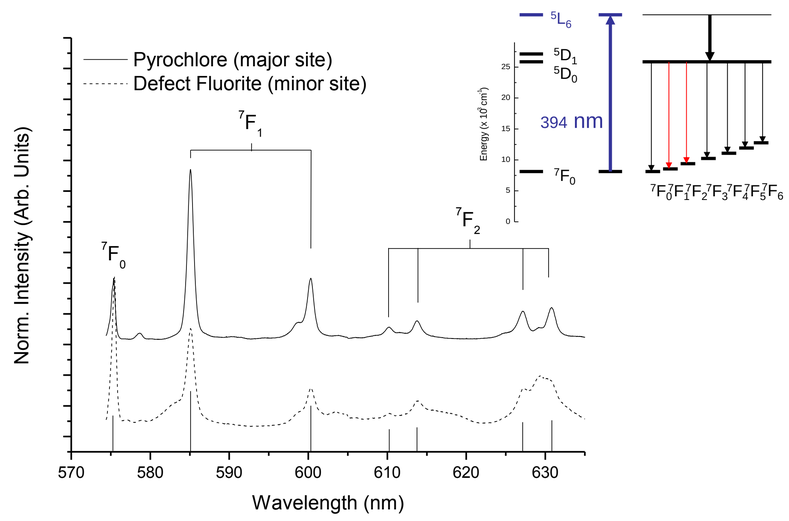


- Synthesis via coprecipitation according to Chen[2].
- Crystallisation took place during sintering



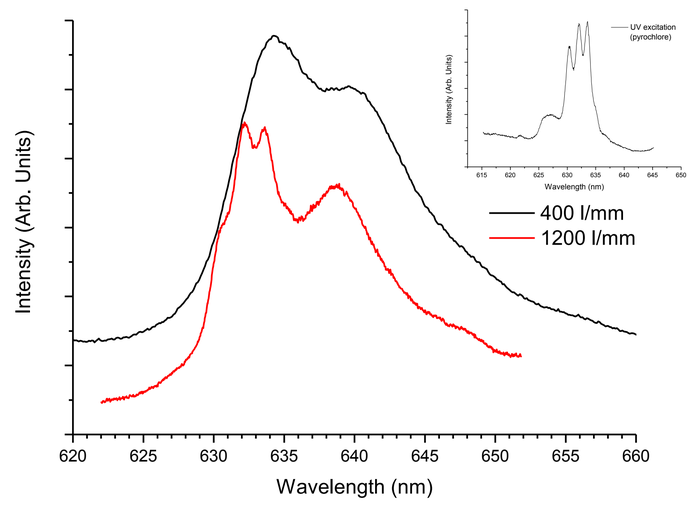
Superstructural reflexes of pyrochlore are marked with asterisks.

Emission spectra after direct excitation of Eu to the $^5D_0$ band.



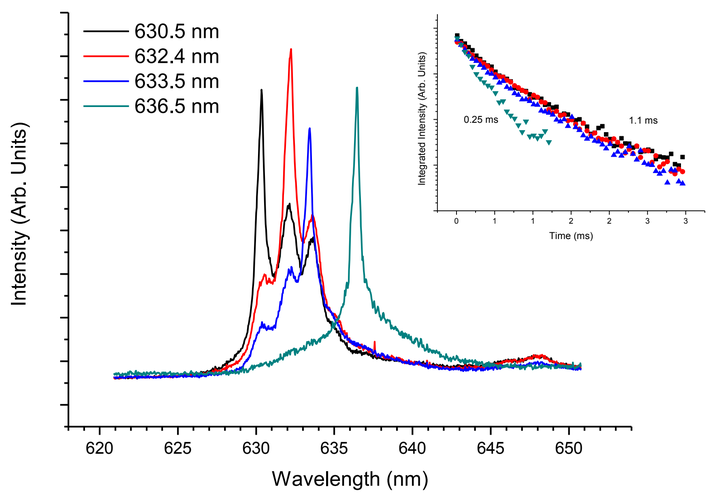
→ Minor species in the defect fluorite structure has already adopted pyrochlore environment.
→ Expected splitting for D_{3d} symmetry within the pyrochlore structure[3].

UV excitation (396.6 nm) spectra of Cm doped $La_2Zr_2O_7$.



→ Spectrum shows an extreme bathochromic shift.
→ Two Cm species are present.

Emission spectra after direct excitation of Cm to the $^6D_{7/2}$ band.



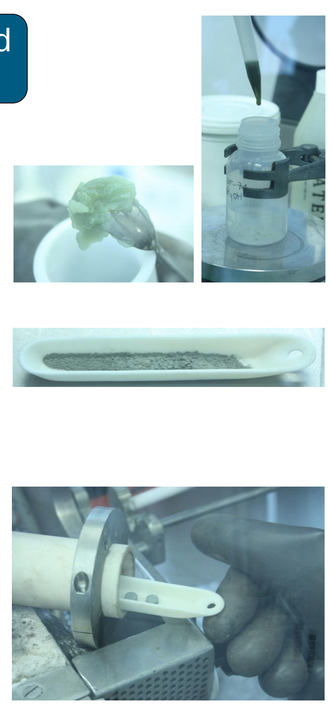
→ Triplet (630.5 – 633.5 nm) is caused by the minor species.
→ Broad peak at 639 nm (UV excitation) consists of a multitude of peaks.
→ Major species in the defect fluorite structure is poorly defined due to the random nature of the oxygen vacancies.

Conclusions from TRLFS

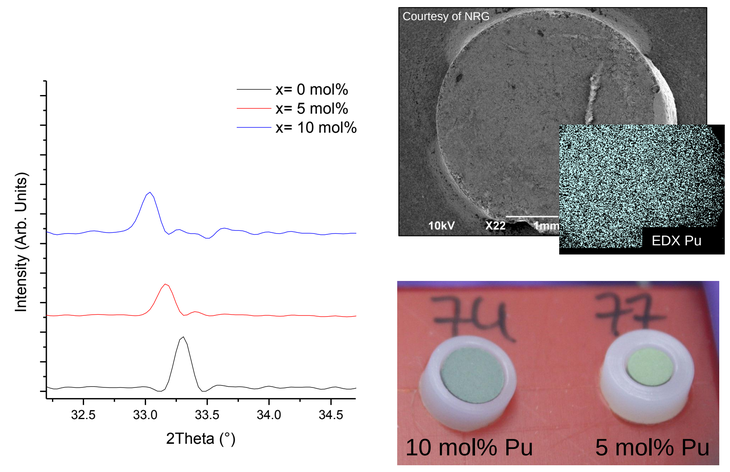
- Minor species with pyrochlore environment was determined in the defect fluorite structure and vice versa.
- Two non-equivalent sites for the trivalent dopants were found in both structures.
  → TRLFS may be used in future studies to quantify radiation damage.
- Cm and Eu occupy regular positions within the crystal structures.
  → Coprecipitation is a suitable synthesis route for An doped pyrochlores and is applied to synthesis pyrochlores with Pu as major component.

Fabrication of Pu-pyrochlore

Coprecipitation of Pu-, Nd- and Zr-hydroxides in NH_4OH
↓
Washing steps
↓
Calcination: 2 h, 600 °C Ar-5% H_2 atmosphere
↓
Pellet fabrication
↓
Sintering: 80 h, 1450 °C Ar-5% H_2 atmosphere



Characterisation by XRD, SEM & EDX



→ Shift of (400) reflex in the XRD pattern for $Nd_{2-x}Pu_xZr_2O_7$ indicates structural uptake of Pu. However, additional PuO_2 presence cannot be excluded by XRD.
→ EDX mapping shows homogeneous distribution of Pu within the whole pellet.

Conclusion & Outlook for Pu-pyrochlore

- Coprecipitation was applied to Pu-pyrochlores.
- XRD, SEM & EDX indicate the structural uptake of Pu within the pyrochlore structure.
- Pu is expected to be reduced to Pu(III) during sintering and to occupy the eightfold coordinated A position within the pyrochlore crystal structure.
- XANES will help to identify the valence state of Pu and the cationic position within the pyrochlore crystal structure.
- EXAFS will determine Pu-O bond length and provide further information about the cationic position of the Pu within the pyrochlore.
- After complete characterisation the dissolution kinetics of the Pu pyrochlores will be studied.

References:
[1] Sickafus, K.E. et al. (2007) Nature Mater. 6, 217. [2] Chen, H. et al. (2009) J. Alloys Compd. 480, 843. [3] Hirayama, M. et al. (2008) J. Lumin. 128, 1819. [4] Holliday, K.S. et al. (2013) J. Nucl. Mat., 433, 479.

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