Supporting Information

Incorporation of U(IV) in monazite-cheralite ceramics under oxidizing and inert atmospheres

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The average ionic radius of cations incorporated in the monazite-cheralite were calculated as follows:

$$\bar{r} = (1 - 2x) \times r_{Nd^{(IX)}} + x \times \left(r_{Ca^{(IX)}} + r_{U^{(IX)}}\right) \quad \textbf{(1)}$$

The different effective ionic radii used to calculate this average ionic radius, in the case of our study are reported in Table S1.

Table S1: Selected effective ionic radius, reported for Nd^{3+}, Ca^{2+} and U^{4+} in 9-fold coordination [1].

	$r_{Nd^{3+}}$ (Å)	$r_{Ca^{2+}}$ (Å)	$r_{U^{4+}}$ (Å)
CN9	1.163	1.18	1.05

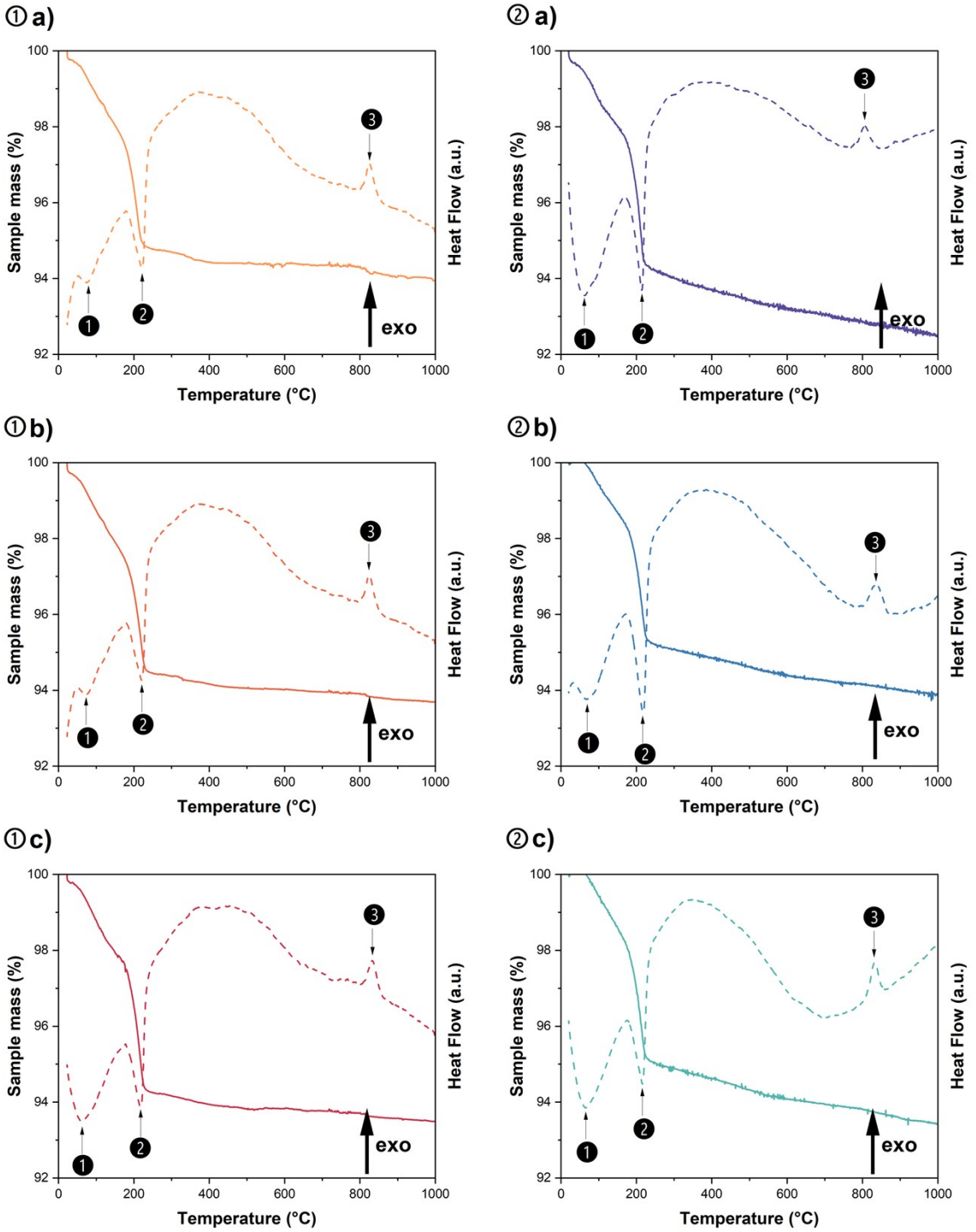

Figure S1: TG and DT scans obtained for $Nd_{0.95}Ca_{0.025}U_{0.025}PO_4{\cdot}nH_2O$ (a), $Nd_{0.9}Ca_{0.05}U_{0.05}PO_4{\cdot}nH_2O$ (b), $Nd_{0.85}Ca_{0.075}U_{0.075}PO_4{\cdot}nH_2O$ (c), converted under air ① and under argon ②.

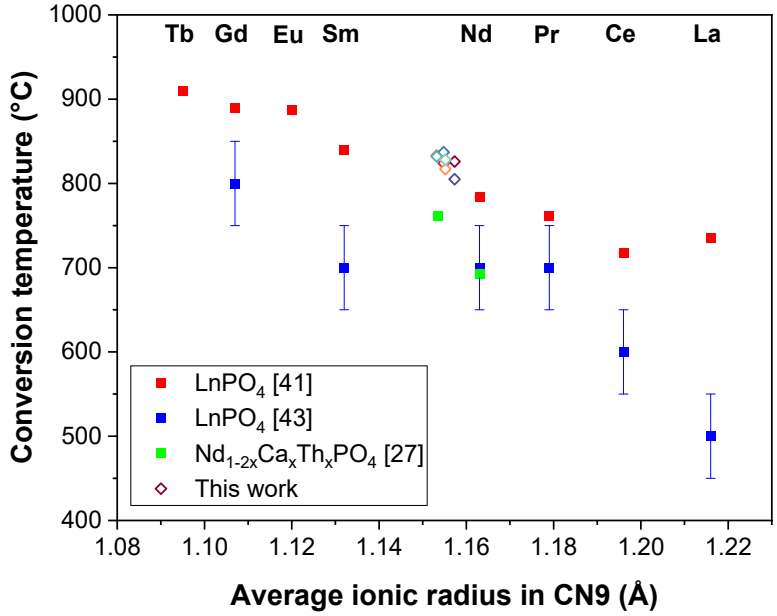

Figure S2: Variation of the temperature of phase transition from rhabdophane to monazite-cheralite solid solution as a function of the average ionic radius in CN 9. The data for the monazite end-members were extracted from Kijkowska et al. [2], Jonasson and Vance [3], the data for Th-monazite-cheralite were taken from Qin et al. [4].

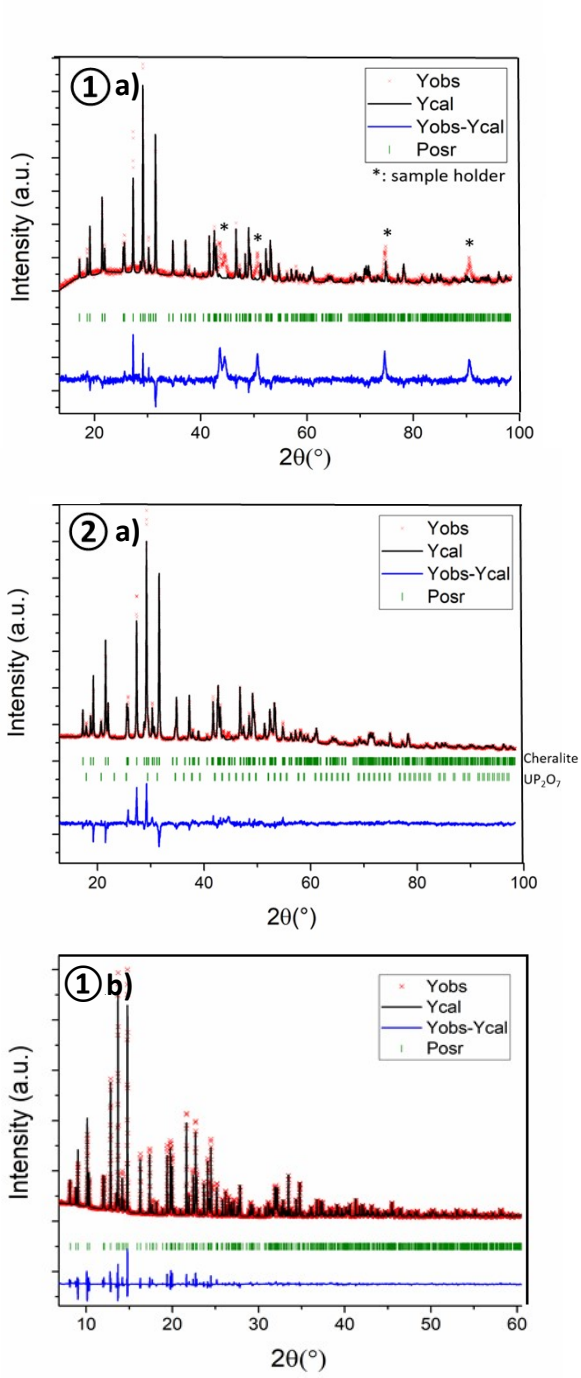

Figure S3: Rietveld refinement of PXRD (a) and SPXRD (b) of $Nd_{0.8}Ca_{0.1}U_{0.1}PO_4$ samples converted under air ① and under argon atmosphere ②.

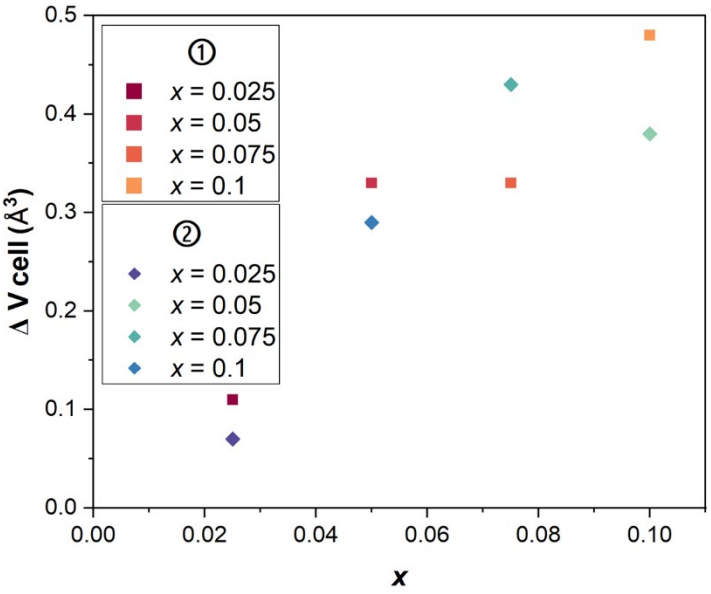

Figure S4: ΔV cell represent the difference between the experimental cell volume obtained by Rietveld refinement of PXRD diagrams of U-monazite-cheralite solid solutions $Nd_{1-2x}Ca_xU_xPO_4$ *prepared in air ① and in Ar ② with that calculated from the proportional combination of the endmembers.*

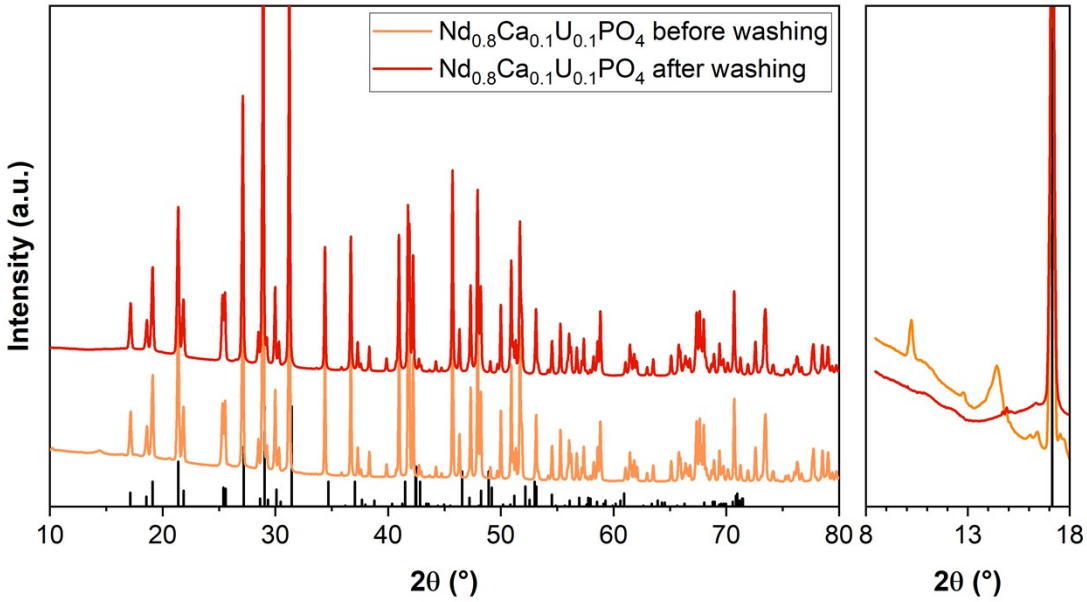

Figure S5: SPXRD patterns obtained by synchrotron analysis of $Nd_{0.8}Ca_{0.1}U_{0.1}PO_4$ converted under air at 1100 °C for 6 h. The red and orange lines represent monazite-cheralite before and after the washing step, respectively. Peaks positions of cheralite reference are taken from [6].

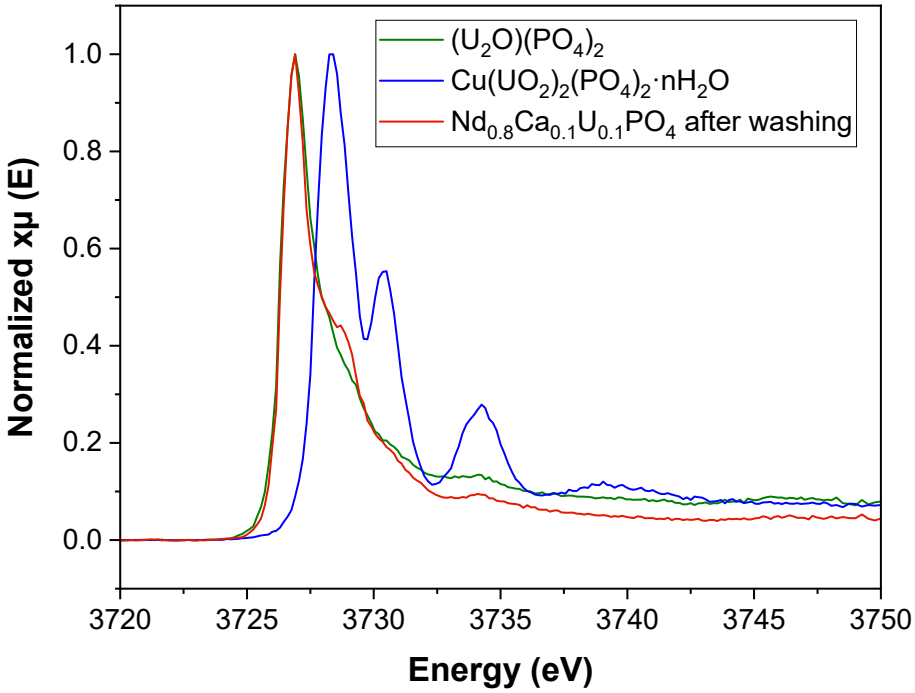

Figure S6: U M_4-edge HERFD-XANES spectrum of $Nd_{0.8}Ca_{0.1}U_{0.1}PO_4$ converted under air after washing step. Reference spectra for U(IV) and U(VI) were obtained by using $(U_2O)(PO_4)_2$ and $Cu(UO_2)_2(PO_4)_2 \cdot H_2O$, respectively.

References

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