Experimental report

05/02/2020

Proposal: CRG-2680 **Council:** 4/2019

Title: Understanding phase separation complex sub-stoichiometric oxidesapplication to in (U1-yPuy)O2-x

Research area:

This proposal is a new proposal

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Samples: U0.54Ce0.46O1.94

Instrument	Requested days	Allocated days	From	To
D1B	2	2	27/01/2020	29/01/2020

Abstract:

Report on the CRG-2680 proposal

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Mixed Plutonium-uranium OXides (MOX) are commonly used as fuels in pressurized water reactors. They also constitute reference fuels for fast breeder reactor applications. As a result of the manufacturing process, these mixed oxides can be hypo-stoichiometric in which case they exhibit a phase separation at low temperature (below 1000K)which has been reported many times in the past [1,2]. It appears essential to characterize and understand it both for its implications in terms of fuel behavior and to gain a basic understanding of these systems

Results:

The aim of this ILL experiment (2680-CRG) on D1B, was to gain insight into the nature and the temperature dependence of the phase transition. We collected two diffraction patterns at room temperature and at 773K

Figure 1a displays the comparison between the experimental and the refined neutron diffraction patterns collected at room temperature on an $U_{0.56}Ce_{0.44}O_{1.933}$ sample. As pointed out by previous authors [2,3] from the analysis of X-ray diffraction patterns, two distinct phases exist at room temperature:

- the stochiometric $U_{0.56}Ce_{0.44}O_2$ phase associated with the Fm-3m space group
- a hypo-stochiometric $U_{0.56}Ce_{0.44}O_{1.91}$ phase assumed before this work began to be also associated with the Fm-3m space group but exhibiting a a-3 symmetry according to [3].

From the results of the Rietveld refinement of neutron patterns collected on D1b, it was possible to confirm that the space group of the hypo-stochiometric phase at room temperature (figure 1b) is Ia-3 and not Fm-3m as previously claimed. As shown in figure 1b, cerium atoms (in yellow) preferentially occupy 24d Wyckoff positions in the hypo-stochiometric $U_{0.56}Ce_{0.44}O_{1.91}$ phase thus demonstrating that the space group of this phase can not be Fm-3m as previously claimed. The good values of the Bragg reliability and weighted profile factors (Rwp=3% and 6.8% respectively) illustrate the quality of the refinement.

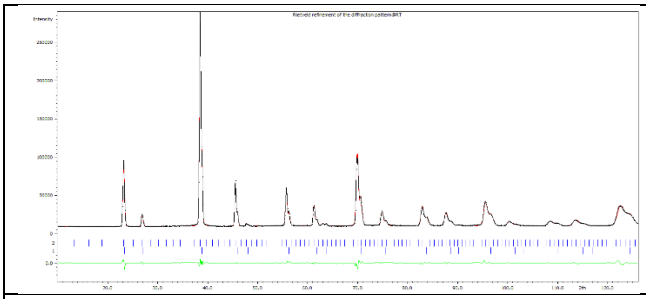

Fig1a: Comparison between experimental and refined neutron diffraction patterns collected at room temperature on D1B
(R_B=2% for the Fm-3m $U_{0.56}Ce_{0.44}O_2$ phase and R_B=3% for the hypo-stochiometric Ia-3 $U_{0.54}Ce_{0.44}O_{1.91}$ phase)

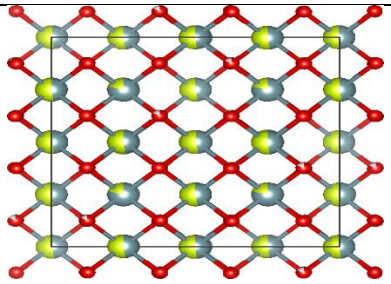

Fig1b: Crystalline structure of the hypo-stochiometric phase obtained from the Rietveld refinement of the neutron diffraction pattern collected on D1b. This figure illustrates the preferential occupancy of Ce atoms for 8b Wyckoff sites which appear in yellow.

To investigate further the effect of temperature on the stability of the hypo-stoichiometric phase, neutron diffraction patterns were collected on D1b at temperatures ranging from room temperature to 773K. Figure 2 displays the evolution of the unit cell parameters of the stoichiometric Fm-3m phase $U_{0.56}Ce_{0.44}O_2$ (black squares) and the Ia-3 hypo stoichiometric $U_{0.56}Ce_{0.44}O_{1.91}$ phase as a function of temperature from the analysis of Rietveld refinements (Refinements were performed with the Jana06 package. R_B and R_{wp} reliability factors were always less than 5% and 10% thus guaranteeing the accuracy of refinements.)

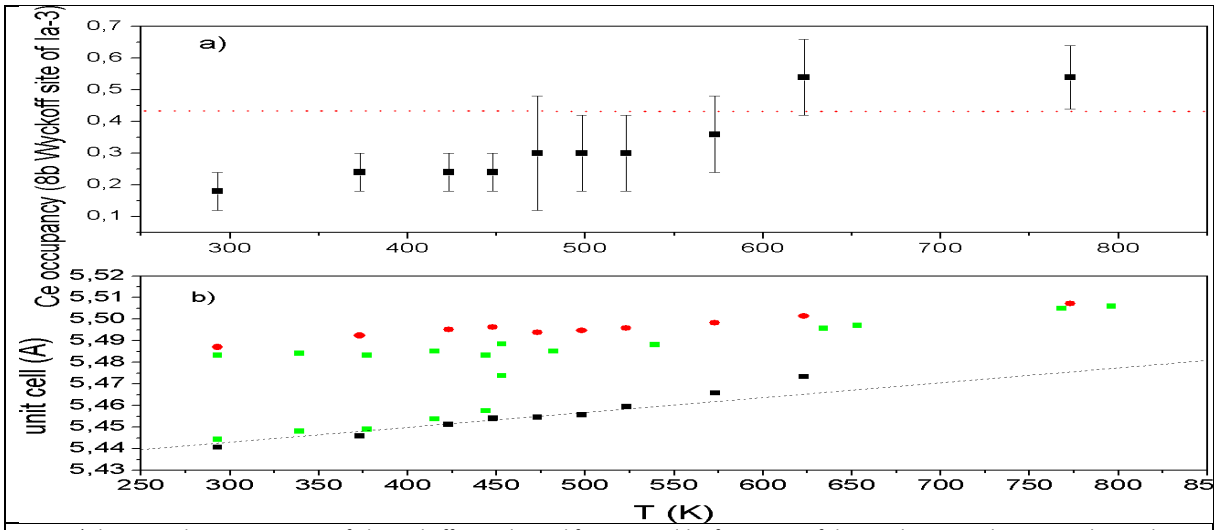

Fig2 : a)Change in the Ce occupancy of 8b Wyckoff sites derived from Rietveld refinements of the Ia-3 hypo-stoichiometric phase. The Ce occupancy value of 0.46 (red line) is the assumed average Ce content of the hypo-stoichiometric phase (Fm-3m).

b) Comparison between unit cell parameters of the hypo-stoichiometric Ia3 phase (red circles) and the stoichiometric Fm-3m phase (black squares) at all temperatures studied (the dotted is a fit through unit cell parameter values of the $U_{0.56}Ce_{0.44}O_2$ Fm-3m phase). The unit cell parameter values for the two phases (for a similar overall oxygen content) reported in the literature [1,2] are also plotted (green squares).

The neutron diffraction patterns collected on D1B (l=1.28A) shown in figure 3 indicate that the transformation is not complete at 470K as claimed by previous authors [1,2].

Summary of results

Results obtained from the analysis of neutron diffraction patterns collected on a $U_{0.56}Ce_{0.44}O_{1.933}$ sample using the D1b diffractometer indicates that:

- The space group of the hypo-stoichiometric phase is Ia-3 at room temperature. This result is at odds with those based on the analysis of x-ray diffraction for which the authors assume both phases are fluorite [1,2].
- A phase transition occurs in this material at a temperature between 600 and 800K. This result disagrees with previously published data pointing to a transition between the two phase to the single fluorite phase region at around 473K (see green squares in figure 1b).
- The space group of the hypo-stoichiometric phase becomes Fm-3m at 773K when the transformation is complete.

Prospects for a future proposal:

Experimental data (unit cell parameter variations, changes in volume fractions of different phases, cation and oxygen occupancies) resulting from the refinement of neutron diffraction patterns are key to understanding this phase transformation within the framework of phase transitions

In order to identify the phase transformation occurring in this material unequivocally, we propose:

- To verify the space group of super-structures associated with oxygen displacements by collecting a high resolution diffraction pattern on D2B (easy access request)
- to determine whether there exists a hysteresis from the analysis of diffraction patterns collected at different temperatures during the heating and cooling. (2 days requested using the D1b facility). The results we have obtained during this preliminary experiment require being completed so that the temperature transitions may be identified unequivocally.

Bibliography :

[1] Markin T., Crouch E., J. of Inorg. Chem., 1970, 32,77-82

[2] Lorenzelli R., Touzelin B., J of Nucl Mat 1980, 95, 290-302

[3] Simeone D., Garcia P., Miard A., Baldinozzi G., Porcher F., J.F. Berar, J. of Inorg. Chem., 2019, 58(17),11599-11605