

AnO₂ Nanocrystals via Hydrothermal Decomposition of Actinide Oxalates

Olaf Walter, Karin Popa, Luca Balice, Oliver Dieste Blanco, Philippe E. Raison, Laura Martel, Mohamed Naji, and Marco Cologne

European Commission, Joint Research Centre, Directorate G - Nuclear Safety and Security
P.O. Box 2340, D-76125 Karlsruhe, Germany
olaf.walter@ec.europa.eu

Abstract - We have recently proposed the hydrothermal decomposition of An^{IV}-oxalates as a simple access to produce highly crystalline, reactive actinide oxide nanocrystals. The method could be easily applied at low temperature (95-250 °C) in order to produce highly crystalline nano-AnO₂ (An= Th, U, Np, Pu). The size and shape of the crystals, together with their increased reactivity, enables the consolidation of homogeneous nanostructured mixed oxides as intermediates toward very dense nuclear fuels for advanced reactors. Spark plasma sintering studies indicates that such nanopowders have increased sinterability compared to powders obtained by conventional thermal decomposition of An^{IV}-oxalates.

We have studied the formation conditions, stability, and thermal expansion of AnO₂ (An= Th, U, Np, and Pu). U_{1-x}Th_xO₂ solid solutions have been produced under similar conditions by hydrothermal treatment of U_{1-x}Th_x(C₂O₄)₂ × n H₂O obtained from oxalate co-precipitation. Ongoing experiments are aimed to show the validity of the method towards associate tri-, or even tetra-component associate solid solutions.

The involvement of the water molecules in the oxalate hydrothermal decomposition mechanism has been proven by studying the isotopic exchange reaction during the thermal decomposition of An(C₂O₄)₂ × n H₂O in H₂¹⁷O through MAS-NMR and Raman techniques.

Keywords: actinide dioxide, nanocrystals, hydrothermal, pellets

1. Introduction

Nanocrystals (NC's) represent fundamental building blocks in nanoscience and nanotechnology because of their size and shape dependent properties and have attracted high interest. Much has been published on nanomaterials with stable elements. Due to the radioactive nature of the actinides combined with safety issues and restrictions in handling as well as reduced availability and difficult access in case for the trans-uranium elements, less is published on actinide nanoparticles, and then practically all on actinide dioxides (AnO₂).

The synthesis of NC's in hot compressed water under hydrothermal conditions or other solvents is today well known and established. The production of NC's in continuous flow reactors is applied successfully. However, for the synthesis of AnO₂ NC's under hydrothermal decomposition and the characterisation of the obtained NC's only our first report exists in the literature up to now [1] even if nanocrystalline AnO₂ is already objective of the research at our institute since several years [2 – 10].

In this contribution we extend our first report on the synthesis and characterisation of AnO₂ NC's formed under hydrothermal decomposition of An(C₂O₄)₂ × n H₂O in batch reactors towards the actinide series Th, U, Np, Pu including the synthesis of mixed oxides plus the first results obtained from pellets produced from ThO₂ or UO₂.

2. Results and discussion

As can be seen from the XRD data shown in Fig. 1, nanoparticles are formed in all cases; EELS analyses proved clearly the purity of the actinide in the AnO₂ NC's. From the shifts in the peak position in fig.1 one can easily deduce that the cell parameters of the cubic cell with a = 5.47 Å for UO_{2(+x)} go to smaller values over Np to Pu whereas for ThO₂ the cell length are with 5.60 Å longer. The particle sizes can be calculated from the XRD data based each on the full width at half maximum

for at least six selected peaks in the 2θ range between 25 and 100° . They have been determined to $7.2(1.0)$ nm for ThO_2 , $13.8(1.2)$ nm for UO_2 , $9.6(1.8)$ for NpO_2 , and $3.7(1)$ nm for the PuO_2 nanoparticles, respectively.

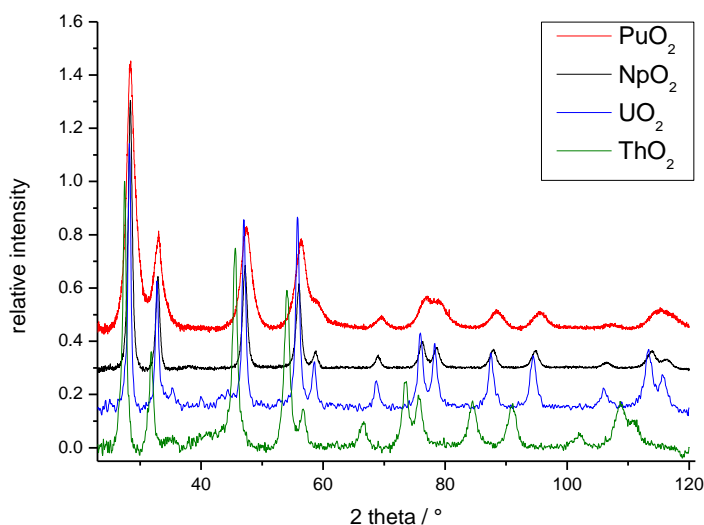


Fig. 1: powder xrd of the AnO_2 comparison from Th (bottom) to Pu (top).

Concerning the reactivity in the particle formation we concluded that it increases from Th to Pu, i.e. ThO_2 NC's can only be obtained at reaction temperatures of 250°C , UO_2 NC's are nicely formed at temperatures above 150°C , for the formation of the NpO_2 NC's a temperature of 170°C was applied (it is not optimised), but the PuO_2 NC's are already formed at 95°C (but the reaction takes several days). Due to the low temperature decomposition, the size of the PuO_2 NC's is smallest, which can be derived obviously from the increased line broadening in Fig. 1. In the case of the UO_2 NC's it turned out that it is of real advantage to work under oxygen free conditions as otherwise (especially at low temperatures and long reaction times) oxidation of the U^{IV} to $\text{UO}_2(\text{OH})_2$ or U_4O_9 might proceed. Furthermore, it is essential, in order to control the size of the UO_2 NC's, to work in a non-oxidising environment.

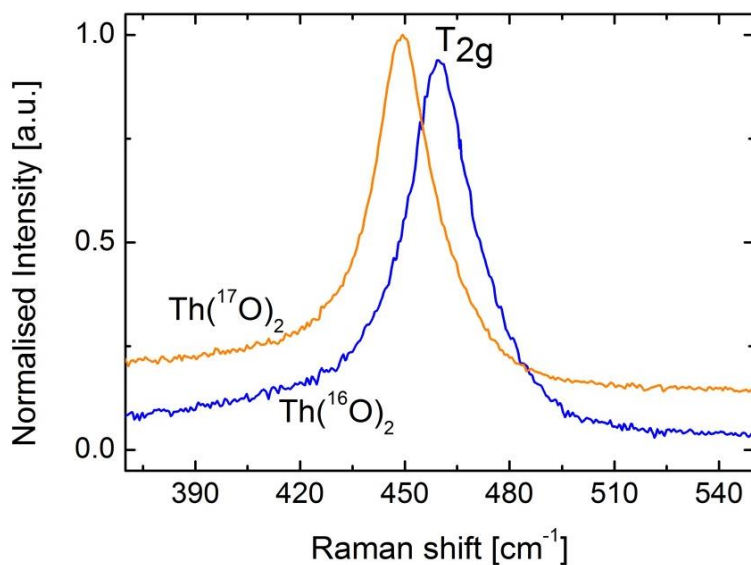


Fig. 2: comparison of Raman spectra of Th^{16}O_2 and Th^{17}O_2 , obtained by thermal decomposition of $\text{Th}(\text{oxalate})_2 \times 2 \text{H}_2\text{O}$ in H_2^{17}O .

We were interested on the mechanism of the particle formation. So when the thermal decomposition of the $U(C_2O_4)_2 \times 6 H_2O$ is carried in the absence of water at $250^\circ C$ over 3 h no particles are formed at all, only an amorphous material is obtained. However in the small reactor used by us already the amount of water present in the oxalate itself is sufficiently high to promote the formation of nanocrystalline UO_2 from $U(C_2O_4)_2 \times 6 H_2O$ at $250^\circ C$.

In order to explore the role of the water more in detail we performed an experiment for the thermal decomposition of $Th(C_2O_4)_2 \times 2 H_2O$ in with more than 98% enriched $H_2^{17}O$ and analysed the product then via Raman spectroscopy and compared it the product obtained in normal water (fig. 2). It can be seen that performing the thermal decomposition reaction leads to a practically complete replacement of all ^{16}O atoms in the ThO_2 formed by ^{17}O resulting in a Raman shift of the Th-O stretching vibration of $8-9\text{ cm}^{-1}$ from 458 to 450 cm^{-1} . However, more detailed information on the mechanism of the thermal decomposition of $An(C_2O_4)_2 \times n H_2O$ in water cannot be taken at the present stage of our research, but it is evident that water is involved in the reaction and that exchange takes accordingly place.

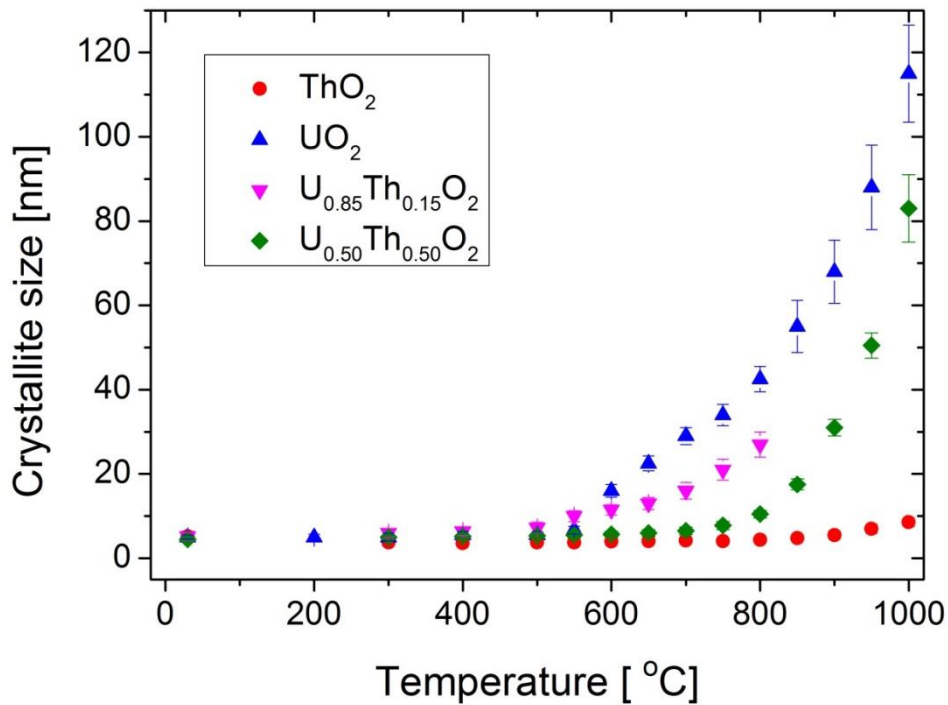


Fig. 3: results from high temperature XRD measurements, crystallite size as function of temperature.

NC's offer the possibility to studying the sintering behaviour of AnO_2 in more details e.g. the growth of the particles as a function of temperature. This examination contributes to our knowledge on how fast particles can change their shape in a nuclear fuel where easily temperatures $1500^\circ C$ are reached in the core of the fuel. Especially when the particles are small significant growth can be detected already at much lower temperatures. This behaviour is exactly found as well for the here presented AnO_2 NC's (fig. 3). In Fig. 3 the particle size of $U_{1-x}Th_xO_2$ NC's of a starting size of ca 5-6 nm is shown as a function of temperature. In the row for $x = 0$ to 1 a noteworthy decrease in the particle size at each given temperature can be observed giving evidence for strongly reduced sintering properties for ThO_2 compared to UO_2 . However the mixed oxides show much higher particles growth than the pure ThO_2 . For a nuclear fuel excellent sintering properties are of advantage as then the fuel production in form of dense pellets becomes easier.

3. Experimental

All work has been carried out at the JRC-KA in certified laboratories with the licence for handling the radioisotopes of Th, U, Np, Pu with respect to the German radioprotection regulations. Experimental details are extensively reported in [1]. More details will follow in a more extended full paper. XRD analyses were performed on a Rigaku Miniflex 600

diffractometer for the obtained ThO₂ and UO₂ NC's, whereas the PuO₂ NC's have been analysed on a Bruker D8 diffractometer equipped with a LinxEye position sensitive detector. Transmission electron microscope analyses (TEM) performed on a TecnaiG2 (FEI™) 200 kV microscope equipped with field emission gun, modified during its construction to enable the examination of radioactive samples. The TecnaiG2 TEM is equipped with a Gatan™ Tridiem GIF camera, an energy dispersive X-ray (EDX) analysis system, and a high-angle annular dark-field (HAADF) detector for the scanning transmission electron microscope (STEM) imaging. The elemental analysis of the sample during the TEM study was performed using Electron Energy Loss Spectroscopy (EELS). Raman spectroscopic measurements were performed at room temperature with a Horiba Jobin-Yvon T64000 spectrometer at 647 nm.

4. Conclusion

We present an effective and easy access to small NC's of AnO₂ (size less than 10 nm) on a preparative scale by the hydrothermal decomposition of An(C₂O₄)₂ × n H₂O at temperature lower than 250 °C. The process exhibits the potential for scale-up. At these low temperatures NC's of the corresponding AnO₂ are formed. We are convinced that our approach exhibits a key step forward to the examination of the size dependence of AnO₂ physical properties as it is applicable to the minor actinides Th, U, Np, Pu and even mixed oxides can be produced like shown here for U_{1-x}Th_xO₂.

The results from these investigations will contribute directly to the safety of the nuclear materials in nuclear fuels.

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