An addendum to IS652

The peculiarities of reduction and doping of vanadium oxides probed by TDPAC spectroscopy at ISOLDE

Speakers: A. Burimova, A. W. Carbonari, J. Schell
Local contacts: J. Schell, J. G. M. Correia

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IS652 S1, Ep1:

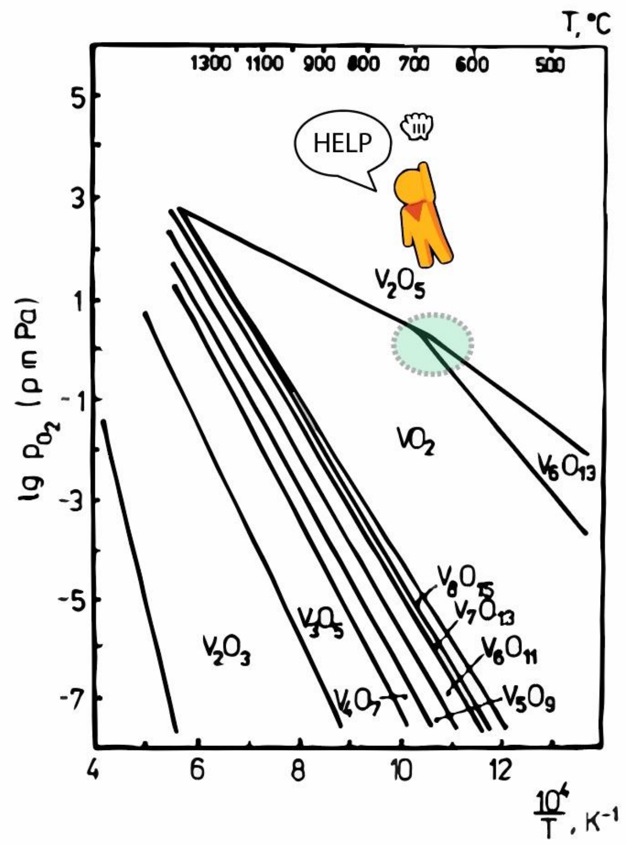
Influence of valence of doping element on local electronic and crystal structure in vanadium oxides: Time-Differential Perturbed Angular Correlations spectroscopy at ISOLDE

Interest to vanadia is driven by its applications. Doping allows to tune the properties. **New wave of battery-research** (Zn^{2+}/H_2O):

"Water-Lubricated Intercalation in V2O5·nH2O for High-Capacity and High-Rate Aqueous Rechargeable Zinc Batteries", **Yan *et al.*** Adv. Mater. 1703725: 1-6
Nov 2017 [IF: 25.809] Citations: 276
"Freestanding graphene/VO2 composite films for highly stable aqueous Zn-ion batteries with superior rate performance", **Dai *et al.*** Energy Storage Mater. **17** p. 143
Feb 2019 [IF: 15.97] Citations: 74

A TDPAC + DFT study of dopant environment in V_2O_5 and VO_2 was proposed, it implied variation of dopant element and concentration

Available probe parents comprised
^{181}Hf, ^{111}In (IPEN) and ^{111m}Cd (ISOLDE)



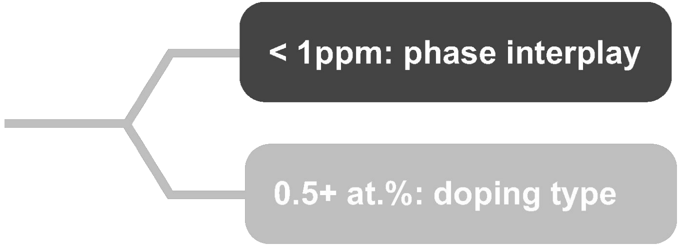
Haber *et al.* Appl. Catal. A Gen **157** (1997) p. 6

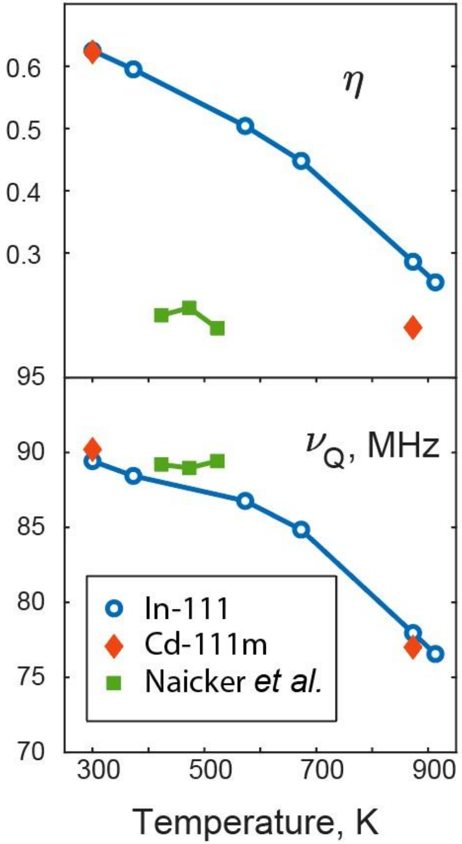
< 1ppm: phase interplay

0.5+ at.%: doping type

< 1ppm: phase interplay

0.5+ at.%: doping type





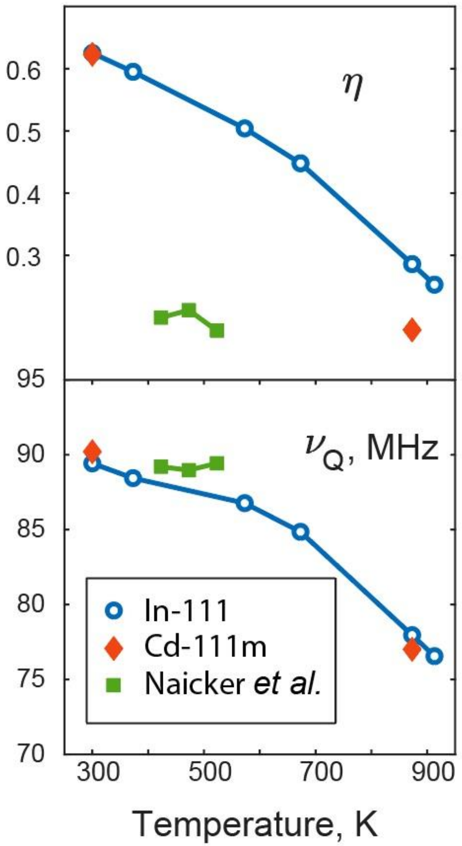
Naicker ***et al.*** Hyperfine Interact. **80** (1993) p. 969

< 1ppm: phase interplay

0.5+ at.%: doping type

Observations:

- Relaxation threshold near 823K
- Annealing in air, O_2, N_2 hinders relaxation
- Dynamic evacuation catalyzes relaxation
- Monochromatic interaction after relaxation
- Smooth reversible transition with temperature similar to that observed for other compounds, e. g. TiO_2



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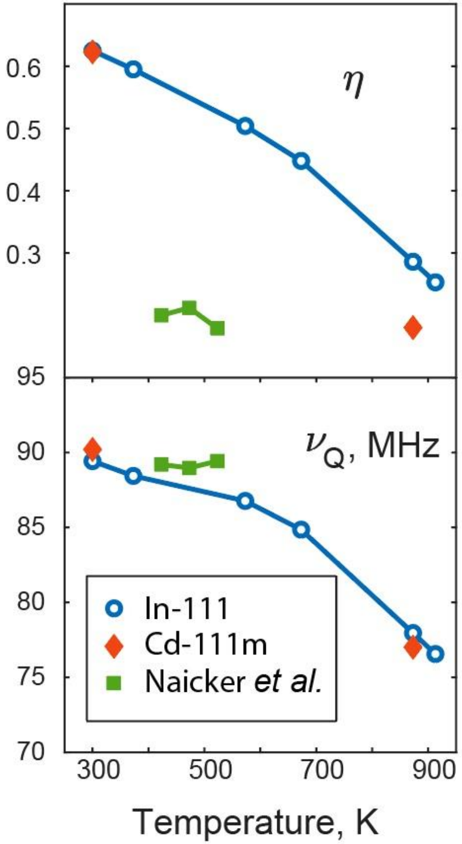
⇩

Working hypothesis:

Probe at V^{4+} site in formed VO_2

Transition: m-VO_2 → t-VO_2



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0.5+ at.%: doping type

Objectives:

Eliminate the ambiguity concerning the observed site

Thus, elucidate the peculiarities of charge density distribution in the vicinity of the dopant

Thus, contribute to the understanding of reduction mechanism in vanadium oxides

Problem statement extended to:

What is the mechanism of reduction in V_2O_5 ?

- **Topotactic**
  $V_2O_5 \rightarrow VO_2$
- **Consecutive**
  $V_2O_5 \rightarrow V_6O_{13} \rightarrow VO_2$
- **Comproportionation**
  $V_2O_5 \rightarrow VO_2$
  $VO_2 + V_2O_5 \rightarrow V_6O_{13}$
- **Competitive**
  $V_2O_5 \rightarrow VO_2$
  $V_2O_5 \rightarrow V_6O_{13} \rightarrow VO_2$

< 1ppm: phase interplay

0.5+ at.%: doping type

Objectives:

Eliminate the ambiguity concerning the observed site

Thus, elucidate the peculiarities of charge density distribution in the vicinity of the dopant

Thus, contribute to the understanding of reduction mechanism in vanadium oxides

Approach:

- TDPAC measurements with ^{111m}Cd at intermediate temperatures:
  473 - 873K
- Adapt the samples to enhance reduction*:
  - Thin films
  - Porous V_2O_5
- Include V_6O_{13} blend to sample list
- Proceed with complementary DFT*

*in progress at home institution, infrastructure available

- < 1ppm: phase interplay
- 0.5+ at.%: doping type

Objectives:

Eliminate the ambiguity concerning the observed site

Thus, elucidate the peculiarities of charge density distribution in the vicinity of the dopant (❖)

Thus, contribute to the understanding of the reduction mechanism in vanadium oxides

Argumentation:

- **Why TDPAC?**
  - XRD can be insensitive to parasitic phases at low concentrations; texture of V_2O_5 and oxygen deficiency induced defects add uncertainty to XRD analysis
  - ND (used to probe the reduction of other compounds) is useless for vanadium
  - Hyperfine methods allow the mapping of the local environment (❖)
- **Why ISOLDE?**
  - Catalytic effect of implantation induced defects on transition was detected
  - Cd as a vacancy trap
  - In contrast to ^{111}In with associated aftereffect, ^{111m}Cd may endow TDPAC spectra with info on **relaxation dynamics in intermediate temperature range** - of interest in reduction mechanism studies

< 1ppm: phase interplay

0.5+ at.%: doping type

< 1ppm: phase interplay

0.5+ at.%: doping type

Tested synthesis routes:

- Coprecipitation
- Solid state reaction route
- Hydrothermal synthesis
- Sol-gel
- Electric arc fusion of metallic vanadium and cadmium

TDPAC with ^{111}In at home institution:

	Cd atomic fraction	site 1			site 2			site 3		
		ν_Q, MHz	η	δ, %	ν_Q, MHz	η	δ, %	ν_Q, MHz	η	δ, %
XRD limitation	**< 0.01**	118.647	1	7.3	109.331	0.3621	6.24	138.852	0.2892	55.02
	0.05	117.873	0.949	2.65	108.581	0.3802	1.19			
	0.1	116.851	0.9442	0.93	106.602	0.4431	22.17			

⇩

substitution?

< 1ppm: phase interplay

0.5+ at.%: doping type

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	0.1	116.851	0.9442	0.93	106.602	0.4431	22.17			

~~substitution?~~

formation of vanadates

< 1ppm: phase interplay

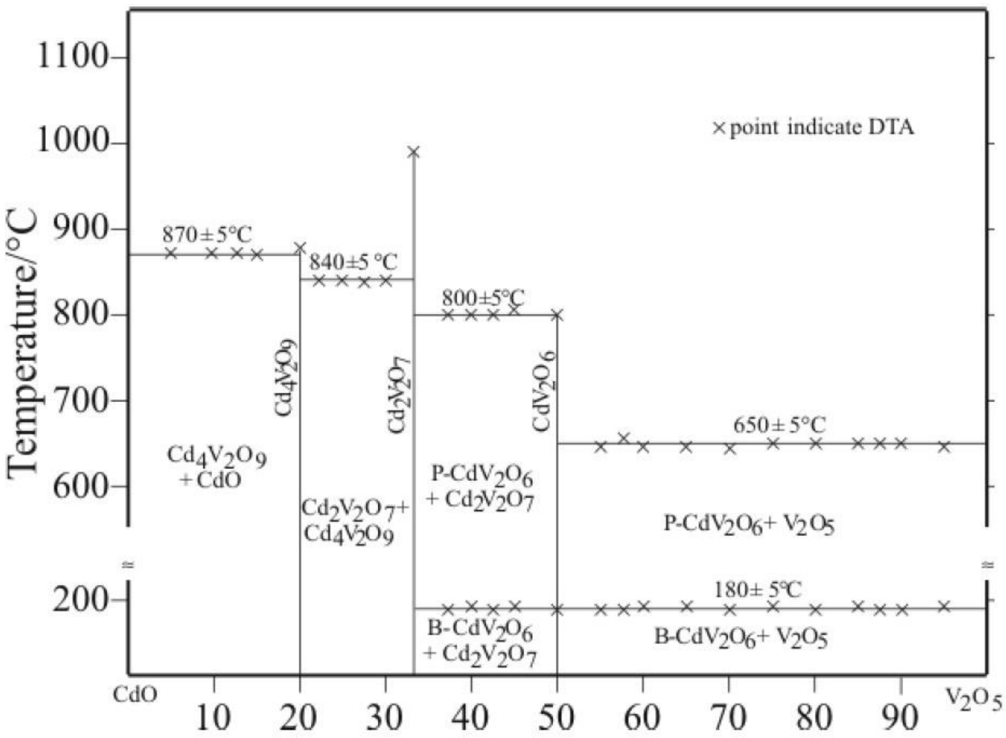
0.5+ at.%: doping type

Pyrovanadate ($Cd_2V_2O_7$)

Metavanadate (CdV_2O_6)

Metavanadate phase transition
β-CdV_2O_6 → α-CdV_2O_6
at ~ 473K

Cadmium vanadates

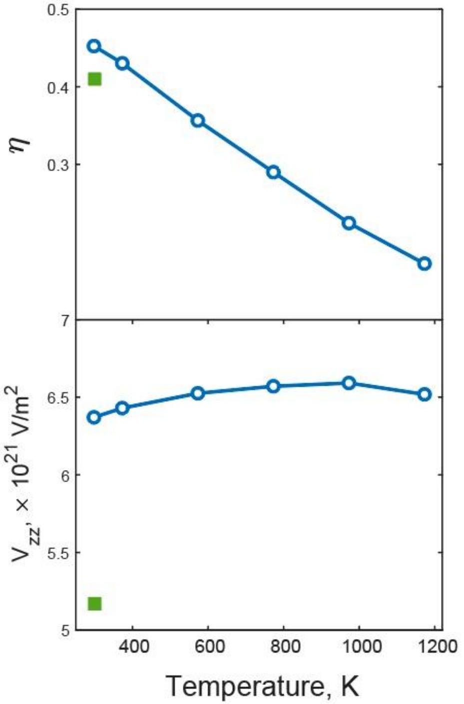


M. Bosacka and A. Blonska-Tabero J. Therm. Anal. Calorim. **93** (2008) p. 814

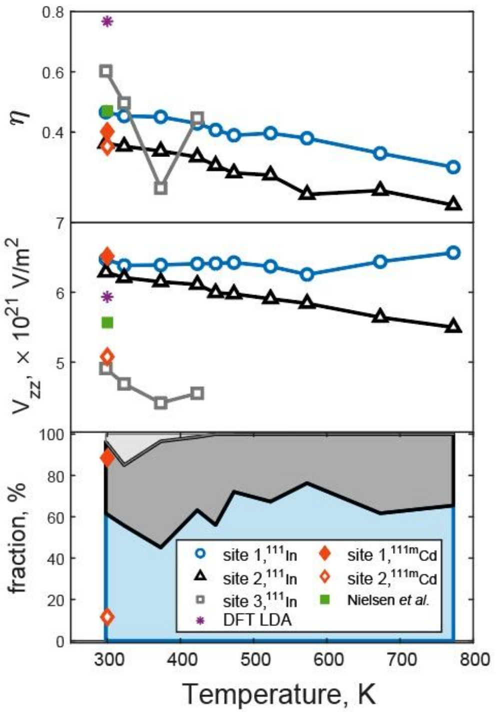
< 1ppm: phase interplay

0.5+ at.%: doping type

$Cd_2V_2O_7$



CdV_2O_6

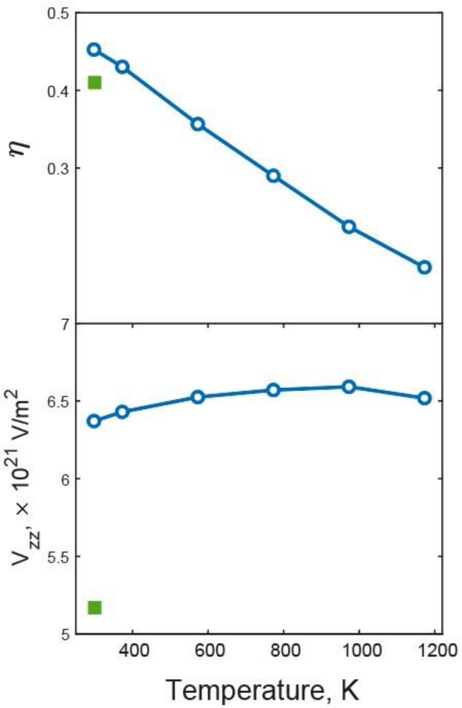


Gro Nielsen *et al.* Inorg Chem **39** (2000) p.2137

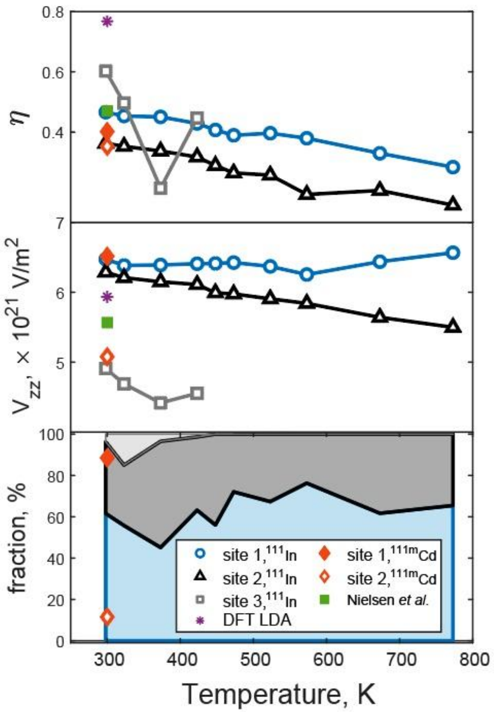
< 1ppm: phase interplay

0.5+ at.%: doping type

$Cd_2V_2O_7$



CdV_2O_6



Objectives:

Identification of the well-defined sites

Thus, getting details on phase transition in cadmium metavanadate* and evolution of local environment with temperature

Thus, final classification of the doping

*to our knowledge, pioneer TDPAC and first transition mapping with hyperfine techniques in these compounds

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- **0.5+ at.%: doping type**

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Approach:

- TDPAC measurements of CdV_2O_6 with ^{111m}Cd probe at temperatures > RT: **300K+****
- ^{111m}Cd TDPAC of $Cd_2V_2O_7$: **RT+****
- Fine fitting of dynamic interactions if any
- Full control over structure with XRD and other conventional methods†
- Full DFT analysis: β-CdV_2O_6, α-CdV_2O_6, $Cd_2V_2O_7$

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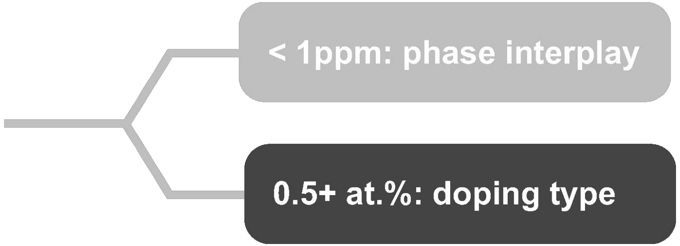
** 1023K+ range not explored

† the scope of equipment available at home institution was recently extended to Raman+SPM platform



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Argumentation:

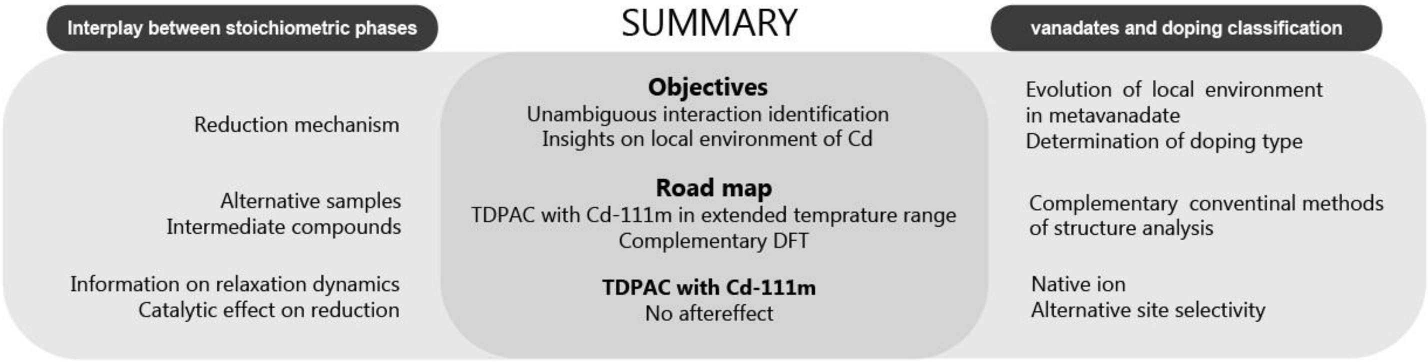
- **Why vanadates?**

  Non-stoichiometric: interlayer expansion in Zn-batteries, "Expanded hydrated vanadate for high-performance aqueous zinc-ion batteries", **Liu *et al.*** Energy Environ. Sci. **12** 2273 **2019 [IF: 33.25] Citations: 54**

  Stoichiometric: Essential components of vanadium slag processing. Understanding intrinsic properties ⇒ increase in the effectiveness of vanadium leaching and reduction of its environmental impact

- **Importance of ^{111m}Cd probe**
  - Native element of cadmium vanadates
  - No aftereffect
  - Can express site selectivity different from ^{111}In

- **^{111m}Cd source: implantation vs. irradiation**
  - $^{52}V \rightarrow {}^{52}Cr$ ⇒ sample contamination
  - Safety issues after irradiation ⇒ sample deactivation



Perspectives

Uncertainty of reduction mechanism, local environment issues, formation of oxoanions, etc, are actual questions not only for vanadium. We assume that the series extends to other oxides, including molybdenia and tungstenia.

Beam request

Required Isotope	Implanted beam	Probe element	Type of experiment	Approx. Intensity (at/muC)	Target/Ion source	Required atoms per sample	# of shifts
^{111m}Cd (48m)	^{111}Cd	^{111}Cd	TDPAC	10^8	Sn target; VD 5 ion source	2×10^{10}	4
^{117}Cd (2.49h)	^{117}Ag	^{117}In	TDPAC	10^8	UC target; RILIS (Ag) ion source	5×10^{10}	2
Total # of shifts							**6**

TAC meeting: complementary measurements ⇒ flexibility. Beam sharing with other groups possible, short-time beam use possible

Supplementary Information

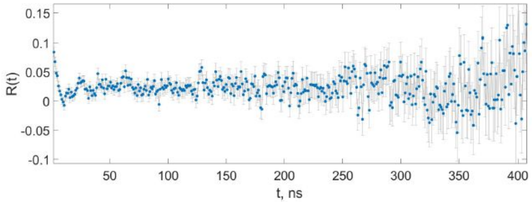
Examples of data obtained with ^{111m}Cd

Vanadia series

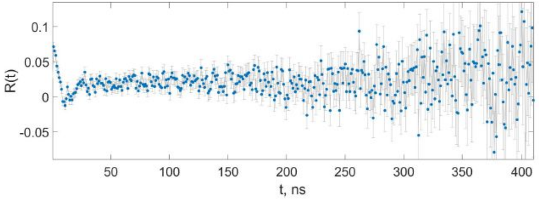
Starting point: bulk (polycrystalline) V_2O_5

Note: 5-5-5 = 5 mins air + 5mins vacuum + 5 mins dynamic vacuum

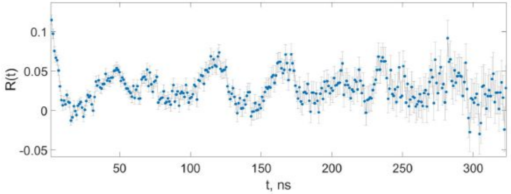
Sol-gel synthesized, annealed in air after implantation, TDPAC at RT



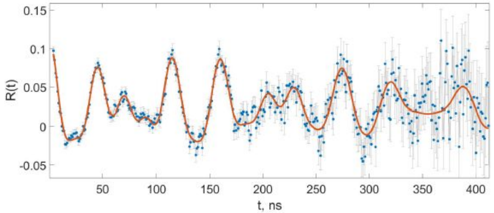
Annealed with 5-5-5 route at 500C, measured at RT



Annealed with 5-5-5 route at 570C, measured at RT

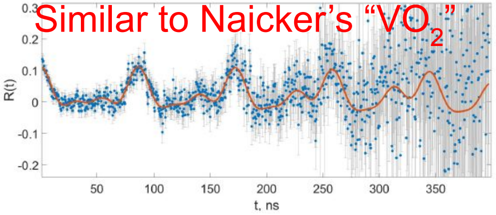


Pure, commercial, measured at RT after annealing with 5-5-5 route at 570C



Site #	f, %	ν_Q, MHz	η	δ
Site 1	8.4736	83.3258	0.5445	0.0680
Site 2	91.5354	90.2028	0.6230	0.0215

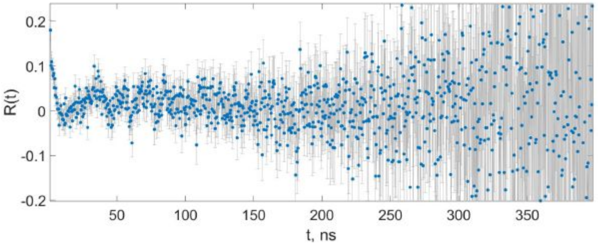
Pure, commercial, measured at 600C



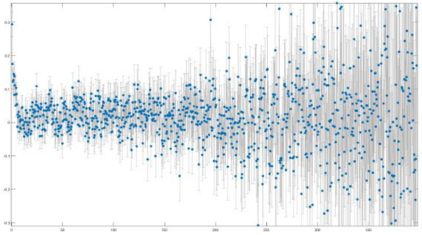
Site #	f, %	ν_Q, MHz	η	δ
Site 1	100	77.0161	0.1802	0

Couldn't get to it with In-111!

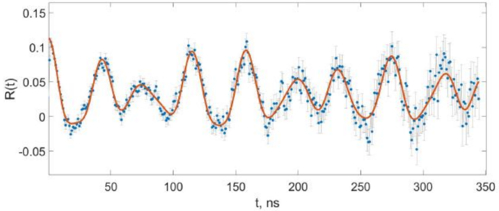
Pure, measurement at 300C in air



Sol-gel measurement at 300C in air



Incident UV



Site #	f, %	ν_Q, MHz	η	δ
Site 1	15.6655	92.6806	0.7006	0
Site 2	58.3614	90.2508	0.6119	0
Site 3	25.9731	96.5650	0.9999	0.0224

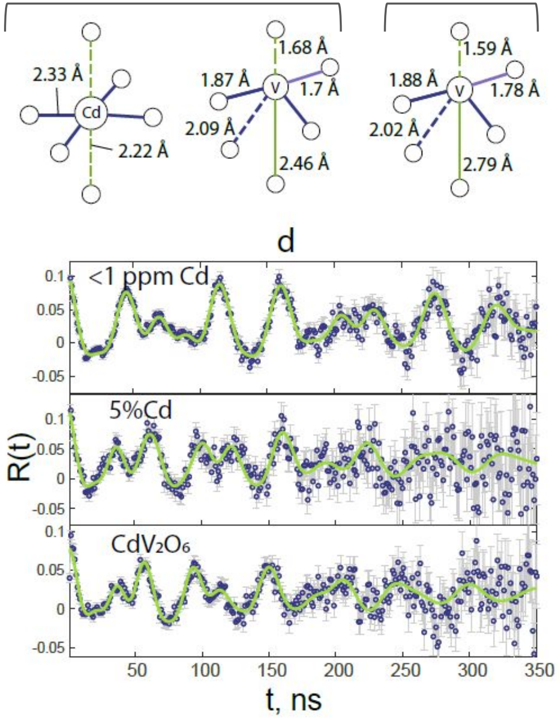
Time invested in the adjustment of the post-implantation treatment necessary to reach probe relaxation

Examples of data obtained with ^{111m}Cd

“Vanadates” series

Nearest oxygen shells

Sites in metavanadate In vanadium oxide



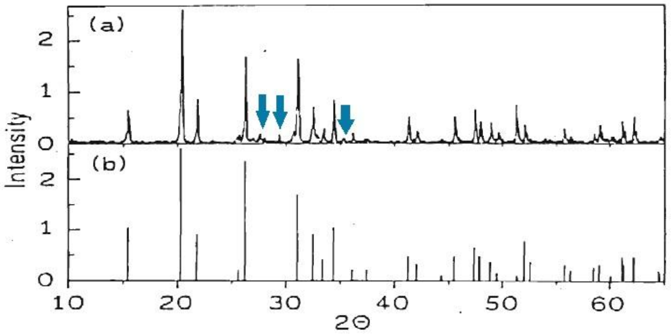
Previous findings: vanadia with TDPAC by Naicker *et al.*

! In V_2O_5, loss of physically absorbed water: **100C**, loss of structural water: **340C**

Naicker1993 and Naicker thesis, experimental details:
Probe: In-111 implanted at IONAS
[phases attributed to V_2O_5]

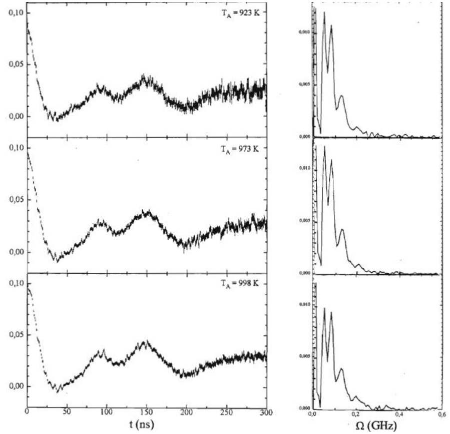
Sample [V_2O_5] annealed in vacuum at 870K for 1h:
ν_Q = 88.1 MHz, η = 0.62 (f (fraction) ↑ with T)

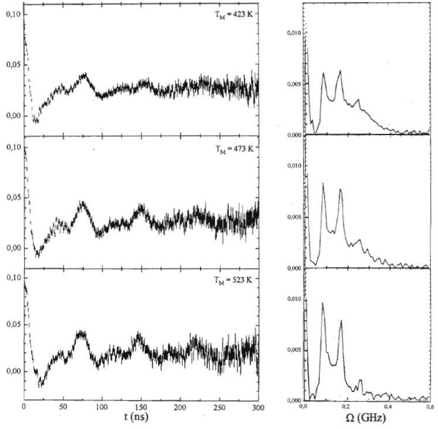
Sample [V_2O_5] annealed in air, 870K? for 0.5h:
ν_Q = 91.4 MHz, η = 0.61 (smaller f, f ↓ with T)



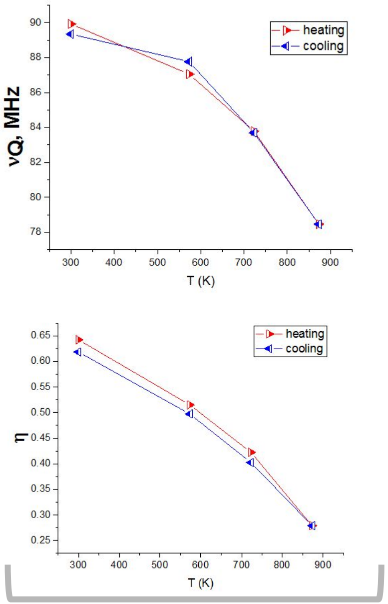
Sample [VO_2], measured at RT after annealing in vacuum in a sequence 923, 973K
ν_Q = 43.79 MHz, η = 0.329 [attributed by Naicker to monoclinic? VO_2]

Sample [VO_2], measured at 423K after implantation (in lower vacuum):
ν_Q = 89.15 MHz, η = 0.22 [attributed by Naicker to rutile VO_2]

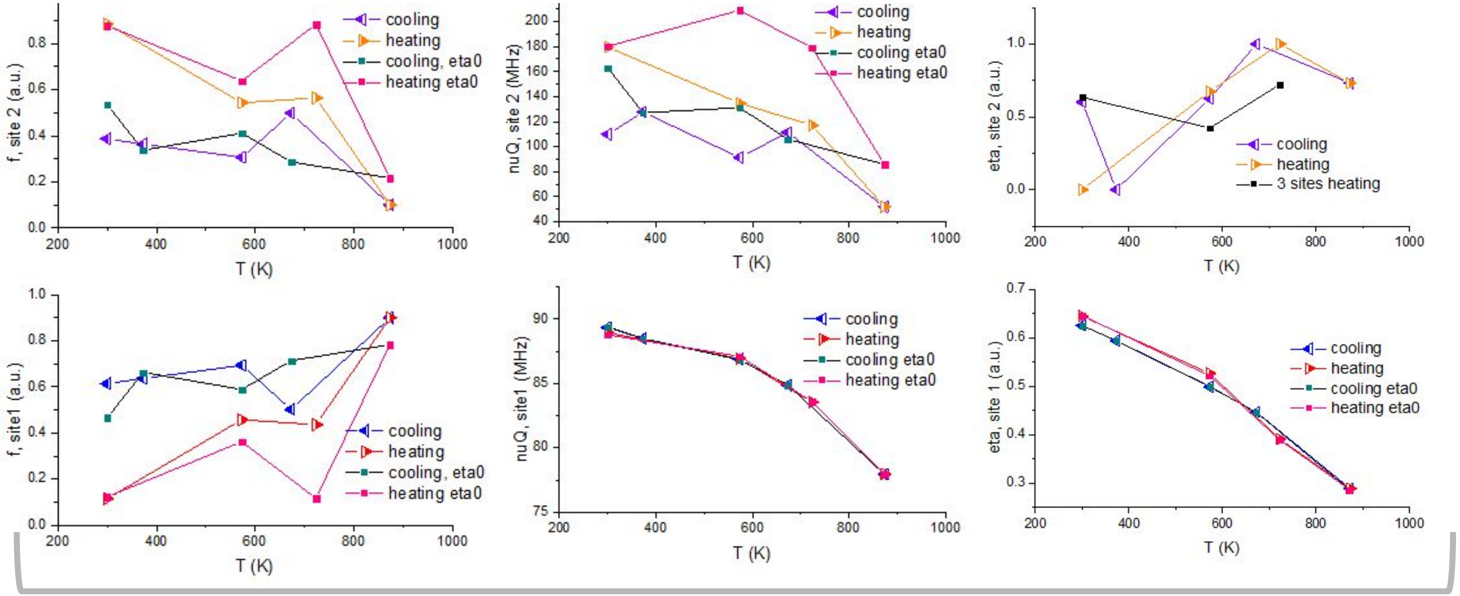




The **reversibility** of the transition in initially divanadium pentoxide probed with In-111:



1 site fit



2 sites fit

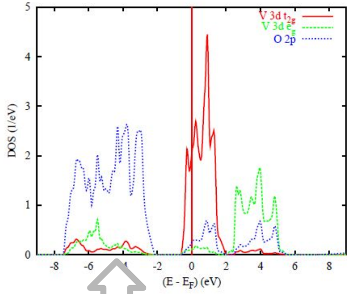
The TDPAC spectra were taken after pre-annealing in vacuum and consequent probe relaxation!

Preliminary DFT results:

For Cd metavanadate in β-phase, obtained with Wien2k (APW+lo)

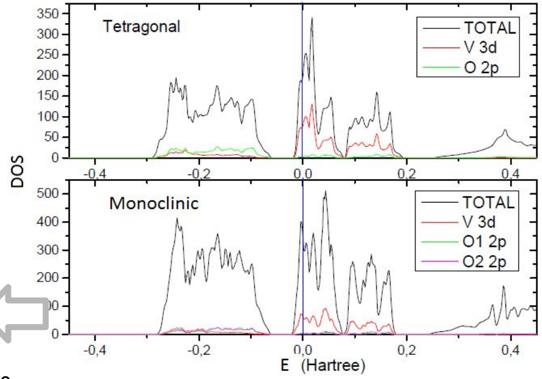
Method	Site	Vzz, 10^21 V/m^2	eta	nuQ, MHz, V-51	nuQ, MHz, Cd-111	[Vzz(Cd)-Vzz(V)]/Vzz(Cd)
PBE, triclinic	**Cd1**	-28.41736	0.45079		-569.8476366	
	V1	6.55704	0.74418	7.624465116	131.4870117	
	V2	10.97877	0.342	12.76601163	220.1550791	
PBE, monoclinic	**Cd1**	-6.00173	0.93851		-120.3514913	0.2778165629
	V1	4.33435	0.66119		86.91585368	
WC, monoclinic	**Cd1**	5.93722	0.89003		119.0578852	0.2017594093
	V1	4.73933	0.75448	5.510848837	95.03683662	
LDA, monoclinic	**Cd1**	5.93436	0.7679		119.0005342	0.1438857771
	V1	5.08049	0.86838	5.907546512	101.8780499	

Eyert Ann. Phys. (Leipzig) 11 (2002) 9, 650

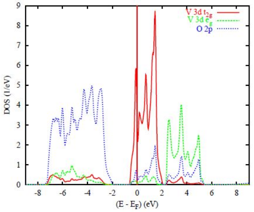


For VO_2, DOS ok, but generally unsatisfactory results for EFG obtained with the Elk code (LAPW+lo)

Sample	eta	Vzz, 10^21 V/m^2	Vzz ext, 10^21 V/m^2
t-VO2	0.48	3.39	0.3941860465
m-VO2	0.96	2.01	0.2337209302



Next step - Hubbard term?



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