Optimization Of Hydrothermal Processing Time And Temperature For $Na_3V_2(PO_4)_3$ Cathode Synthesis For Sodium-ion Batteries

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Why Batteries Matter

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Renewable integration

Store electricity when solar or wind output is high; return it when generation falls.

Grid flexibility

Fast response helps balance supply and demand and support electricity reliability.

Electric transport

Batteries provide onboard energy storage for electric vehicles.

Why it matters: reliable storage makes renewables and electrification more practical at scale. [1]

[1] Tapia-Ruiz, N., et al. (2021). 2021 roadmap for sodium-ion batteries. Journal of Physics: Energy, 3(3), 031503.

Why Sodium Over Lithium

Lithium

Higher energy density and manufacturing maturity [1]

Supply-chain risks due to non-uniform distribution and limited resource [3]

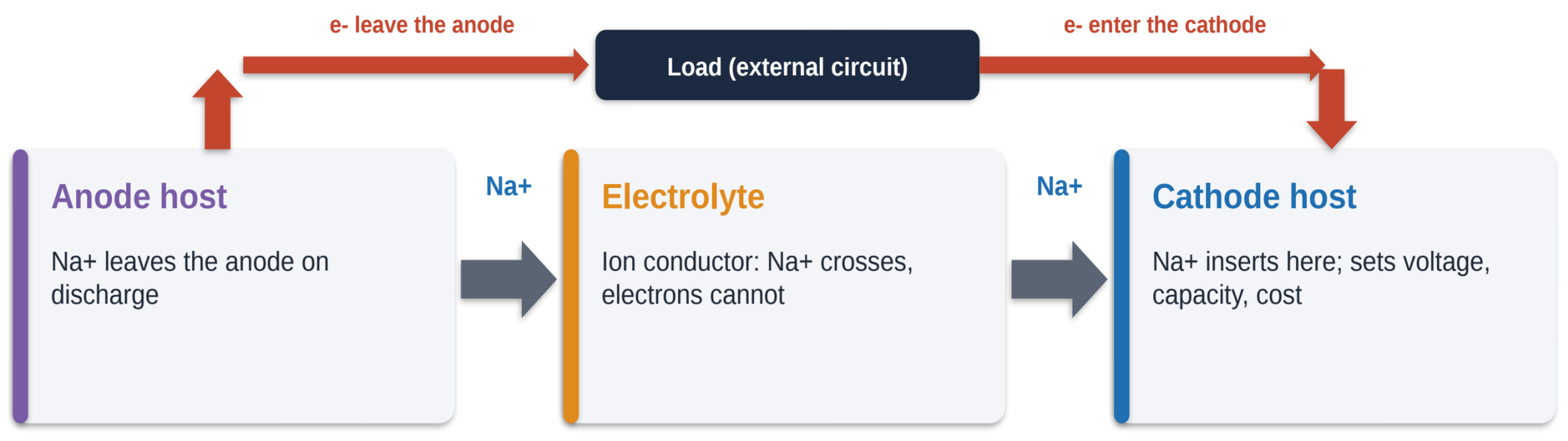
Sodium

- Sodium is around thousand times more abundant in the Earth's crust than lithium and occurs globally in rock salt and seawater [2]
- Similar battery operating principle to Li-ion [2]
- Potential low-cost complement for Li-ion Batteries [3]

Trade-off: current sodium-ion cells generally have lower energy density; cost competitiveness depends on technology progress and supply-chain conditions. [2,3]

[2] Pan, H., Hu, Y.-S., & Chen, L. (2013). Room-temperature stationary sodium-ion batteries for large-scale electric energy storage. Energy & Environmental Science, 6(8), 2338.
[3] Sun, X., Hao, H., Hartmann, P., Liu, Z., & Zhao, F. (2019). Supply risks of lithium-ion battery materials: An entire supply chain estimation. Materials Today Energy, 14, 100347.

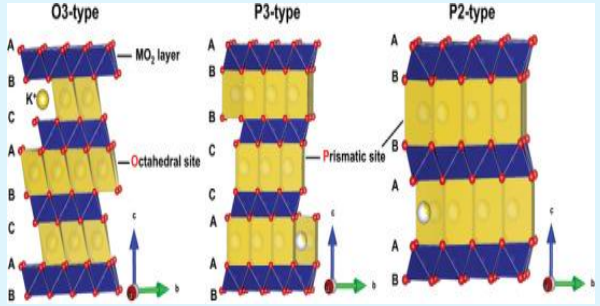
A Battery In Three Moves



During discharge, stored chemical energy is delivered as electrical energy to the external circuit.

Sodium-ion Cathode Families

Layered Oxides ($NaMO_2$)



Layered Oxides ($NaMO_2$)

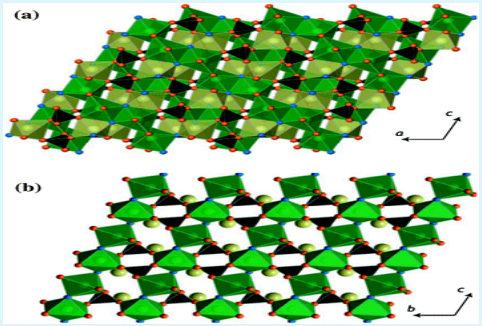
✓ High capacity

❖ Safety concerns

❖ Low voltage

❖ Poor stability

Polyanionic Compounds ($NaFePO_4$, etc.)



Polyanionic Compounds ($NaFePO_4$, etc.)

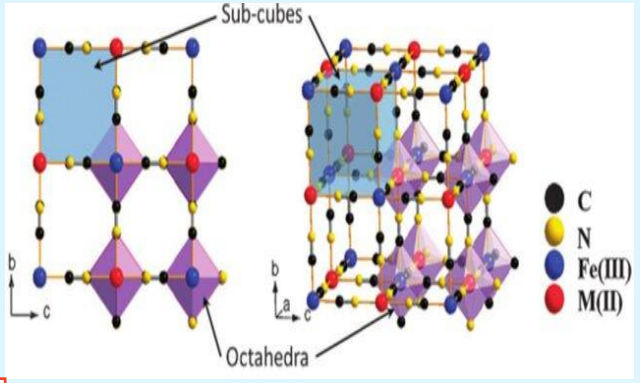
✓ Strong covalent framework → structural stability

✓ Excellent thermal & chemical stability

✓ Minimal volume change during Na^+ insertion/extraction

❖ Slightly lower energy density

Prussian Blue Analogues (PBAs)



Prussian Blue Analogues (PBAs)

✓ Low cost

✓ open framework

❖ Water instability

❖ Low voltage

$Na_3V_2(PO_4)_3$ (NVP) As A Cathode Material

Structure:
(i) NVP crystallizes in a rhombohedral NASICON structure (**figure 1**) and has 3D Na^+ diffusion pathways.

Advantages:
(i) High structural stability (the phosphate group (po_4^{3-}) in NVP stabilizes the structure by strong covalent bonding). [4]

(ii) Fast sodium-ion diffusion

(iii) Stable voltage plateau around 3.4 v and a good capacity retention of around ~117mah/g theoretical value. [5]

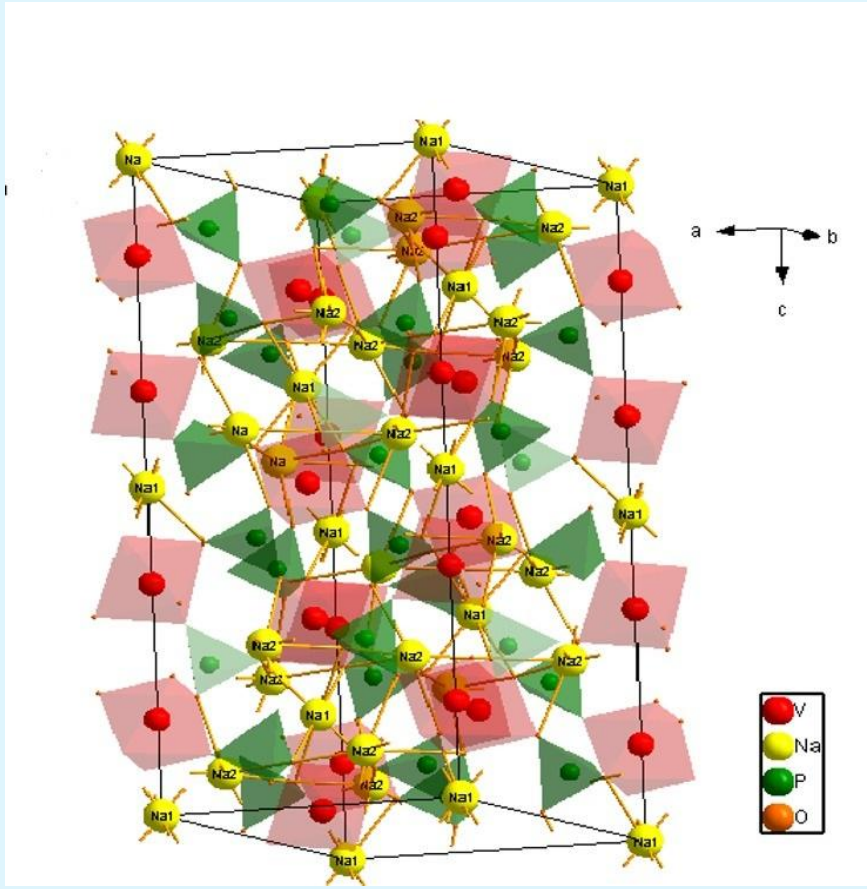


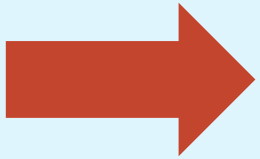
figure 1: Crystal structure of NVP

[4] Y. Liang, L. Xu, Z. Chen, D. Ning, Z. Sun, Recent research progress in the application of $Na_3V_2(PO_4)_2F_3$ cathode materials in sodium-ion batteries: synthesis, modification, and battery optimization, Energy Materials 5 (2025).
[5] Q. Zhu, B. Nan, Y. Shi, Y. Zhu, S. Wu, L. He, Y. Deng, L. Wang, Q. Chen, Z. Lu, Na3V2(PO4)3/C nanofiber bifunction as anode and cathode materials for sodium-ion batteries, Journal of Solid State Electrochemistry 21 (2017) 2985–2995.

But NVP Has A Conductivity Problem

NVP has lower electronic conductivity (1.63×10^{-6} S cm^{-1}) which Limits rate capability and cycle life of bare NVP

Every reported fix is benchmarked against the base NVP - so the quality of the base material itself decides how fair the comparison is.



- Carbon coating
- Doping
- Morphology design

The Gap: Synthesis Window Treated As Fixed

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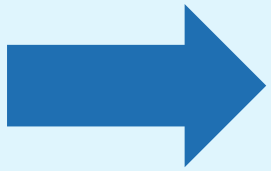
What most studies do

Fix hydrothermal temperature and time,

Optimize only calcination afterwards.

One-factor-at-a-time, rarely mapped.



What we do

Systematically vary BOTH parameters

3 temperatures x 3 times = 9 samples

Quantify crystallinity by XRD

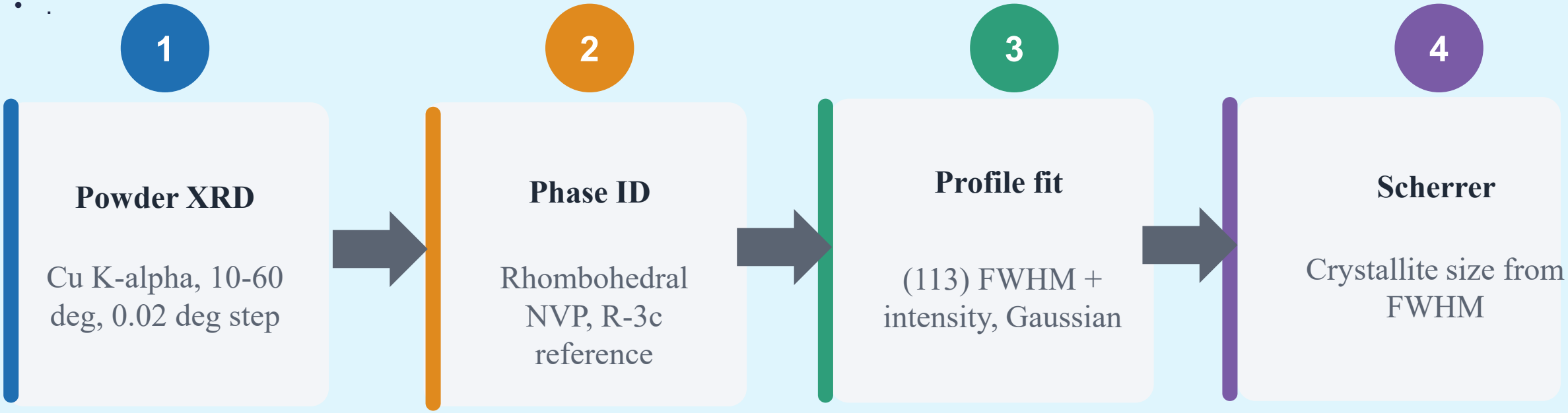
3 X 3 Full-factorial Synthesis Matrix

	30 h	40 h	50 h
160 °C	NVP	NVP	NVP
180 °C	NVP	NVP ★	NVP
200 °C	NVP	NVP	NVP

Common recipe for all nine samples: 40 mL DI water • magnetic stirring • 100 mL Teflon-lined autoclave

Full-factorial design: every temperature-time combination is measured, so parameters can be separated

Characterization: XRD And Scherrer Analysis



One metric set per sample: FWHM, (113) intensity and crystallite size - the quantitative fingerprints of crystallinity.

All Nine Samples: Phase-pure NVP Everywhere

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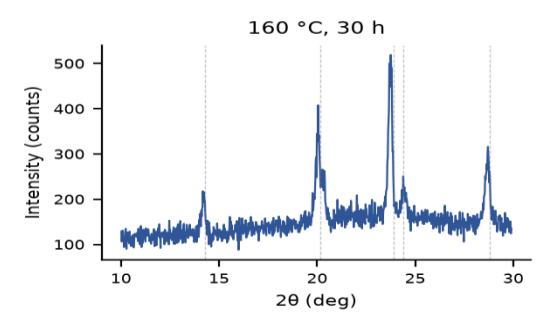
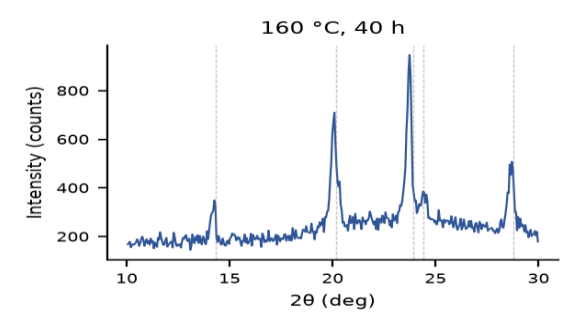
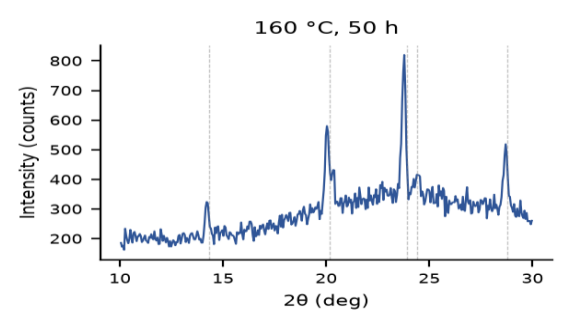


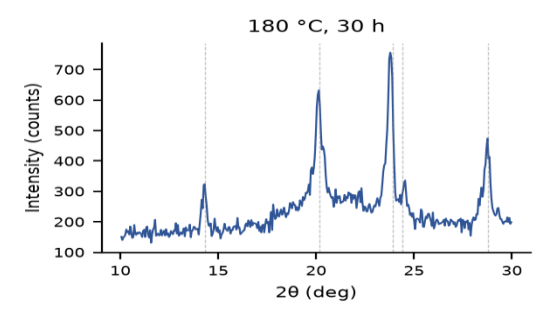
160 ºC 30h



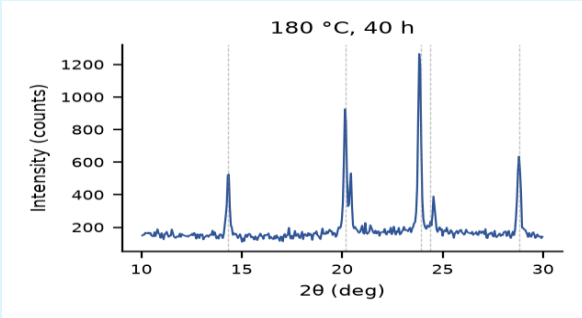
160 ºC 40h



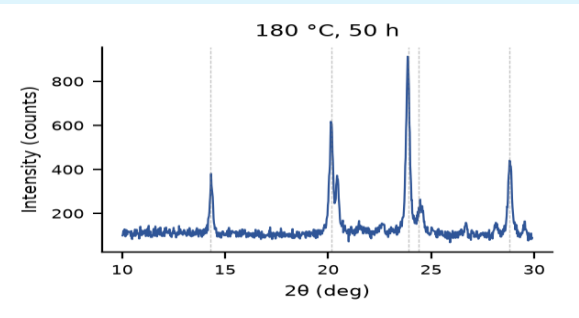
160 ºC 50h



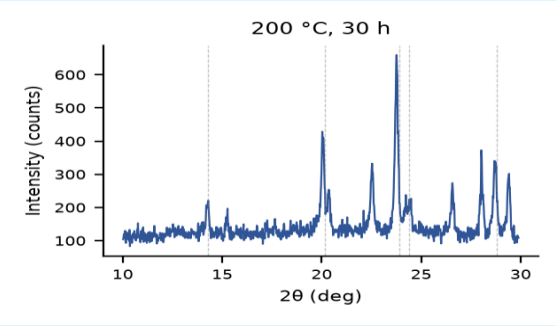
180 ºC 30h



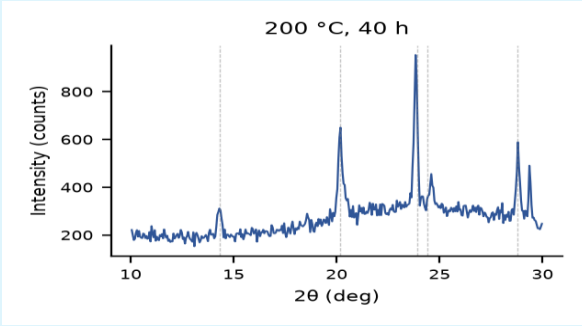
180 ºC 40h



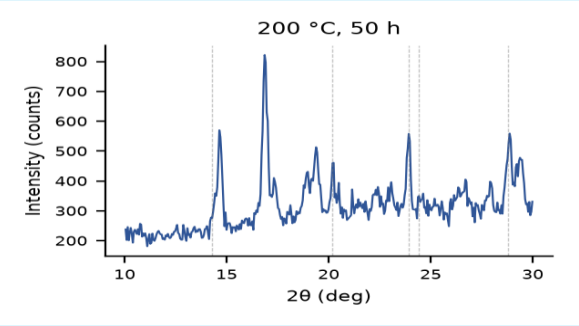
180 ºC 50h



200 ºC 30h



200 ºC 40h



200 ºC 50h

At 180 Deg C, 40 H Is The Clear Optimum

40 h FWHM

0.160

deg - narrowest of the series

40 h intensity

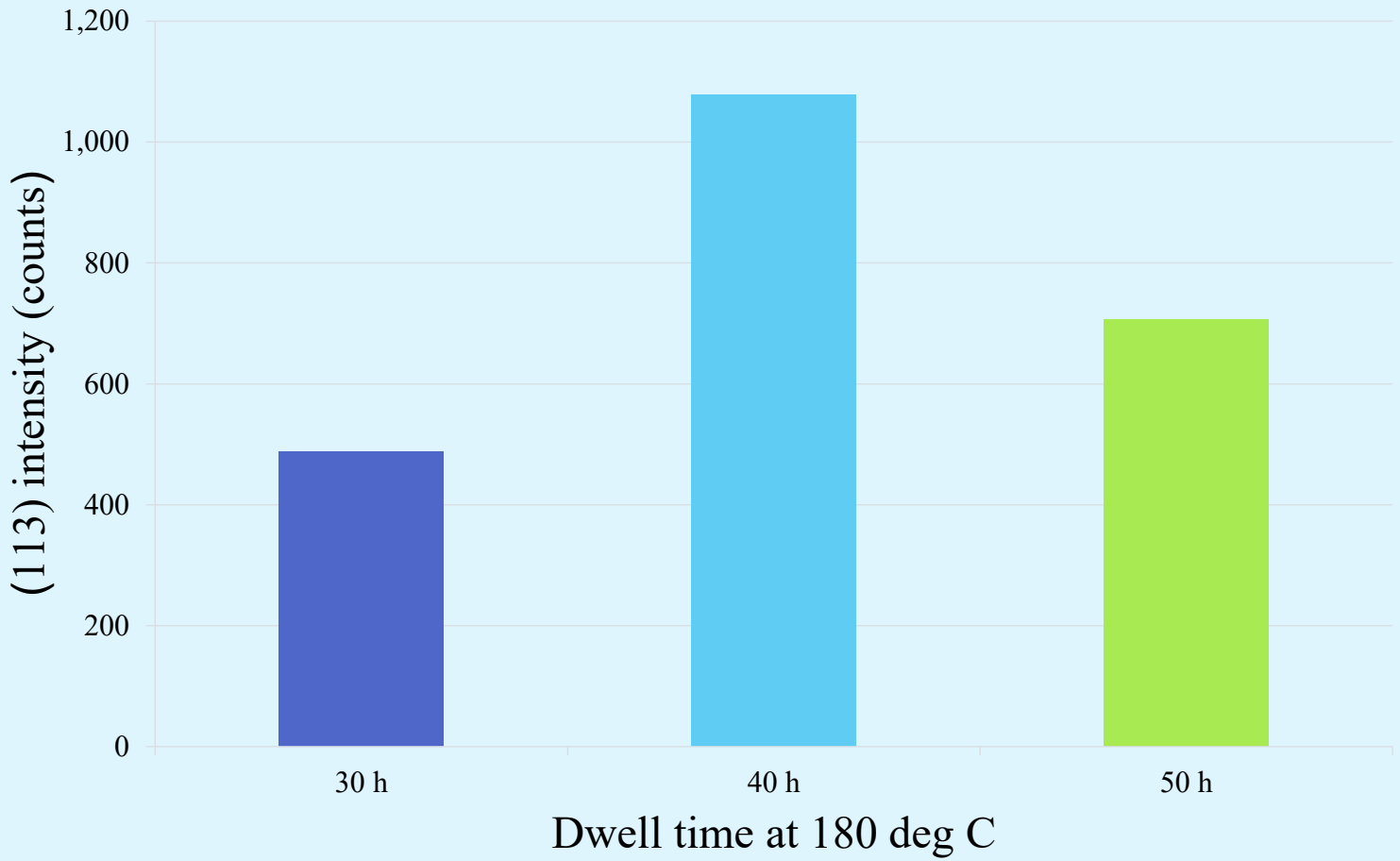
1079

counts, 2.2x the 30 h sample

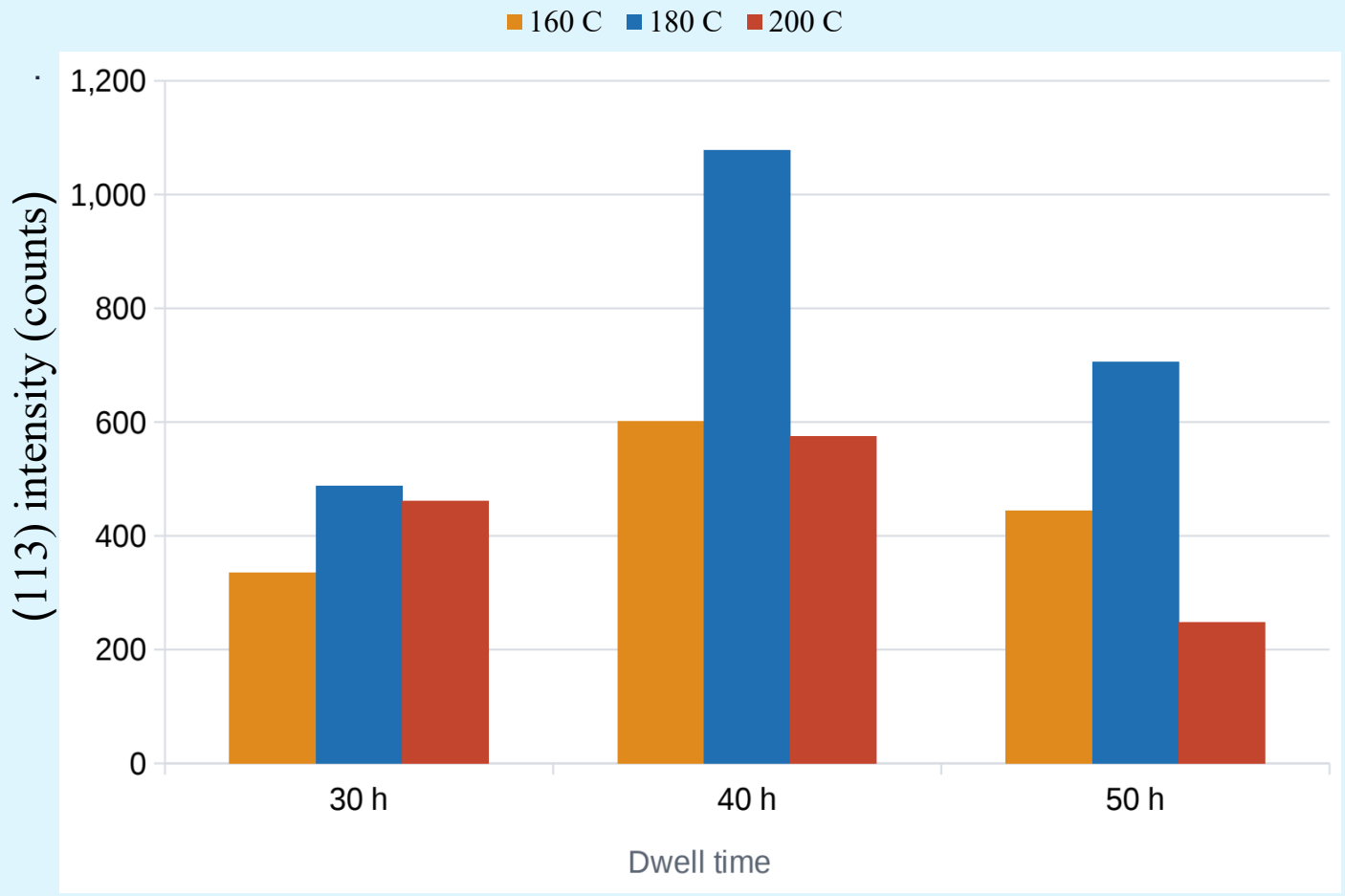
40 h size

507

nm by Scherrer analysis



180 Deg C Wins At 40 And 50 H On Both Metrics



40 h FWHM

0.160

vs 0.204 (160 C) / 0.180 (200 C)

40 h intensity

1079

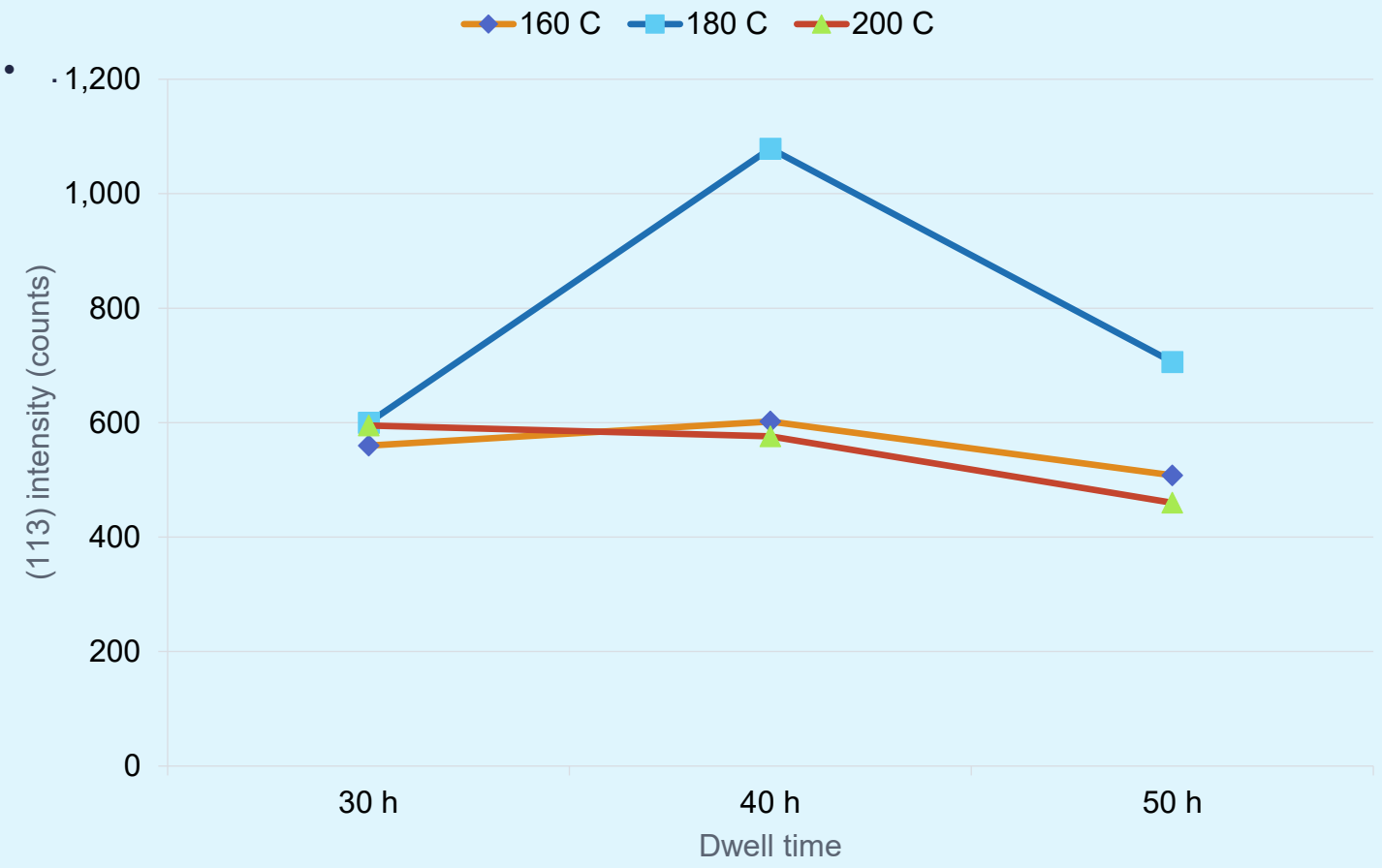
vs 602 / 576 counts

50 h intensity

706

vs 508 / 460 counts

Only 180 Deg C Shows Orderly Growth



160 C

FWHM broadens with time: 0.197 -> 0.222 deg

180 C

Sharpen-strengthen to 40 h, relaxes at 50 h

200 C

Degrades after 40 h: 0.180 -> 0.210 deg

Conclusions And Outlook

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Optimal window

180 deg C for 40 h: narrowest FWHM, highest (113) intensity, largest crystallites

Two first-order parameters

Temperature and dwell time act independently on NVP crystallinity

Phase purity

Same phase everywhere: R-3c NVP. What changes with temperature and time is how well it crystallizes.

THANK YOU!