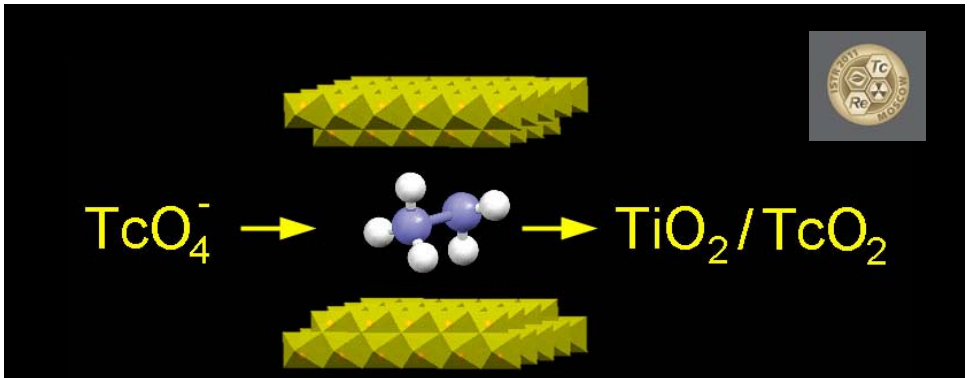
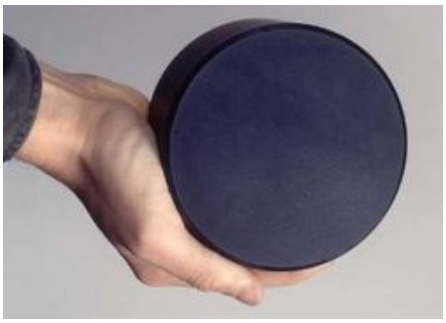


Layered Hydrazinium Titanate: Reductive Adsorbent for Irreversible Immobilization of Technetium

S.N.Britvin,[1] Y.I.Korneyko,[2] L. Kienle,[3] S.V. Krivovichev,[1] W. Depmeier[3]
[1]*St. Petersburg State University,* [2]*V.G.Khlopin Radium Institute,* [3]*Kiel University*

Titanate-based Waste Forms: SYNROC



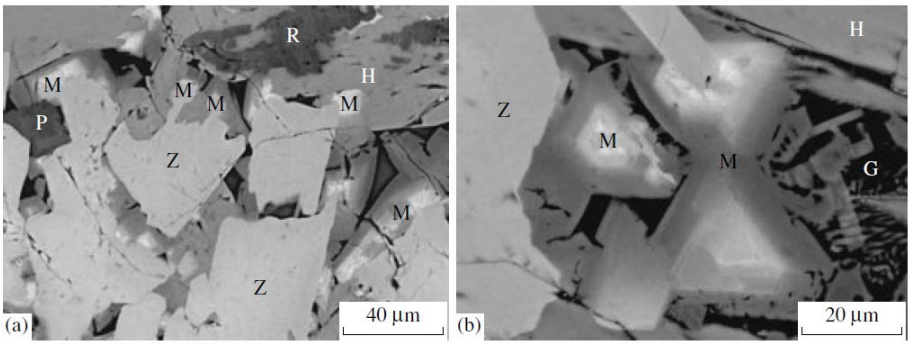
Hollandite	$Ba(Ti,Al)_8O_{16}$
Zirconolite	$CaZrTi_2O_7$
Perovskite	$CaTiO_3$
Pyrochlore	$Ln_2(Ti,Zr)_2O_7$
Rutile	TiO_2

Ringwood et al. 1978

www.eoearth.org

Titanate-based Waste Forms: Murataite

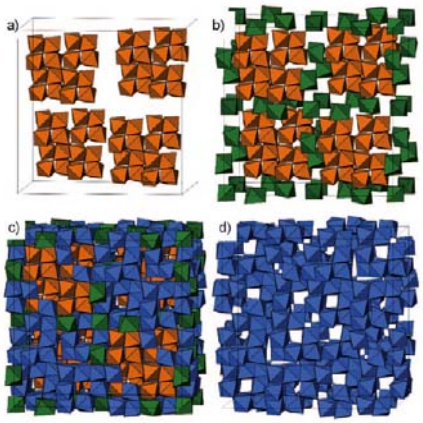
$(Ln,Na)_6(Zn,Fe)_5Ti_{12}O_{29}(OH,F)_{10}F_4$



Laverov N.P.; Yudintsev S.V.; Stefanovsky S.V.; Omel'yanenko B.I.; Nikonov B.S. *Geol. Ore Deposits* 2006, 48, 335-356.

Titanate-based Waste Forms: Murataite

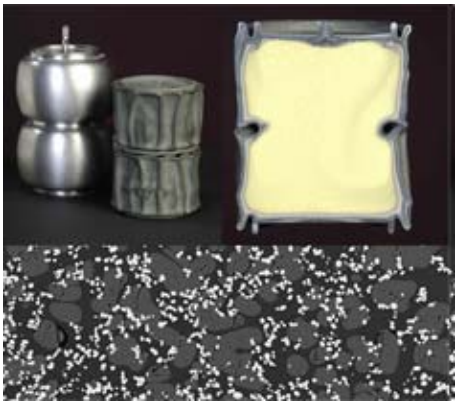
$(Ln,Na)_6(Zn,Fe)_5Ti_{12}O_{29}(OH,F)_{10}F_4$

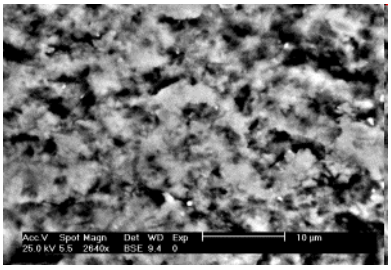


Krivovichev S.V.; Yudintsev S.V.; Stefanovsky S.V.; Organova N.I.; Karimova O.V.; Urusov V.S. *Angew. Chem*. 2010, 122, 10178-10180.

Titanate-Based Waste Forms: How to Prepare Suitable Matrix ?

Classic Approach:

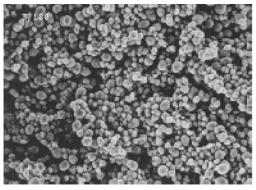




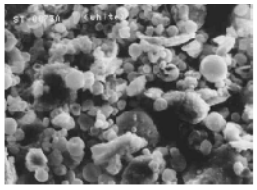
Grinding &
Calcination

In-situ Formation of Titanate Waste Precursor: "Sandia Solidification Process"

Amorphous Monosodium Titanate $NaTi_2O_4(OH)\cdot nH_2O$



MST #33180
1020x Magn.



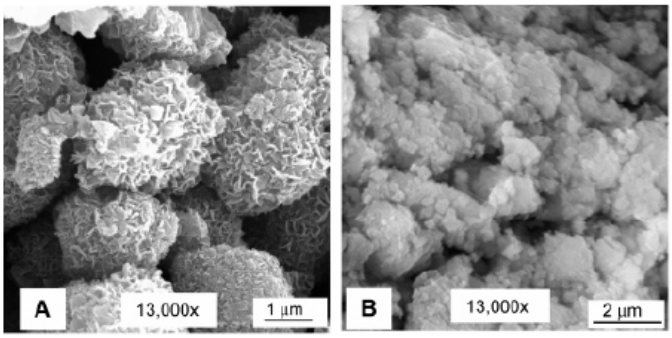
ST-0073A
1810x Magn.

ST-0073B
1820x Magn.

Direct Adsorption and Calcination

Lynch R., Dosch R., Kenna B., Johnstone J., Nowak E.
IAEA Symp. Management Rad. Waste. Vienna, 1976

In-situ Formation of Titanate Waste Precursor: Peroxo Complexes of Titanium



Chem. Mater. 2006, *18*, 6425−6435

A Family of Peroxo-titanate Materials Tailored for Optimal Strontium and Actinide Sorption

May Nyman*,† and David T. Hobbs*,‡

Drawbacks of Titanate Adsorbents

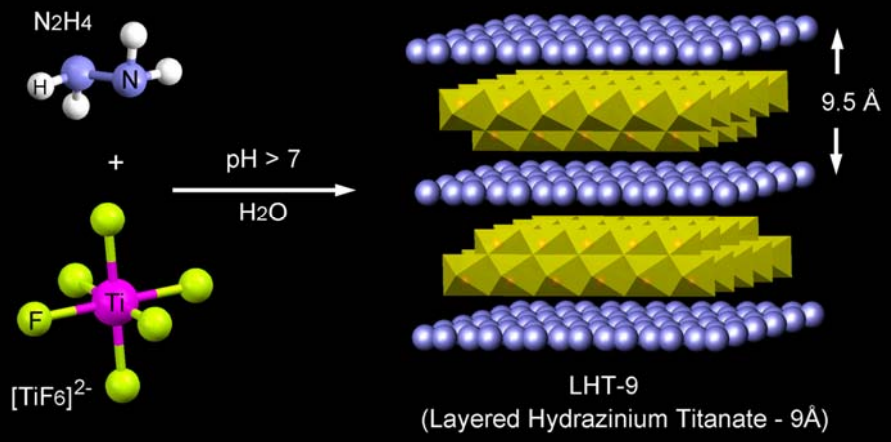
Enrichment in Sodium

Lack of Reductive Properties

~~TcO_4^- SeO_3^{2-} Pd^{2+}~~

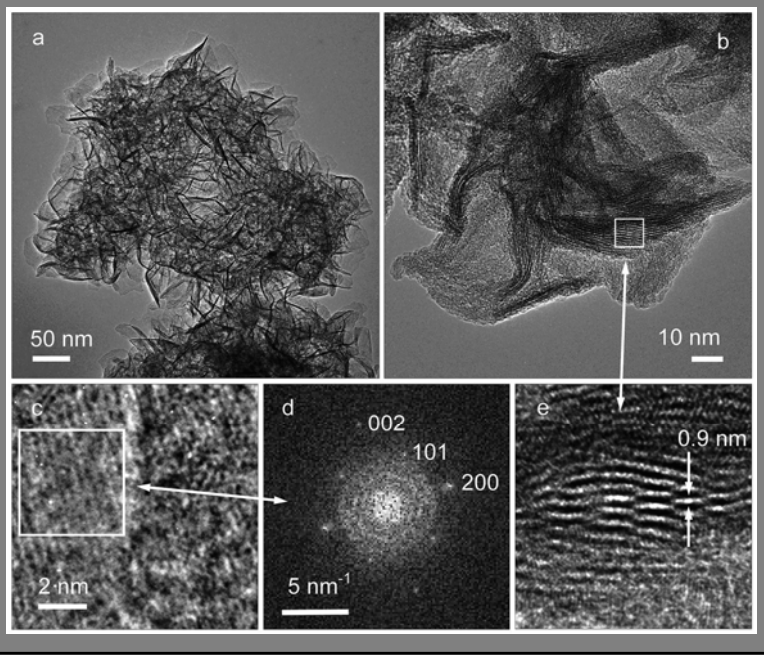
Layered Hydrazinium Titanate LHT-9

$(N_2H_5)_{0.5}Ti_{1.87}O_4$



S.N.Britvin, A.Lotnyk, L.Kienle, S.V.Krivovichev, W.Depmeier.
J. Am. Chem. Soc. 2011, 133, 9516-9525.

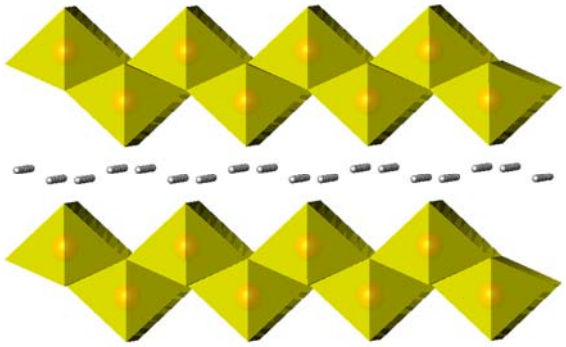
LHT-9: Layered Hydrazinium Titanate – 9 Å



Acta Cryst. (1968). B24, 1228

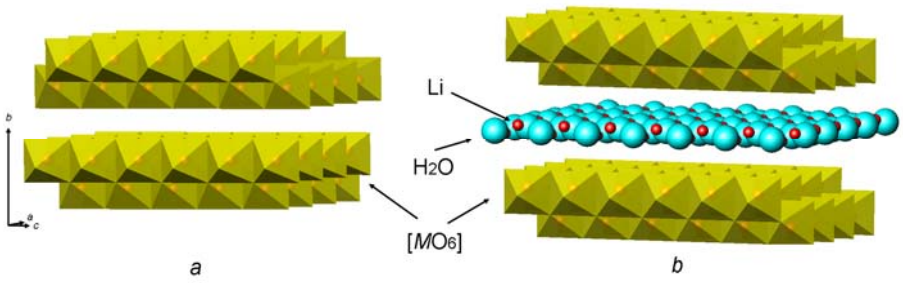
A New Class of Compound $M_x^+A_x^{3+}Ti_{2-x}O_4$ ($0{\cdot}60 < x < 0{\cdot}80$) Typified by $Rb_xMn_xTi_{2-x}O_4$

BY A. F. REID, W. G. MUMME AND A. D. WADSLEY
Division of Mineral Chemistry, CSIRO, Melbourne, Australia



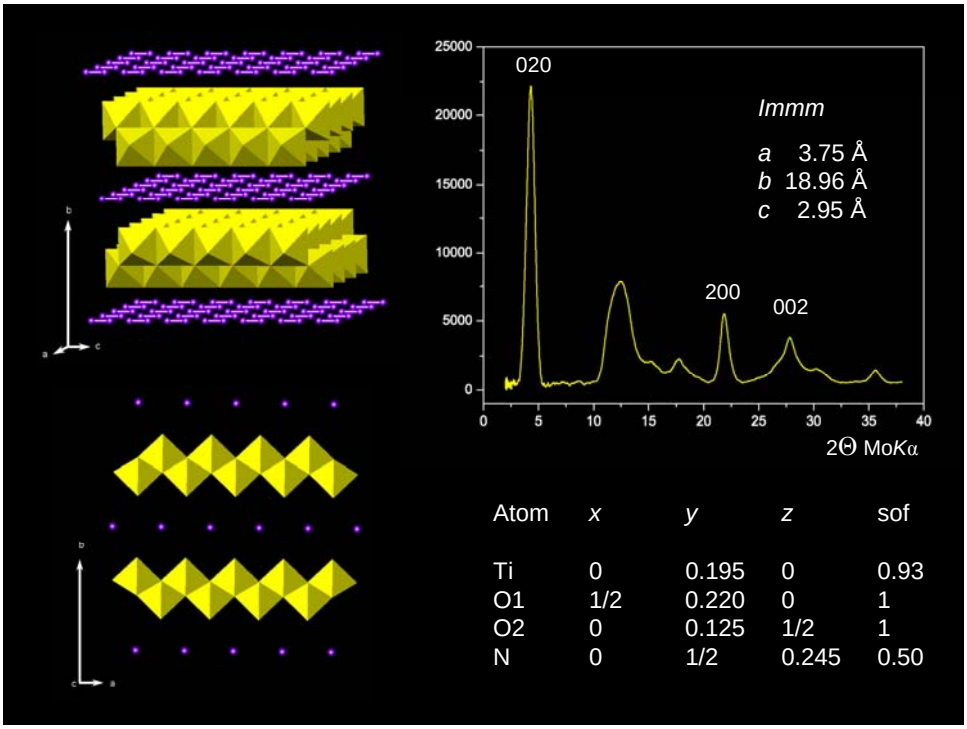
Lepidocrocite *γ*-FeOOH

Layered Titanates: Negatively Charged Octahedral Layers



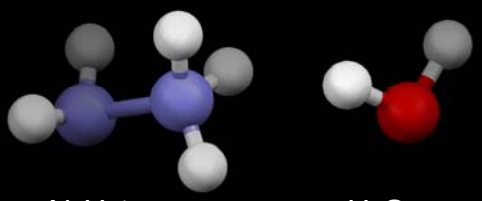
Lepidocrocite
***γ*-FeOOH**

$A_xTi_{2-4/x}\square_{4/x}O_4 \cdot nH_2O$
A **= alkali cation**

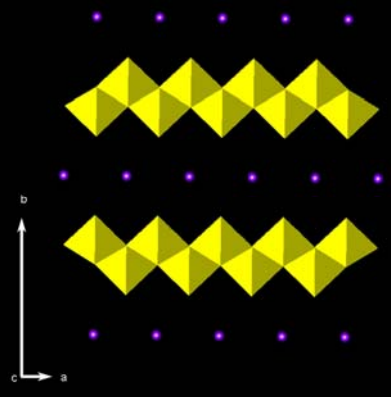


Atom	*x*	*y*	*z*	sof
Ti	0	0.195	0	0.93
O1	1/2	0.220	0	1
O2	0	0.125	1/2	1
N	0	1/2	0.245	0.50

Role of Hydrazinium: no H_2O or cations are required

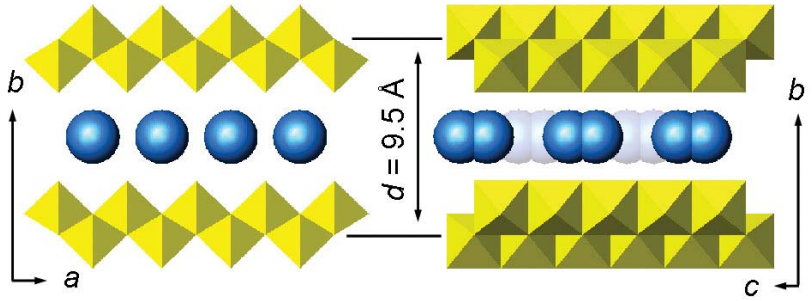


$N_2H_5^+$ H_2O



$(N_2H_5)_{0.5}Ti_{1.875}O_4$

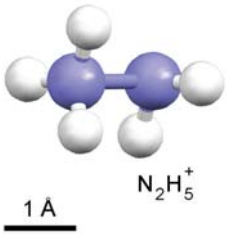
LHT-9: Advanced Functionality

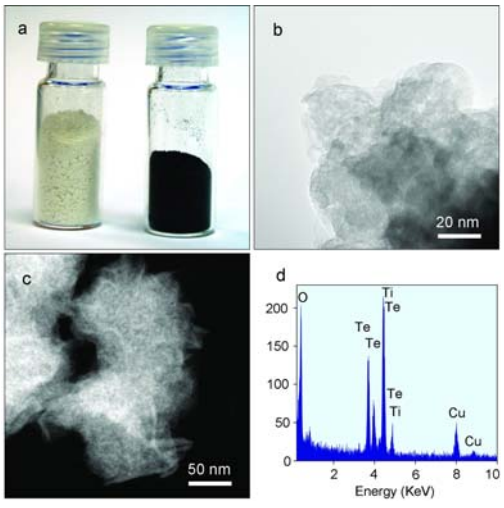


Ion Exchange: Layered Titanate

i.e. $(N_2H_5)_{0.5}Ti_{1.87}O_4 \longrightarrow Rb_{1/4}(N_2H_5)_{1/4}Ti_{1.87}O_4 \cdot nH_2O$

LHT-9: Advanced Functionality

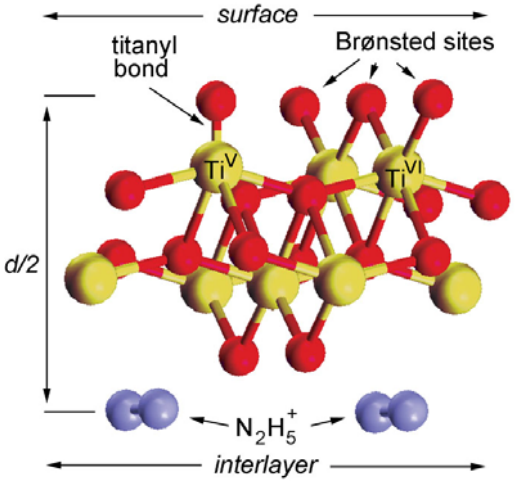




LHT-9 $\xrightarrow{H_6TeO_6}$ **TiO_2 / Te**

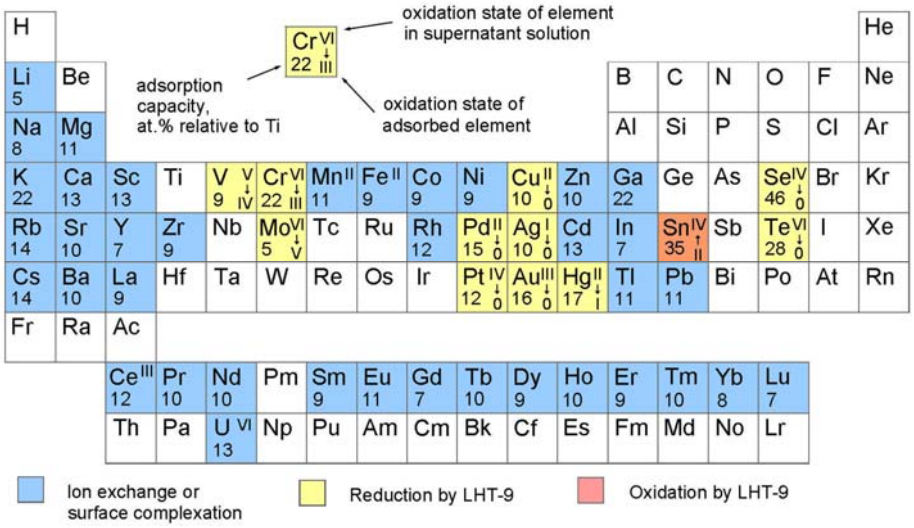
Redox Properties: Hydrazinium

LHT-9: Advanced Functionality

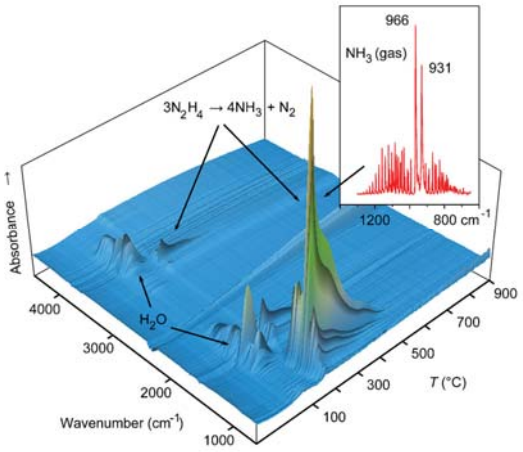


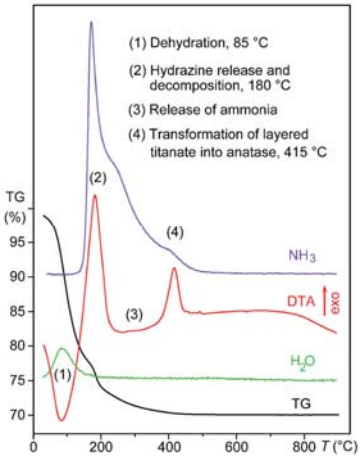
Surface Activity: Brønsted Sites & Titanyl Bonds

LHT-9: Combination of Reductive and Ion Exchange Properties



Final Product of Thermal Decomposition: Rutile TiO_2





Reductive Properties of LHT-9

$VO_3^- \longrightarrow V^{4+}$

$CrO_4^{2-} \longrightarrow Cr^{3+}$

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$

$MnO_4^- \longrightarrow Mn^{4+}$

$Fe^{3+} \longrightarrow Fe^{2+}$

$SeO_3^{2-} \longrightarrow Se^0$

$TeO_6^{6-} \longrightarrow Te^0$

$MoO_4^{2-} \longrightarrow Mo^{4+}$

$TcO_4^- \longrightarrow Tc^{4+}$

$Hg^{2+} \longrightarrow Hg_2^{2+}$ ↓ precipitation

Duration: 1 to 60 min

Cu Ag Au Pd Pt

↓

metals

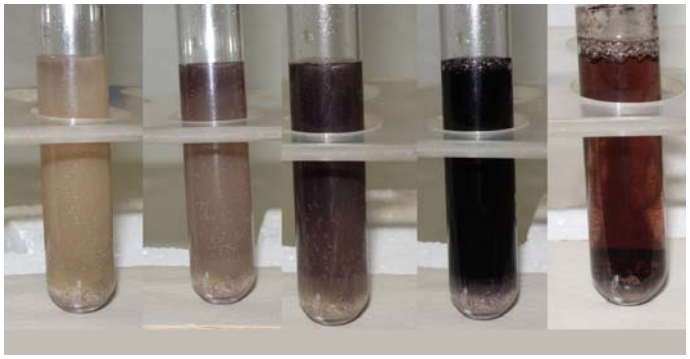
Reduction of Technetium by Hydrazine

$$4TcO_4^- + 3N_2H_4 \rightarrow 4TcO_2 + 3N_2\uparrow + 4OH^- + 4H_2O$$

Technetium and LHT-9

fast precipitation of Tc from:

- **neutral ($KTcO_4$)**
- **acid ($HTcO_4$)**
- **alkaline ($KTcO_4$) solutions**



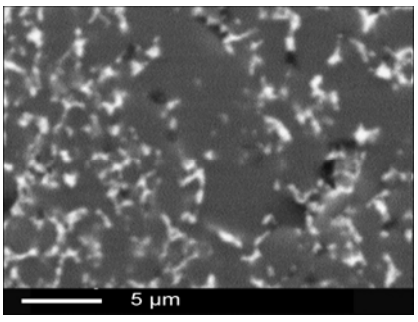
start **1 min** **3 min** **30 min** **1 day**

LHT-9 and Radionuclides

Radionuclide, compound	Initial concentration	Duration, hours	Removal, % of injected	Adsorption capacity, wt.%
^{99}Tc ($KTcO_4$)	**2 g/L**	**24**	**93**	**10**
^{137}Cs ($CsNO_3$)	87 MBq/L	1.5	94	11
^{90}Sr ($Sr(NO_3)_2$)	10 MBq/L	1.5	90	8
^{239}Pu ($PuCl_3$, pH 3)	40 g/L	24	95	12
^{238}U ($UO_2(NO_3)_2$)	50 g/L	24	97	15

Potential reducing additive to cement grout

Ready-to-use homogeneous precursors for stable titanate-based ceramics



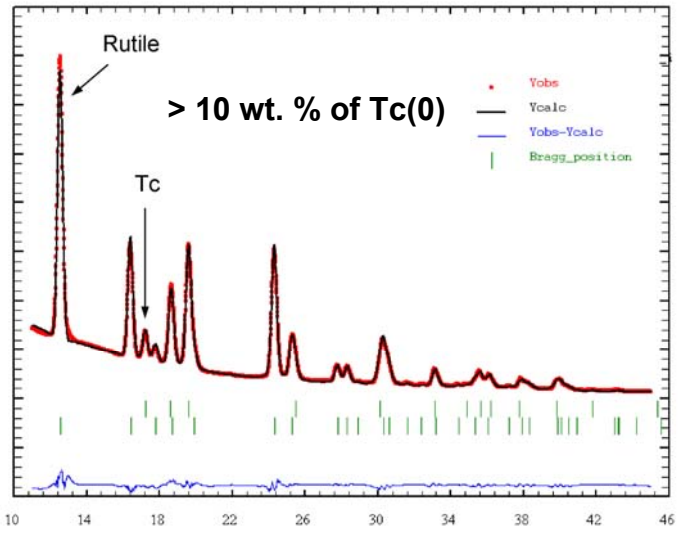
Ceramic pellet (8 mm) prepared by reductive sorption of pertechnetate on LHT-9 followed by sintering at 1200 °C in extrapure Ar.

Ready-to-use homogeneous precursors for stable TiO_2-based ceramics

Rutile	**$(Ti,Tc)O_2$**
Hollandite	**$K_{1-x}(Ti,Tc)_8O_{16}$**
Jeppeite	**$K_2(Ti,Tc)_6O_{13}$**
Metallic Tc	**Tc**

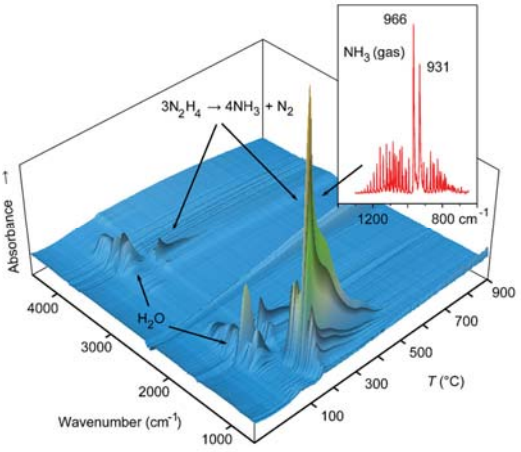
Tc(IV) → Tc(0) **H_2 CO CH_4**

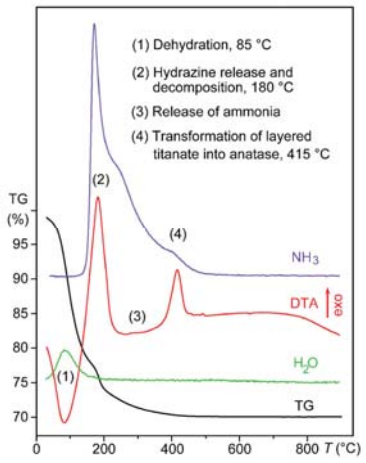
Thermally Induced Reduction of Tc to Tc (Metal)



$TcO_2 + N_2H_4 \rightarrow Tc + N_2 + 2H_2O$

Thermally Induced Reduction of Tc to Tc (Metal)





$TcO_2 + N_2H_4 \rightarrow Tc + N_2 + 2H_2O$

LHT-9: a Convenient Adsorbent and Precursor for Titanate Ceramic Forms

Thank you for your attention

This research was carried out under financial

support of DFG project DE 412/39-1 and

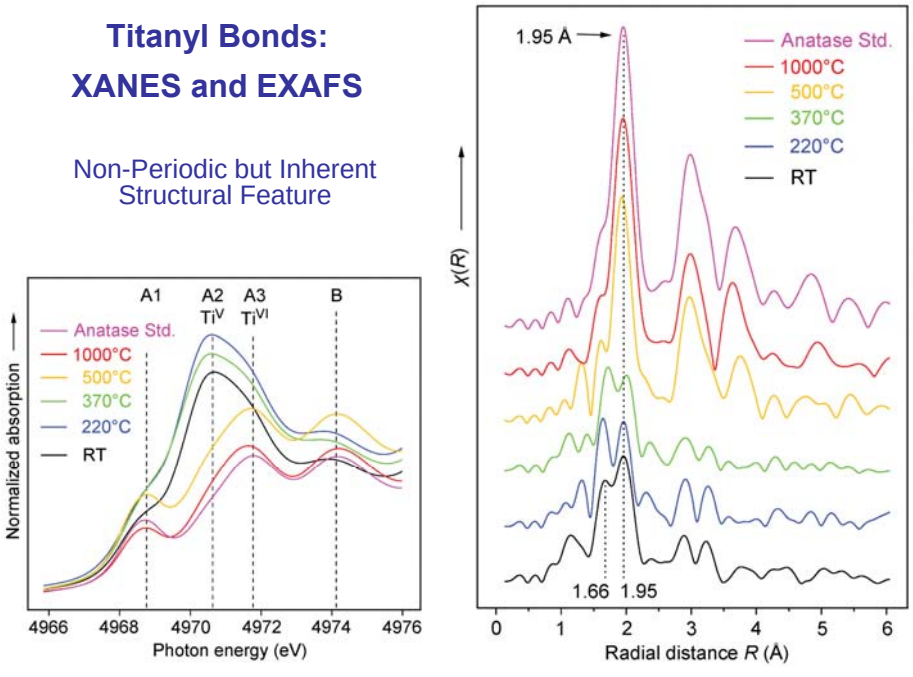
the Russian Federal Program "Scientific Cadres for

Innovative Russia“

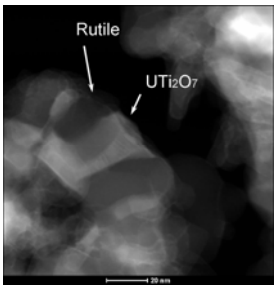
(state contract # 02.740.11.0326).

Titanyl Bonds: XANES and EXAFS

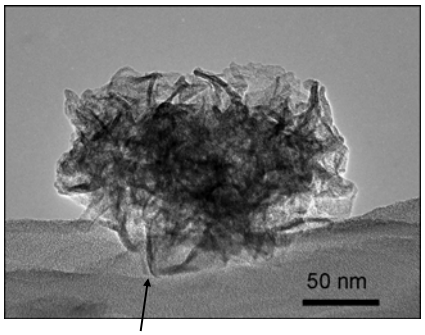
Non-Periodic but Inherent Structural Feature



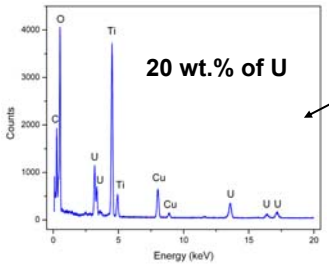
Sorption of U from 5%-$UO_2(NO_3)_2$ solution

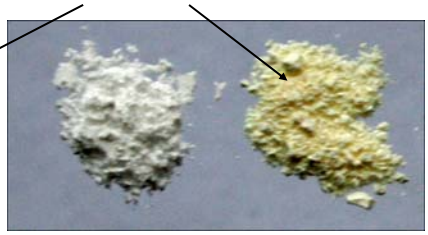


After 1000°C (Z-contrast)



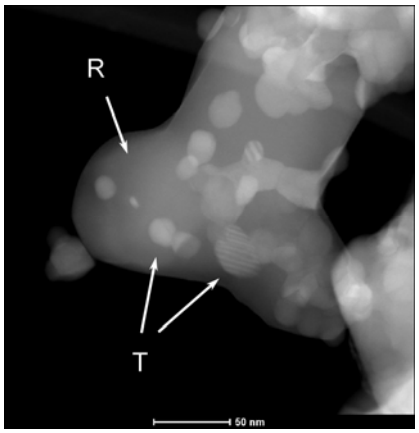
LHT-9 / U: as synthesized



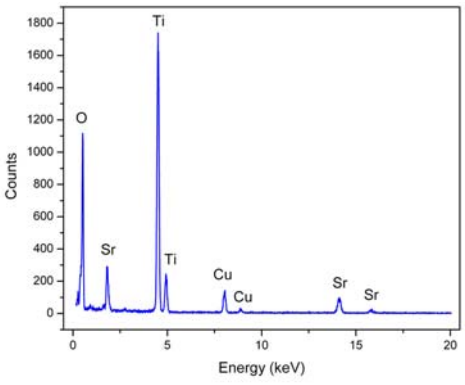


0 min 30 min

Sorption of Sr

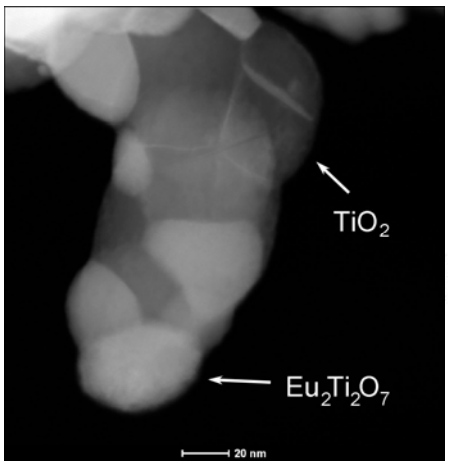


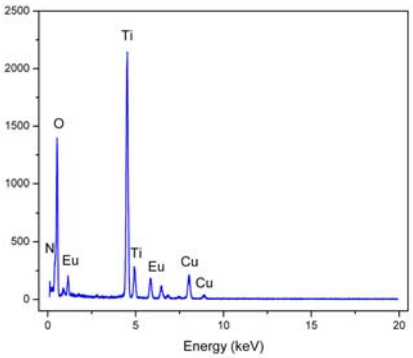
After 1000°C:
rutile TiO_2 + tausonite $SrTiO_3$
(Z-contrast)



~ 8 wt.% of Sr

Sorption of Lanthanides





Sintered at 1000°C: rutile TiO_2 + pyrochlore $Eu_2Ti_2O_7$

~ 12 wt.% of Eu