

Probing structural transitions in M(II) vanadates (M = Zn, Mn, Cd, Ca) with TDPAC spectroscopy

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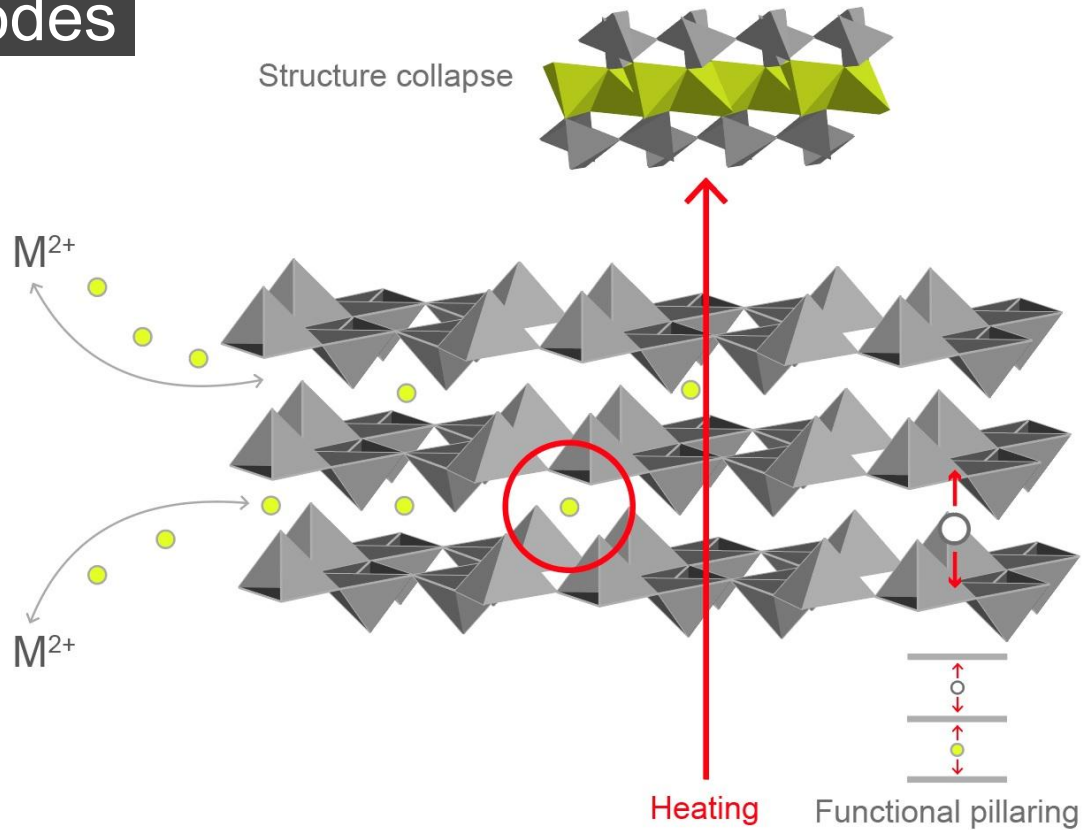
Inspo: MAB electrodes

Local structure studies

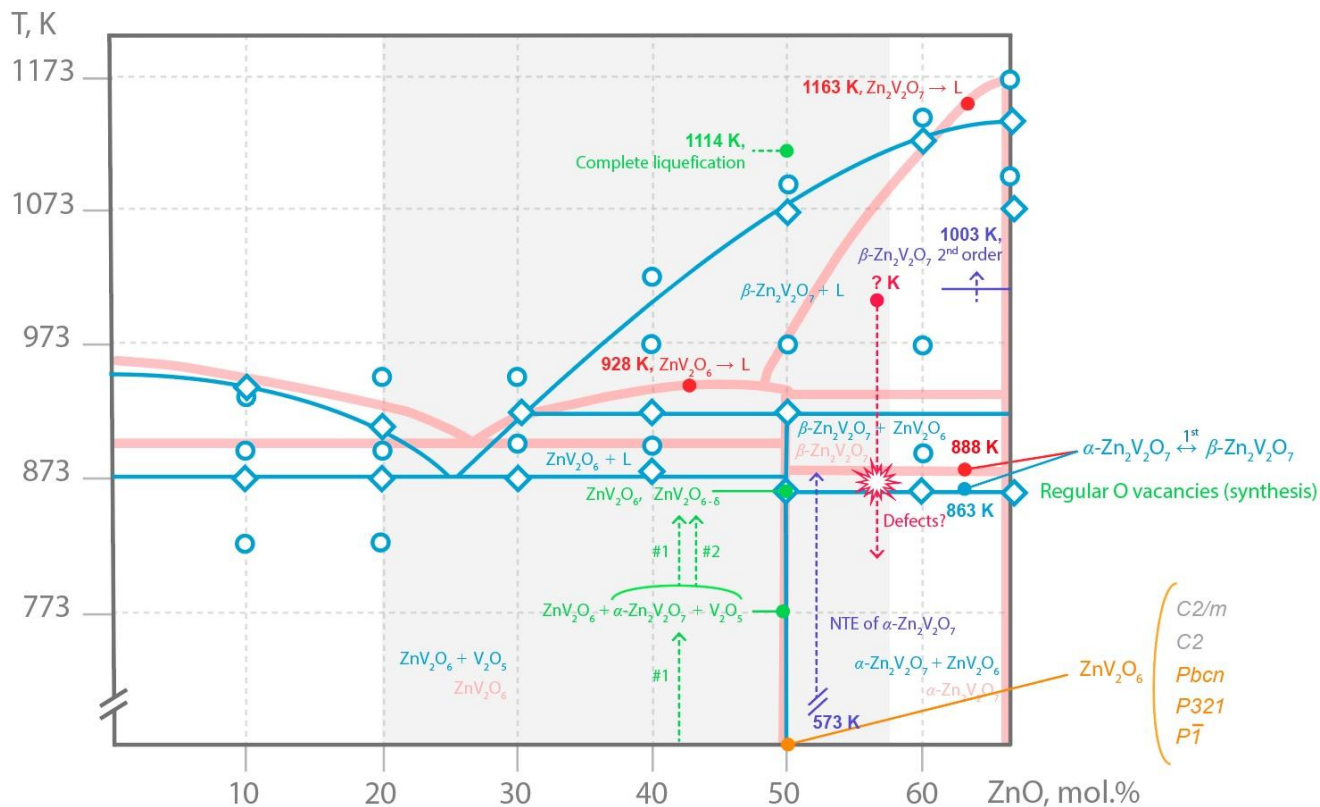
M^{2+} ion localization and adherence

Structure vs. Temperature

- Operation + operation conditions
- Production scaling
- Recycling



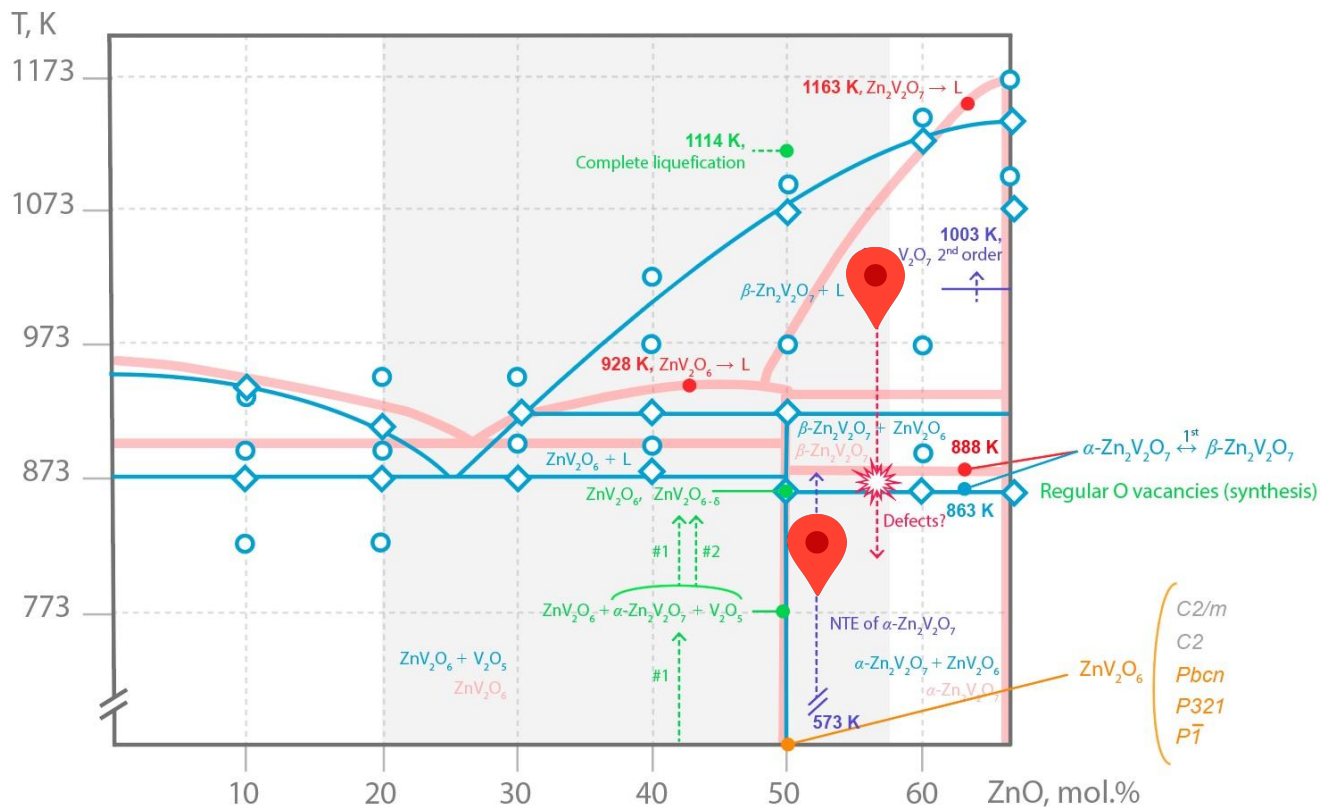
Example: ZnO — V₂O₅ system



Refs:

- Fotiev *et al.* 1985
- Kurzawa *et al.* 2001
- Krasnenko *et al.* 2003
- Tang *et al.* 2014
- Rotermel *et al.* 2017
- Beltran *et al.* 2019
- Hong *et al.* 2021

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TDPAC + DFT vs.

Experiment feasibility for observing the effect



NTE of α -Zn₂V₂O₇

Reported T range: 573 — 873 K

Reported pressure: 1 atm

High local sensitivity of TDPAC

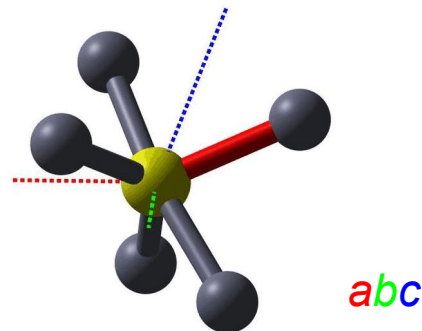
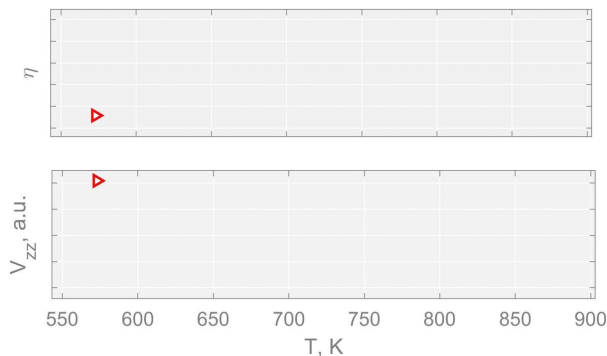


Reported expansion: $\alpha_V = -17.94 \times 10^{-6} \text{ 1/K}^*$

η response



Zn—O bond lengths in ZnO₅ change non-uniformly over T*



[Rotermel et al. 2017](#)

Expansion coefficient was scaled for visualization

TDPAC + DFT vs.



Experiment feasibility:

- Small amount of sample required
- A thicker and safer holder may be used without compromising significantly the acquisition rate and quality
- TDPAC may be carried out under dynamic vacuum



Reported temperature: 863 —893 K
Reported pressure: 1 atm
Reported as an abrupt $C2/c \rightleftharpoons C2/m$ transition
Explosive upon cooling

The non-autonomous phase (if any) is expected to appear as an additional site fraction comprising $R(t)$ (low δ , high η may indicate to regular defects; high δ indicates to site irregularity)



Non-autonomous phase (XRD experiments failed to define) depending on grain size)

Plan

- (1) Acquisition and unambiguous identification of HF parameter sets for a series of M (II) vanadates with TDPAC+DFT combo
- (2) Tackling phase transitions in meta- and pyrovanadates with TDPAC
- (3) Bonus: tackling magnetic interactions in $\text{MnO}-\text{V}_2\text{O}_5$ at lower temperatures

(attributed) Site	Experimental		Theoretical	
	$V_{zz}, 10^{21} \text{ V/m}^2$	η	$V_{zz}, 10^{21} \text{ V/m}^2$	η
Metavanadates				
ZnV ₂ O ₆ (B): [Zn]	-	-	-7.96 [choudhary2020]	0.46 [choudhary2020]
ZnV ₂ O ₆ (B): [V]	5.46 [nielsen2001]	0.4 [nielsen2001]	4.88 [choudhary2020] -5.40 [lo2007]	0.42 [choudhary2020] 0.45 [lo2007]
MnV ₂ O ₆ (B): [Mn]	-	-	-6.27 [choudhary2020]	0.69 [choudhary2020]
MnV ₂ O ₆ (B): [V]	-	-	4.87 [choudhary2020]	0.11 [choudhary2020]
MnV ₂ O ₆ (P): [Mn]	-	-	-	-
MnV ₂ O ₆ (P): [V]	-	-	-	-
CdV ₂ O ₆ (B): [Cd]	6.25	0.38	-5.34 [choudhary2020] 5.93	0.97 [choudhary2020] 0.77
CdV ₂ O ₆ (B): [V]	5.14 [nielsen2001]	0.47 [nielsen2001]	4.25 [choudhary2020] 5.08	0.48 [choudhary2020] 0.87
CdV ₂ O ₆ (P): [Cd]	-	-	-	-
CdV ₂ O ₆ (P): [V]	1.35 [nielsen2001]	1 [nielsen2001]	-	-
CaV ₂ O ₆ (P): [Ca]	-	-	-	-
CaV ₂ O ₆ (P): [V]	2.43 [nielsen2001]	0.51 [nielsen2001]	-	-
Pyrovanadates				
α -Zn ₂ V ₂ O ₇ : [Zn]	9.62	0.41	-	-
α -Zn ₂ V ₂ O ₇ : [V]	-	-	-2.71 [lo2007]	0.69 [lo2007]
Cd ₂ V ₂ O ₇ : [Cd]	6.52	0.36	-	-
Cd ₂ V ₂ O ₇ : [V]	-	-	-4.28 [lo2007]	0.36 [lo2007]

Sample prep

To be performed at home institution

Methods to be employed include

- Solid state reaction (control samples)
- Hydrothermal (electrode imitation)
- Sol-gel* (fine powder)

Sample quality control with powder XRD

EM for morphology control

Challenge: obtaining single-phase samples

*tested for $\text{ZnO} - \text{V}_2\text{O}_5$ and $\text{CdO} - \text{V}_2\text{O}_5$

TDPAC with ^{111}In

To be performed at home institution

Mapping within 300 — 1173 K

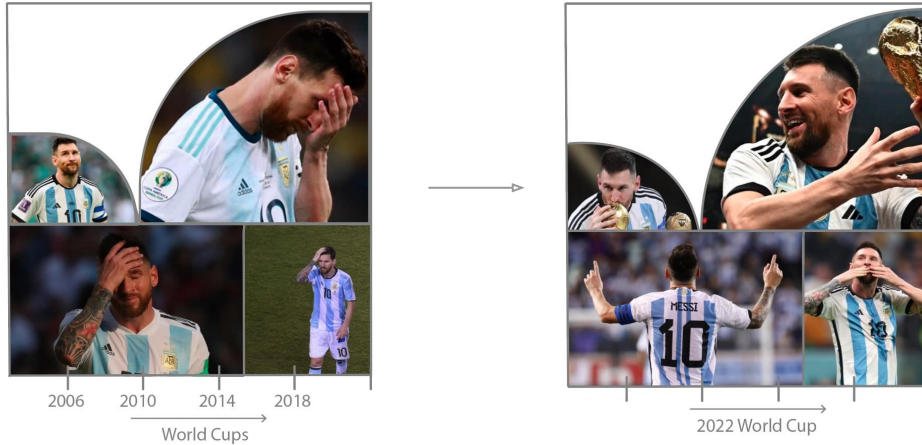
Probe incorporation options

- Wet impregnation
- Admixture at synthesis

$^{111\text{m}}\text{Cd}$ parent at ISOLDE

- **Isovalent to M(II): substitution and isotropic NN relaxation expected**
- **Inter-solubility of Cd and Ca vanadates**
- Site selectivity alternative to ^{111}In parent / variation in charge state of the probe site
- No after-effect

Summary



Bringing phase diagrams for M (II) vanadates to a different [messy] state

Beam request

Required Isotope	Implanted beam	Probe element	Type of experiment	Approx. Intensity (at/ μC)	Target/Ion source	Required atoms per sample	# of shifts
$^{111\text{m}}\text{Cd}$ (48m)	^{111}Cd	^{111}Cd	γ — γ TDPAC	10^8	Sn target; VD 5 ion source	2×10^{10}	8
Total # of shifts							8