



2020 VIRTUAL MRS® SPRING/FALL
MEETING & EXHIBIT

Chemical bond complexity in δ -phases (fluorite-related ternary oxides).

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Complexity in δ -phases.

Oxides with generic stoichiometry M_7O_{12} occupy, in a generic phase diagram, an intermediate place between pyrochlore (or weberite) and bixbyite structure types. Their structure is derived from the ideal fluorite structure, and it is characterized by a more or less pronounced ordering of the O vacancies within the average fluorite sublattice.

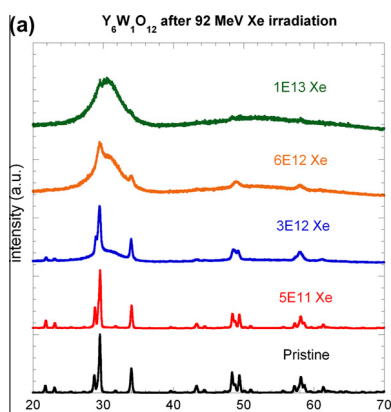
We believe that ternary oxides with this generic formula $(A^{III}_{1-x}B_x)_7O_{12}$ display some structural flexibility relevant to fission product stabilization in nuclear fuels and to the understanding of actinide waste forms as well.

Typically the A^{III} cation can be either an actinide or a rare earth element, whereas the B cation can be either a transition metal or U. We would like to discuss the chemical bonds in the ordered prototype systems (Bader's AIM theory) and compare to disordered systems.



Complexity in δ -phases.

In **ordered** compounds the crystal structure transforms from ordered rhombohedral to amorphous under irradiation



M. Tang et al. / Journal of Nuclear Materials 425 (2012) 193–196

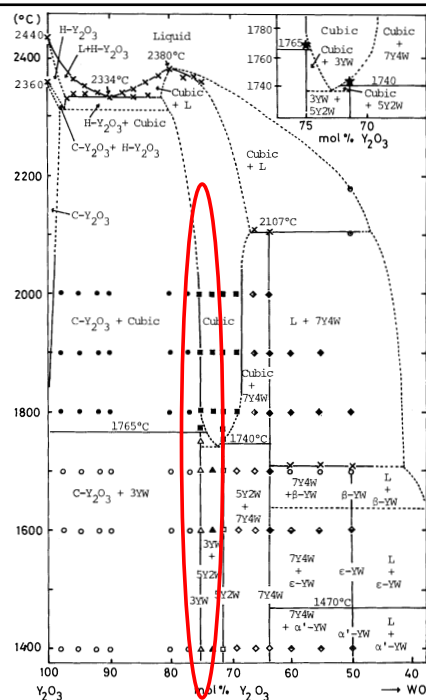


Fig. 5. Phase diagram of the system Y_2O_3 - Y_2O_3 - WO_3 , determined by DTA, \times , by thermal analysis (Ref. 17); \star , by high-temperature X ray; and \circ , \triangle , \square , \diamond , ∇ , \circ , \triangle , \square , \diamond , ∇ , by quenching.

Kuribayashi, J. Amer Ceram Soc 63 644-647 (1981)



Complexity in δ -phases.

In the **ordered** compounds (Y_6MoO_{12} , Y_6WO_{12} , ...) a competitive oxygen deficient cubic fluorite phase can be observed at high temperature, suggesting that the irradiation behavior (amorphization) is not following the thermally driven polymorphism.

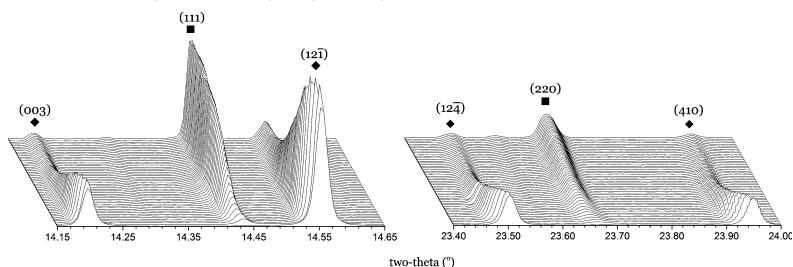
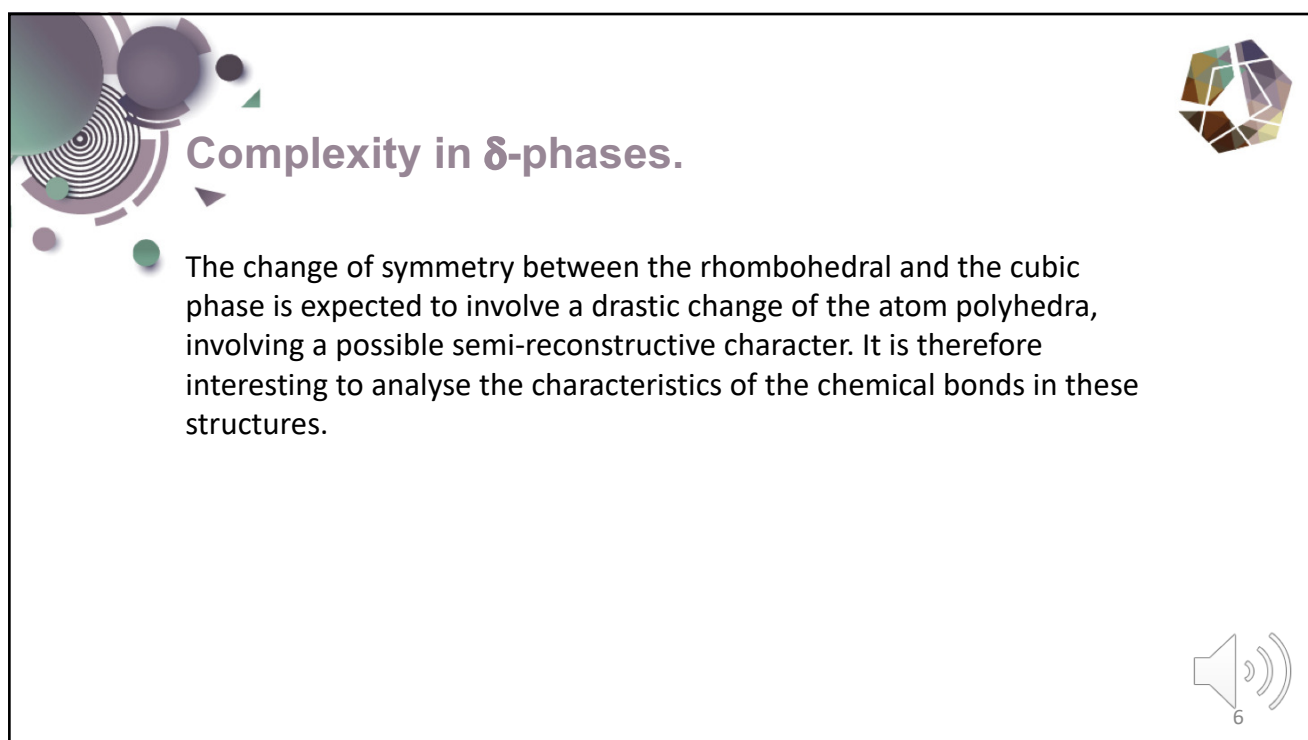
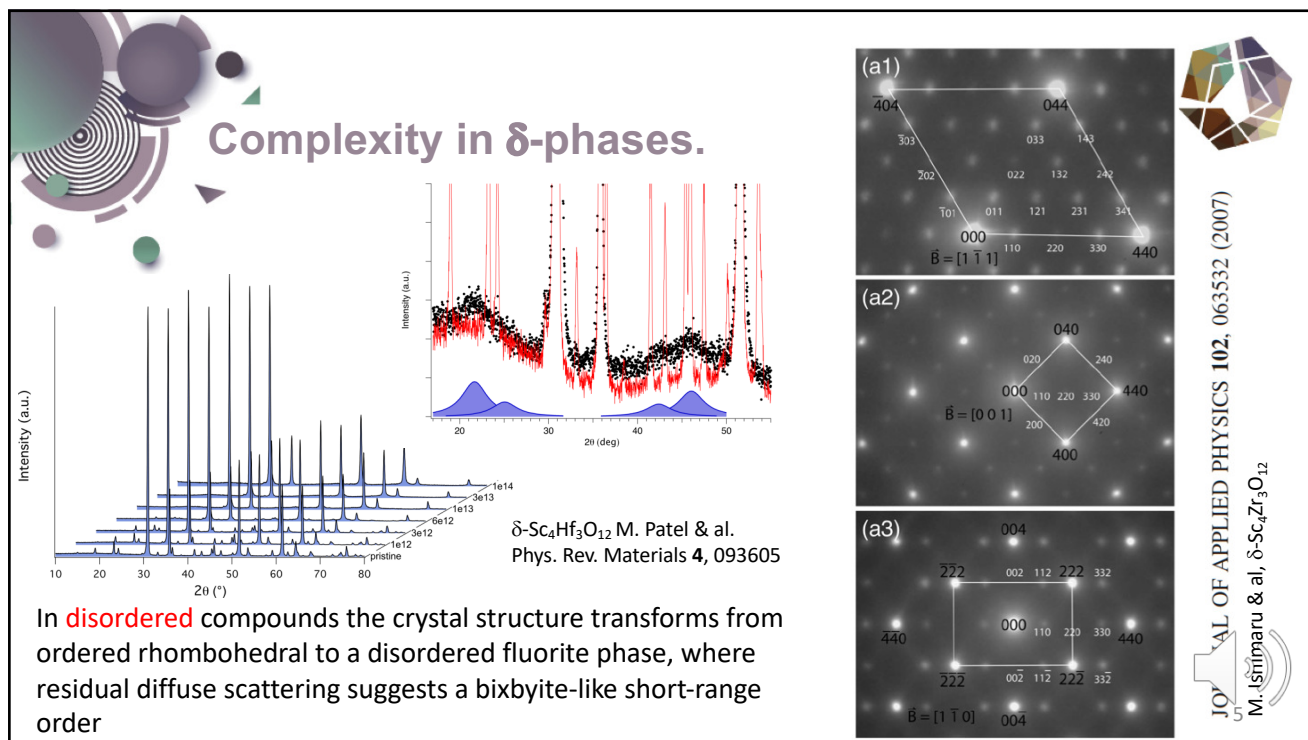


Fig. 4. Sections of the *in situ* XRD pattern for Y_6WO_{12} , isothermally heated at 1680°C for 11 h ($\lambda = 0.7787$ Å). Annotated are the rhombohedral (\blacklozenge) and h-fcc (\blacksquare) peaks.



Z. Apostolov J. Am. Ceram. Soc. 97 1256–1263 (2014)

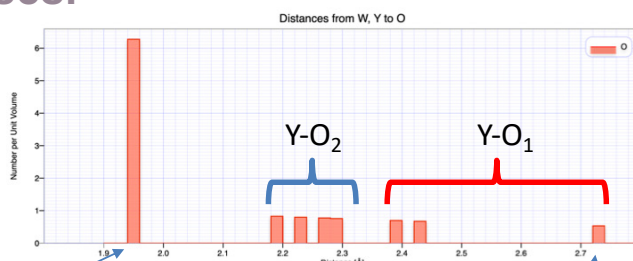


Complexity in δ -phases.

DFT: GGA+U

Site	x/a	y/b	z/c	m
A	0.6843	0.3895	0.8563	6
B	0.0000	0.0000	0.0000	1
O1	0.4313	0.1770	0.5917	6
O2	0.9225	0.7049	0.0341	6

$\text{Y}_6\text{MoO}_{12}$	bcp density	curvature	laplacian	dist
Mo-O1 x6	0.9718	0.2475	11.1031	1.950
Y-O1	0.1526	0.1655	2.0966	2.723
Y-O1	0.3028	0.2032	3.7058	2.481
Y-O1	0.3184	0.2068	3.9526	2.412
Y-O2	0.4057	0.2112	4.9286	2.337
Y-O2	0.4241	0.2136	5.2572	2.317
Y-O2	0.4701	0.2106	5.9289	2.256
Y-O2	0.5103	0.2104	6.7130	2.221



Y_6WO_{12}	bcp density	curvature	laplacian	dist
W-O1 x6	1.0041	0.2429	11.8996	1.957
Y-O1	0.1497	0.1645	2.0662	2.720
Y-O1	0.3012	0.2018	3.7216	2.460
Y-O1	0.3213	0.2088	3.9900	2.399
Y-O2	0.4069	0.2115	4.9402	2.323
Y-O2	0.4258	0.2131	5.2955	2.302
Y-O2	0.4698	0.2100	5.9504	2.249
Y-O2	0.5101	0.2085	6.7419	2.212

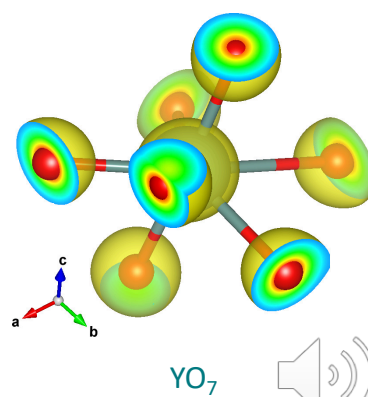
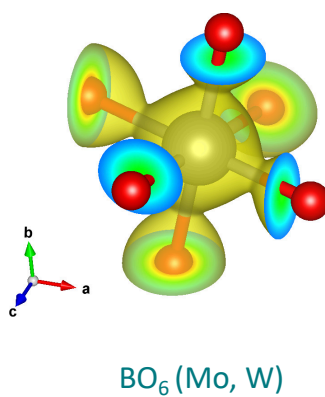
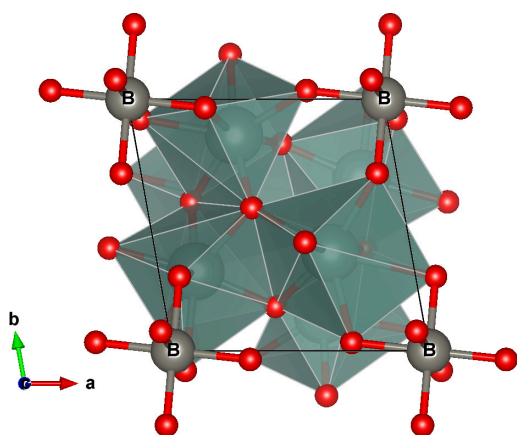
Complexity in δ -phases.

$R = 3$

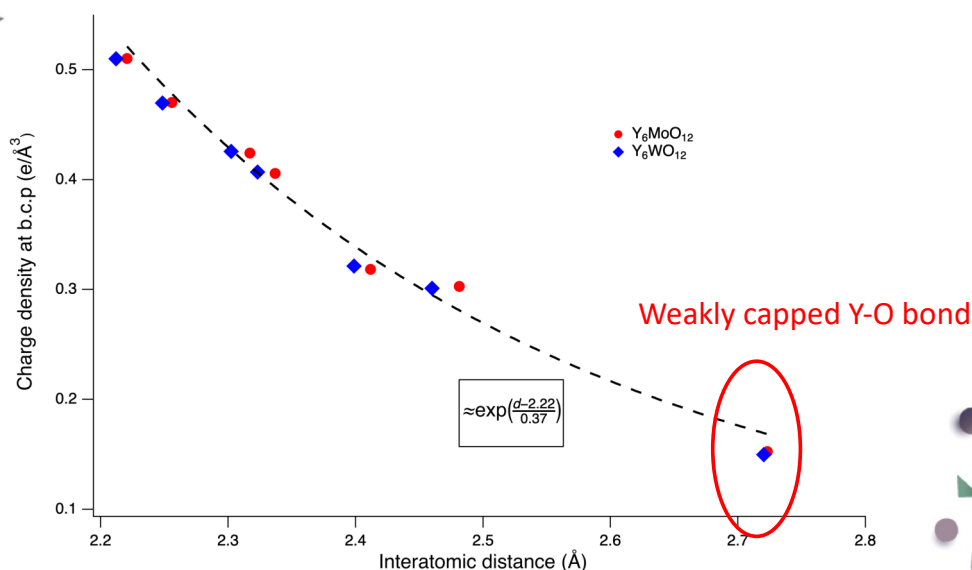
$a: \sim 6.475 \text{ \AA}$

$\alpha: \sim 98.64^\circ$

DFT: GGA+U



Complexity in δ -phases.



Complexity in δ -phases.

We believe that the characteristics of the polyhedron of the 7-fold coordinated A^{III} ion is particularly relevant: these polyhedra are often described in the literature as a mono-capped trigonal prisms, with bond lengths exhibiting a large dispersion.

This bond length spread is also encountered in the disordered compounds.

The weak bond of the 7-fold polyhedron, shared with the BO_6 octahedron, seems to easily re-arrange, producing the observed change of stacking of the O vacancies, that changes from δ -type to **bixbyite-type**.



Complexity in δ -phases.

$(A^{III}_{1-x}B_x)_7O_{12}$ structures involve the regular stacking of two building blocks, an octahedron and a 7-fold capped prism.

α irradiation and ion recoils produce a cation mixing that destabilizes the structure.

In ordered compounds, as for instance Y_6WO_{12} , the radiation induced irregular stacking of the two polyhedra produces a severe charge imbalance that quickly leads to amorphisation.

In disordered compounds, as $Sc_4Hf_3O_{12}$, the smaller charge difference of the two polyhedra is more favorable to the cation mixing and a partial reconstruction of the chemical bond (e.g. a different distribution of the O vacancies) can efficiently stabilize the irradiated structure, thus avoiding amorphisation.