Behaviour of materials containing actinides and long lived radionuclides

Part I

Artificial crystalline materials doped with Pu-238

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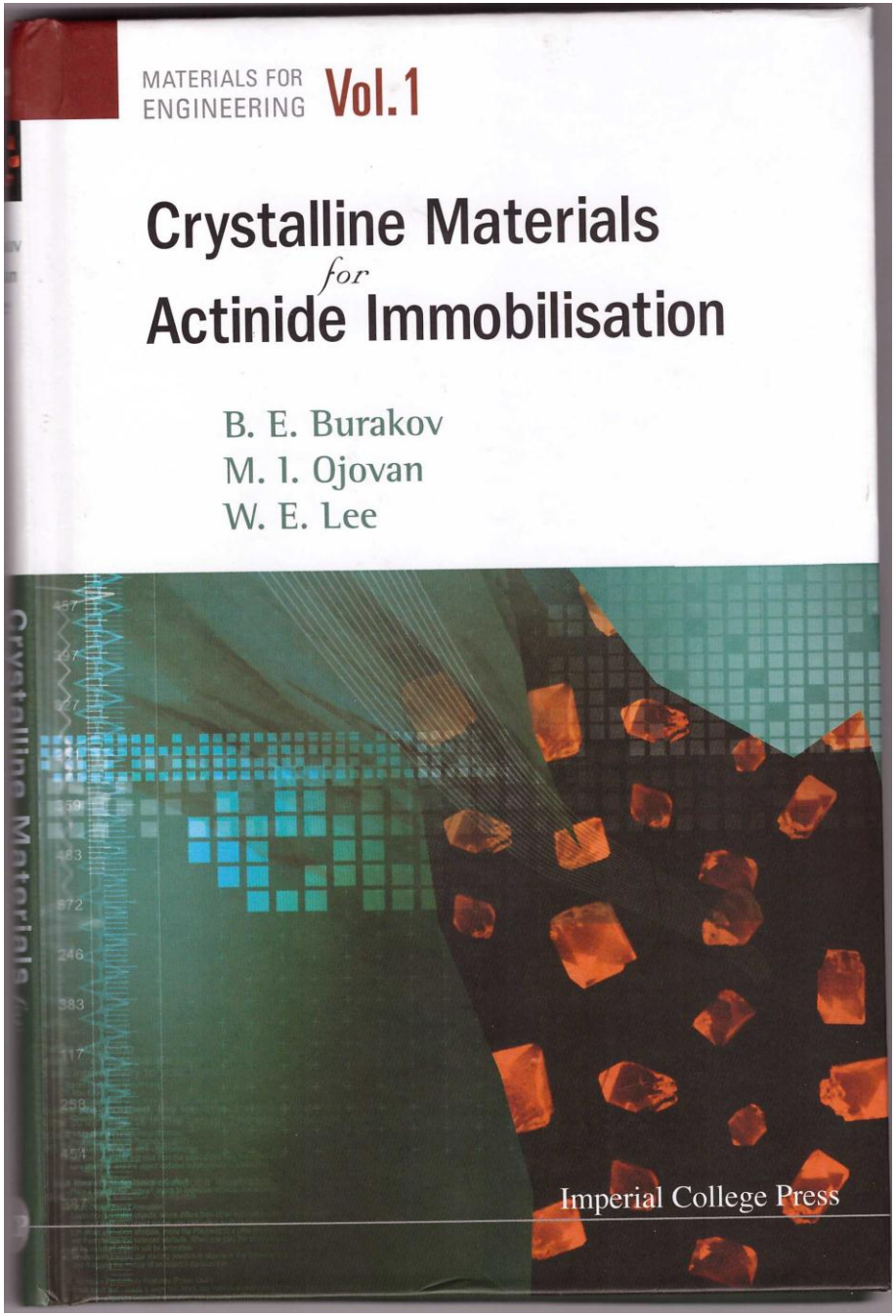
Main target of this presentation is to overview all uncertainties related to the modeling of long-term behavior of radwaste forms under self-irradiation


MATERIALS FOR ENGINEERING Vol. 1
Crystalline Materials for Actinide Immobilisation
B. E. Burakov
M. I. Ojovan
W. E. Lee
Imperial College Press

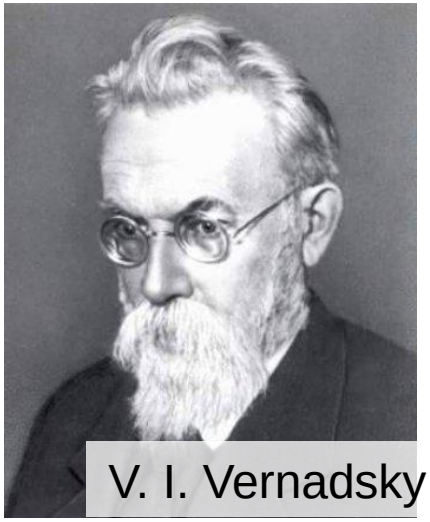
V.G. Khlopin Radium Institute (KRI) is located in
St. Petersburg *(Main Site and Historical Site)*
and Gatchina *(hot-cell facility)* – 40 km from St. Petersburg

About V.G. Khlopin Radium Institute (KRI)

- Radium Institute was established in 1922 under the guidance of academician V. I. Vernadsky. It is the oldest research institute included into the State Corporation “Rosatom”

- Academician Vitaliy Grigoryevich Khlopin initially was a deputy director of Radium Institute (and later he became a formal Director). Now institute has his name

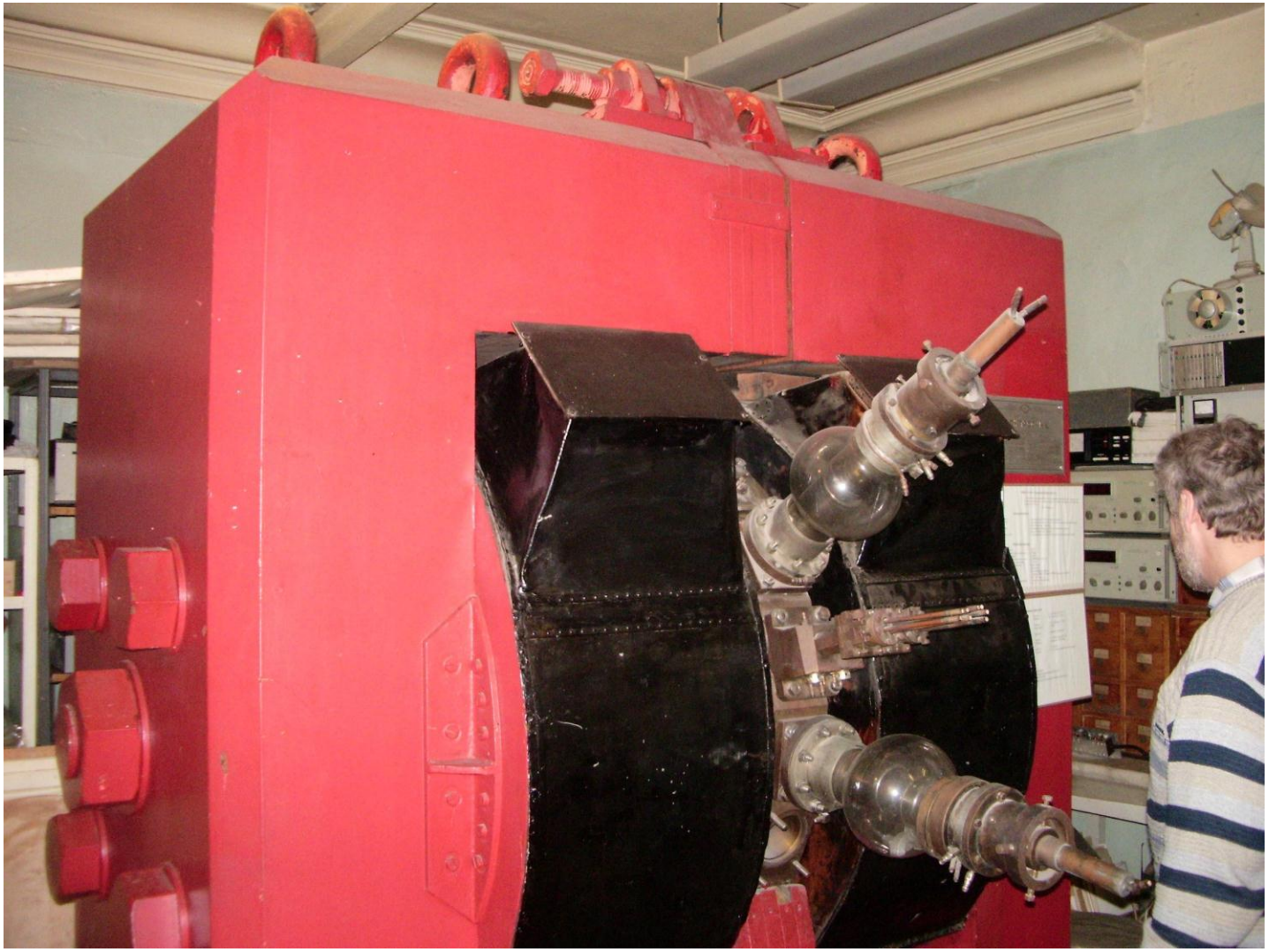
- First European cyclotron was built in KRI (1936-1937) and the first sample of Soviet plutonium (Pu) was obtained here (1945)



V. I. Vernadsky

V.G. Khlopin

Cyclotrone (first in Europe) built at KRI in 1936-1937



Main fields of current KRI research and activity

- Reprocessing of spent nuclear fuel
- Nuclear waste management
- Development of glass and ceramic waste forms for HLW immobilization
- Study of radiation damage effects in solids
- Monitoring of contamination
- Isotope production
- *Training of young international scientists in the field of applied radiochemistry and nuclear waste management. Tutorials with real radionuclides*

KRI hot-cell facility (Gatchina, 40 km from Saint-Petersburg)

Chain of glove-boxes at KRI for work with highly radioactive actinides

Background (1)

- Self-irradiation affects (destroys) crystalline structure of radionuclide host-phase, which can become fully amorphous
- Damage of crystalline structure under self-irradiation can be accompanied with essential decrease of chemical durability. Matrix swelling is possible. As a result of swelling the crack formation (and mechanical destruction) is possible
- Self-irradiation affects glass matrix too. As a result glass recrystallization and mechanical destruction is possible

Background (2)

- Some crystalline phases demonstrate high resistance to irradiation: zirconia (cubic, tetragonal and monoclinic), $(Zr,\ldots)O_2$; monazite, $(Ce,Ln,Gd)PO_4$; UO_2 and PuO_2
- Zr-pyrochlore, $Zr_2Gd_2O_7$, remains crystalline at very high dose of irradiation but it changes crystalline structure from pyrochlore to fluorite
- Zircon, $ZrSiO_4$, and Ti-pyrochlore, $Gd_2Ti_2O_7$, become amorphous at comparable doses, however, their chemical durability changes differently

Self-corrosion of metallic can with PuO_2

Actinide Research Quarterly, LANL, 2004, 2-nd quarter, p.4

Gas release as a result of radiolysis

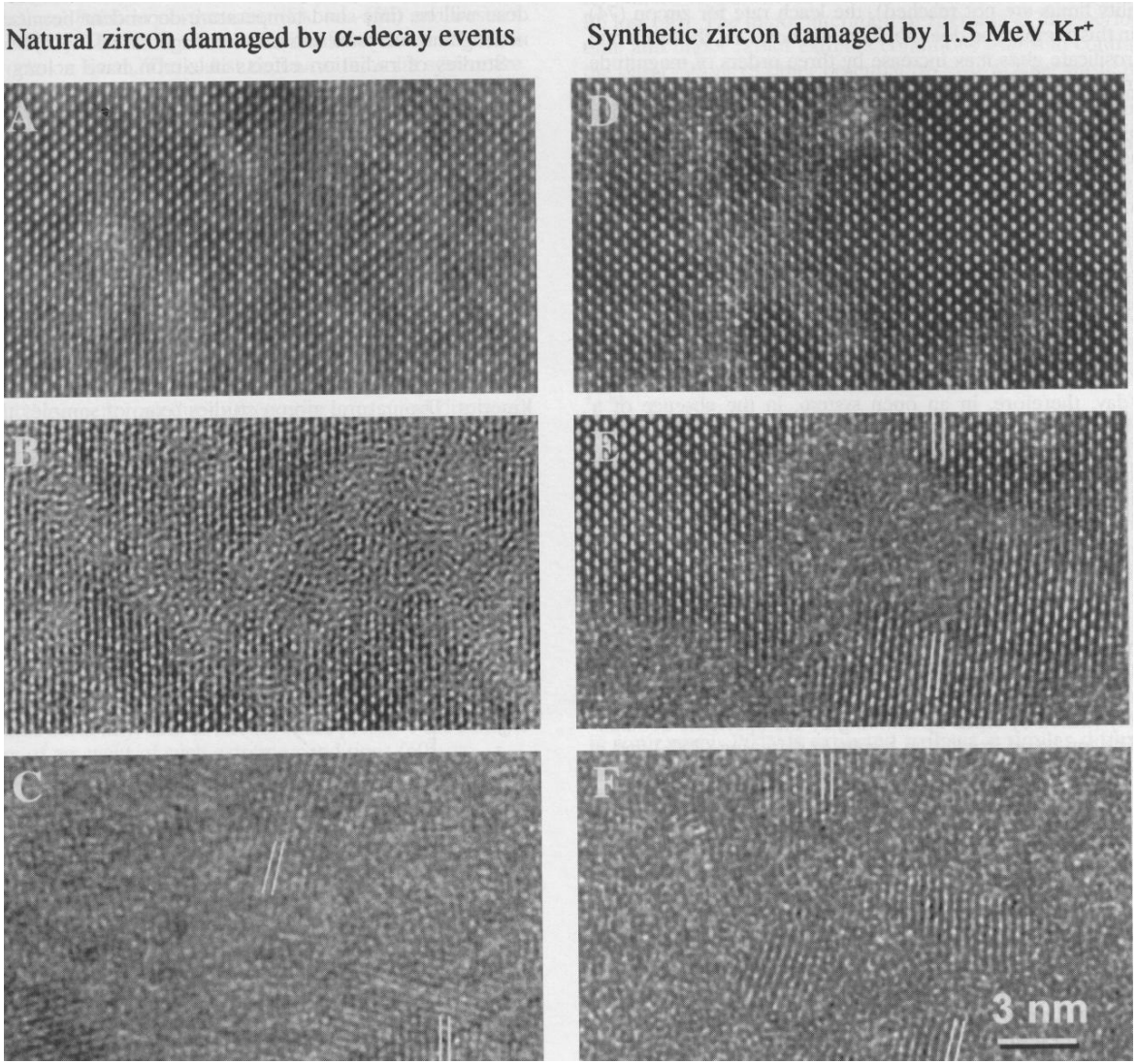
La-monazite ceramic (La,Pu)PO_4 doped with 8.1 wt.% Pu-238 in water after 6 years of storage at KRI

Main uncertainties

- Behavior of solid solution under self-irradiation is not the same to one of pure undoped host-phase under external irradiation (for example, by heavy ions)
- Optimal level of radionuclide loading into crystalline lattice of host-phase is unclear
- Destruction of solid solutions (with formation of separate phases of radionuclides) under self-irradiation is possible

HRTEM images of non-radioactive natural and synthetic zircon after at different cumulated dose

(*Weber W.J. et al. 1994*)



Radiation damage study: how to simulate thousands of years?

ACTIVITY (Bq/g)

^{239}Pu – 2.3E+09 (usual valence state 4+)

^{241}Am – 1.3E+11(usual valence state 3+)

^{238}Pu – 6.3E+11

(almost 275 times higher than ^{239}Pu !)

^{244}Cm – 3.0E+12 (usual valence state 3+)

Accelerated radiation damage study using ^{238}Pu and ^{244}Cm is very informative

However

Only few laboratories in the world can handle such extremely radioactive materials

Ceramic based on Ti-pyrochlore, $(Ca,Gd,Hf,Pu,U)_2Ti_2O_7$

developed by Lawrence Livermore National Laboratory, USA, for excess Pu immobilization

RECIPE (in wt.%)

- UO_2 – 23.7
- PuO_2 – 11.9
- Gd_2O_3 – 8.0
- HfO_2 – 10.7
- CaO – 10.0
- TiO_2 – 35.7

Ti-pyrochlore ceramic
$(Ca,Gd,Hf,Pu,U)_2Ti_2O_7$

doped with 8.7 wt. % Pu-238

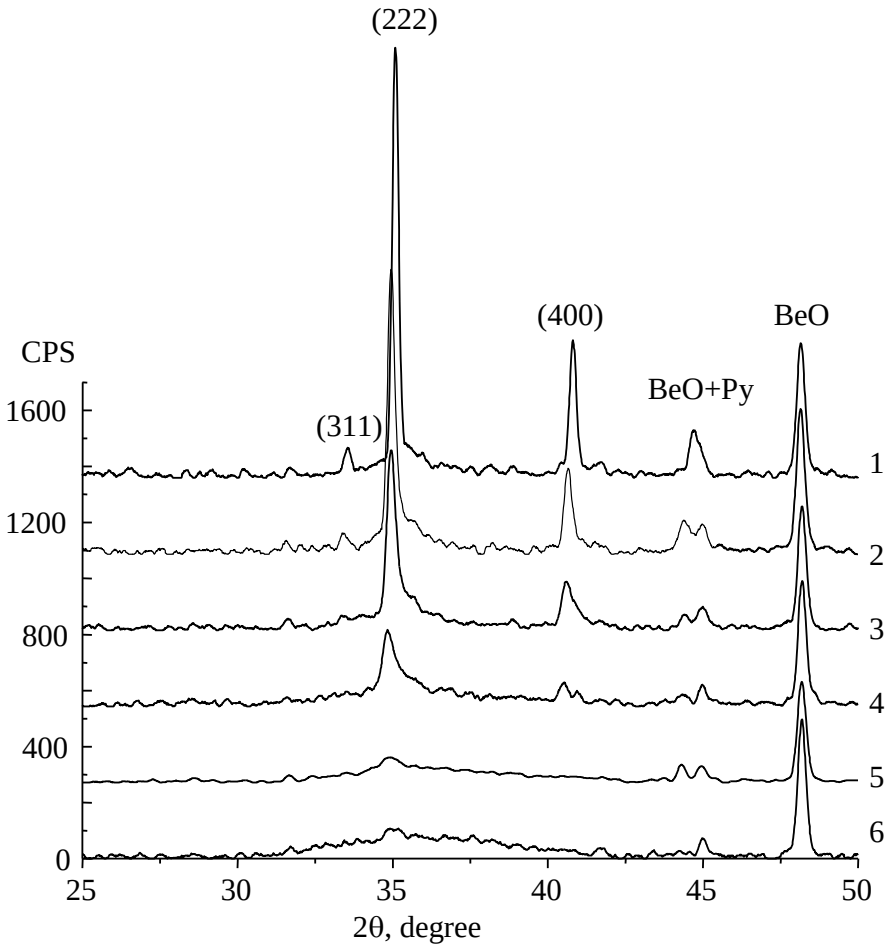
Samples of this ceramic were synthesized in NIIAR (Dimitrovgrad, Russia) and sent to the V.G. Khlopin Radium Institute for investigation under support of Lawrence Livermore National Laboratory

Zircon/zirconia ceramic
$(Zr,Pu)SiO_4/(Zr,Pu)O_2$

doped with 4.7 wt. % Pu-238

Samples of this ceramic were synthesized at V.G. Khlopin Radium Institute

XRD patterns of ^{238}Pu-doped (8.7 wt.%) Ti-pyrochlore ceramic $(Ca_{1.16}Gd_{0.23}Hf_{0.30}Pu_{0.24}U_{0.42})Ti_2O_7$ after cumulative dose (in alpha decay/m^3x10^{23}): 1) 26; 2) 43; 3) 57; 4) 82; 5) 110; 6) 130



New-formed phases in matrix of Ti-pyrochlore ceramic ?

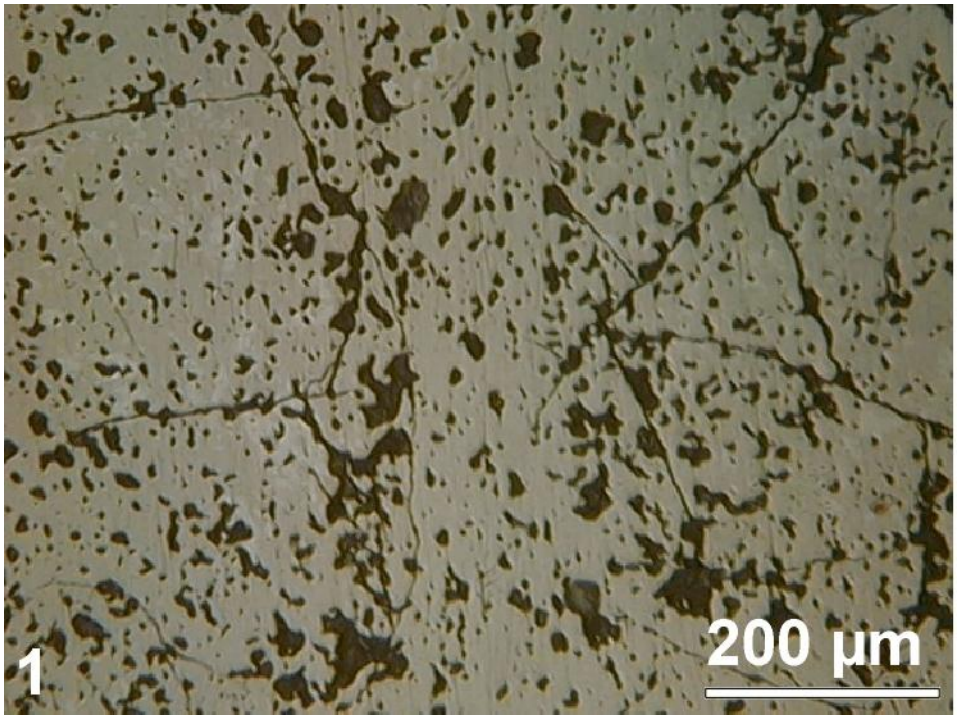
Destruction of solid solution under self-irradiation ?

Matrix swelling !

Change of pyrochlore ceramic density from 4.8 to 4.3 g/cm^3

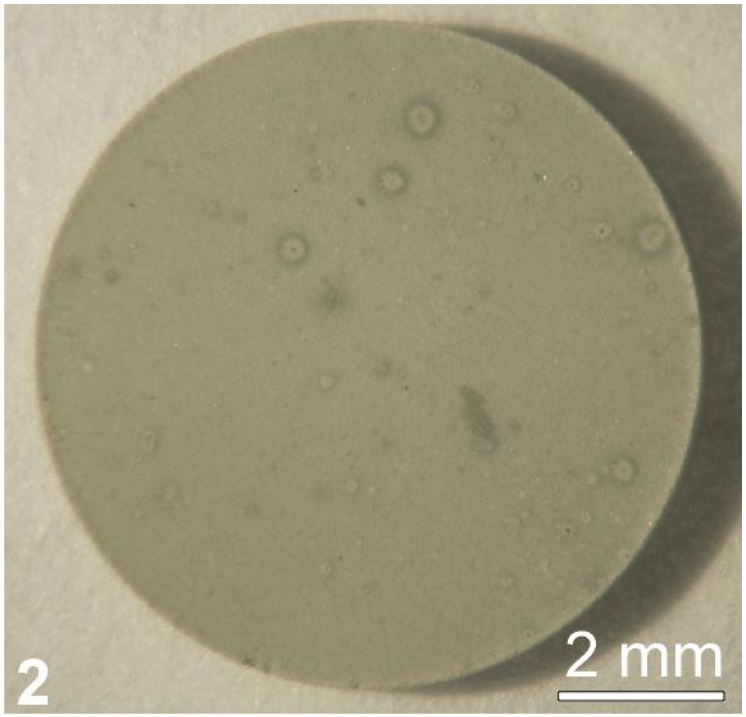
Ceramic behavior under self-irradiation

1) $(Ca_{1.16}Gd_{0.23}Hf_{0.30}Pu_{0.24}U_{0.42})Ti_2O_7$ with pyrochlore structure
2) $(Zr_{0.955}Pu_{0.045})SiO_4$ – zircon and tetragonal $(Zr_{0.964}Pu_{0.036})O_2$



Start of metamictization

dose 26 alpha-decays/m^{3}x10^{23}



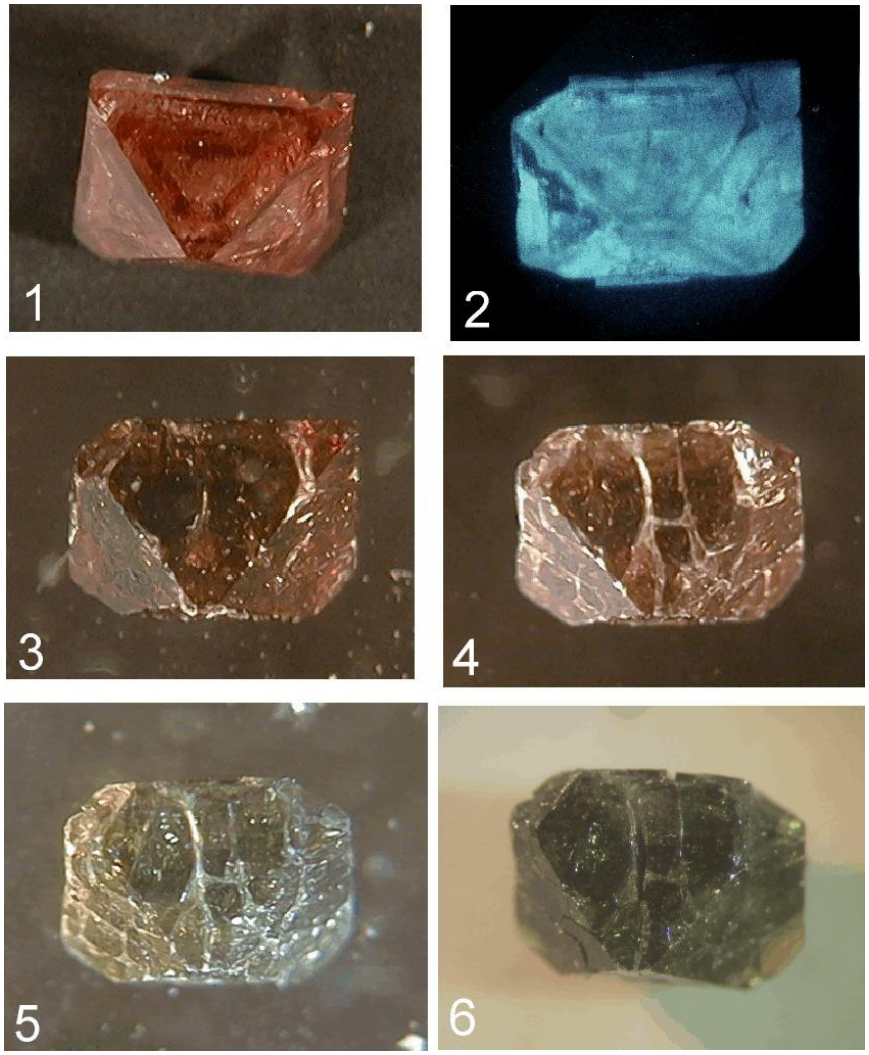
Zircon phase is fully metamict

dose 530 alpha-decays/m^{3}x10^{23}

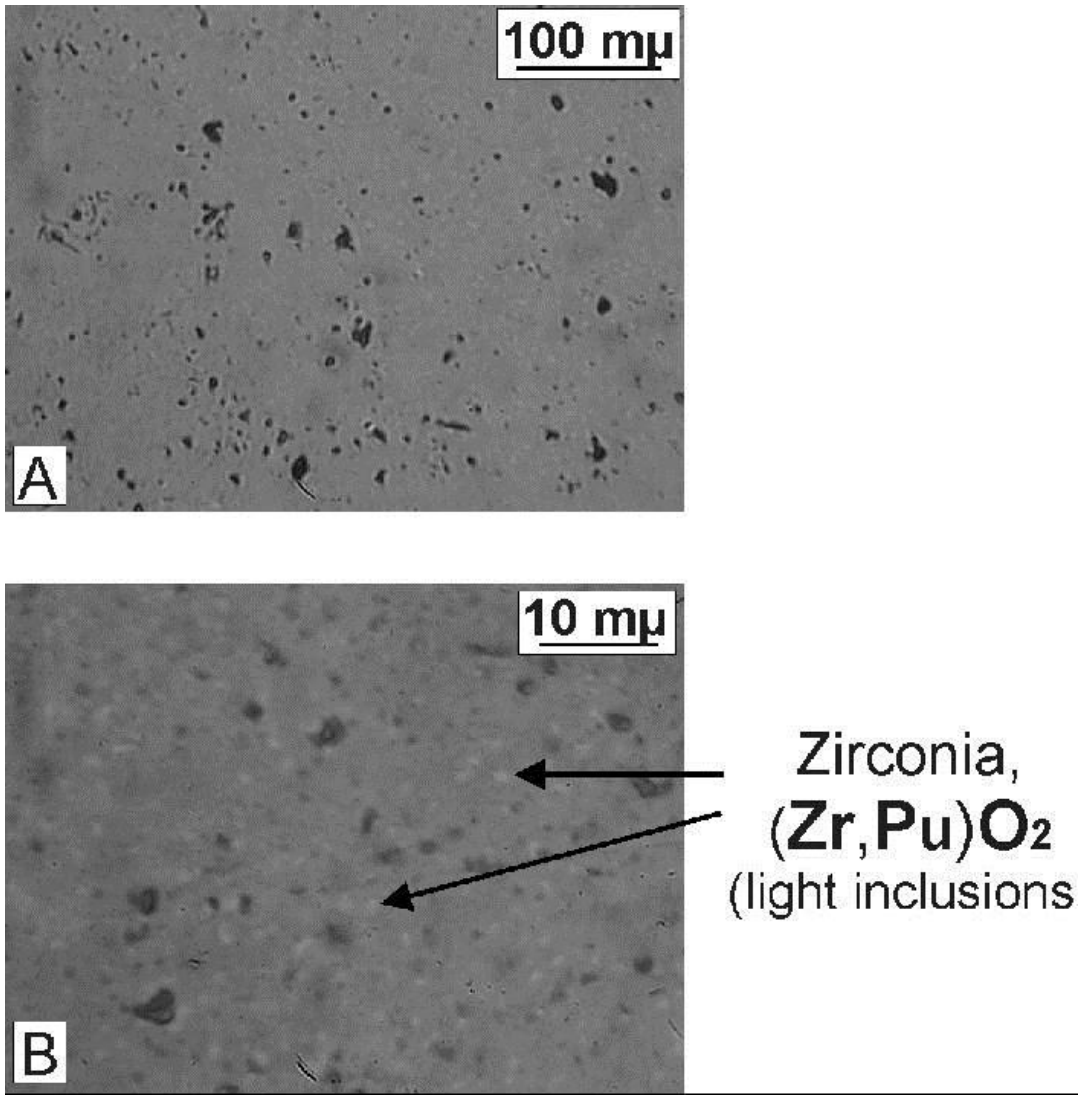
Synthetic zircon $(Zr_{0.977}Pu_{0.023})SiO_4$ 2.4 wt.% ^{238}Pu

accumulated dose (alpha-decays/g x10^{17}):

1) и 2) 0,1 3) 2 4) 51 5) 22 6) 51



Reflected light microscope image of ^{238}Pu-doped (4.7 wt.%) ceramic based on zircon, $(Zr,Pu)SiO_4$ and 15 wt.% tetragonal zirconia, $(Zr,Pu)O_2$ (obtained by cold pressing followed by sintering in air)



Matrix swelling ?

Should take place for zircon-based ceramic

but we did not observe

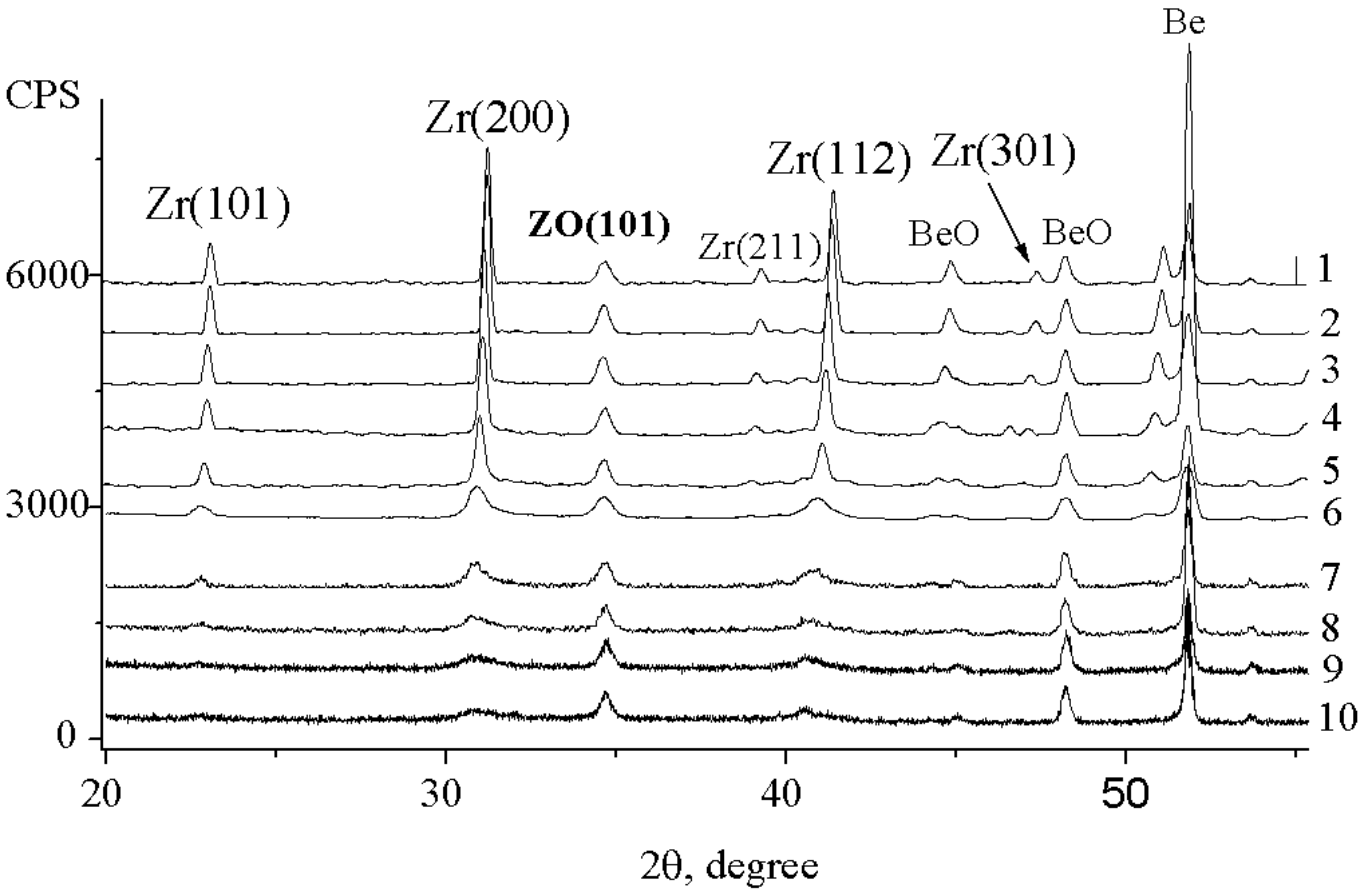
XRD patterns of double-phase ceramic based on:

$(Zr_{0.955}Pu_{0.045})SiO_4$ – *zircon phase Zr*

$(Zr_{0.964}Pu_{0.036})O_2$ – *tetragonal zirconia ZO*

accumulated dose (alpha-decays/m^3x10^{23}):

1) 3; 2) 13; 3) 30; 4) 51; 5) 65; 6) 91; 7) 113; 8) 134; 9) 151; 10) 188



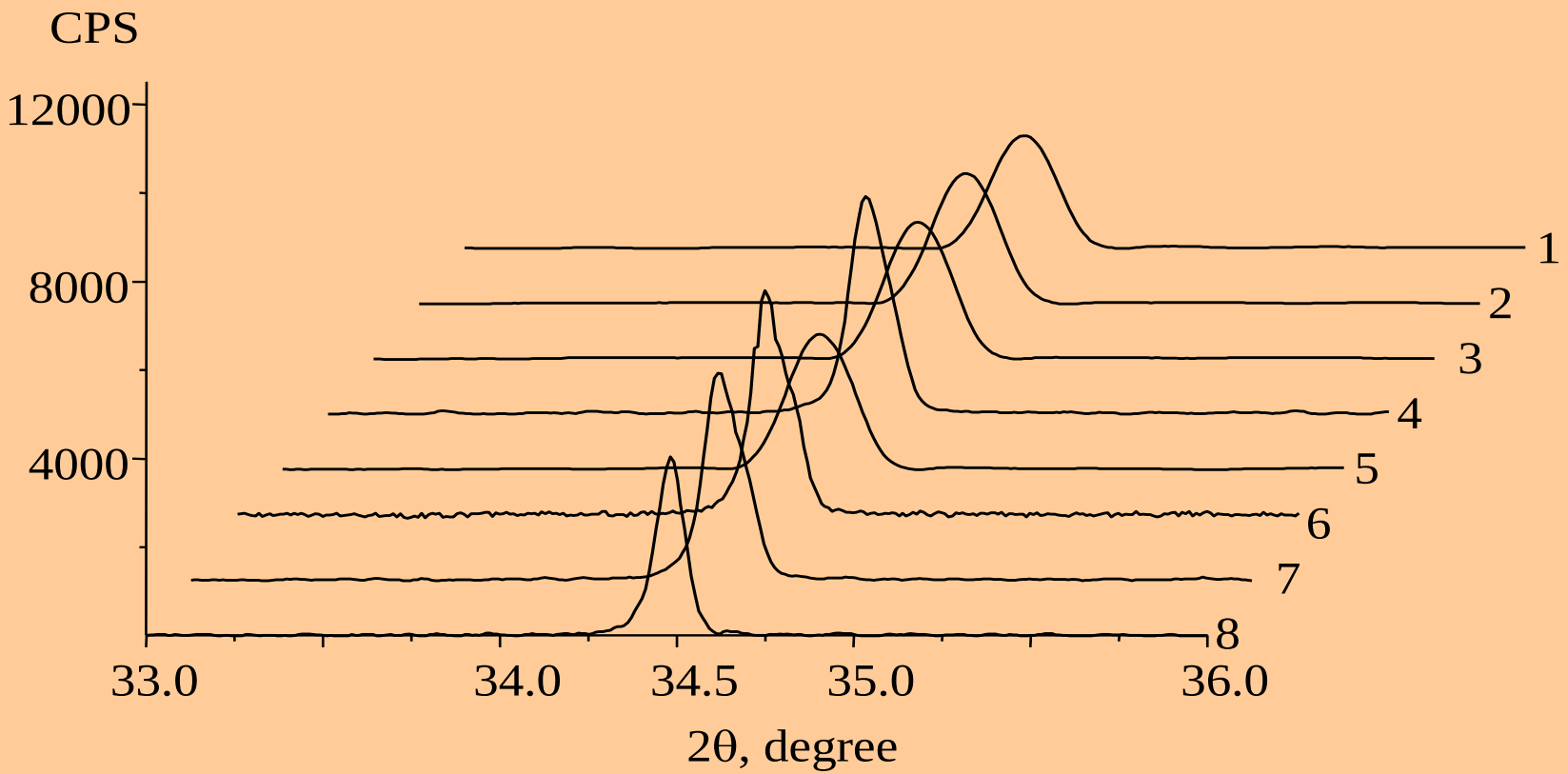
Cubic zirconia ceramic

$Zr_{0.79}Gd_{0.14}Pu_{0.07}O_{1.93}$

doped with 9.9 wt. % Pu-238

Samples of this single-phase ceramic were synthesized at V.G. Khlopin Radium Institute

Behavior of (111) XRD reflection of ^{238}Pu-doped (9.9 wt. %) cubic zirconia after cumulative dose (in alpha decay/m^{3}x10^{23}):
1) 3; 2) 27; 3) 62; 4) 110; 5) 134; 6) 188; 7) 234; 8) 277

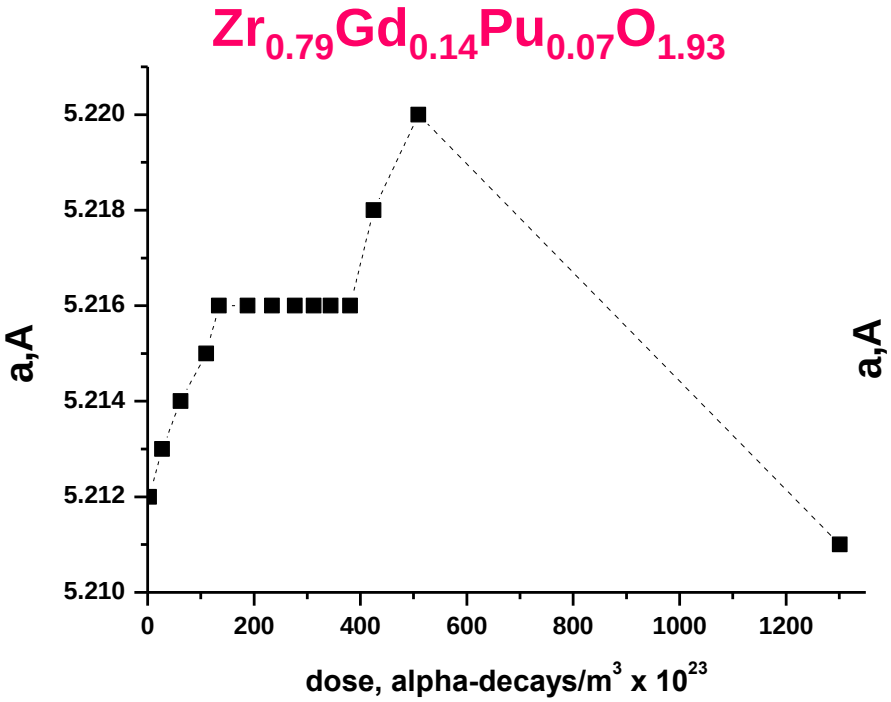


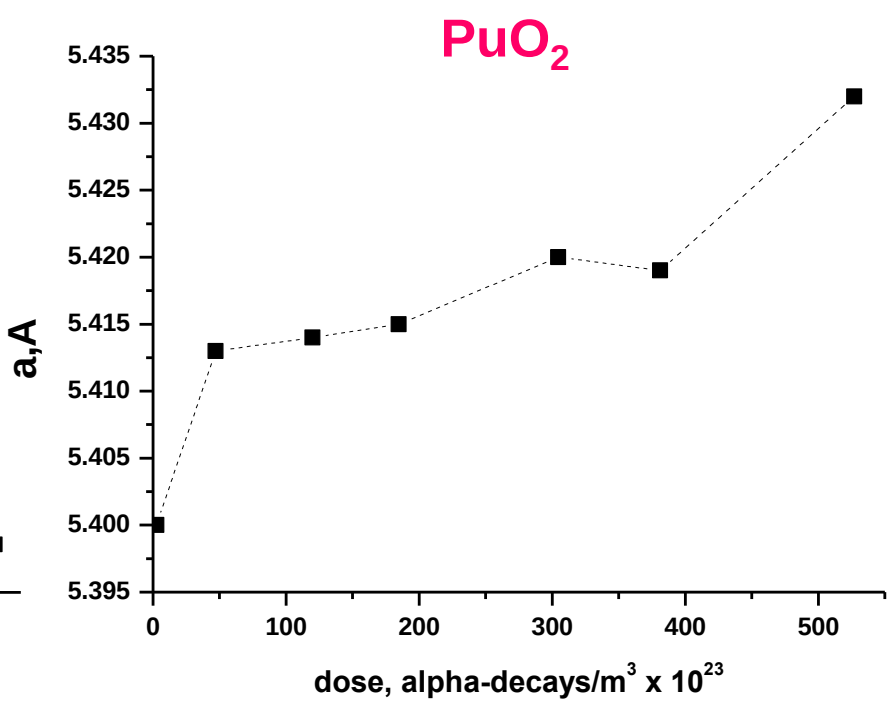
Accumulation of defects under self-irradiation and repeated self-annealing?

No swelling for cubic zirconia ceramic!

What about other crystalline phases with the same cubic fluorite-type structure?

Behavior of unit-cell parameter in ^{238}Pu-doped cubic fluorite-type structured zirconia and plutonia





Burakov B.E. and Yagovkina M.A., A study of accelerated radiation damage effects in PuO_2 and gadolinia-stabilized cubic zirconia, $Zr_{0.79}Gd_{0.14}Pu_{0.07}O_{1.93}$, doped with ^{238}Pu. J. Nucl. Mater., Vol. 467, pp. 534-536
more than 11 years of this research

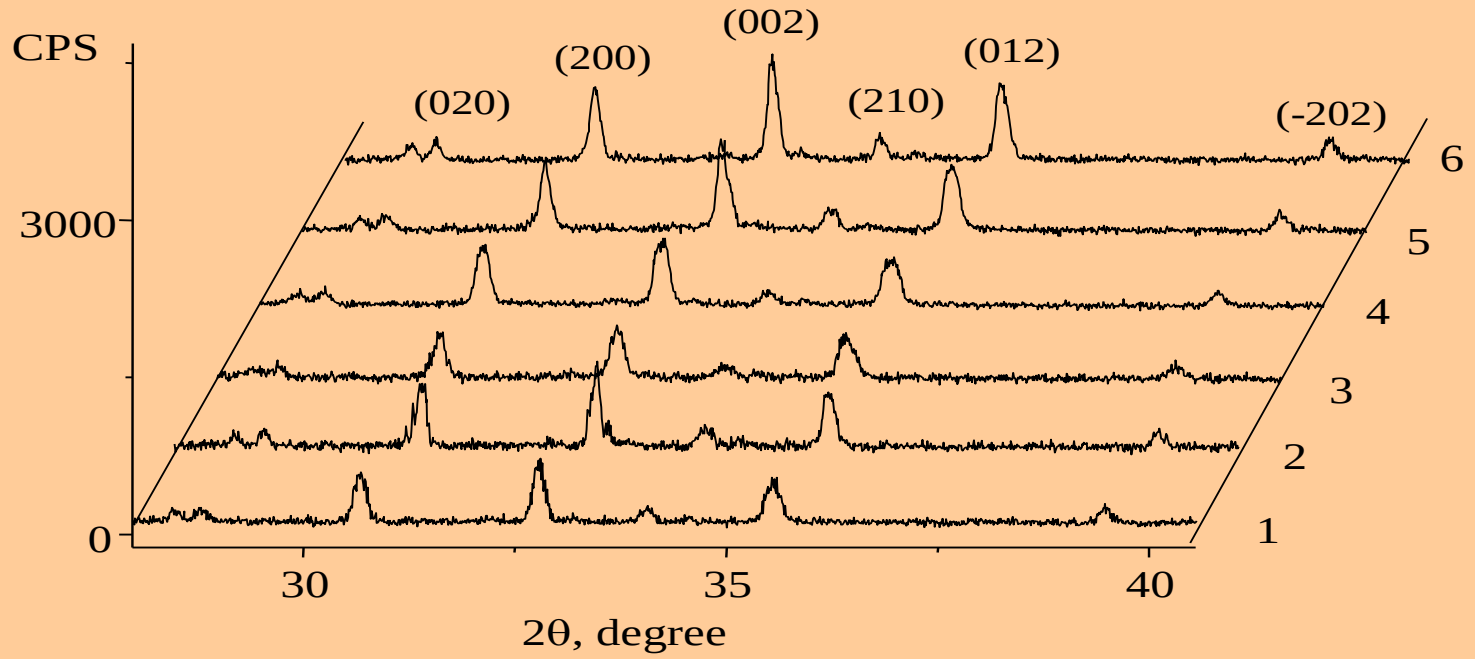
Different behavior of phases with the same crystalline structure under self-irradiation!

La-monazite ceramic
$(La,Pu)PO_4$

doped with 8.1 wt. % Pu-238

Samples of this ceramic were synthesized at V.G. Khlopin Radium Institute

XRD patterns of ^{238}Pu-doped (8.1 wt.%) La-monazite (La,Pu)PO_4 ceramic after cumulative dose (in alpha decay/m^3x10^{23}):
1) 1.5; 2) 19; 3) 47; 4) 72; 5) 93; 6) 119



La-monazite, $(La,Pu)PO_4$
doped with 8.1 wt. % Pu-238
completely different crystalline structure – but similar to cubic zirconia behavior under self-irradiation (so far !)

No swelling in ceramic based on La-monazite

doped with 8.1 wt.% Pu-238

Change of La-monazite ceramic color !

light-blue → grey

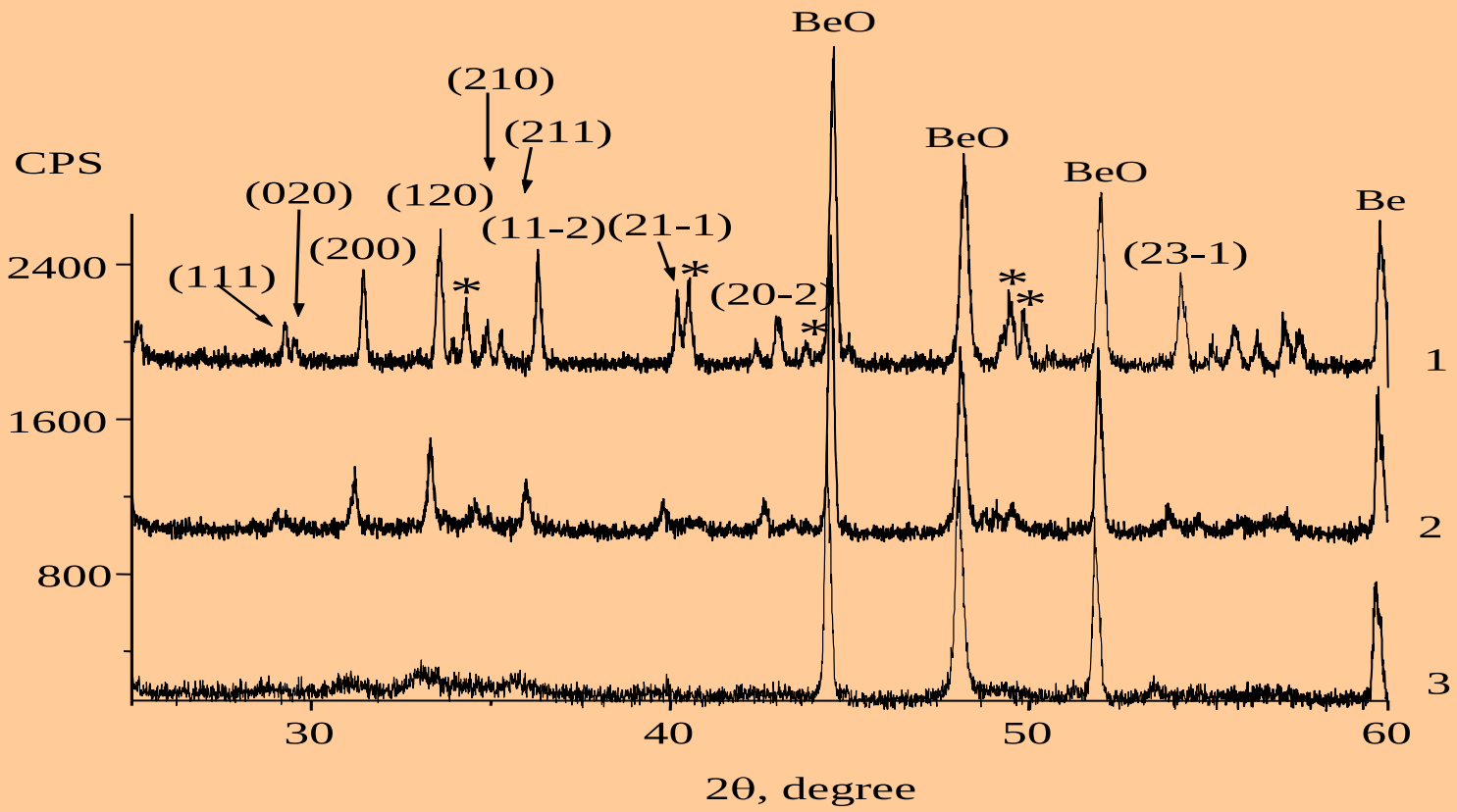
change of Pu valence state ?

Pu-monazite ceramic
$PuPO_4$

content of Pu-238 – 7.2 wt.%

Samples of this ceramic were synthesized at V.G. Khlopin Radium Institute

XRD patterns of ^{238}Pu-doped monazite $PuPO_4$ ceramic after cumulative dose (in alpha decay/m^3x10^{23}): 1) 1.3; 2) 17; 3) 42



Pu-monazite, $PuPO_4$
containing 7.2 wt. % Pu-238

very unstable under self-irradiation!

What is optimal actinide loading into monazite structure?

we do not know

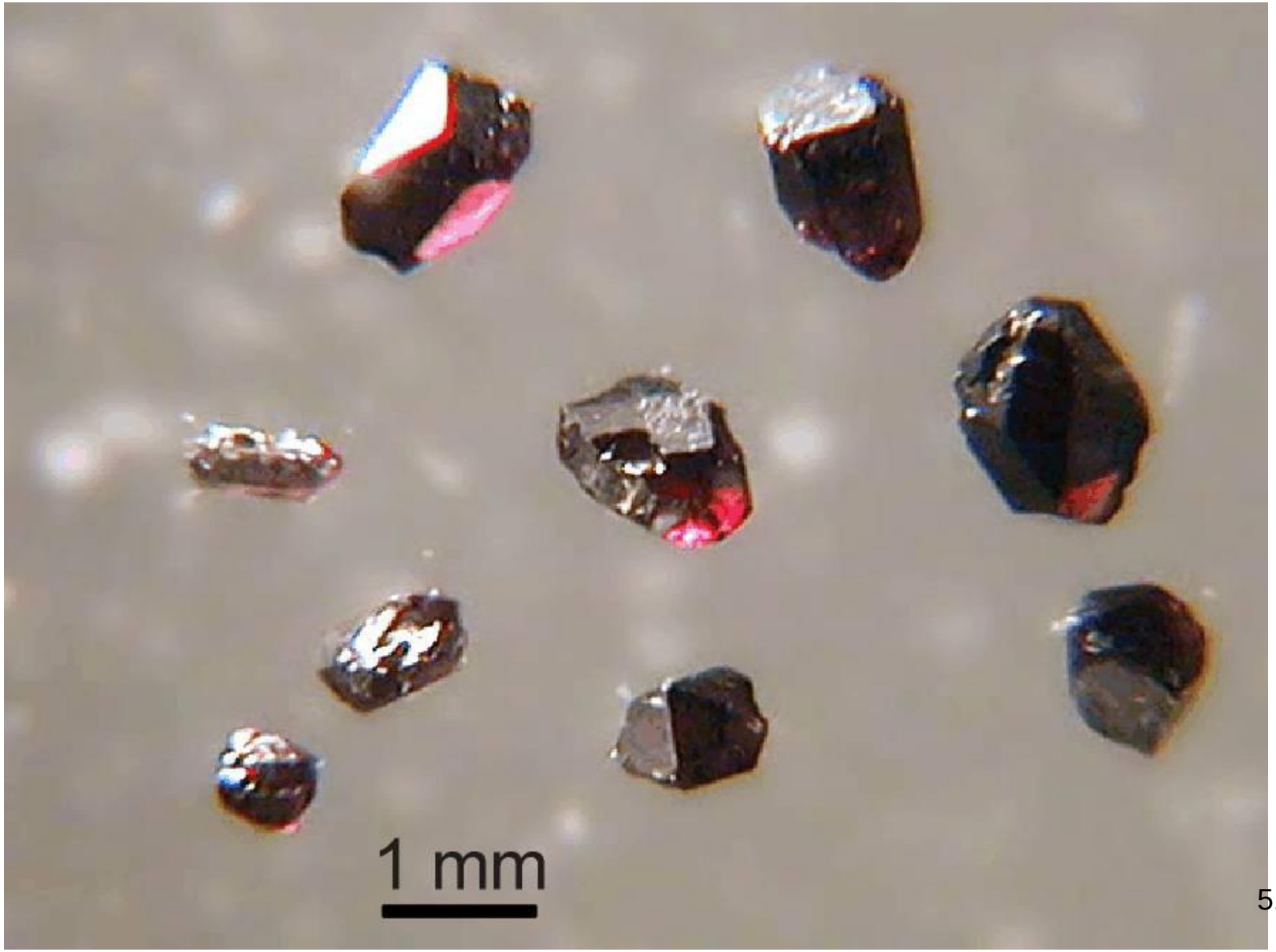
Strong swelling (even breaking into separate pieces) of ceramic based on Pu-monazite!

Change of Pu-monazite ceramic color !

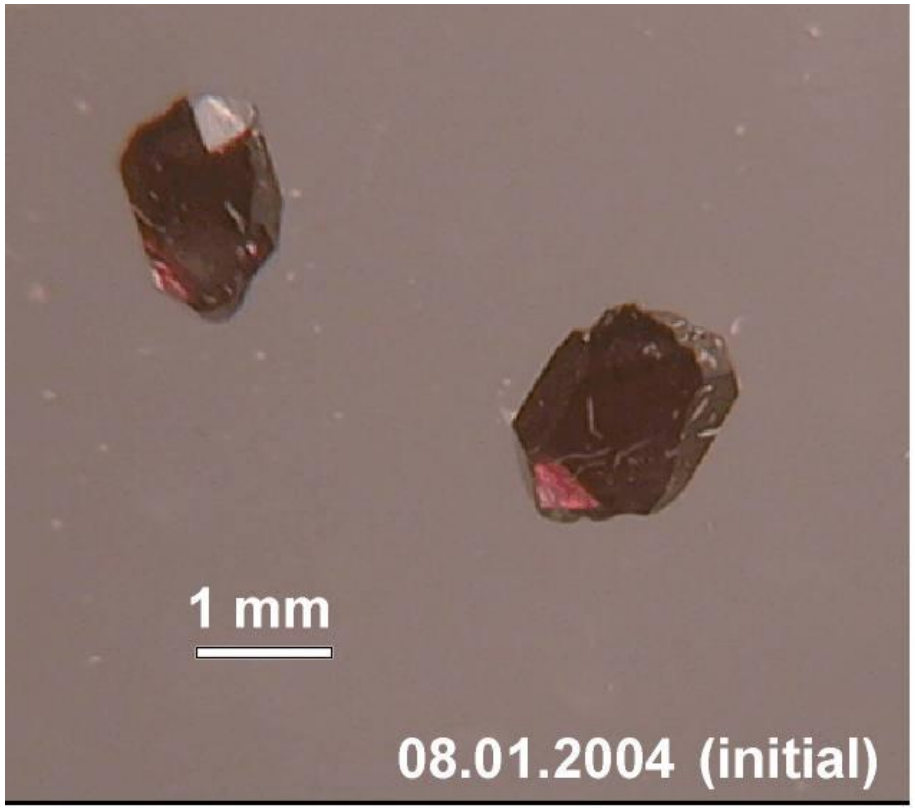
dark-blue → black

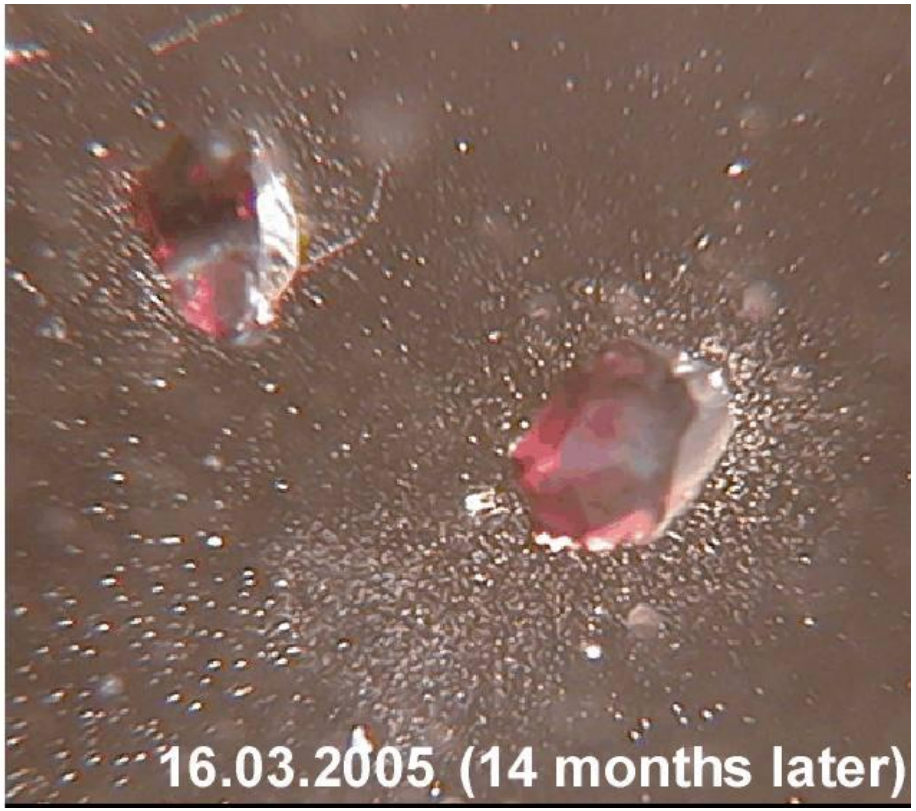
change of Pu valence state ?

Single crystals of Eu-monazite, $(Eu_{0.937}Pu_{0.063})PO_4$ doped with 4.9 wt.% ^{238}Pu



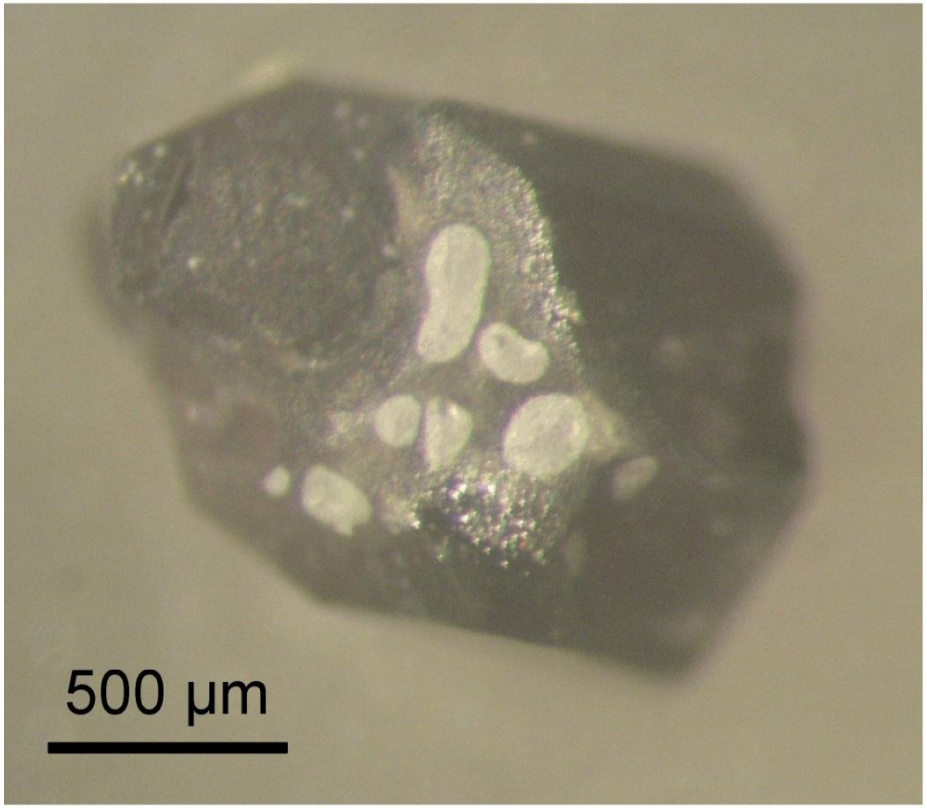
Single crystals of Eu-monazite, $(Eu_{0.937}Pu_{0.063})PO_4$ doped with 4.9 wt.% ^{238}Pu

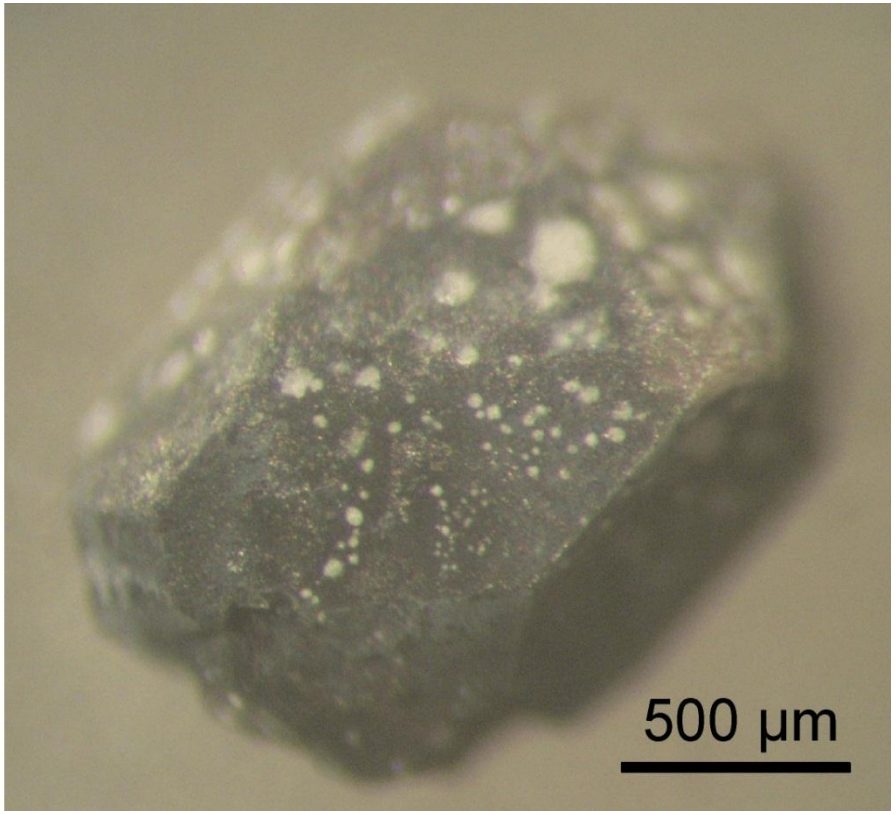




Single crystals of Eu-monazite, $(Eu_{0.937}Pu_{0.063})PO_4$ doped with 4.9 wt.% ^{238}Pu

7 years after sinthesis
accumulated dose 52 x10^{17} alpha-decay/g





Mechanical destruction and particle formation as a result of alpha-decay?

Possible mechanism of colloid formation ?

Principal features of ceramics and crystals doped with Pu-238

Sample, formula of main phase	Bulk Pu content and distribution, wt. % el.	^{238}Pu content, wt.% el.	Geometric density, g/cm^3	
			initial	at highest cumulative dose
Ti-pyrochlore ceramic $(Ca,Gd,Hf,Pu,U)_2Ti_2O_7$	10.5 inhomogeneous from 3.4 to 26.8	8.7	4.8	4.3 visually observed cracks
Zircon/zirconia ceramic $(Zr,Pu)SiO_4/(Zr,Pu)O_2$	5.7 homogeneous	4.7	4.4	no data no cracks visually observed
Cubic zirconia ceramic $Zr_{0.79}Gd_{0.14}Pu_{0.07}O_{1.99}$	12.2 homogeneous	9.9	5.8	5.8
La-monazite ceramic $(La,Pu)PO_4$	9.9 homogeneous	8.1	4.7	4.7
Pu-monazite ceramic $PuPO_4$	65.2 homogeneous	7.2	4.9	no data visually observed cracks
Zircon single crystal $(Zr,Pu)SiO_4$	3.3 inhomogeneous from 1.9 to 4.7	2.7	no data	no data visually observed cracks
Eu-monazite single crystal $(Eu,Pu)PO_4$	6.0 homogeneous	4.9	no data	no data visually observed shelling and particle formation

Normalized Pu mass losses (NL) from matrices of ^{238}Pu-doped ceramics after leach test (in deionized water, at 90° C for 28 days) depending on cumulative dose

Corrections for ceramic porosity were not estimated

Cumulative dose in ceramic doped with ^{238}Pu alpha decays/m^3 x 10^{23}	NL g/m^2	Equal years of storage calculated for the same ceramic but doped with ^{239}Pu
Cubic zirconia ceramic, $Zr_{0.79}Gd_{0.14}Pu_{0.07}O_{1.99}$		
11	0.04	30
56	0.35	140
81	0.37	200
127	0.24	320
Zircon/zirconia ceramic, $(Zr,Pu)SiO_4$ + 15 % $(Zr,Pu)O_2$		
7	0.01	30
31	0.04	150
43	0.05	210
66	0.04	330
Ti-pyrochlore ceramic, $(Ca,Gd,Hf,Pu,U)_2Ti_2O_7$		
29	0.22	80
49	0.28	140
100	0.84	280
133	1.93	380

Conclusions or questions ?

- Possible destruction of solid solution (in Ti-pyrochlore ceramic) as a result of self-irradiation?
- What is optimal loading level of actinides into host-phases to preserve stability of solid solution?
- Mechanical destruction and formation of tiny particles as a result of alpha-irradiation? *Possible mechanism of colloid formation?*
- Change of Pu valence state (from 3+ to 4+) in monazite under self-irradiation? If so, what does it cause?

Thank you!