Water driven phase transitions in Prussian White cathode materials

ILL/ESS User Meeting

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7/9-2022

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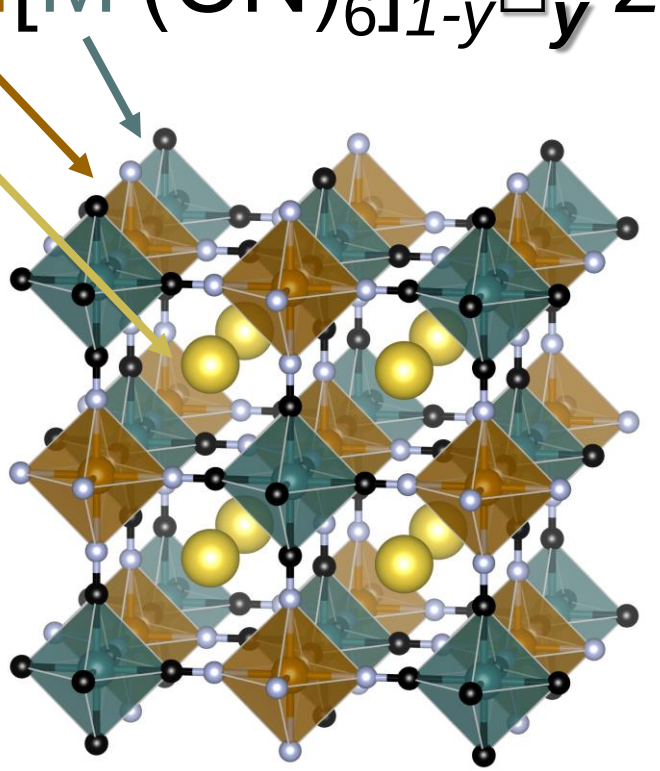
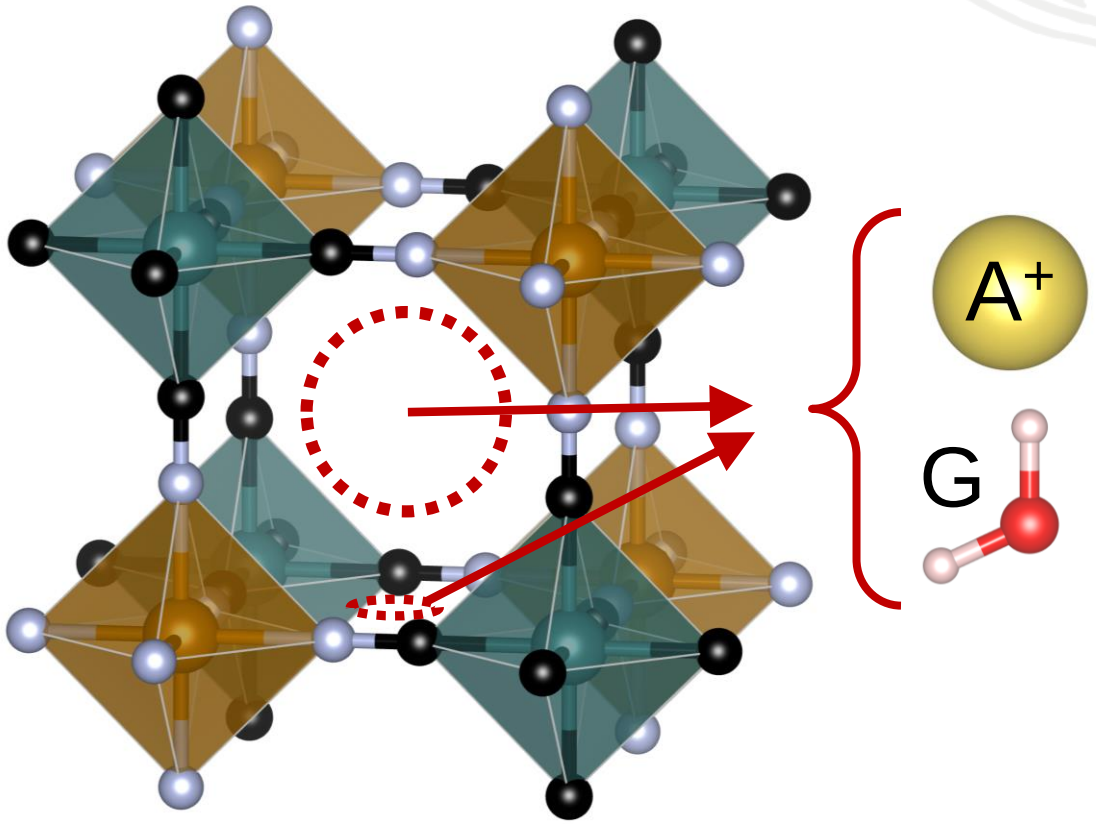
Prussian Blue Analogues

Promising cathode materials for batteries

$A_xM[M'(CN)_6]_{1-y}\square_y \cdot zG$





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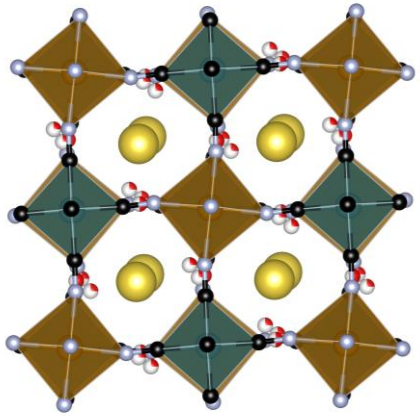
Chem. Mater. 2019, 31, 5933−5942. Chem. Commun. 2019, 55, 10230–10233. Ionics(Kiel). 2020, 26, 531–547.

Prussian White – $Na_2Fe[Fe(CN)_6]\cdot zH_2O$

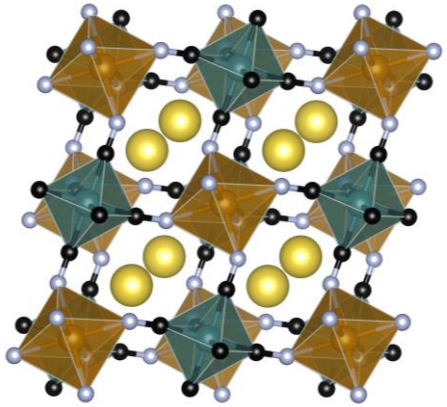
Hydrated $P2_1/n$

Na=2
H_2O=2



$-H_2O$

-18% (volume)

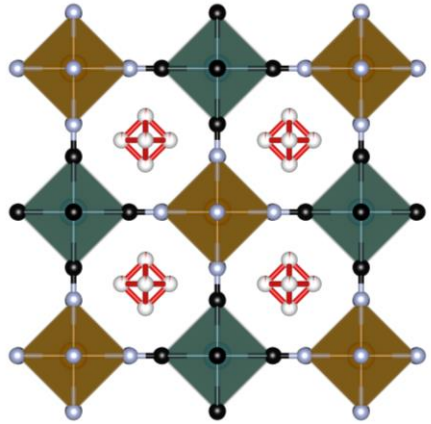


Dehydrated $R\bar{3}$

Na=2
H_2O=0

$-Na^+$

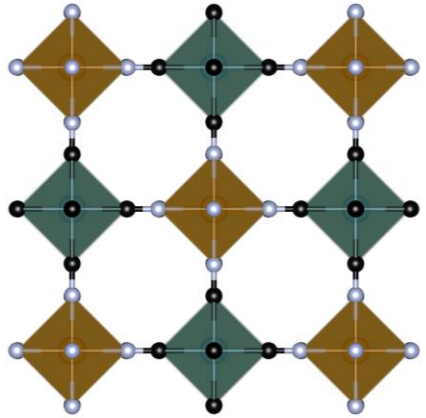
-2%



Hydrated $Fm\bar{3}m$

Na=0
H_2O=0.5

+17%



Dehydrated $Fm\bar{3}m$

Na=0
H_2O=0

$-H_2O$

<1%

Chem. Mater. 2019, 31, 5933−5942.
Chem. Commun. 2019, 55, 10230–10233.
Ionics(Kiel). 2020, 26, 531–547.

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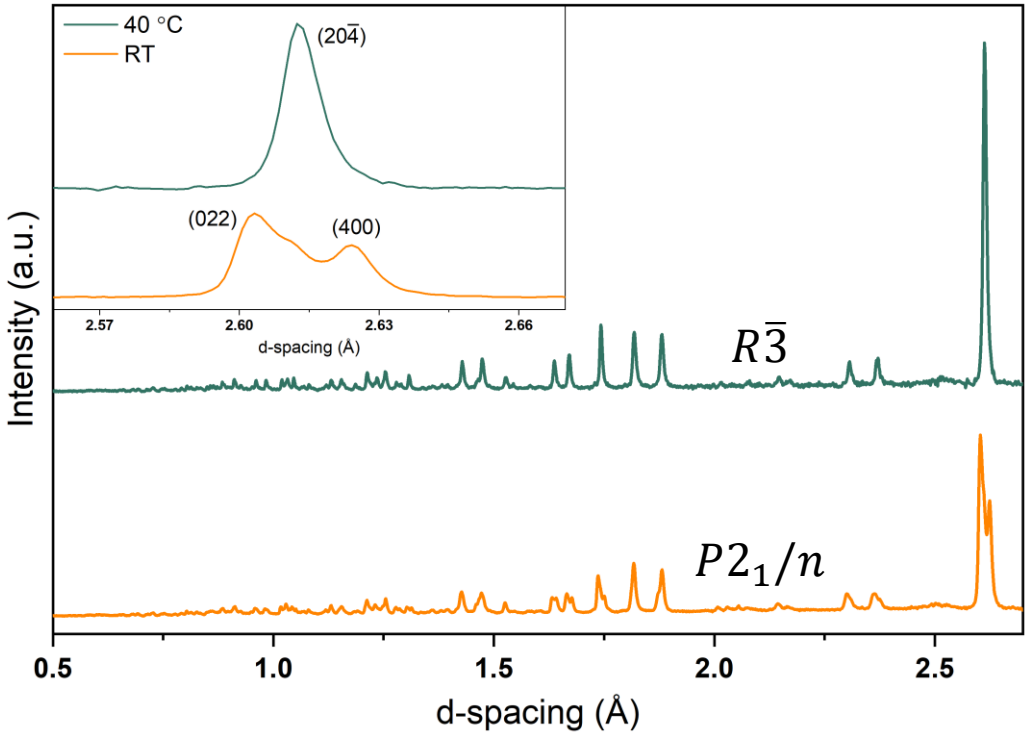
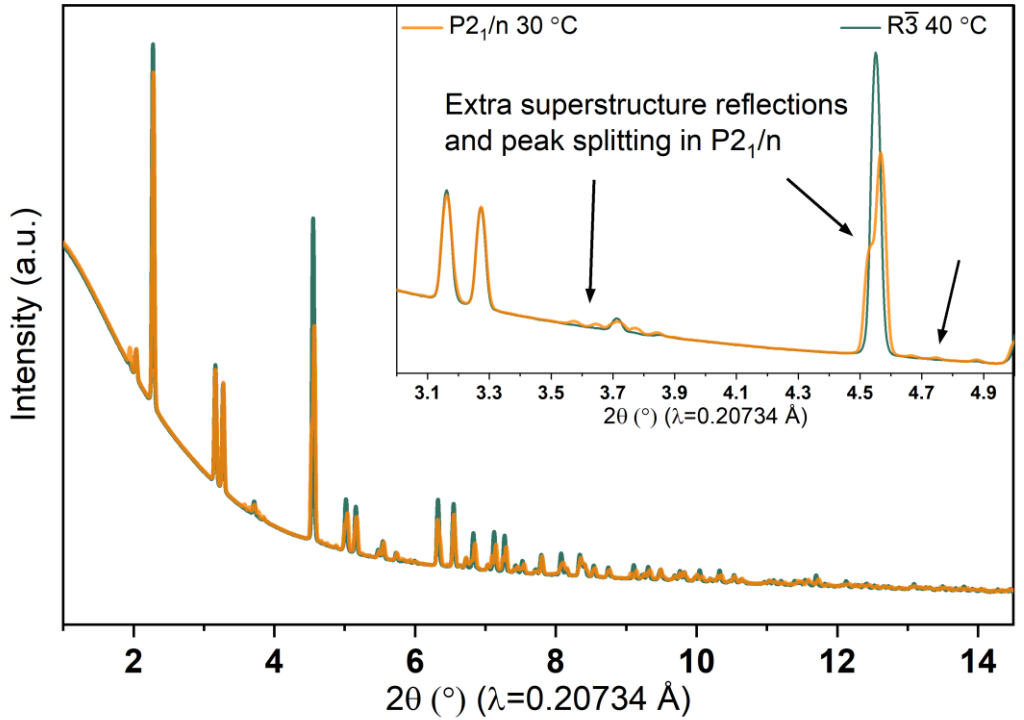
Near room temperature phase transition

Neutron diffraction



Acid decomposition synthesis

Synchrotron X-ray diffraction



Co-precipitation synthesis

Phase transition in Na-rich PW is independent of the synthesis method!

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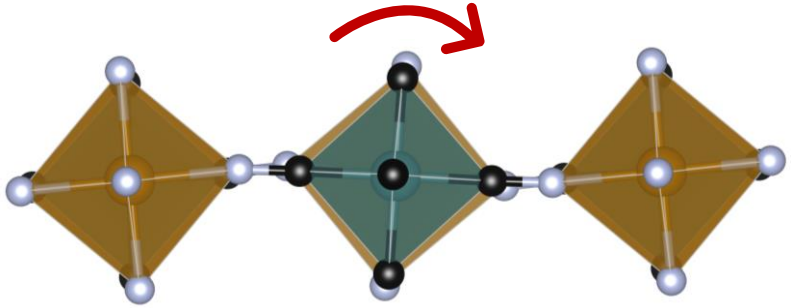
Octahedral tilt transition

Monoclinic $P2_1/n$ symmetry

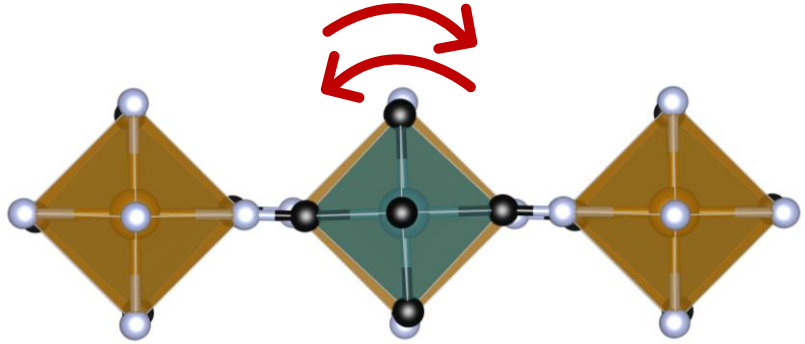
$a^-a^-b^+$



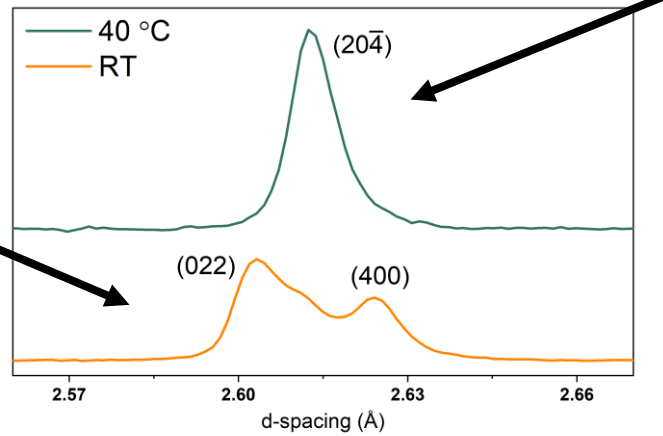
b^+ in-phase tilt

Rhombohedral $R\bar{3}$ symmetry

$a^-a^-a^-$



a^- out-of-phase tilt



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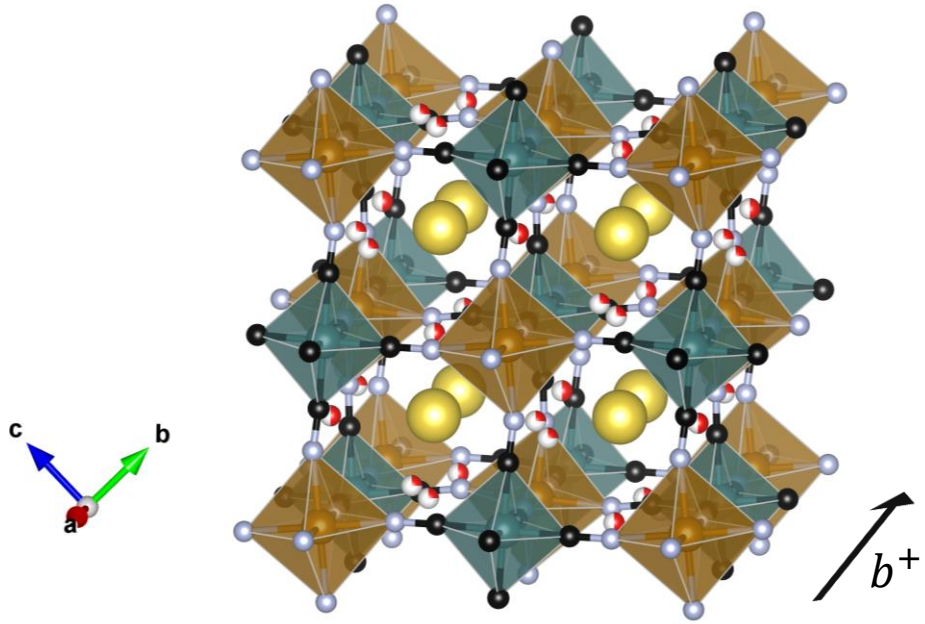
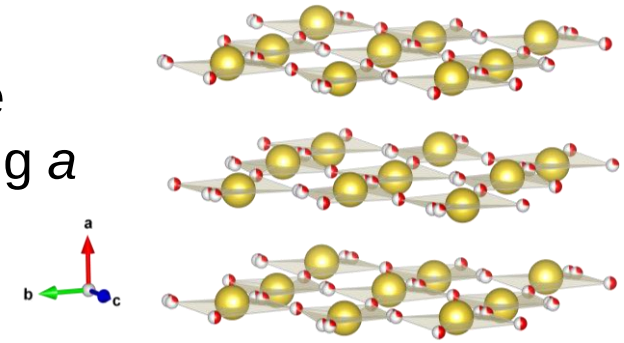
Water disordering during the phase transition

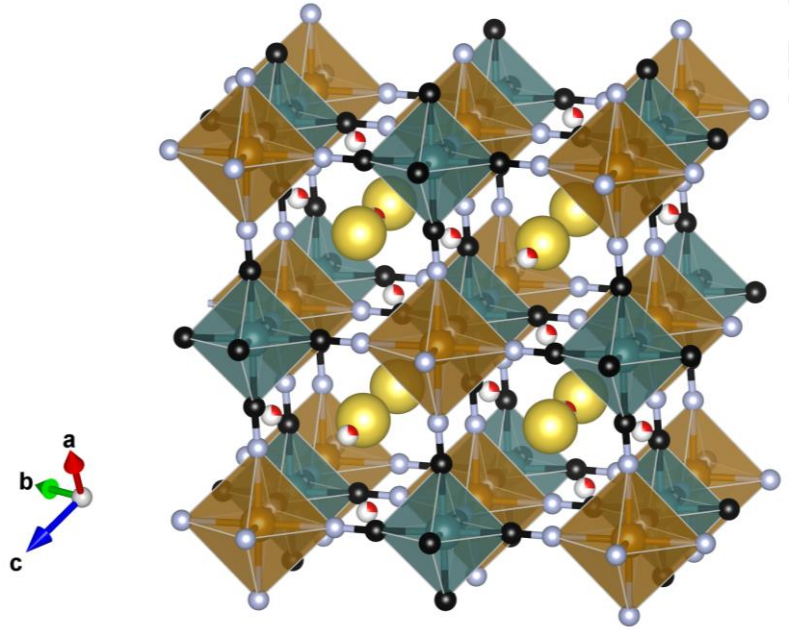
$P2_1/n$



Water in the *bc*-plane
Clear Na^+ channels along *a*



$R\bar{3}$



Disordered relative to the $P2_1/n$ structure

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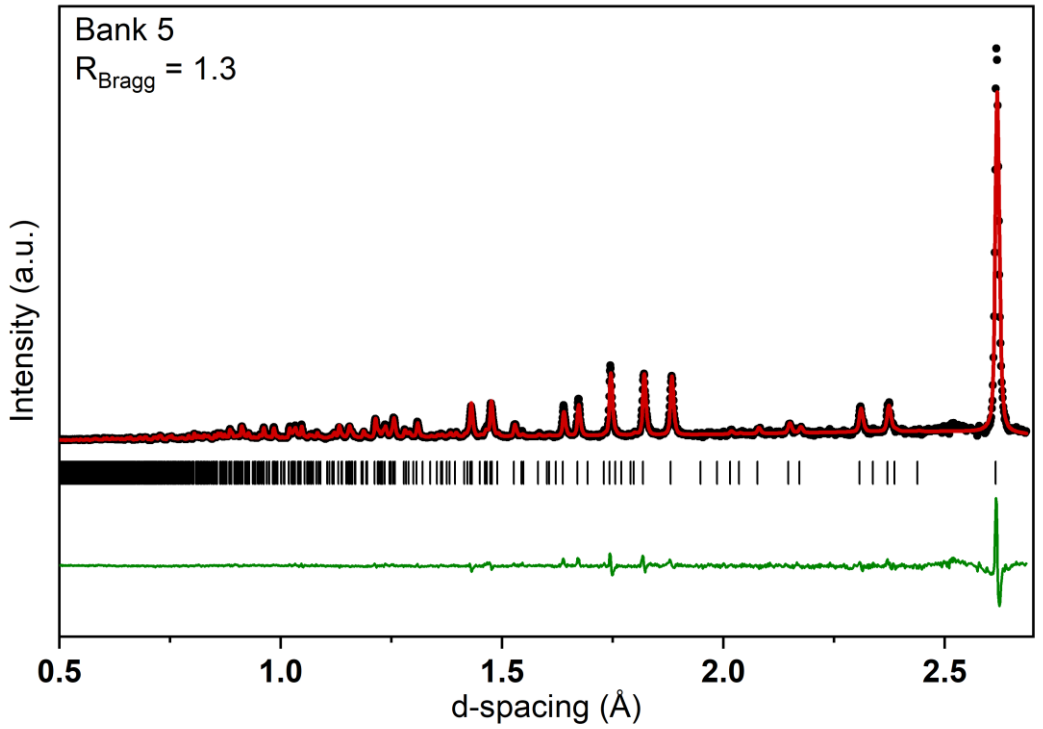
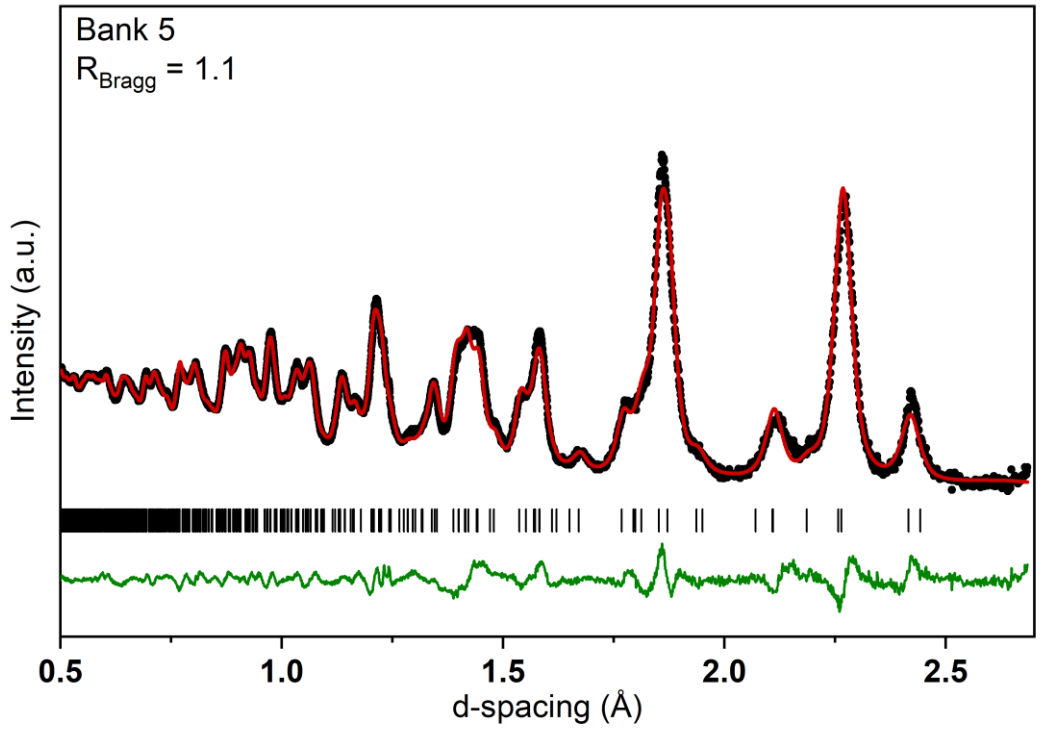
Structural collapse during dehydration of PW



Hydrated $R\bar{3}$



Dehydrated $R\bar{3}$

20% volume contraction and loss of crystallinity during dehydration

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Dehydration modifies the magnitude of pre-existing distortions

Key distortion modes:

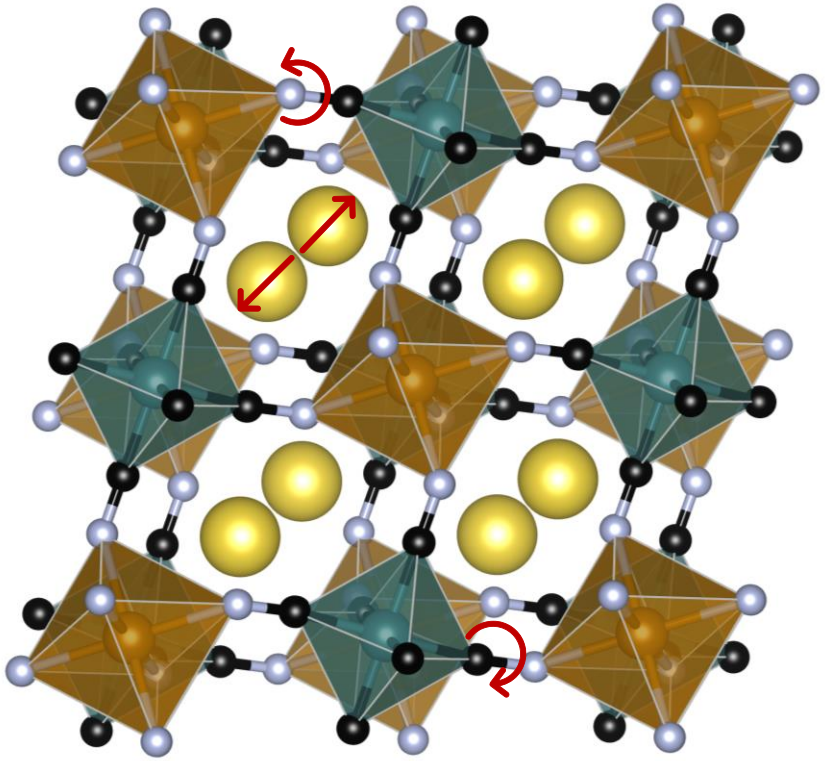
- Tilting of the rigid FeN_6 and FeC_6 octahedra
- Na^+ displacement along *c*

Irrep	Hydrated PW	Dehydrated PW
Γ_4^+ N	0.13(1)	-2.450(2)
Γ_4^+ C	0.10(1)	-1.668(3)
Γ_1^+ N	-0.229(2)	-0.200(2)
Γ_1^+ C	-0.251(3)	-0.270(2)
Γ_5^+ N	-0.069(3)	0.185(2)
Γ_5^+ C	0.074(4)	-0.047(2)
Γ_5^+ Na	0.05(1)	1.358(4)

Unit: Å

Dehydrated $R\bar{3}$

$a^-a^-a^-$



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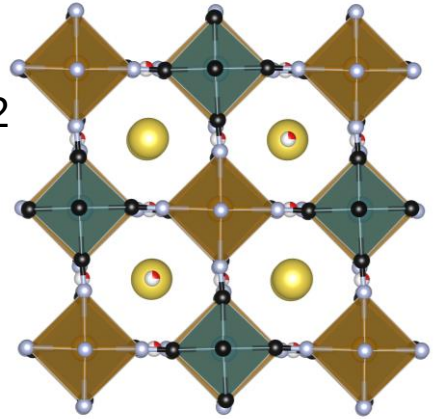
Replacing H_2O is a viable strategy to modify volume changes

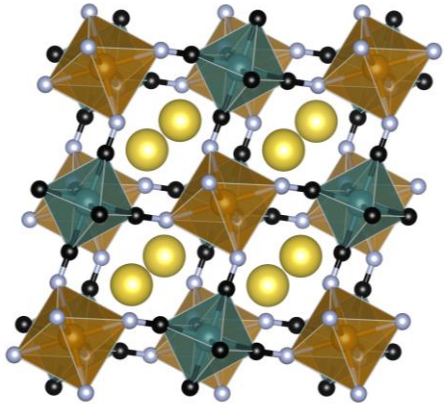
Hydrated $R\bar{3}$

Na=2
H_2O=2



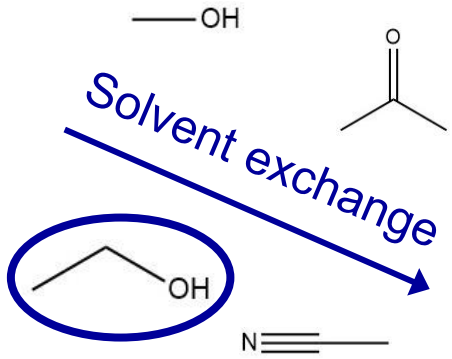
$-H_2O$

-20%
(volume)

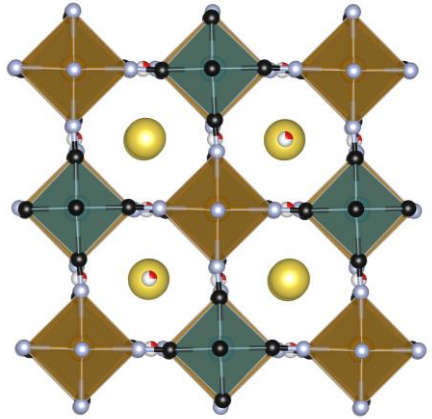


Dehydrated $R\bar{3}$

Na=2
H_2O=0



Solvent exchange



Solvent exchanged $R\bar{3}$

Na=2

Modify the magnitude of the distortions and prevent volume changes

Improve battery performance and life-time

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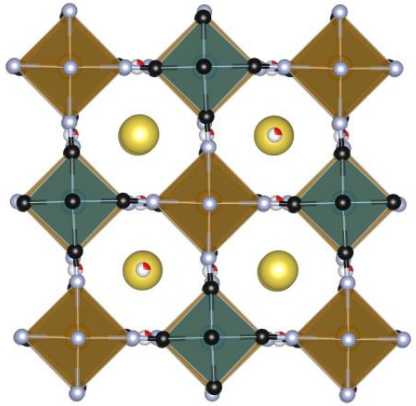
Summary

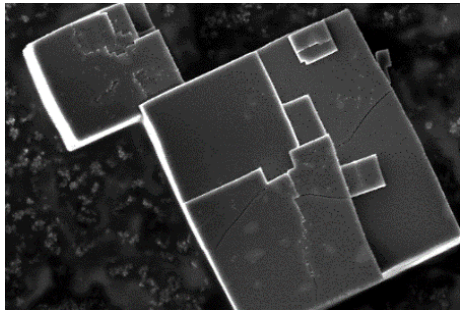
The first time **two structures for PW** were observed near room temperature

Dehydration **modifies pre-existing distortions** rather than inducing phase transitions

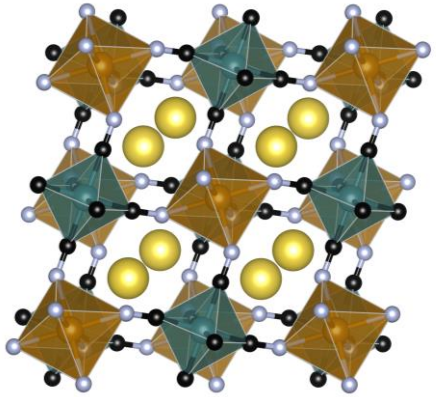
Structures determined with **higher accuracy** using neutron diffraction

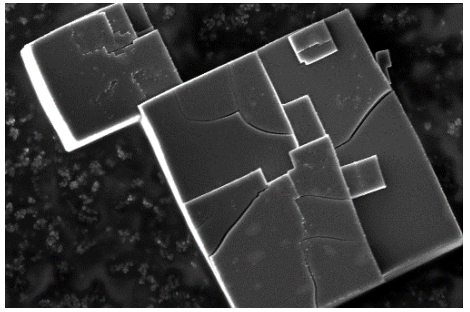
Hydrated $R\bar{3}$





Dehydrated $R\bar{3}$





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ISIS Neutron and
Muon Source

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