

Structural and Microstructural Features Observed in (Ln,U)O_{2-x} Systems



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Invited talk : Monday December 2nd - EN17.04.01

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Motivation, objective

- **Oxides with fluorite (or fluorite related) structures form a large class of compounds with a high radiation tolerance.**
- **This is possibly related to those two peculiar features that are actual situations for nuclear fuels:**
- **Fuels of nuclear reactors must withstand very high radiation damage that produces local compositional fluctuations**
- **Some fission products can replace U atoms and produce aliovalent doping**
- **Radiation resistance and resilience generally involves mastering defects and mechanical stability.**
- **In this presentation we want to review some of the structural features of these systems that might be relevant for structural and mechanical properties.**



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Non-stoichiometry in fluorites

Disorder can display various features.

- The cation sites are all occupied, except possibly at temperatures approaching the melting points; also, the cations may display some relaxation from the ideal fluorite positions.
- **Metastable cation configuration** can be quenched if the annealing time / T is not enough for the system to reach equilibrium.
- The defects introduced into the lattice to account for the wide departure from the ideal composition are generally confined to the anion sublattice
- They can be either O vacancies or O interstitials
- The concentrations of such “defects” can be very large, therefore the term “defect” is misleading. **These anion defects are difficult to quench at intermediate T.**
- The structure can tolerate large numbers of cations with a coordination other than 8



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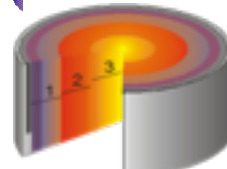
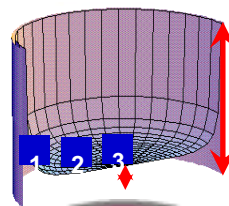


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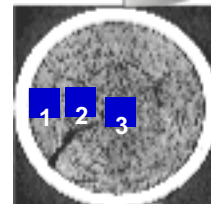
Rare Earths & Zr, Hf, Ce, and U oxides (and Mo, W)

Periodic Table of the Elements

1	2											10	11	12	13	14	15	16	17	18
H	He											Ne	Ar	Kr	Xe	Rn				
Li	Be											B	C	N	O	F	Ne			
Na	Mg											Al	Si	P	S	Cl	Ar			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr			
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe			
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn			
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og			
Lanthanides		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
Actinides		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				



1. 450 °C
2. 950 °C
3. 1150 °C

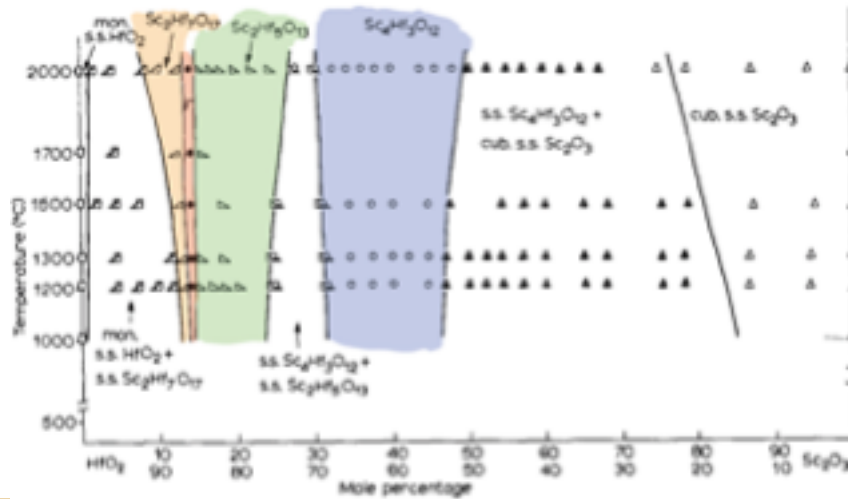


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A prototype $A^{III}_2O_3-B^{IV}O_2$ phase diagram: $Sc_2O_3-HfO_2$ ($Sc_2O_3-ZrO_2$)



Kalinovskaya et.al. Journal of the Less-Common Metals 17 (1969) 151



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The R-3 ferroelastic structures A_mO_{2m-2}

Matrix transformation:

$$\begin{bmatrix} n & \bar{1} & 0 \\ 1 & n-1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The determinant m of the matrix gives the index of the chemical formula

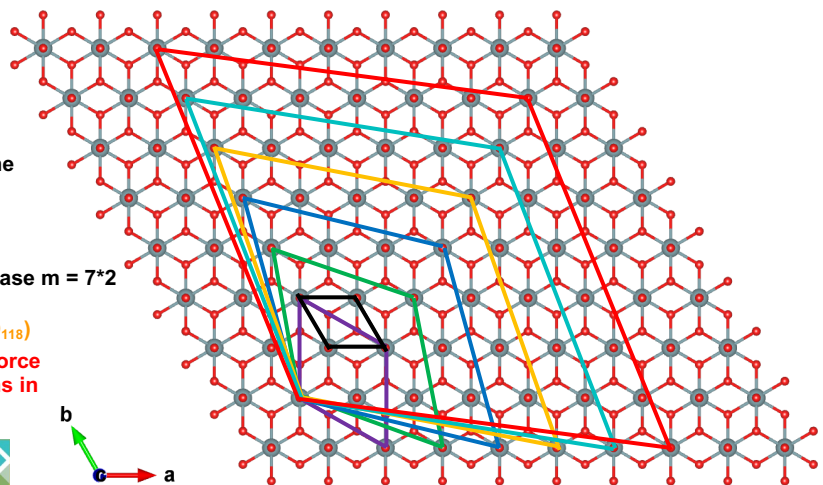
$n = 1 \rightarrow$ fluorite

$n = 3 \rightarrow \delta$ phase $m = 7$ (A_7O_{12})

$n = 3$, c doubled but half vacancies $\rightarrow \gamma$ phase $m = 7 \cdot 2$ ($A_{14}O_{26}$)

$n = 6 \rightarrow c$ doubled β phase $m = 31 \cdot 2$ ($A_{62}O_{118}$)

The 3-fold operator and the R centre enforce symmetry equivalences among the atoms in the structure



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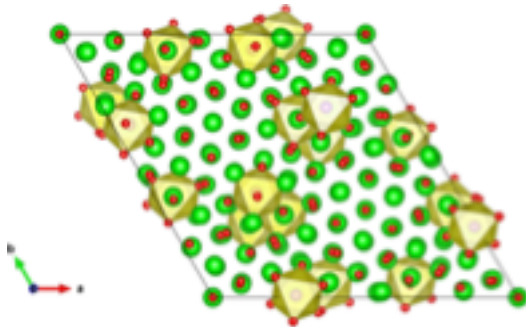


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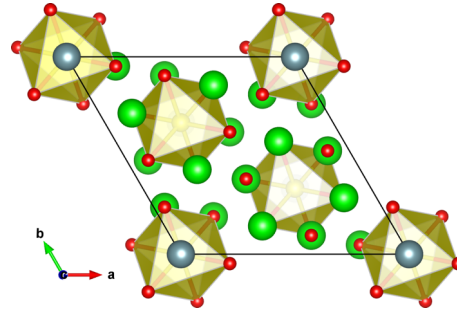
$A_{62-x}B_xO_{118}$ β -phase & $A_{7-x}B_xO_{12}$ δ -phase

Anion vacancy exhibit stacking correlations

Most often they stack along $\langle 111 \rangle_F$ that is the c-axis in the R-3 layered representation



anion octahedral environment
59/62-dense (1.903)



anion octahedral environment
6/7-dense (1.714)

These systems have very limited cation mobility & small charge difference is a limited driving force. Only anion vacancies display long-range order.



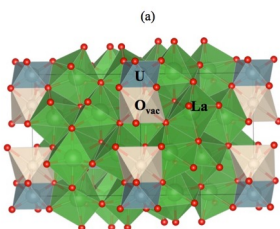
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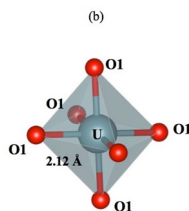
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δ -phase La_6UO_{12} and $O \rightarrow D$ in the stoichiometric phases $LaUO_4$, $CeUO_4$, La_2UO_6 , and Ce_2UO_6 .

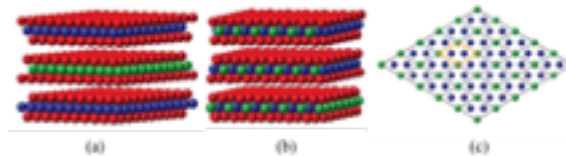
In La_6UO_{12} , large charge difference between cations (U is +6 here) is a strong driving force for promoting long-range order. Both cation and anion vacancies display long-range order.



Casillas, Phys Rev Materials 2017



Casillas, Comp Mat Sci 2016



Standard DFT and DFT+U indicate a lower energy for an ordered phase in each model compound. But the energy differences among different ordered structures are too small to find a clear preference. This suggests a complex metastability situation with lot of competition when diffusion is sluggish



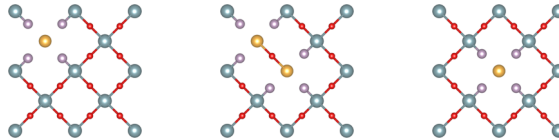
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Mechanisms of charge compensation

- In some oxide compounds a cation charge variation can be compensated by extended defects. This occurs for instance in WO_{3-x} phases where the reduction of the cation leads to the formation of shear phases. **Under some conditions it may apply to U where the polaron mechanism can also occur.**



- The shear changes the connectivity among polyhedra
- A high dielectric constant favours planar faults because cation relaxation can minimize the system energy**
- The structures in the substoichiometric regions of the ternary phases diagrams (U, Ln, O) are still largely unknown. Most of them seem to lack of long range order and are labeled “defect fluorites” though TEM shows that some intermediate range order is likely to occur



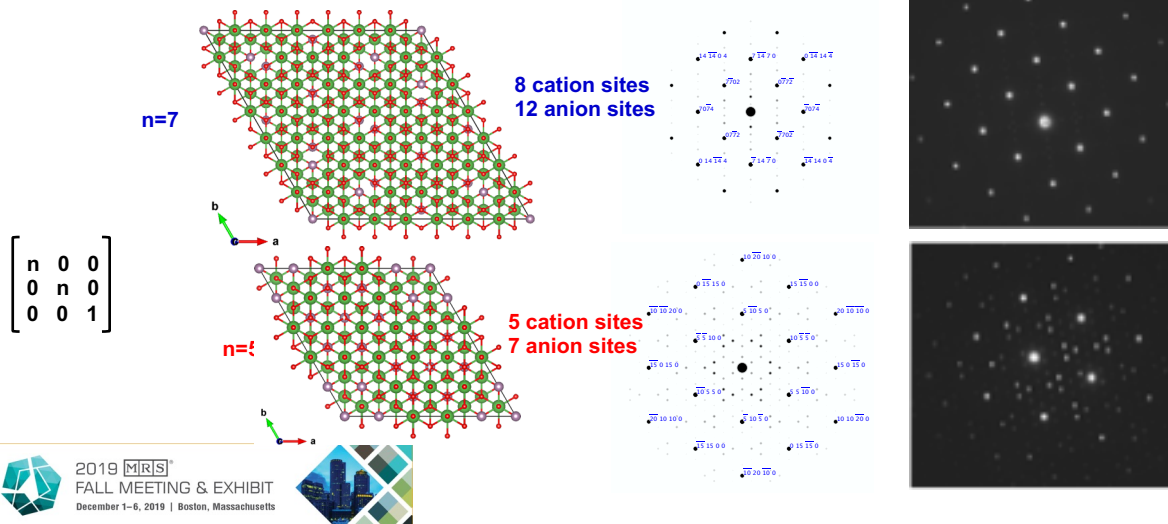
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$\text{La}_{6-x}\text{MoO}_{12-y}$ ($x < 0.8$ here $x = 0.6$)

Slightly different O stoichiometries quenching or annealing in reducing atmosphere lead to different final superstructures (all are R-3m) though the R-type layer stacking seems to hold and vacancies prefer to cluster near Mo atoms.

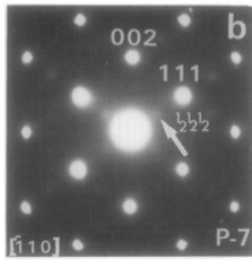


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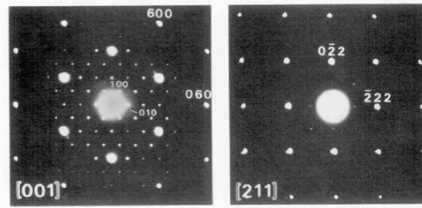
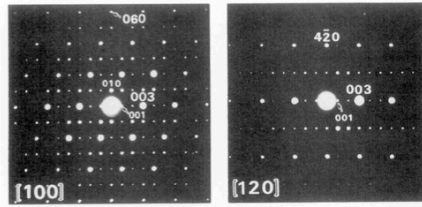
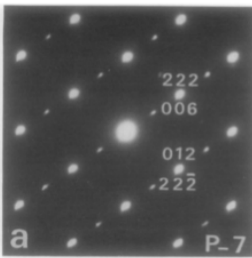


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Cation ordering in $U_xLa_{1-x}O_{2-\delta}$



Cation ordering in $U_{0.40}La_{0.60}O_{1.98}$



Cation ordering in $U_{0.26}La_{0.74}O_{1.89}$

Quenched 1100C



Two weeks ...

Annealed 1100C



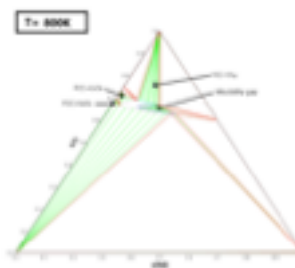
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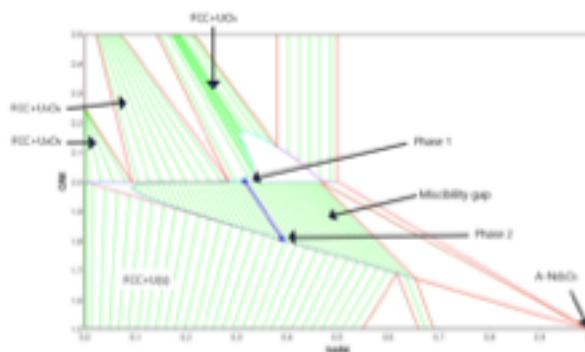
Herrero & al. J solid State Chem 87 (1990) 331
Rojas & al. J solid State Chem 112 (1994) 322

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$Nd_2O_3-UO_2$ systems



Dottavio JNM 2015



The tie lines from the current model suggest cation segregation in addition to O vacancy formation

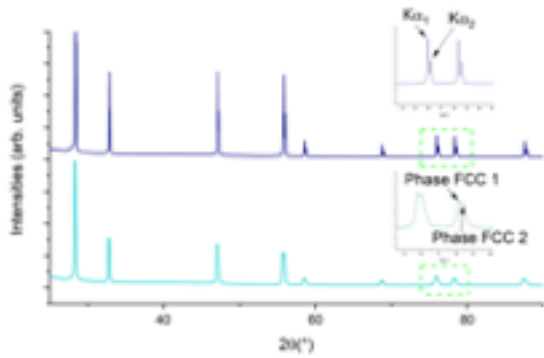


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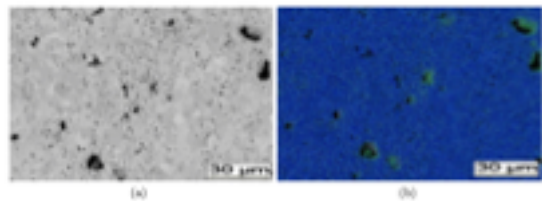


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Microcrystalline $U_{2/3}Nd_{1/3}O_2$



- Different samples exhibit extreme variability
- Single fluorite phase or not
 - Strong microstrain suggesting large **compositional fluctuations** in two-phase samples



There is a significant microstructural trend for cavity formation near the Nd rich regions



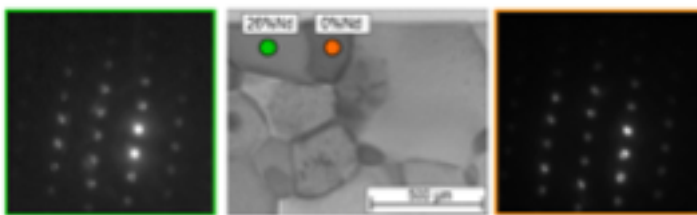
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Microcrystalline $U_{2/3}Nd_{1/3}O_2$

Inhomogeneity (phase separation) seems to occur also within single crystalline grains



TEM microdiffraction suggests the local symmetry of the two phases is slightly different though the long range patterns is still a perfect fluorite
But the two compositions are not compatible with the current Calphad model

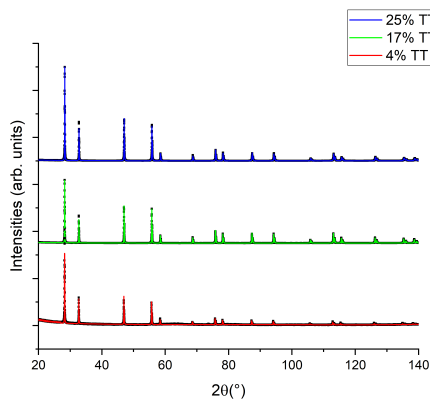


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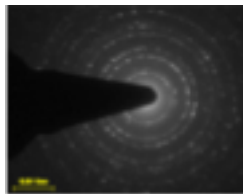
Nanocrystalline $\text{Nd}_2\text{O}_3\text{-UO}_2$ systems



Stoichiometric (not reduced) $\text{U}_{3/4}\text{Nd}_{1/4}\text{O}_2$, $\text{U}_{0.83}\text{Nd}_{0.17}\text{O}_2$ and $\text{U}_{0.96}\text{O}_{0.04}\text{O}_2$

No phase separation and no significant microstrain in annealed nanocrystalline wet route samples.

But the thermal treatment is unlikely to lead to significant long range cation transport.



Fluorite signature on 20 nm grains of $\text{U}_{3/4}\text{Nd}_{1/4}\text{O}$

Reducing annealing below 800C produces a lattice parameter change but no phase separation or symmetry change

Above 800C it induces some grain coarsening but still no phase separation



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$\text{Nd}_2\text{O}_3\text{-UO}_2$ systems

- The U+5 mechanism of charge compensation seems preferred in these systems over the O vacancy formation
- Vacancy formation seems favoured only in extremely substituted Nd samples where the C-type or A-type bixbyite structures are adopted.



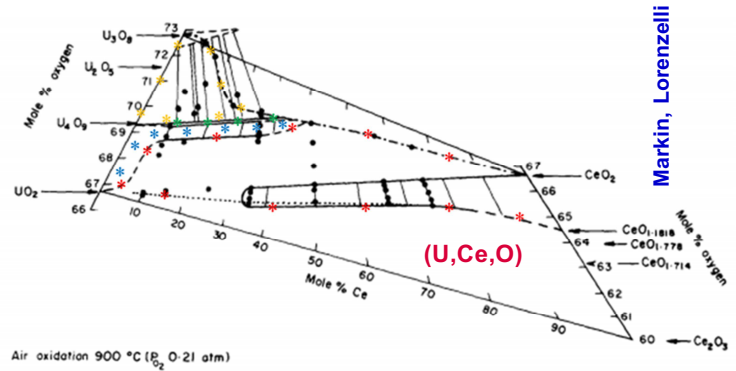
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The ternary systems $Ce_{1-x}U_xO_{2-y}$

- Only Vacancy ordering is expected from the current thermodynamic model
- What is the symmetry of the O deficient phase of the miscibility gap?
- Ferroelastic system?

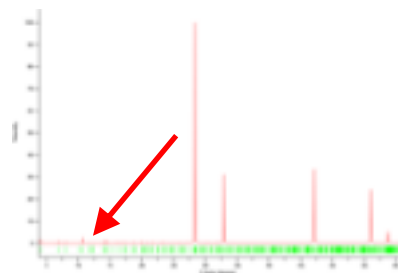
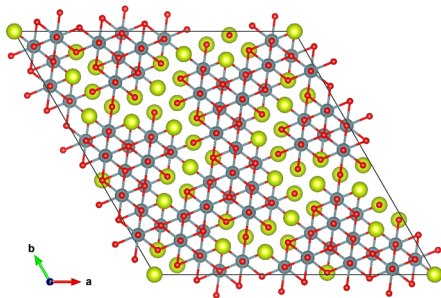


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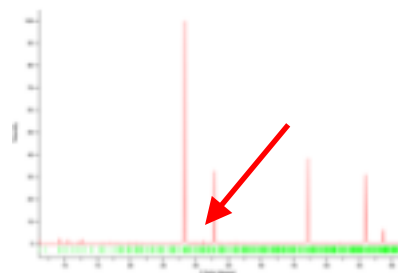


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$Ce_{0.45}U_{0.55}O_{2-\delta}$ quenched at 1700°C (Ar/4H₂)



n=8
Unrelaxed model



Relaxed (refined)

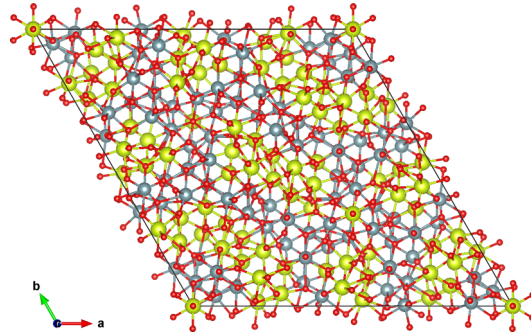
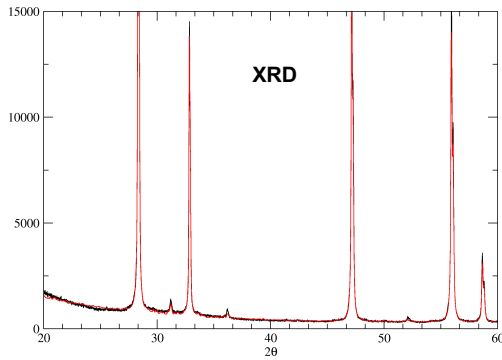


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Ce_{0.45}U_{0.55}O_{2-δ} quenched at 1700°C (Ar/4H₂)



$n = 8$ variant of R-3 but atomic displacement do not exactly respect the R centring so the model symmetry is rather P-3. It might be a problem of correlation length of the displacements rather than a real symmetry change (ferroelastic twins).

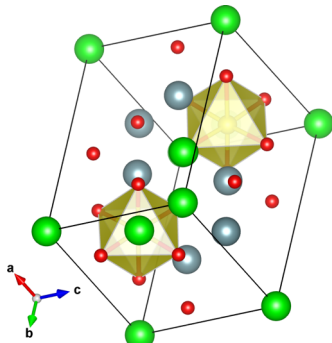


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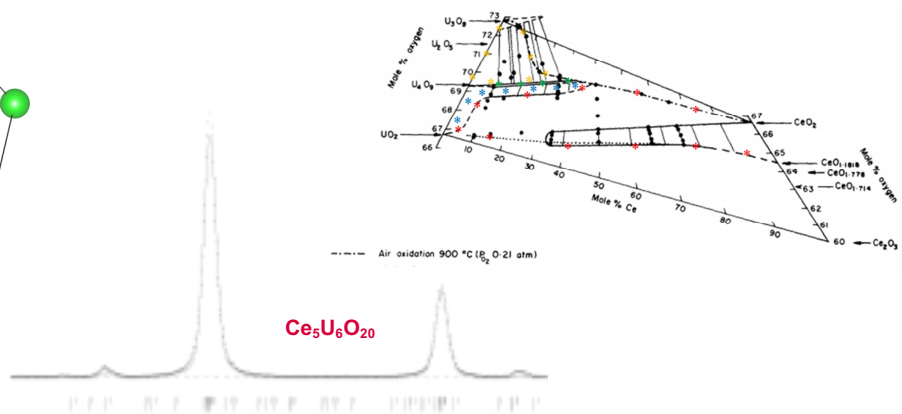


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After reduction of Ce_{0.45}U_{0.55}O₂ by Ar/H₂ at 400°C



A different story ...



The vacancy ordering is extremely sensitive to annealing conditions and so are the cation relaxations and the final symmetry of the system. This structure borrows from Ce₁₁O₂₀.



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Conclusion (for now)

- **Fluorite derived mixed oxide systems can order**
 - The U+5 mechanism of charge compensation seems preferred in these systems over the O vacancy formation (not so clear cut for Ce systems where Ce reduction/oxidation can be competitive)
 - The cations order only occurs when significant atomic transport can take place below the ordering transitions.
 - The anions (→ O vacancies) always order, at least short-range.
 - Most the XRD superlattice intensities are from cation displacive relaxation, and getting the pattern right requires guessing the O vacancy distributions
 - But under irradiation cation order might occur even when atomic transport is not effective
 - More work is still needed to improve our understanding
 - We just scratched the problem of ferroelastic nanotwinning



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