Dipartimento di Fisica e Astronomia Galileo Galilei

INFN PADOVA

The crystallization process in Ta_2O_5 and TiO_2-Ta_2O_5 amorphous films

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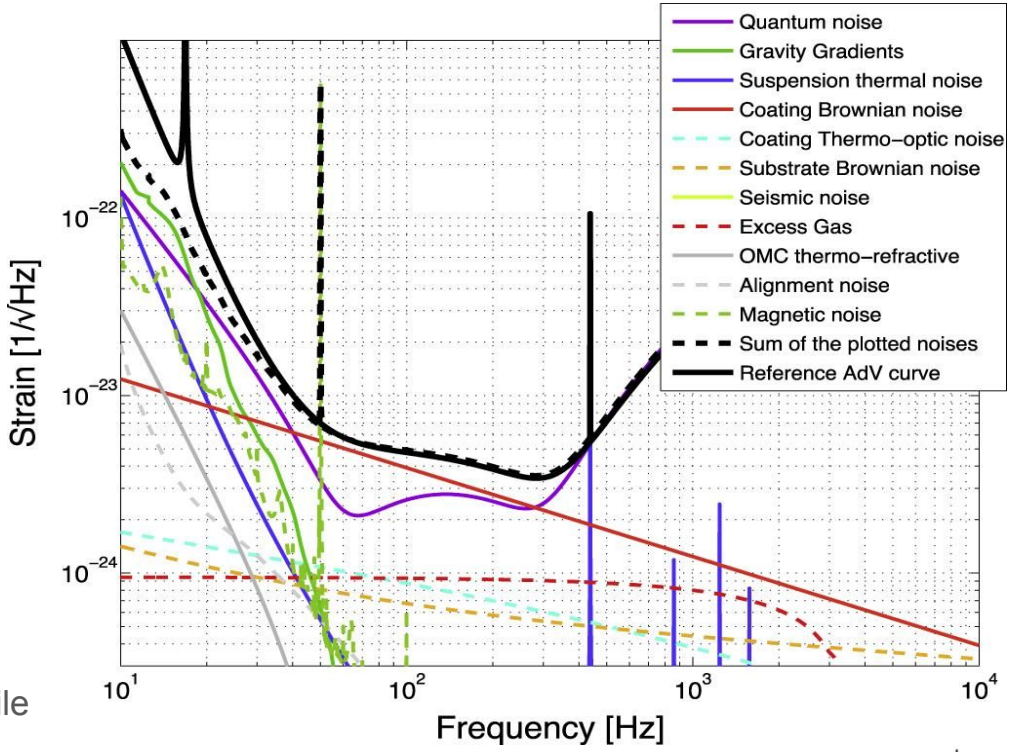
Introduction: Noise Sources in Virgo

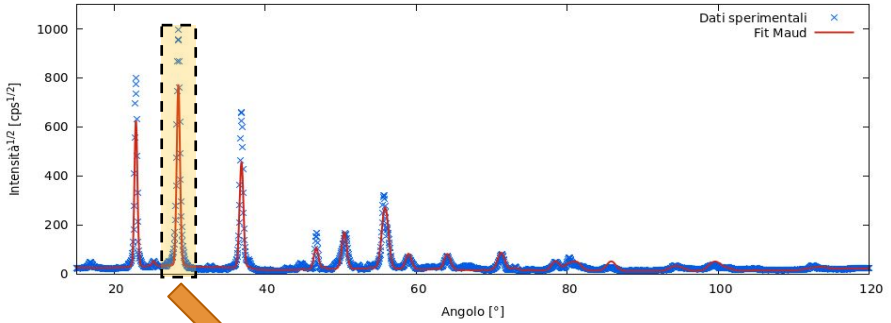
Among the various Noise source in the mid-frequency sensitivity region (50-300 Hz) the limiting detection factor is currently the Coating Brownian Noise **(CBN)**

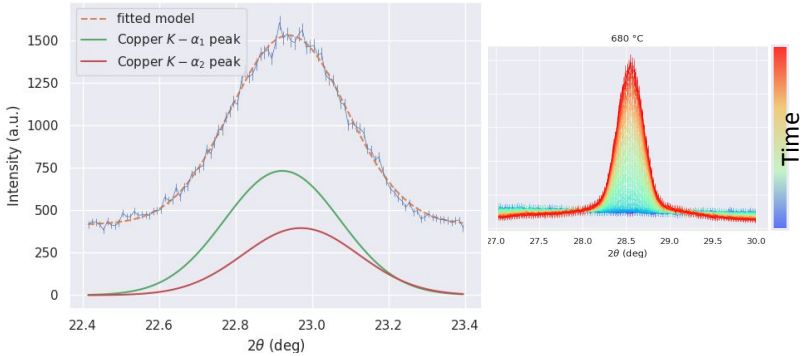
This phenomena originates mainly from the amorphous structure of the coatings materials. Although unavoidable the search for materials with lower losses it's fundamental

The solution we investigate to reduce the CBN consist in creating a crystallites dispersion in the materials while avoiding to have too high optical losses



Controlled Crystallization: Experiment





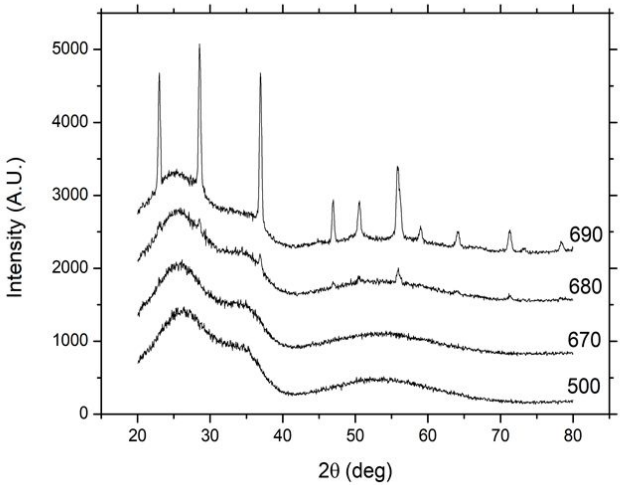
The sample we want to study gets annealed inside our X-Ray facility while being measured at the same time

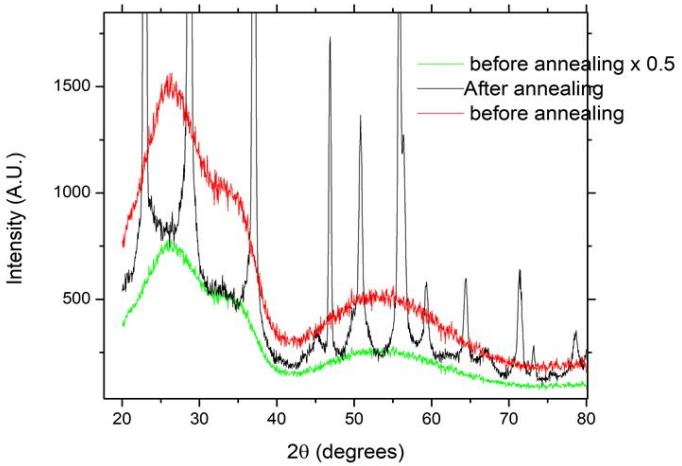
Only one diffraction peak gets measured during the annealing process to reduce dead time.
A full GIXRD spectra of our sample gets acquired at the end of the process

By performing GIXRD experiment we can extract informations regarding the amount of crystallized material and the mean dimension of the crystal grain

Controlled Crystallization: Data

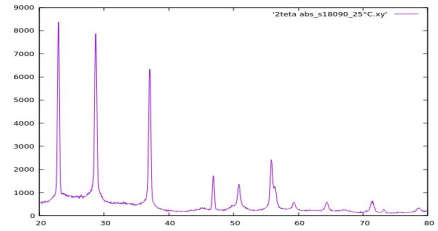
- Ta2O5 is a material with many polymorphs
- The first step is to determine what is the correct structure
- Rietveld analysis on full-profile XRD spectra



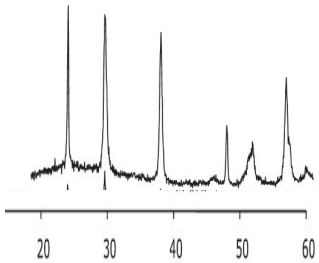


In general, we observe the sum of the amorphous spectrum and of the crystallized fraction

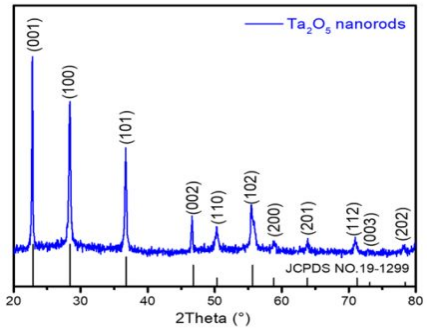
Comparison with literature



Our data (s18090 after annealing at 690°C)



Structure of Amorphous Tantalum Oxide and Titania-Doped Tantala: ^{17}O NMR Results for Sol Gel and Ion-Beam-Sputtered Materials, *Namjun Kim* and Jonathan F. Stebbins*

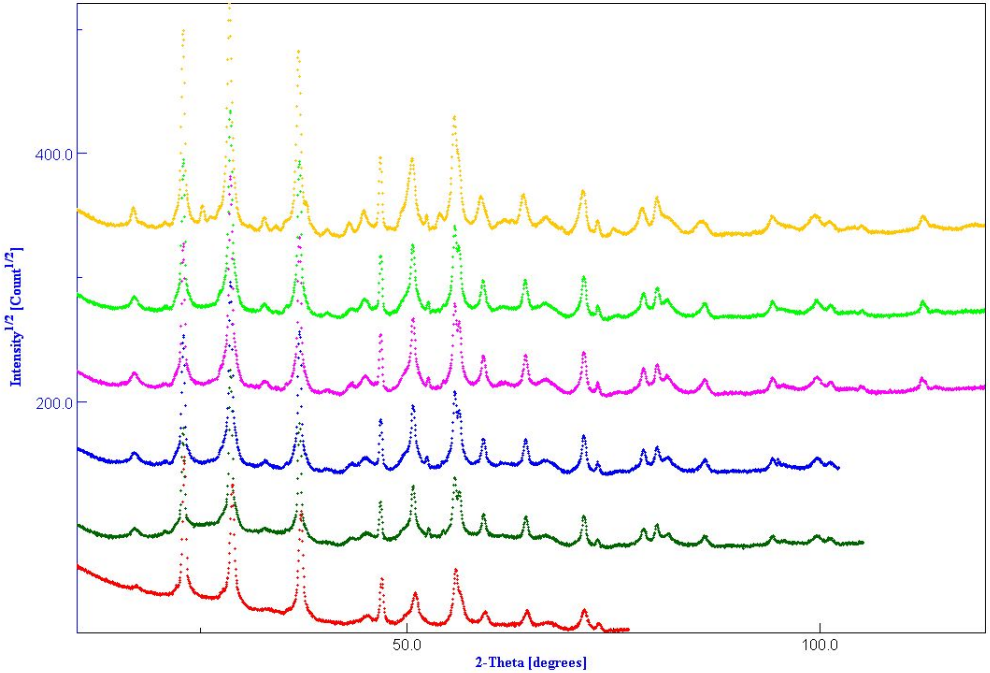


^{17}O Solid-State NMR Studies of Ta2O5 Nanorods, *Meng Xu, Junchao Chen, Yujie Wen, Jia-Huan Du, Zhiye Lin, and Luming Peng*

Experimental XRD spectra are well reproducible and coherent with literature. However:

- Disagreement on the type of structure to be attributed
- The most widely accepted structure (β – Ta2O5 orthorhombic) has a very large unit cell with many degree of freedom which makes the results not very significant.

Spectra comparison



The spectra at different temperatures are consistent → single phase appearing. Difference related to small changes in structure/microstructure

TiO2:Ta2O5, isochronal annealing up to 900 °C

TiO2:Ta2O5, @ 720 °C, 30h

TiO2:Ta2O5, @ 700 °C, 33h

TiO2:Ta2O5, @ 690 °C, 33h

TiO2:Ta2O5, @ 680 °C, 36h

Ta2O5, @ 680, 33h

Phase Diagram: possible TiO2 - Ta2O5 demixing at high T

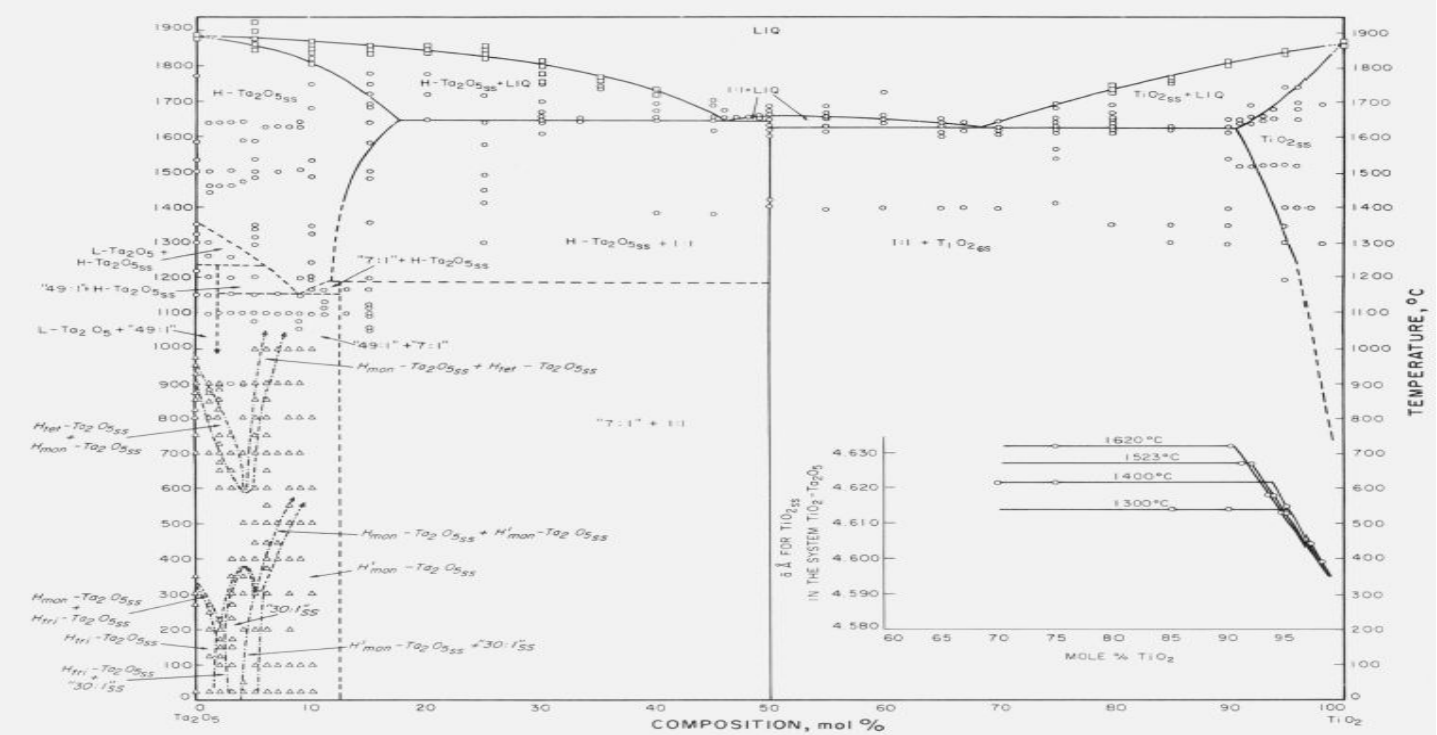
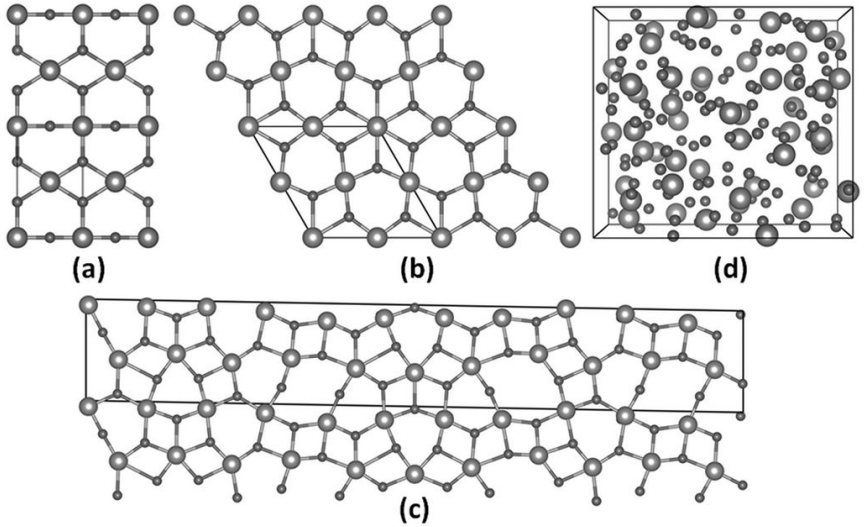


FIGURE 1. *Phase equilibrium diagram for the system* TiO_2-Ta_2O_5.

In all cases, the formation of pure Ta2O5 crystals implies that a demixing process takes place

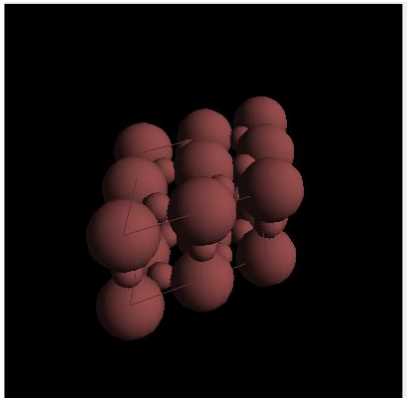
At T>720°C, extra XRD peaks may point to the formation of TiO2 nanocrystals, i.e., three-phase deximing

Ta2O5 candidate structures



Crystal structures of (a) β-Ta2O5, (b) δ-Ta2O5, (c) the 11 f.u. model, and (d) amorphous tantalum pentoxide.

J. Lee; W. Lu; E. Kioupakis; *Appl. Phys. Lett.* **105,** 202108 (2014)
DOI: 10.1063/1.4901939



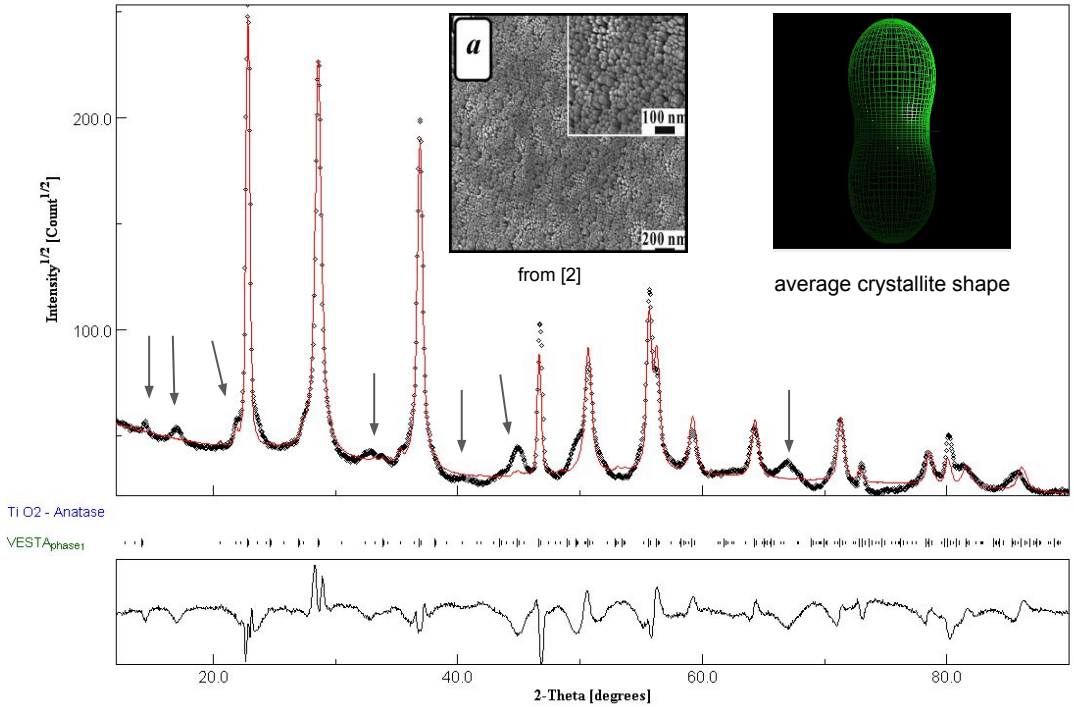
New structure, derived from recent total scattering data (

- Symmetry: hexagonal
- Space group: P6/mmm
- Cell parameters: a = 7.19 Å; c = 3.83 Å

- VIR-0324A-21
- A. Martinelli et al Phys. Rev. Materials 5, 115603 – 2021

Rietveld refinement with the hexagonal model

Ta2O5 (s18118)



Fitting program: MAUD
Model: non spherical crystallites
a = 7.2059(8) Å, c = 3.8898(6) Å
B = 6.7 Å^2 (!)
<R> ≅ 50 nm
Rwp = 16.4 %

- Main peaks are reasonably well fitted with a simple model.
- Elongated crystallites have been observed in Ta2O5 deposited by high-T CVD methods [1,2]

- Several low intensity features are not explained
- High B value

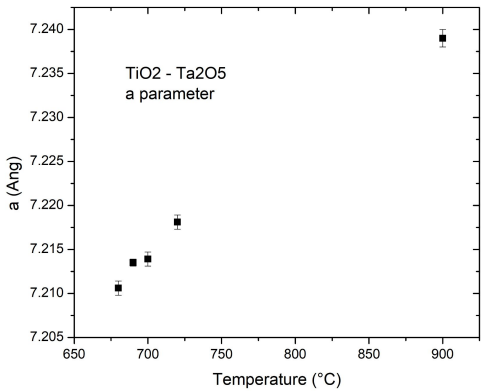
[1] Materials Research Bulletin, 67, 2015, 20-46,
[2] Nanotechnology, 20 (2009), p. 445708

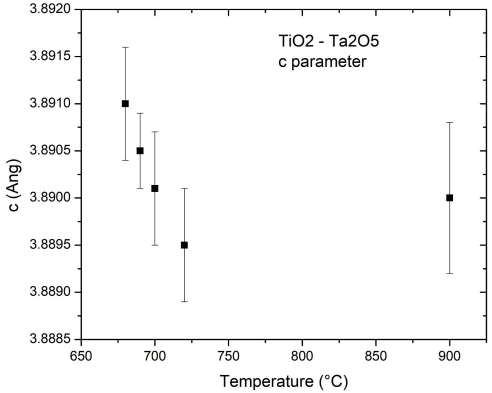
TiO2:Ta2O5 Microstructure vs annealing temperature

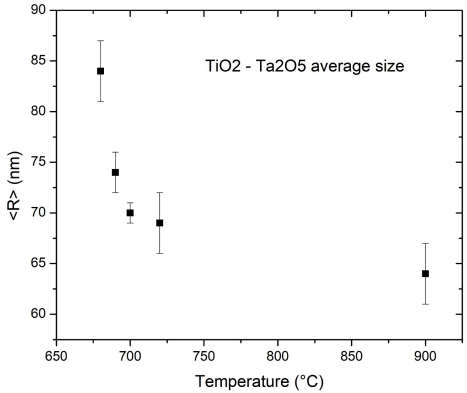
Isotropic model (spherical crystallites)

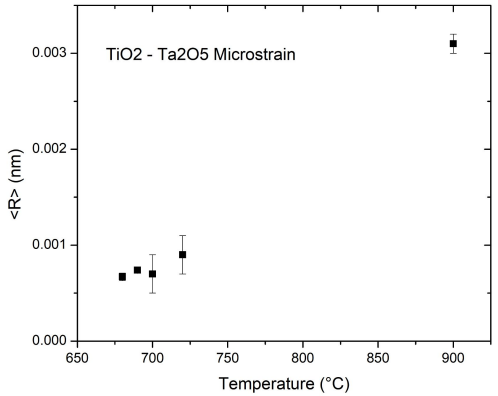
Temperature	a (Å)	c (Å)	<R> (nm)	microstrain	B_{Iso} ($Å^2$)	Rwp
680°C	7.2106 ± 0.0008	3.8910 ± 0.0006	84 ± 3	(6.7 ± 0.4) $\times 10^{-4}$	4.5 ± 0.1	14.7%
690°C	7.2135 ± 0.0004	3.8905 ± 0.0004	74 ± 2	(7.4 ± 0.1) $\times 10^{-4}$	4.6 ± 0.1	18.7%
700°C	7.2139 ± 0.0008	3.8901 ± 0.0006	70 ± 1	(7 ± 2) $\times 10^{-4}$	4.5 ± 0.1	19.6%
720°C	7.2181 ± 0.0008	3.8895 ± 0.0006	69 ± 3	(9 ± 2) $\times 10^{-4}$	4.5 ± 0.1	18.4%
Isochronal annealing up to 900°C	7.239 ± 0.001	3.8900 ± 0.0008	64 ± 3	(31 ± 1) $\times 10^{-4}$	4.4 ± 0.1	18.8%

Microstructure vs Annealing temperature







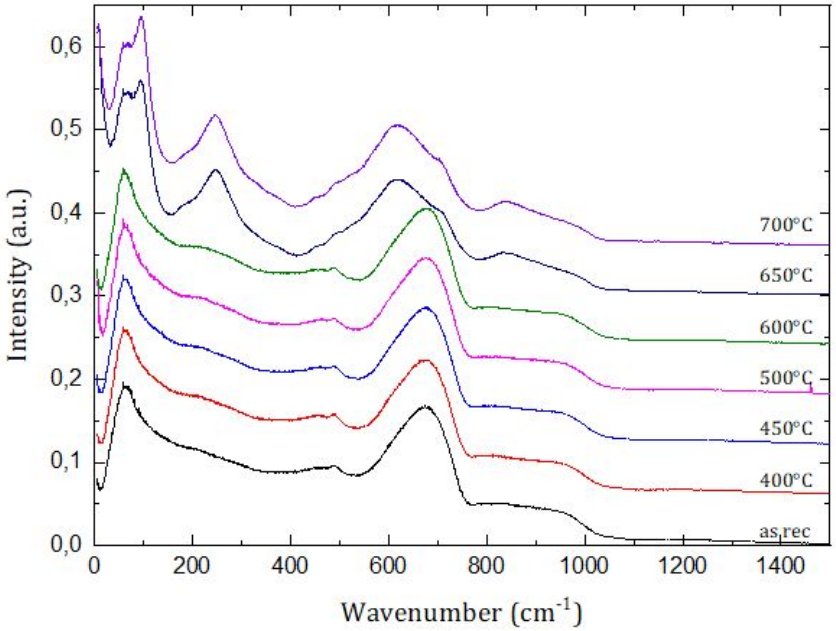


Increasing the annealing temperature both structural and microstructural parameters exhibit a clear trend.

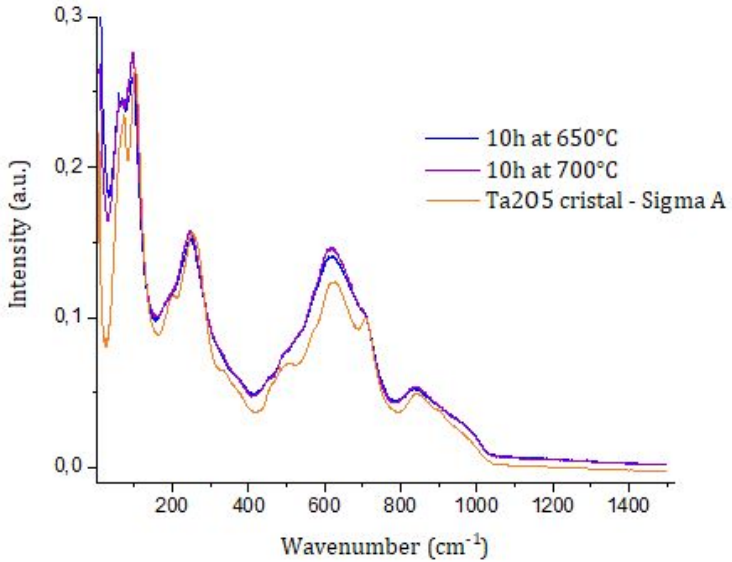
Possible indication that the crystal structures forming at different temperatures are characterized by a different defect structure.

Raman analysis - Ta2O5

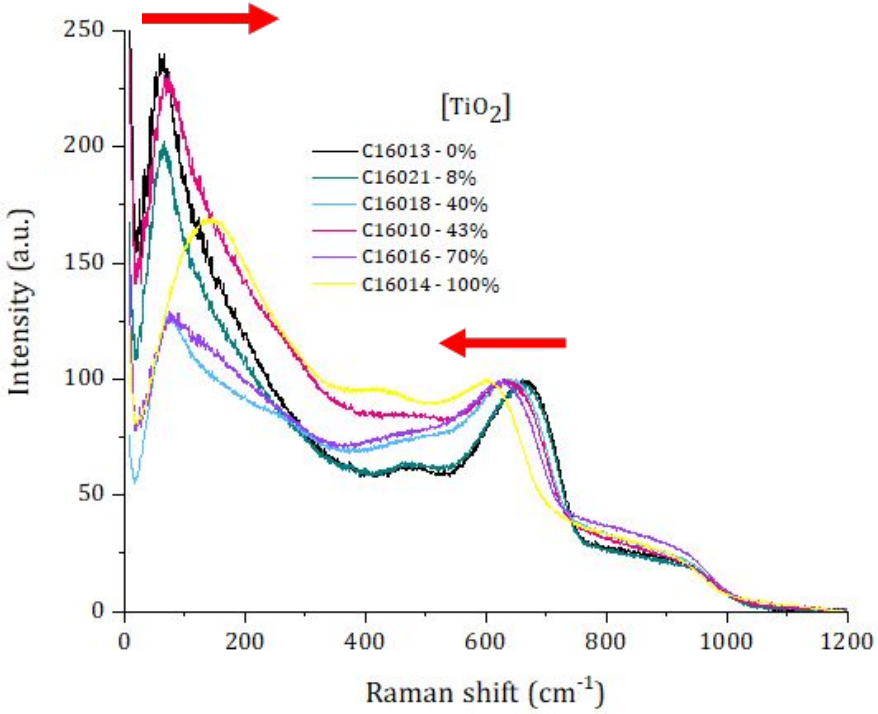
Annealing time = 10h



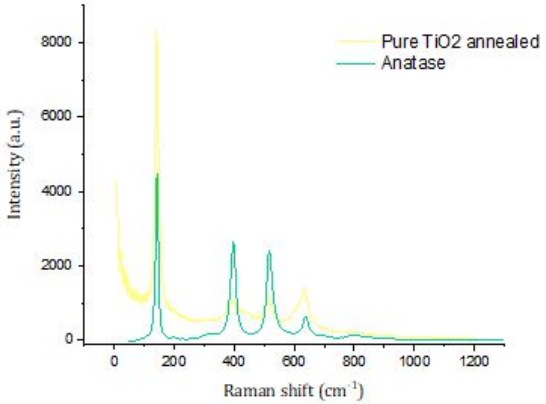
Crystallization can be detected also by Raman spectroscopy



Raman analysis - TiO2 doped Ta2O5



After an annealing in air at 500°C during 10h



Ab initio Raman simulations : crystal *vs* amorphous

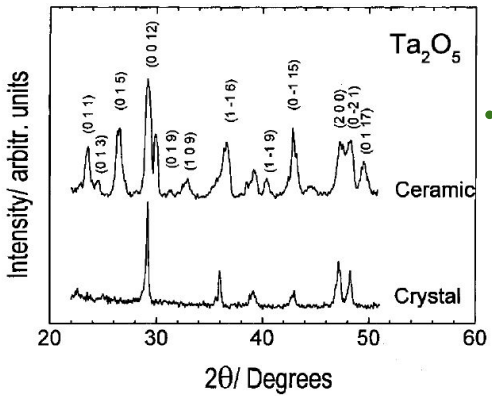
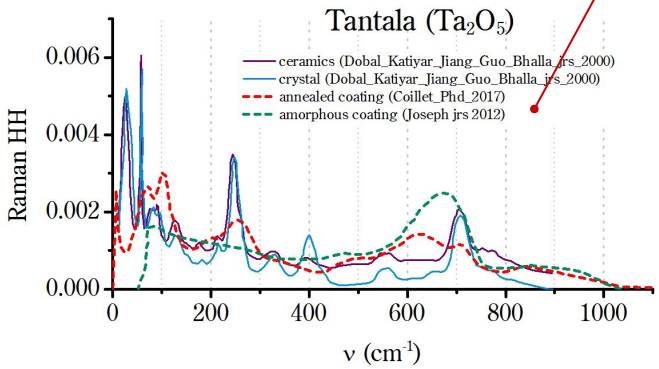
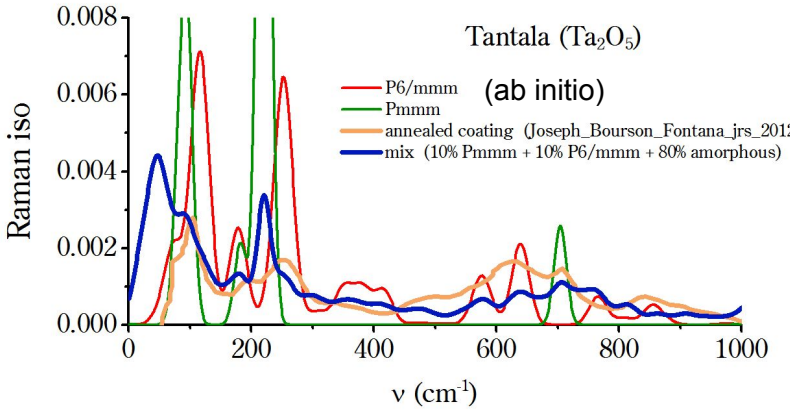


Figure 1. Room temperature x-ray diffraction patterns of ceramic

XRD and **Raman** evidence that an <u>annealed</u> coating is tending to be crystalline but still contain a significant <u>amorphous</u> fraction!

Possible solution: fit the spectrum with amo. and crys. fractions to assess the degree of crystallization and type of crystalline phase



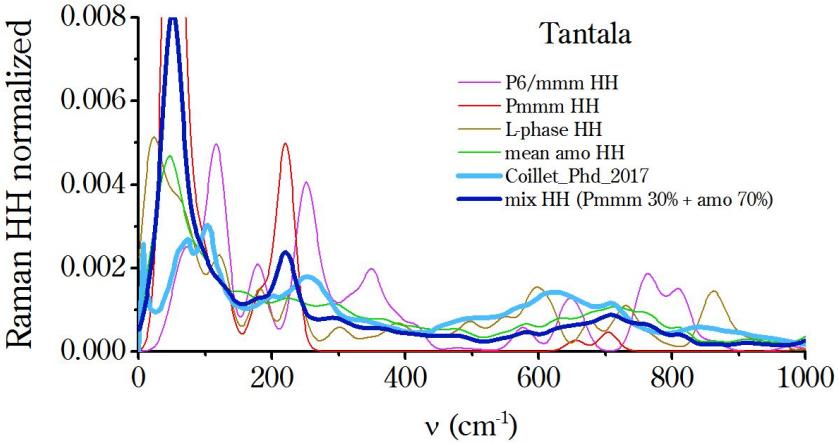


(ab initio)

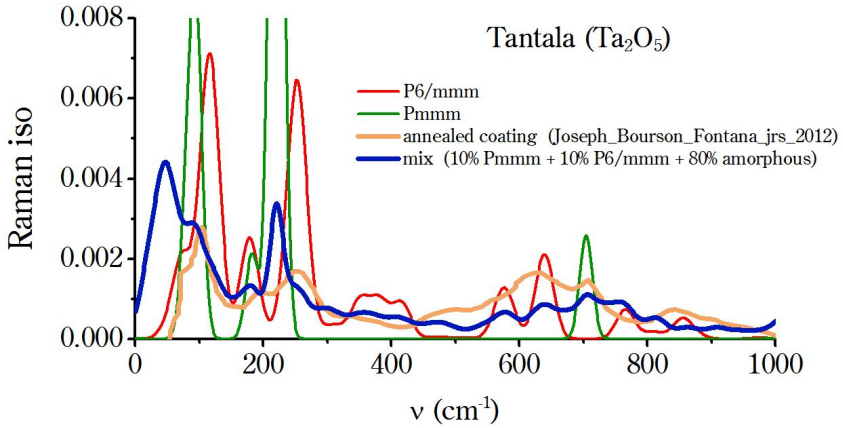
(ab initio data)

Ab initio Raman simulations : fitting

Raman HH (Pmmm vs amo.)



Raman ISO (Pmmm+P6/mmm vs amo.)



Q: one or two cryst. phases are present ?

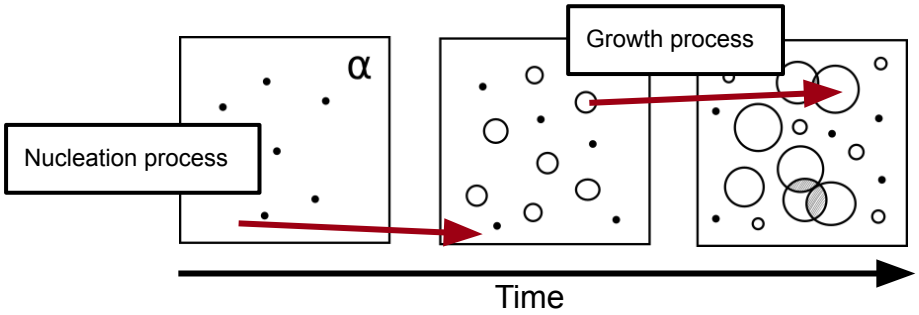
Crystallization kinetics

Avrami equation describes the evolution of the crystal fraction with respect to time

$$\chi(t) = 1 - exp\left[-\left(\frac{t}{\tau_c}\right)^{\alpha}\right]$$

There are two processes that contribute to crystallization: nucleation and crystal growth. These processes are related to the crystallization time by the formula

$$\tau_c = \left(\frac{\alpha\Gamma(\frac{\alpha+1}{2})}{\pi^{\frac{\alpha-1}{2}} j_{ss} v_g^{\alpha-1}}\right)^{1/\alpha}$$



J_{SS} : Nucleation rate
v_g : Growth velocity

α is a characteristic exponent related to the dimensionality of the growth process. For 3D growth α=4.

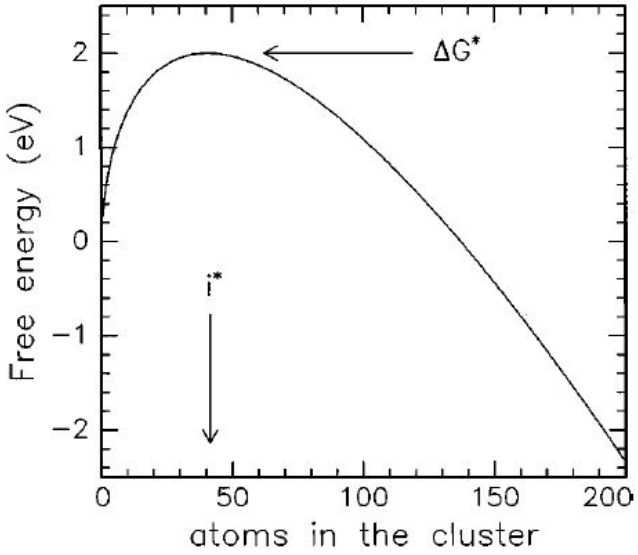
Classical nucleation theory

Nucleation and growth are thermally activated processes. By measuring the energies we are able to compute the effects of an annealing treatment, in terms of average particle size and average density.

$$v_g = \frac{V_0}{k_B T} e^{-\left(\frac{E_f + E_m}{k_B T}\right)}$$

$$j_{ss} = \frac{J_0}{\sqrt{k_B T}} e^{-\left(\frac{E_f + E_m + \Delta G^*}{k_B T}\right)}$$

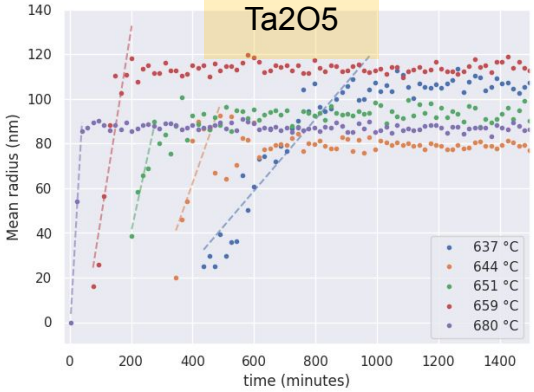
$$\tau_c^{\alpha} = \frac{\alpha \Gamma\left(\frac{\alpha+1}{2}\right)(K_b T)^{\frac{2\alpha-1}{2}}}{\pi^{\frac{\alpha-1}{2}} J_0 V_0^{\alpha-1}} e^{-\left(\frac{\alpha E_f + \alpha E_m + \Delta G^*}{K_b T}\right)}$$



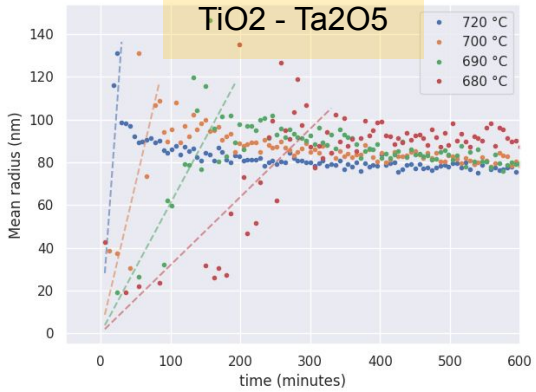
Nucleation barrier

Growth velocity

Ta2O5



TiO2 - Ta2O5

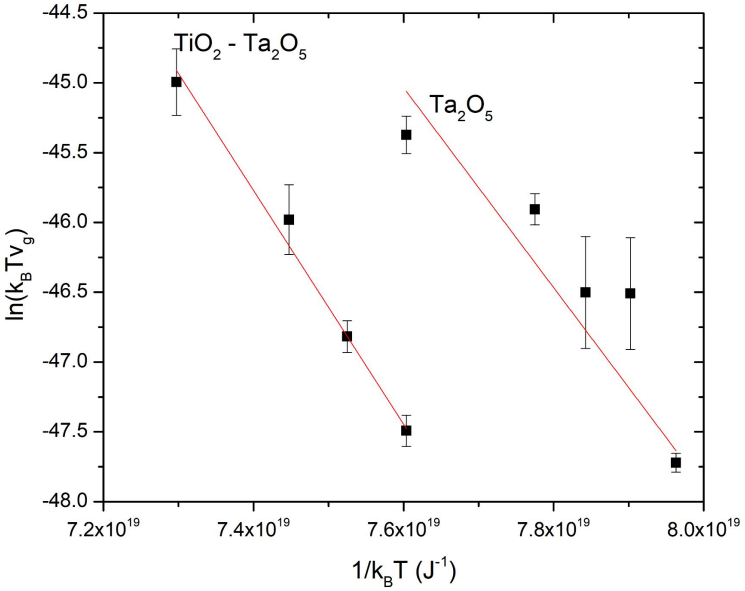


Temperature (°C)	v_g(nm/min)	<R> (nm)
637	0.16 ± 0.02	106 ± 8
644	0.4 ± 0.1	78 ± 5
651	0.6 ± 0.2	93 ± 6
659	0.9 ± 0.2	114 ± 5
680	2.4 ± 0.7	86 ± 3

Temperature (°C)	v_g(nm/min)	<R> (nm)
680	0.32 ± 0.04	80 ± 40
690	0.61 ± 0.06	80 ± 30
700	1.4 ± 0.4	80 ± 30
720	5 ± 1	80 ± 10

- At equal temperatures, Ti-doped tantala displays a much slower growth rates.
- Possibly, Ti atoms form bonds that hinder Ta and O atoms rearrangement
- The observed decrease in particle size for the TiO2 - Ta2O5 is probably an artifact due to the slow buildup of microstrain during the annealing process

Activation energies

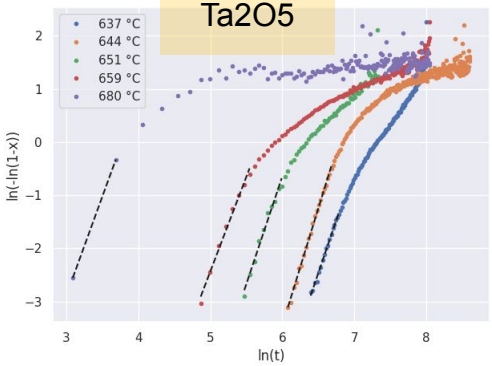


Ta2O5 : Ef + Em = (4.5 ± 0.6) eV
TiO2 - Ta2O5 : Ef + Em = (5.5 ± 0.3) eV

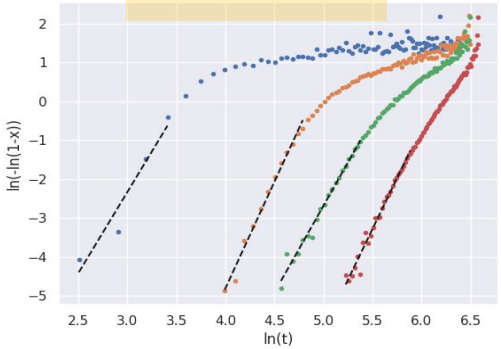
The addition of TiO2 slows down the crystal growth process and seems to increase the activation energy required to rearrange the atoms at the grain surface.

Crystallization Kinetics

Ta2O5



TiO2 - Ta2O5



Avrami equation in double-log anamorphosis:

$$ln\left[-ln\left(1-\chi(t)\right)\right] = \alpha ln(t) + q$$

Temperature (°C)	α	q	τ_c (min)
637	4.0 ± 0.1	-28.4 ± 0.5	1200 ± 200
644	4.4 ± 0.1	-29.9 ± 0.4	900 ± 120
651	4.1 ± 0.2	-25 ± 1	450 ± 50
659	3.9 ± 0.2	-22 ± 2	300 ± 200
680	3.7 ± 0.5	-14 ± 2	50 ± 10

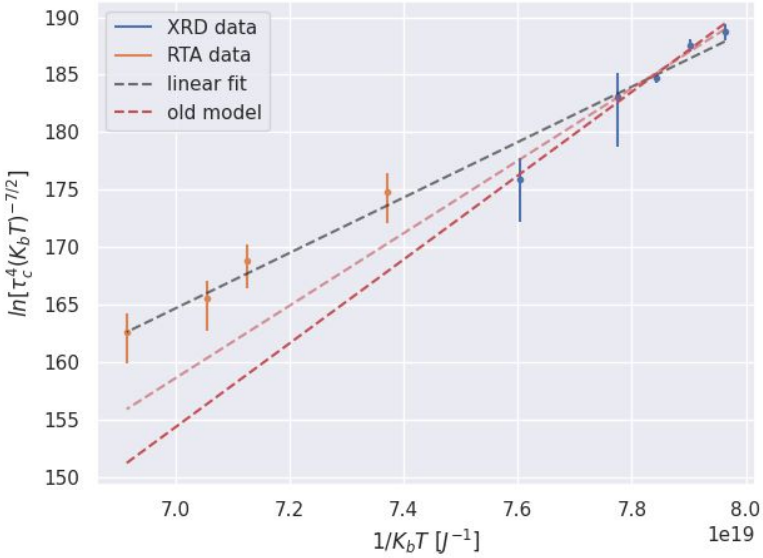
Temperature (°C)	α	q	τ_c (min)
680	5.2 ± 0.1	-32.0 ± 0.7	459 ± 7
690	4.5 ± 0.1	-25.0 ± 0.6	271 ± 4
700	5.5 ± 0.2	-26.7 ± 0.8	131 ± 2
720	4.2 ± 0.8	-14.8 ± 2	35 ± 4

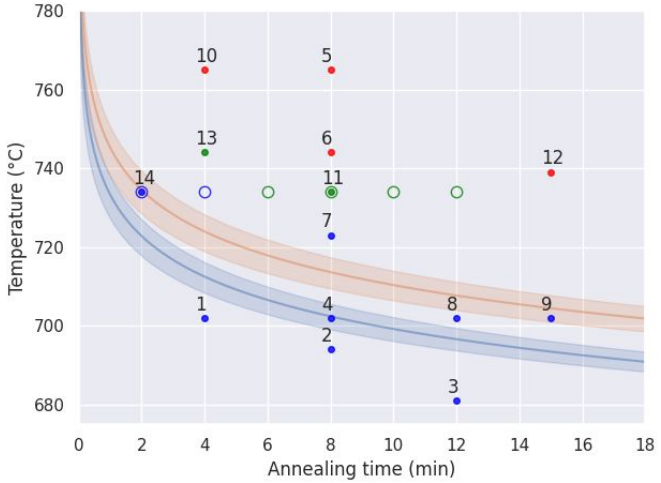
Evidence for 3D growth

Crystallization characteristic time in Ta2O5

$$ln\left[\tau_c^4\left(K_bT\right)^{-\frac{7}{2}}\right] = ln\left[\frac{4\Gamma\left(\frac{5}{2}\right)}{\pi^{\frac{3}{2}}J_0V_0^3}\right] - \left(\frac{4E_f + 4E_m + \Delta G^*}{K_bT}\right)$$

$$ln\left[\tau_c^4\left(K_bT\right)^{-\frac{7}{2}}\right] = a - \left(\frac{Q}{K_bT}\right)$$





- Old Model:
  - Q = (-15.0 ± 0.6) eV
  - a = 0 ± 10
- New Model:
  - Q = (-20 ± 2) eV
  - a = -60 ± 30

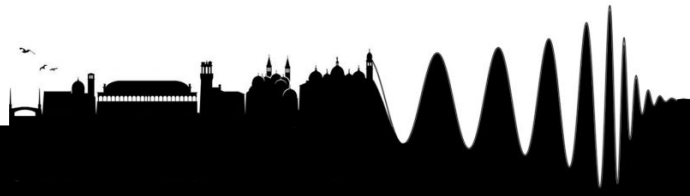
Conclusions

What have we learned?

- XRD suggest that Ta2O5 crystallizes into a P6/mmm phase.
- Crystallization signatures are present in Raman as well.
- Comparison between different samples and with ab initio data suggest that post-annealed samples always contain a mixture of amorphous and crystallized volume
- The microstructure of the crystalline grains have been investigated by means of Rietveld analysis. Higher temperatures produce different amount of defects.
- The crystallization kinetics have been characterized. It proceeds by nucleation and 3D growth of spherical nanoparticles in a typical size of 50-100 nm. The activation energy of the growth process is about 5 eV. The addition of titania (at 21%) to the mixture slows down the growth velocity of about one order of magnitude.

What is still missing?

- Evidence demixing of TiO2 at higher T?
- Combine with TEM analysis to check the microstructure
- Optical scattering analysis
- Loss angle measurements



Thank You

For your Attention