Cation-driven phase separation in internally gelated $(U,Ce)O_{2-x}$ microspheres

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Introduction

Recently Schreinemachers et al. [1] studied calcined and sintered $U_{1-y}Ce_yO_{2-x}$ microspheres (MS) fabricated via internal gelation (IG) with nominal Ce molar metal fractions, χ(Ce), of up to 30 mol%. Sintered IGMS with nominal χ(Ce)={20 mol%, 25 mol% and 30 mol%} were observed to exhibit phase separation at ambient temperature based on X-ray diffraction (XRD) results which were fitted well to two fcc phases with differing Ce content. MS obtained via IG of Uranyl Nitrate and Ce-Nitrate precursor mixtures are generally expected to have homogeneous cation distribution. Given metal (M) cation homogeneity, the literature consensus has long been that for y>~0.2 and moderate hypo-stoichiometry, two fcc phases, $MO_{2.00}$ and MO_{2-x}, are formed due to a miscibility gap below a critical temperature. While possible oxygen hypo-stoichiometry due to the sintering conditions was yet to be ruled out, the results obtained in [1] called for further characterization of the original material. Unexpected observations were made.

Objectives

- **Duplicate thermal treatment in [1] on stored, cured and dried material to obtain additional as-sintered IGMS for present work**
- **Obtain precise and accurate O/M ratios of the as-sintered batches to confirm or rule out oxygen hypo-stoichiometry.**
- **Investigate the nature of the phase separation via XRD, Electron Microprobe Analysis (EPMA) and Energy Dispersive Spectroscopy (EDS).**

Methods

Using a thermogravimetric analyzer, ~450 mg of sintered duplicate IGMS were subjected to a 12 h equilibration treatment at 800 °C using -376 kJ mol^{-1} for all $(U,Ce)O_{2-x}$, following accepted thermodynamic data. O/M ratios for as-sintered batches were determined from the O %wt. change, as shown in Figure 1.

O/M after sintering and calculated δ (2σ)			In-situ Δm		Expected O/M
Phase separation reported	Ce-precursor	χ(Ce) $_{nominal}$	O/M	δ (2σ)	
-	-	0 %	2.000	0.000	2.0001 (a)
NO	Ce(IV)	5 %	2.004	0.002	1.94 (b)
NO		10 %	2.002	0.002	
NO		15 %	2.003	0.002	
NO		20 %	2.000	0.002	
-	-	0 %	1.999	0.002	2.0001 (a)
NO	Ce(III)	5 %	1.998	0.002	1.94 (b)
NO		10 %	2.000	0.000	
NO		15 %	1.998	0.002	
YES		**20 %**	**1.998**	**0.001**	
YES		**25 %**	**2.002**	**0.001**	
YES		**30 %**	**1.997**	**0.001**	

a) Leinders et al. 2015, based on Lindemer and Bessman 1985

b) Graphically extracted from McMurray et al. 2015 Fig.5a

Figure 1: As-sintered O/M ratios obtained via TG for duplicated IGMS

XRD patterns and LPs were obtained on crushed material. Equilibrated and intact IGMS were pressed into Ag pellets and polished to reveal cross-sections suitable for EPMA. Ce(Lα), U(Mα), O(Kα) lines were used with 20 kV for mapping and about 10 kV for elemental quantifications.

Results

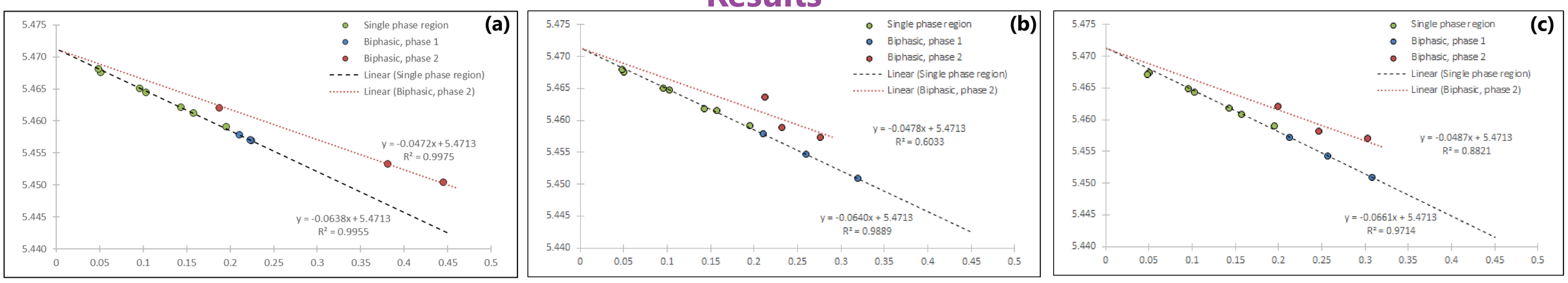
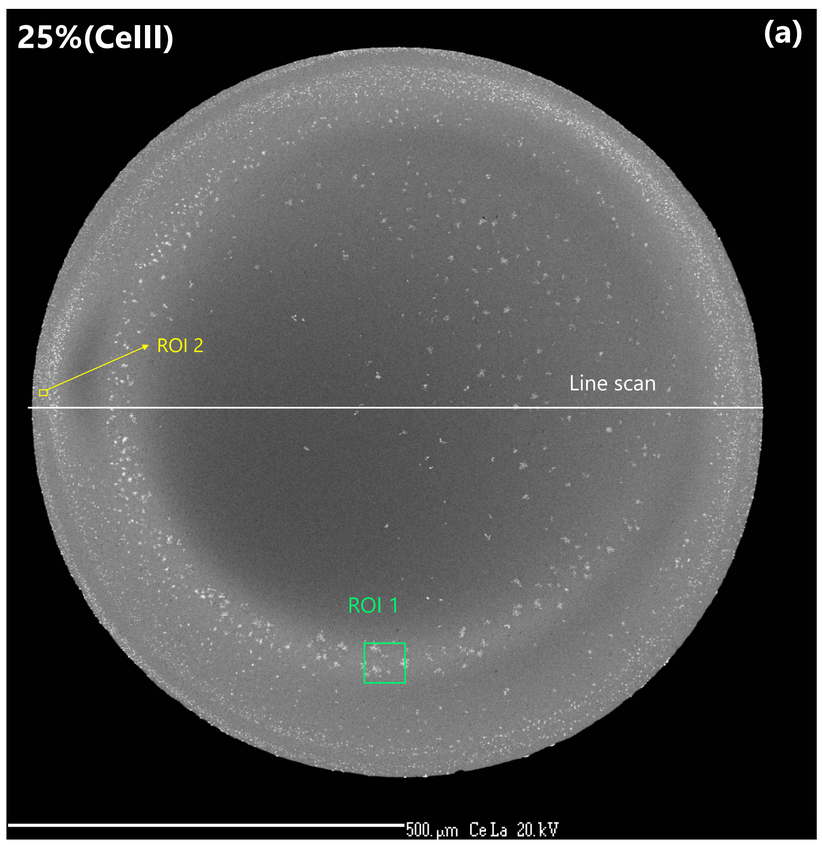


Figure 2: Obtained lattice parameters against global $\chi(Ce)_{real}$ obtained via ICP-MS. Left to right: (a) Schreinemachers et al. as-sintered (b) This work as-sintered (c) This work after 12 h of equilibration



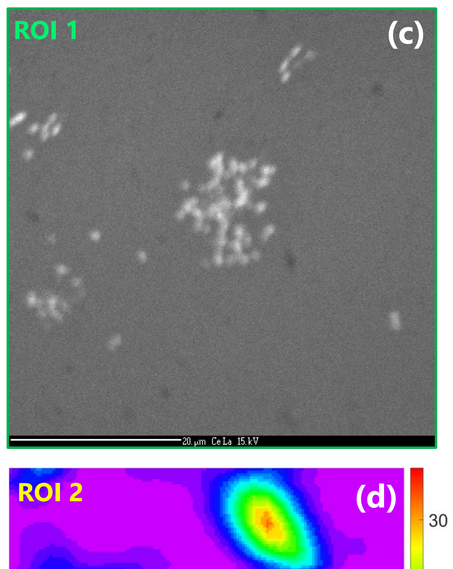


Figure 3, EPMA imaging on equilibrated IGMS cross-section (XS); $\chi(Ce)_{nominal}$=25 mol% Ce(III)-precursor batch: (a) Ce-map on whole IGMS (b) Line scan of IGMS XS given in at% (U & Ce), (c) Ce-map on ROI-1 (d) Quantitative at% (Ce) map of ROI-2

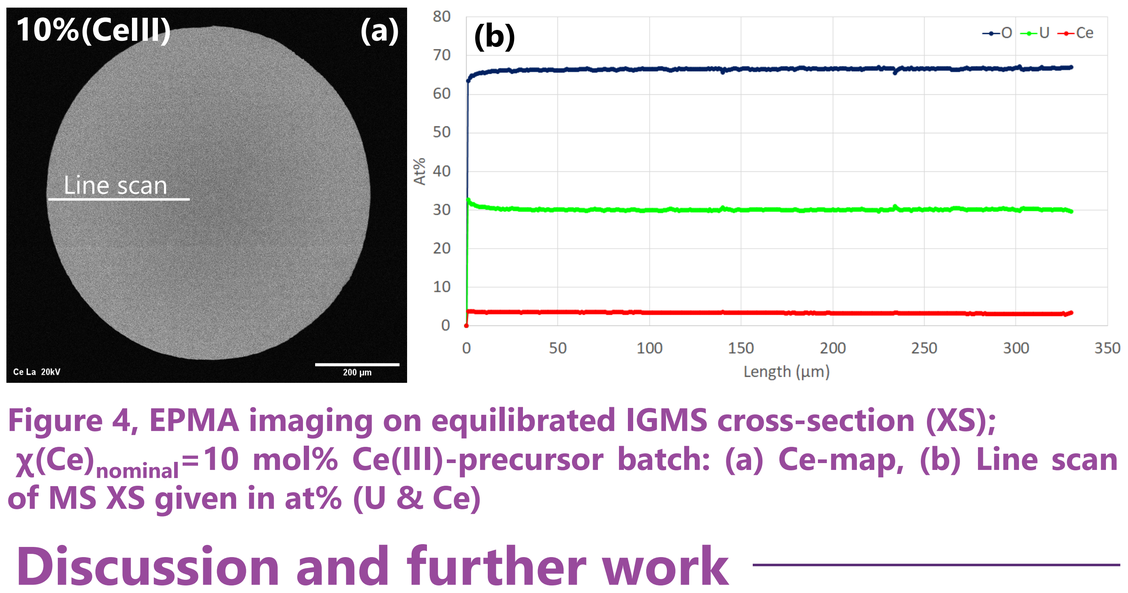


Figure 4, EPMA imaging on equilibrated IGMS cross-section (XS); $\chi(Ce)_{nominal}$=10 mol% Ce(III)-precursor batch: (a) Ce-map, (b) Line scan of MS XS given in at% (U & Ce)

Discussion and further work

- Measured as-sintered global O/M ratios at or very close to 2.00
- As-sintered LPs of single phase batches agree very well with values published in [1]. For the biphasic samples the LP of fcc_1 and fcc_2 as well as $\chi(Ce)_{fcc1}$ and $\chi(Ce)_{fcc2}$ were found to be diverging from published figures, both sets being obtained via Rietveld refinement.
- Equilibration resulted in a higher *R*-value for the linear fit of the LP of the fcc_2 phases for in this work.
- EPMA mapping and line scans on cross-sections of 12 h equilibrated IGMS with χ(CeIII)={20 mol%, 25 mol% and 30 mol%} revealed:
  - **Systematic Ce-gradients increasing from the center to the rim;**
  - **Multiple concentric wave-shaped diffuse Ce-enrichment rings;**
  - **Multiple concentric highly Ce-enriched precipitate cluster chains predominantly found on the diffuse enrichment rings.**
- Role of thermal treatment steps in Ce-segregation currently under study

[1] C. Schreinemachers, G. Leinders, G. Modolo, M. Verwerft, K. Binnemans, and T. Cardinaels, "Fabrication of Nd- and Ce-doped uranium dioxide microspheres via internal gelation," *J. Nucl. Mater.*, vol. 535, p. 152128, 2020.

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