CANADIAN LIGHT SOURCE 2026 WORKSHOP

High Temperature X-Ray Diffraction

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7/16/26

High Temperature X-Ray Diffraction

01 Introduction

02 Experiment Set-up

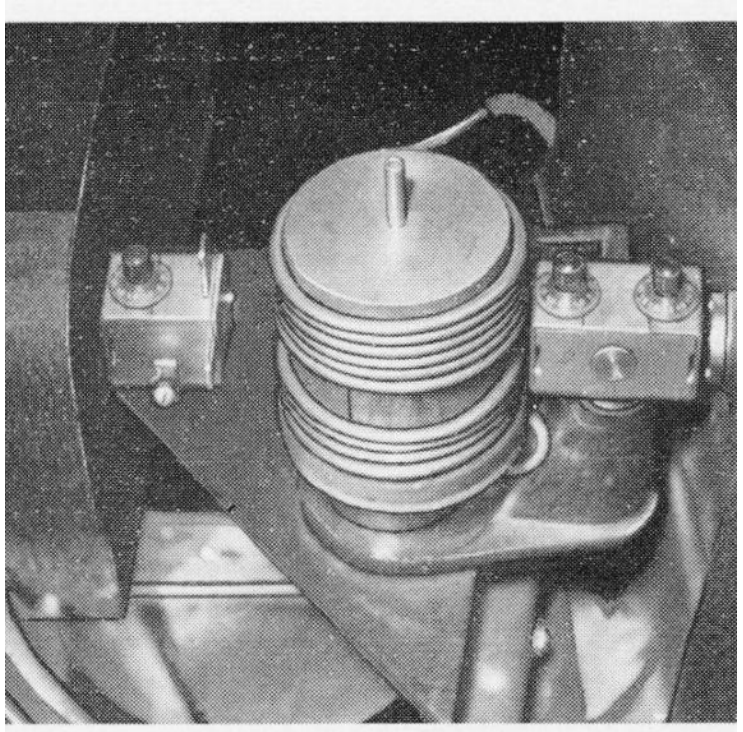
03 Visualization of Results

04 Example Experiments

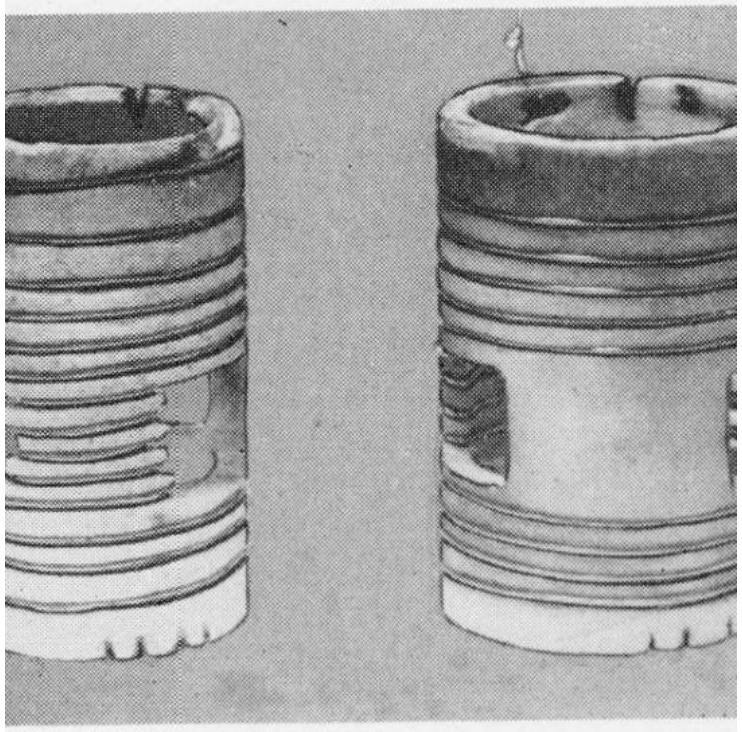
High Temperature X-Ray Diffraction

What is High Temperature X-Ray Diffraction?

- A subset of non-ambient X-Ray diffraction where temperature is primarily used to probe how the material of interest changes within an observed thermal profile.
- Initial attempts were primarily done on inorganic powders looking for structure changes at elevated temperatures.



Prototype in-situ temperature stage from 1947.



Valkenburg, Alvin Van and Howard F. McMurdie. "High temperature X-ray diffraction apparatus." *Journal of research of the National Bureau of Standards* 38 4 (1947): 415-8 .

High Temperature X-Ray Diffraction

Experiment Set-up

Types of Temperature stages

- Low Temperature Stage
  - Direct Cooling
  - Cold Finger
    - Liquid Nitrogen
  - Strip heater
    - Al-Cr
    - Max temperature 400-500 °C
  - Sample holder
    - Ni coated Cu
    - Stainless steel

Experiment Set-up

Types of Temperature stages

- Furnace
  - Indirect Heating
  - Largest Amount of Options

Experiment Set-up

Types of Temperature stages

- Furnace
  - Indirect Heating
  - Largest Amount of Options
    - Maximum temperature 1200-1500 C
      - Alumina sample holder
      - AlCr heating element
      - Option for various atmospheres
        - Air, Inert, Vacuum, Reactive Gases

Experiment Set-up

Types of Temperature stages

- High temperature stage
  - Direct Heating
  - For the most extreme reactions
    - Type of strip determines maximum temperature and atmosphere
      - Platinum
        - Max 1600 °C Air, Inert, Vacuum
      - Tantalum
        - 1600 °C Vacuum
      - Tungsten
        - 2000 - 2300 °C High Vacuum

Experiment Set-up

Sample Considerations

- Knowledge of your sample is necessary for good data collection
  - What temperature range is the focus?
  - What are the main peaks you want to focus on?
  - What is the melting point?
  - Does the material interact with the sample holder?
  - Does your material evolve gases upon heating?

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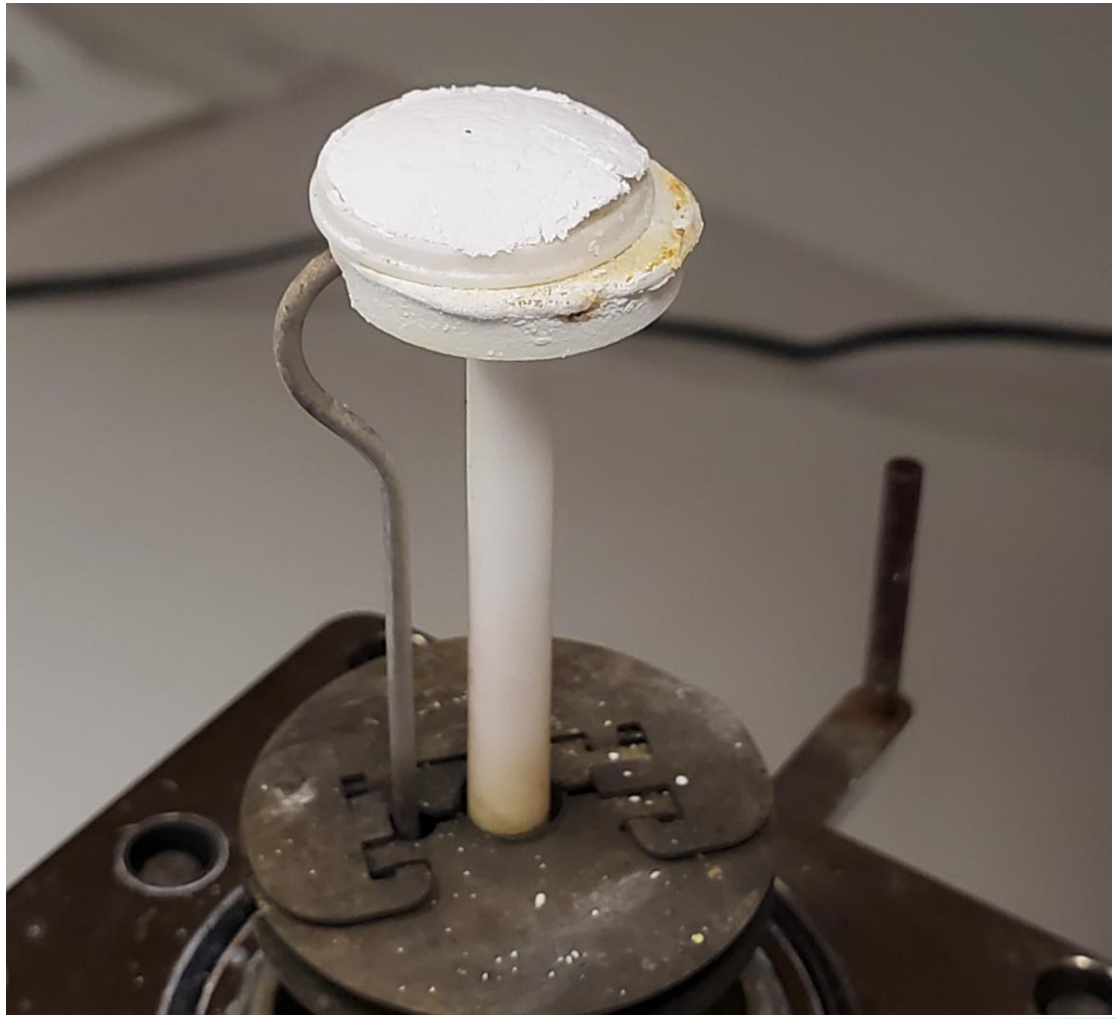
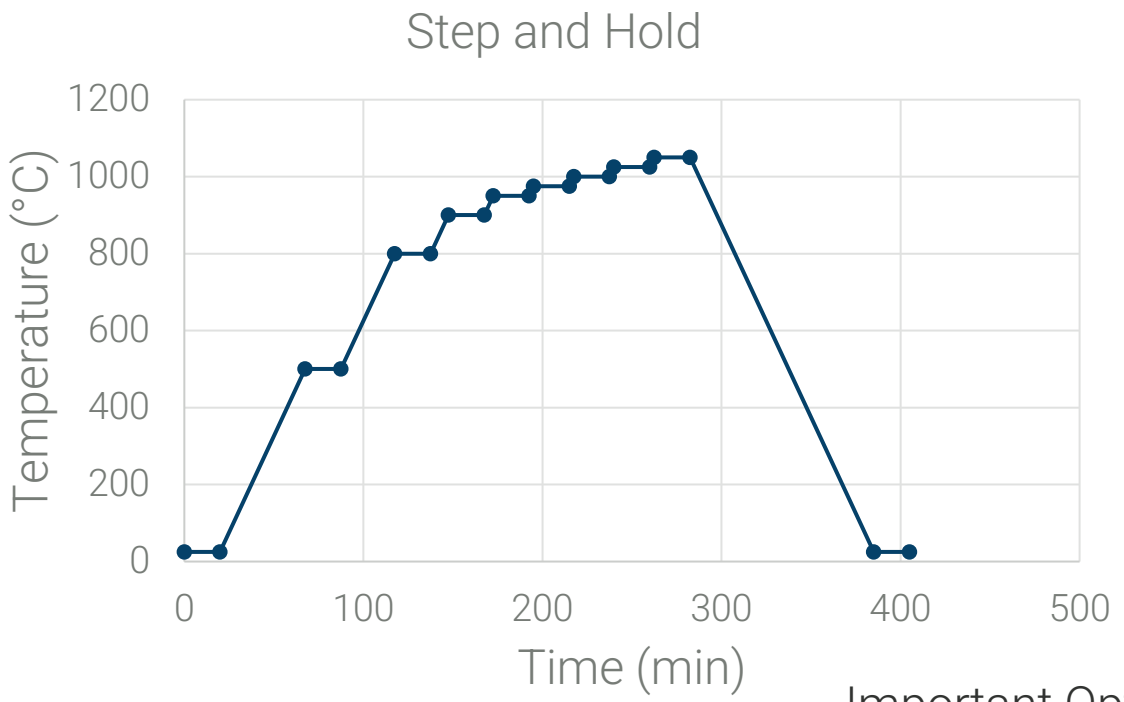
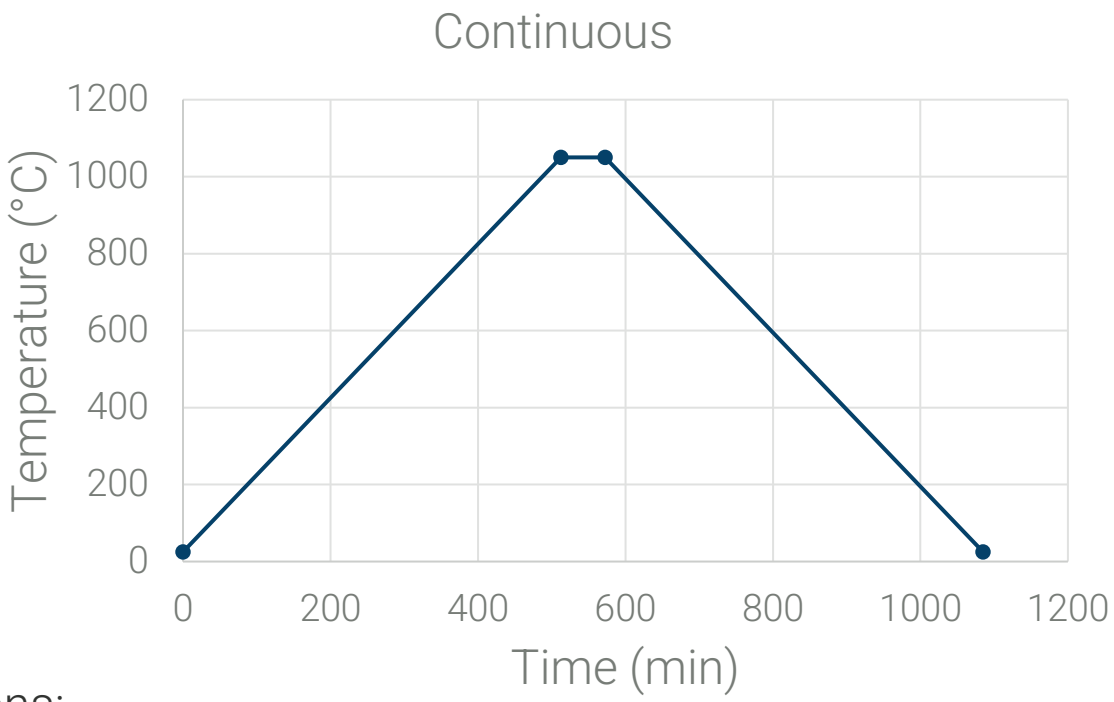


Experiment Set-up

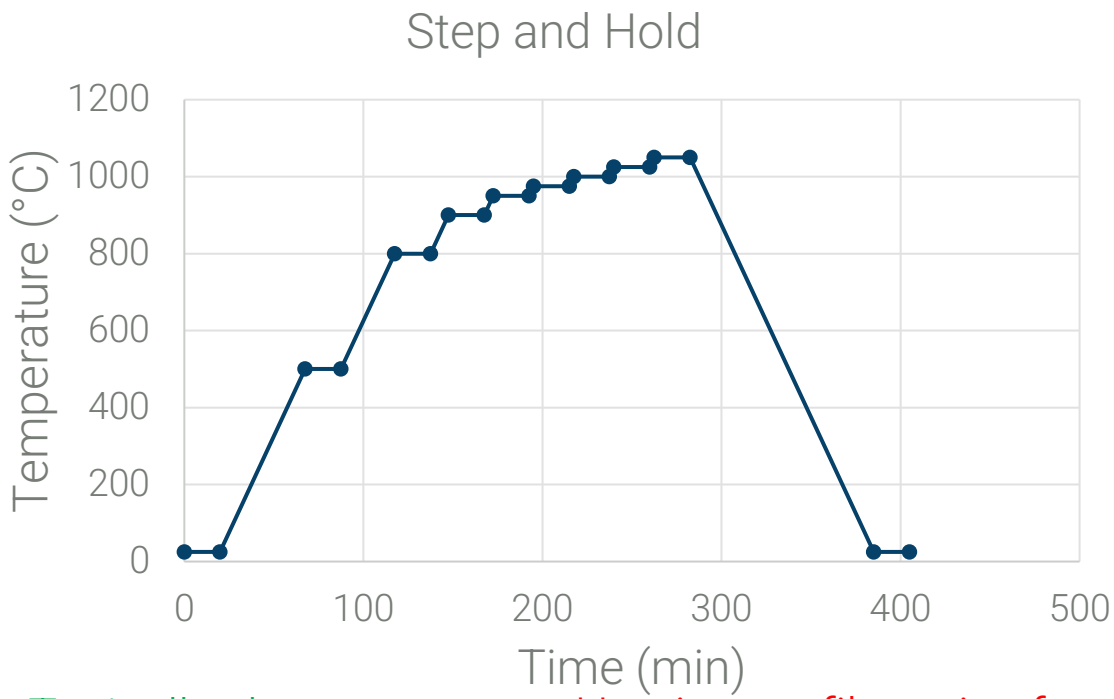




Important Options:

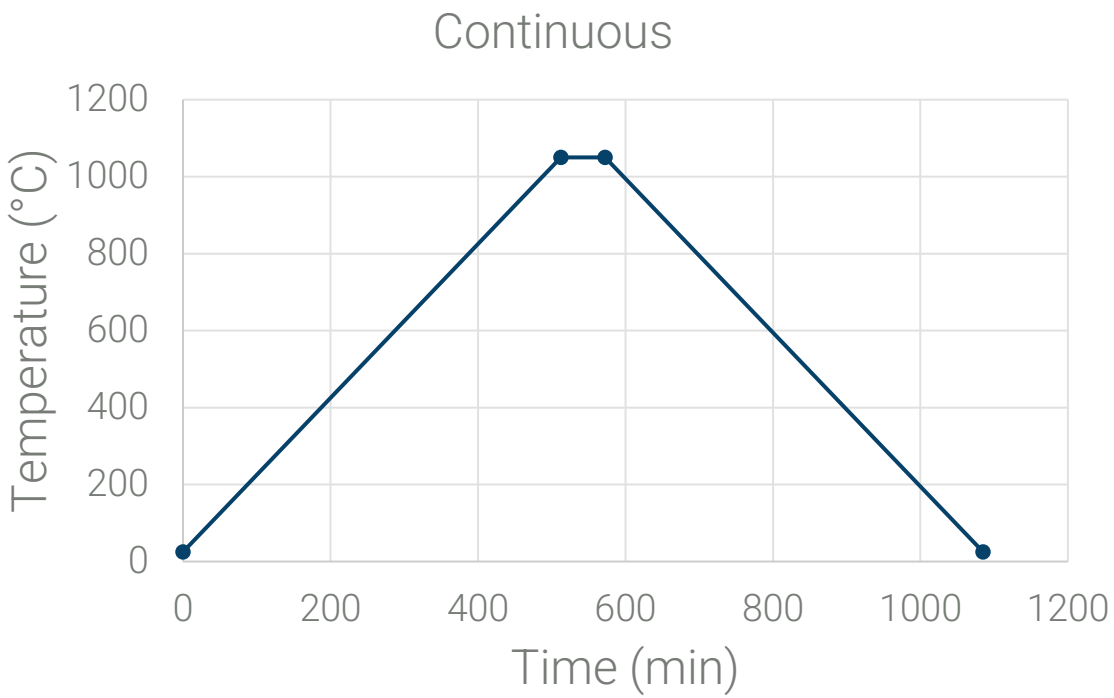
- Ramp Rate
  - Heating and Cooling
- Dwell time
- Measurement Duration
- Measurement Delay

Experiment Set-up



- Typically shorter
- Higher resolution scans
- Temperature certainty

- Heating profile varies from bulk solid state
- Short lived phases can be missed
- Data between steps is interpolated



- Closer to a traditional heating profile
- Able to visualize transient phases and diffusion

- Typically longer
- Noisier data

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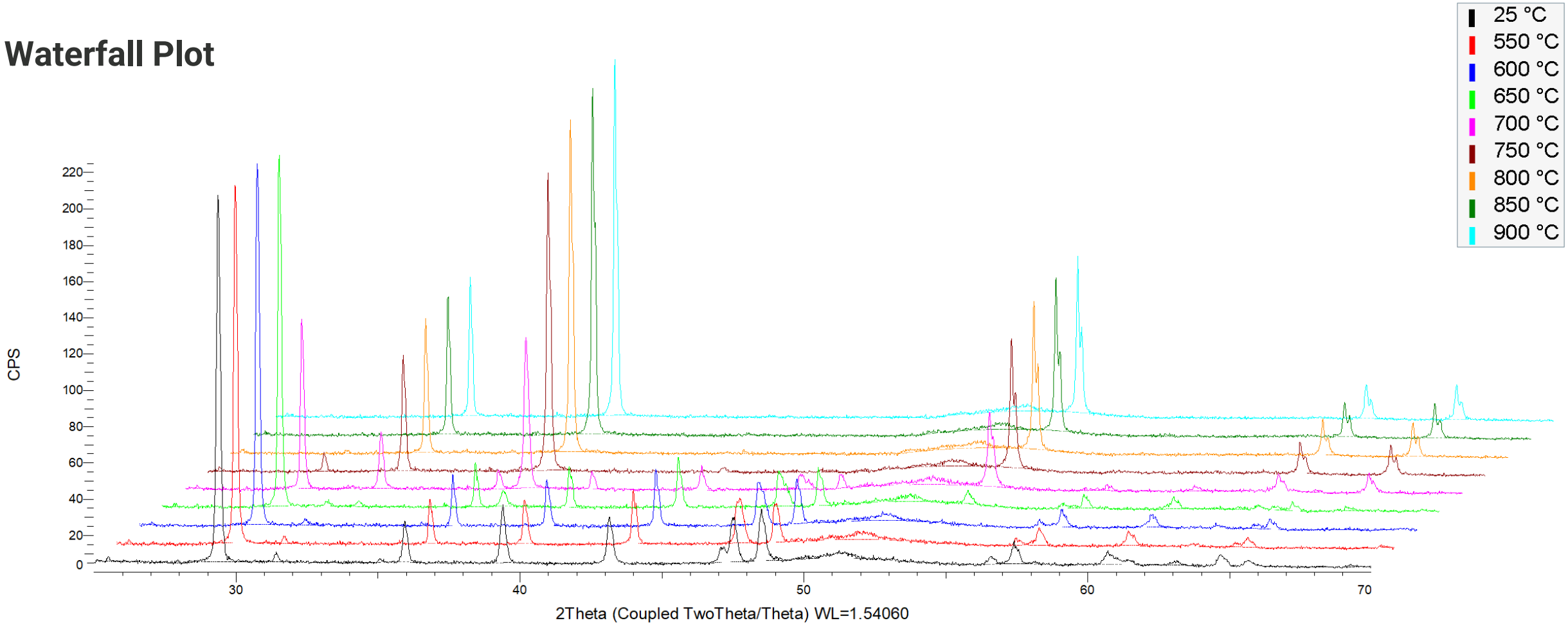
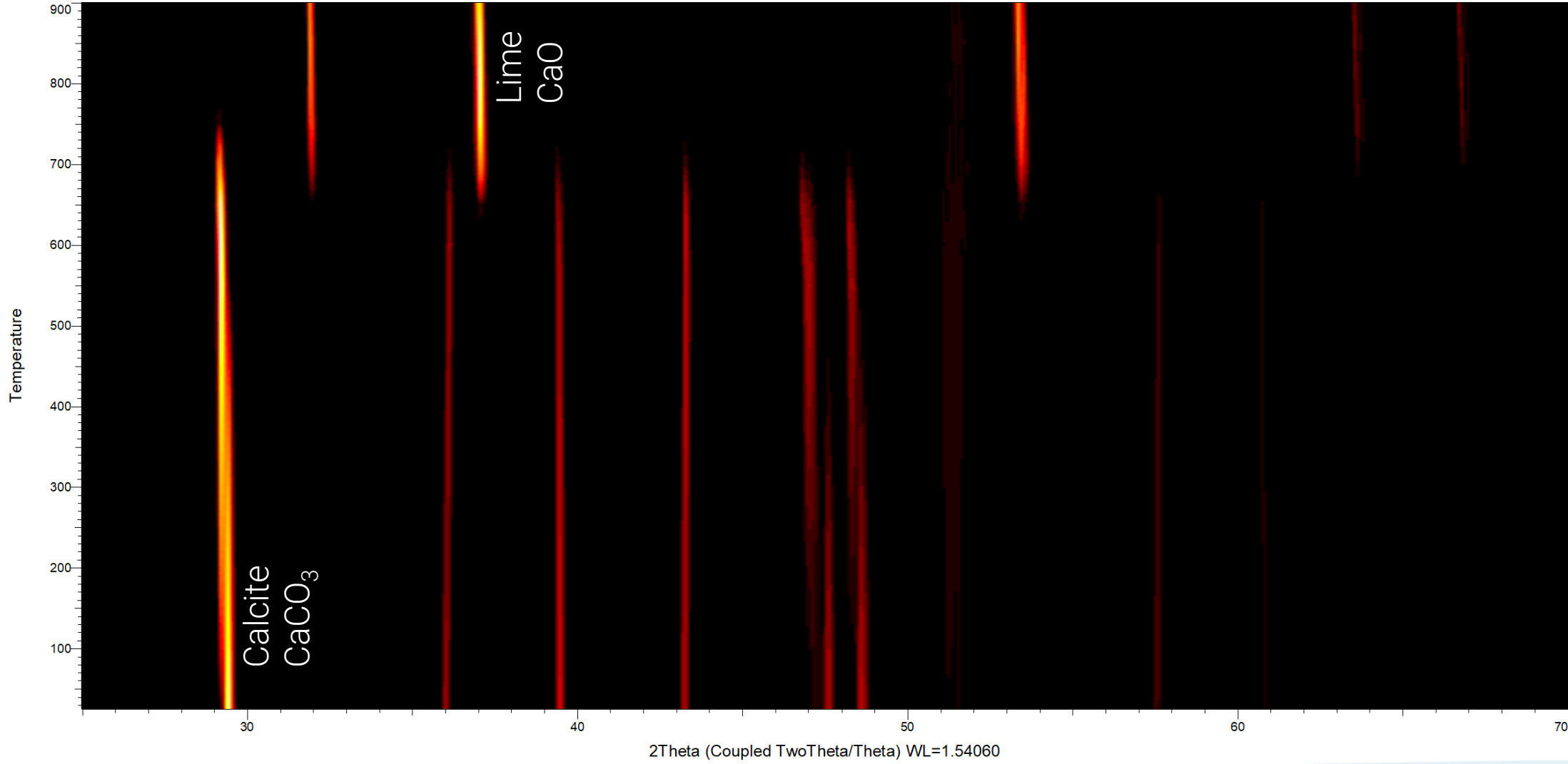
Visualization of Results

Waterfall Plot



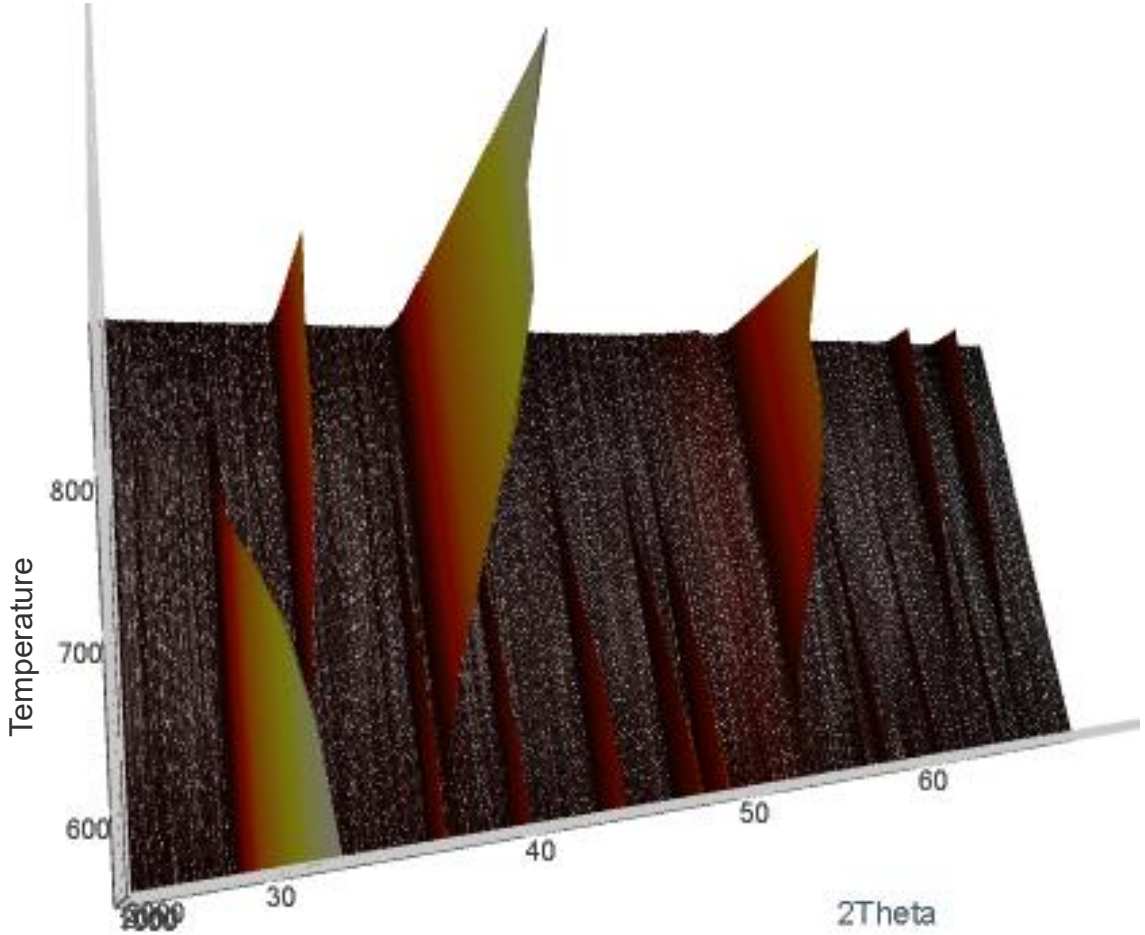
Visualization of Results

2D Plot



Visualization of Results

3D Plot



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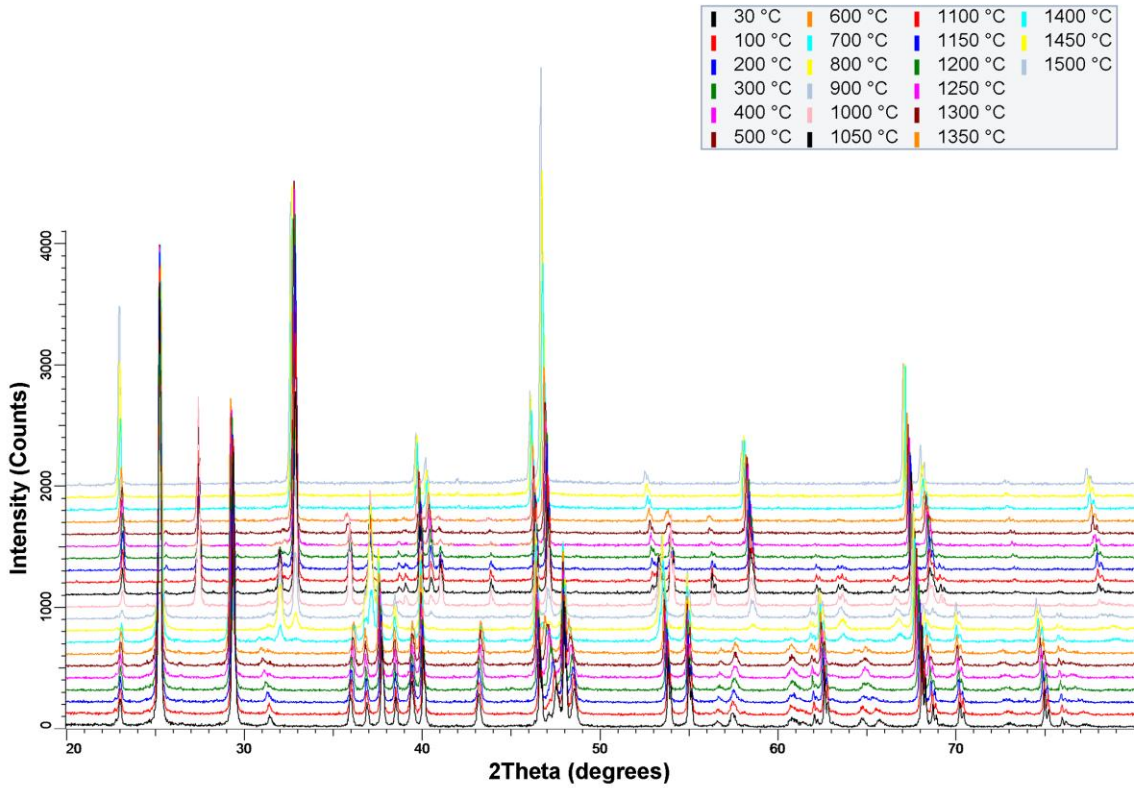
Case Study 1 : Synthesis of $CaTiO_3$

Case Study 1: $CaTiO_3$

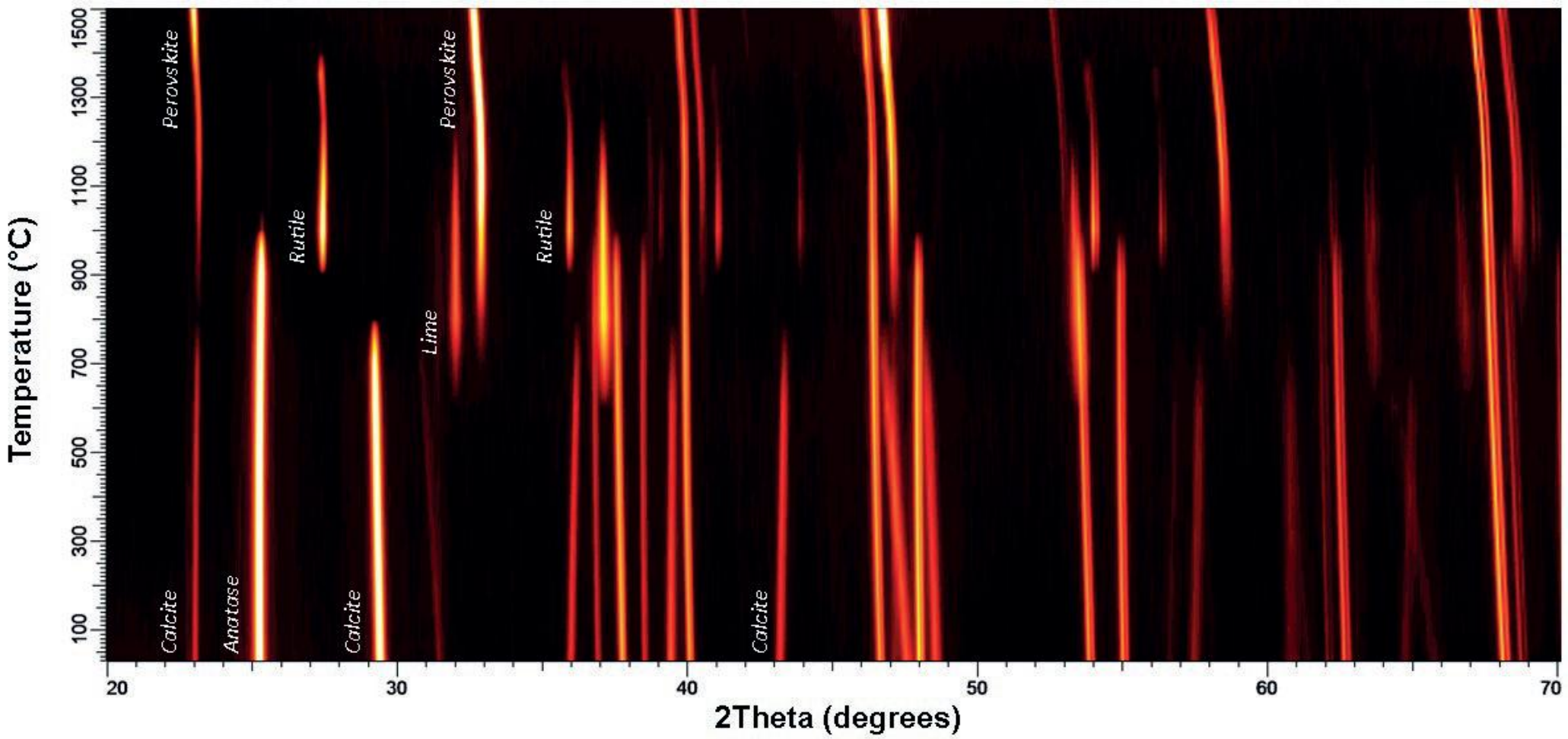
Motivation

- Evaluate the reaction between Calcite and Anatase
- Look into the reaction pathway for the formation of Calcium Titanate
- The end goal of this experiment is to visualize the formation of Calcium Titanate from the starting reagents.

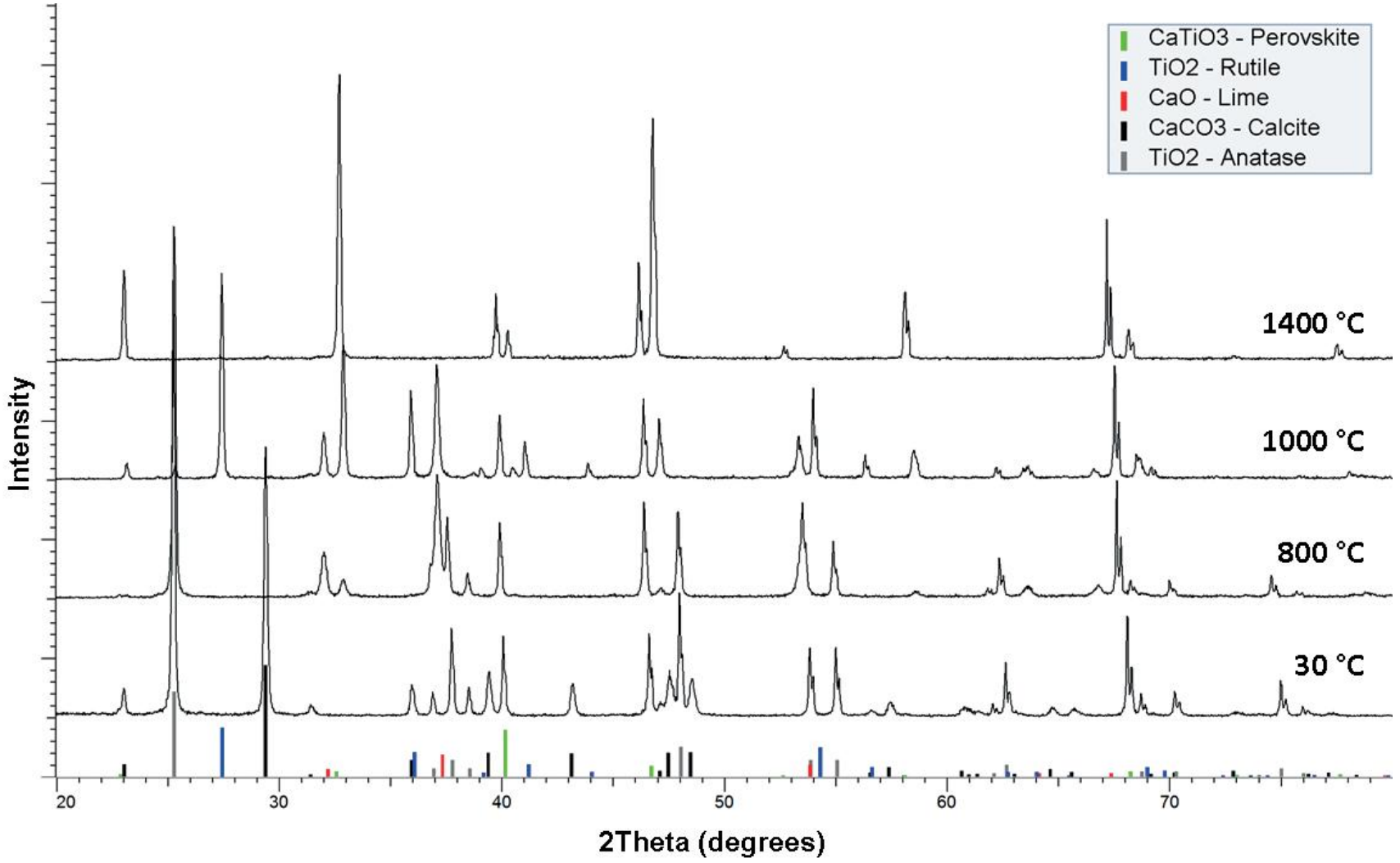
Results - Waterfall



Case Study 1: $CaTiO_3$



Case Study 1: $CaTiO_3$



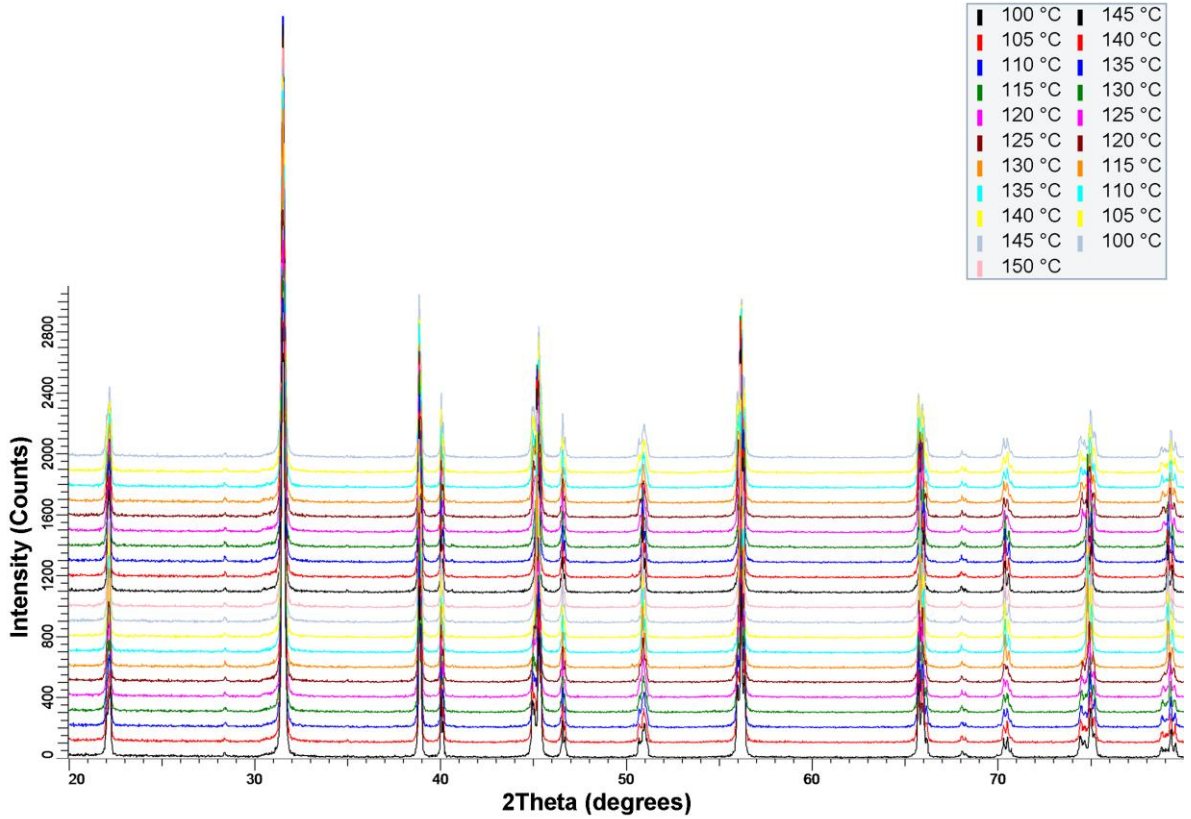
Case Study 2 : Phase Transition of $BaTiO_3$

Case Study 2: $BaTiO_3$

Motivation

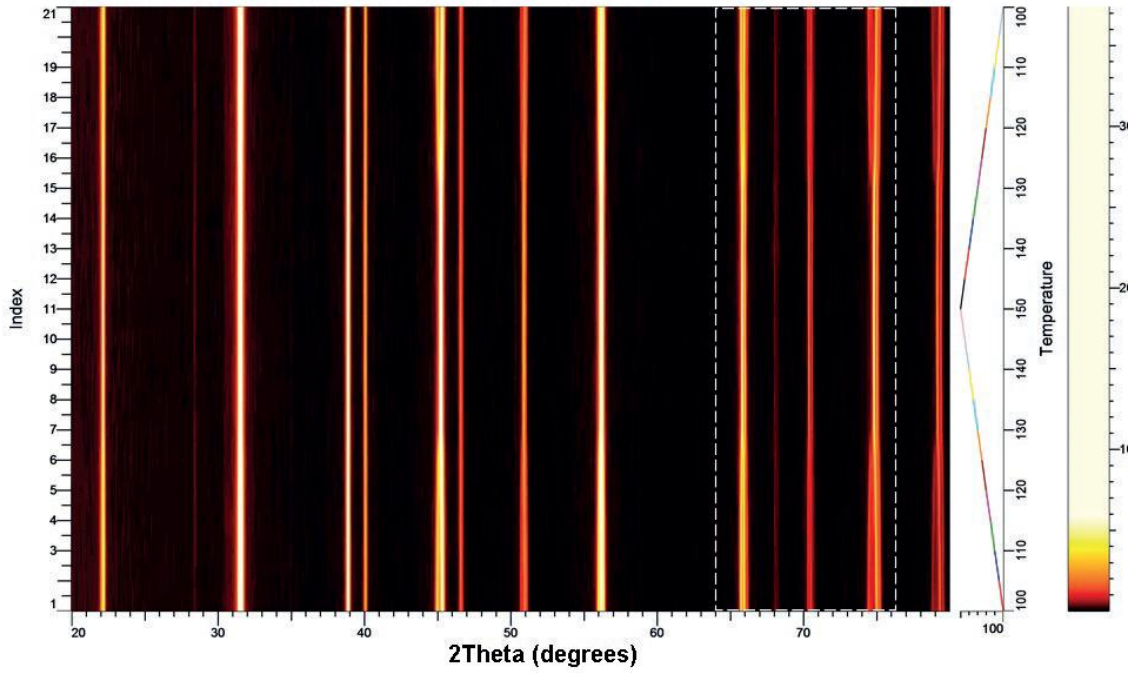
- Barium Titanate was one of the first ferroelectric materials ever synthesized.
- It undergoes a reversible phase transition at the Curie temperature (~130 C) where it changes from a tetragonal to cubic structure.
- The goal of this experiment is to visualize this transition as the crystal structure changes from one to the other.

Results - Waterfall

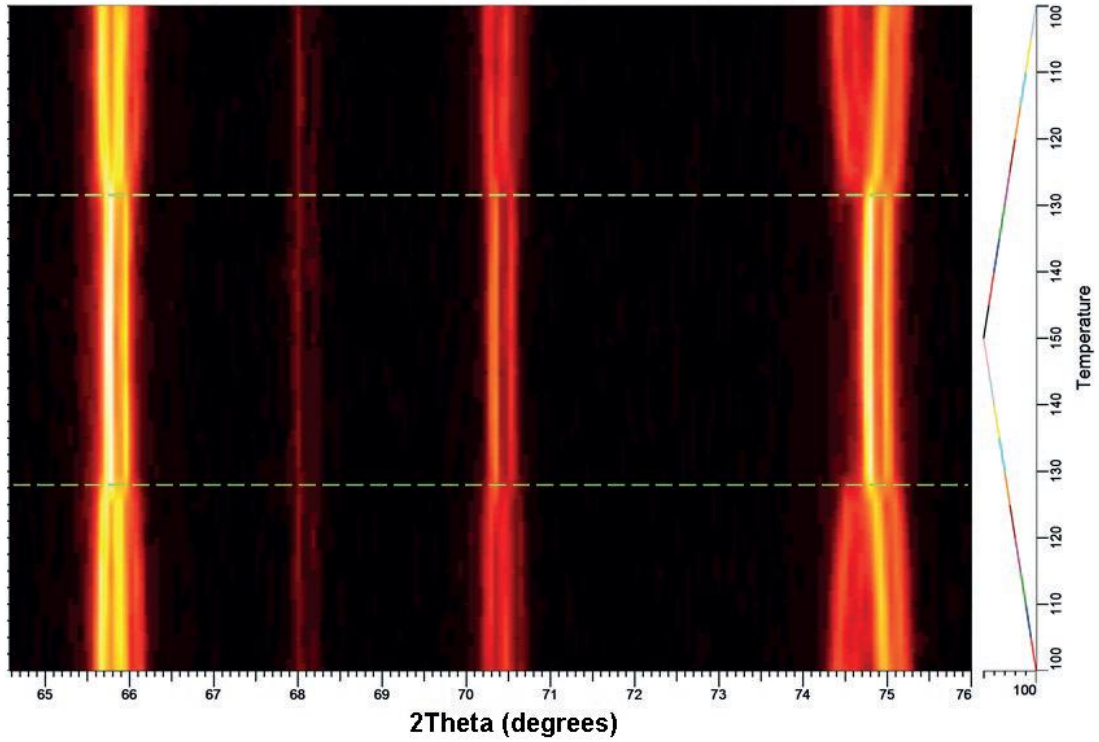


Case Study 2: $BaTiO_3$

Results – 2D View



Results – 2D View Zoom



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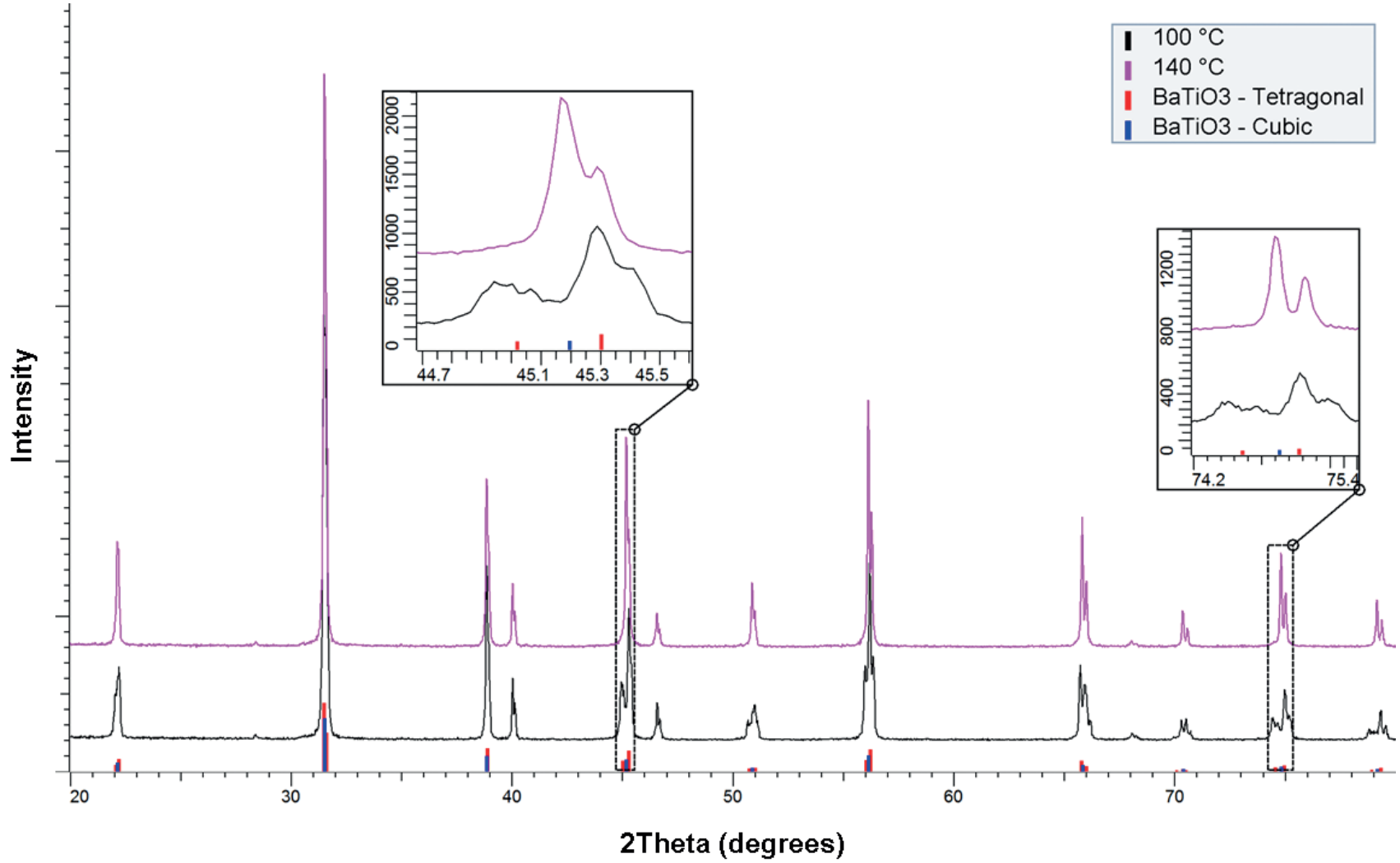
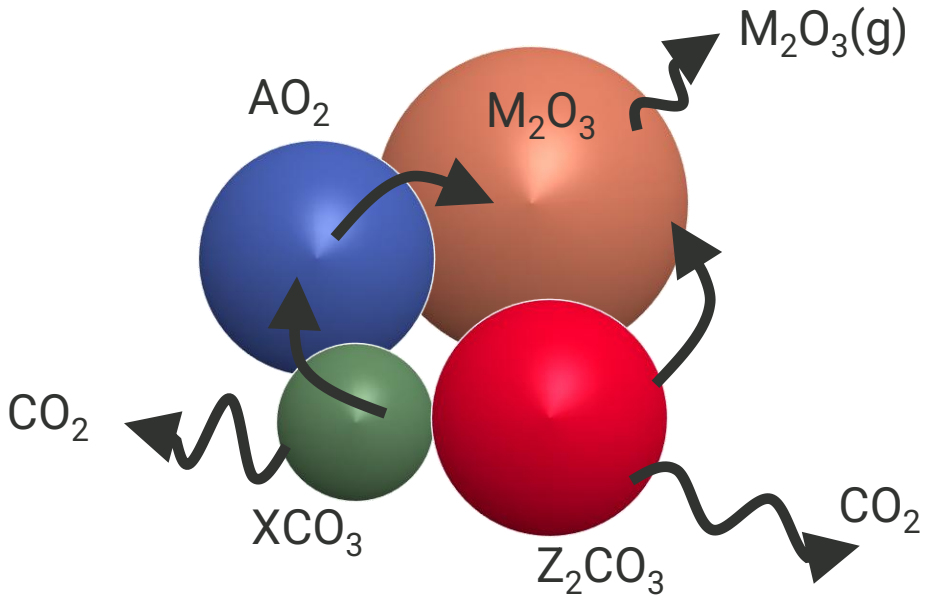


Case Study 3 : Synthesis of (K,Na)NbO3

MOTIVATION

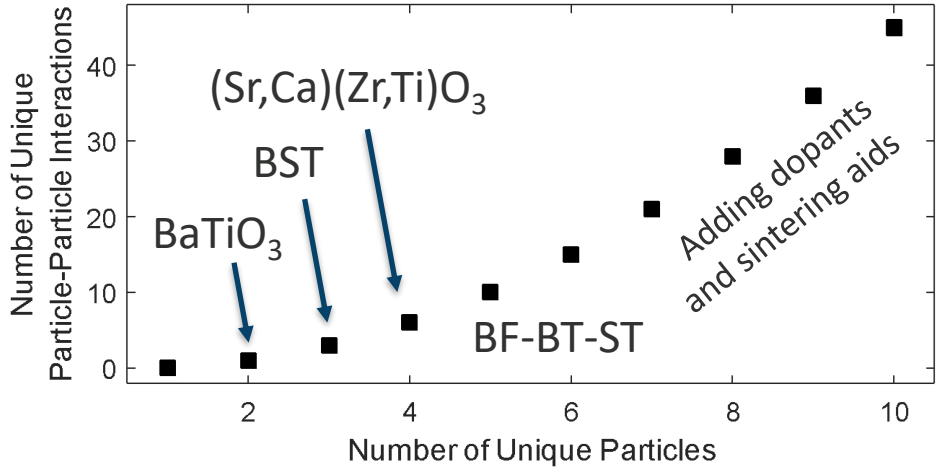
Although simple in formula (e.g., A + B → C), solid state reactions occur through **mass transport**, where the microscopic interactions matter.



Problems exacerbated in increasingly complex compositions due to increasing number of starting materials (n), which:

▷ Increases required diffusion distances

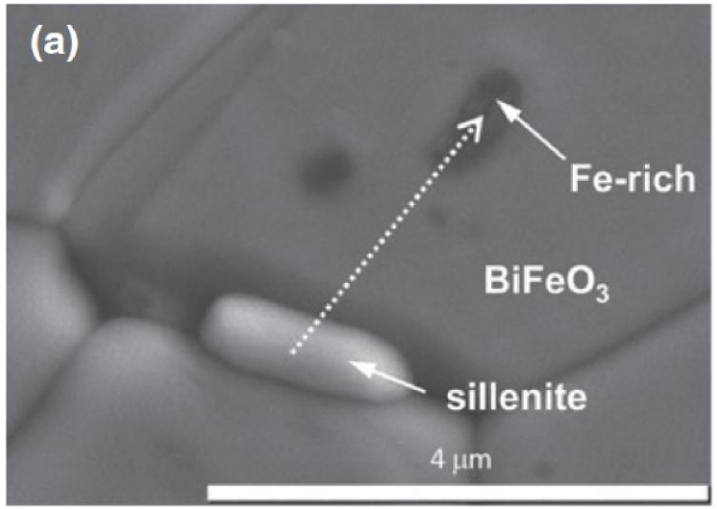
▷ Increases unique particle-particle interactions, according to: **n(n-1)/2**



▷ Deleterious phases may persist at elevated temperatures, even if not thermodynamically favorable

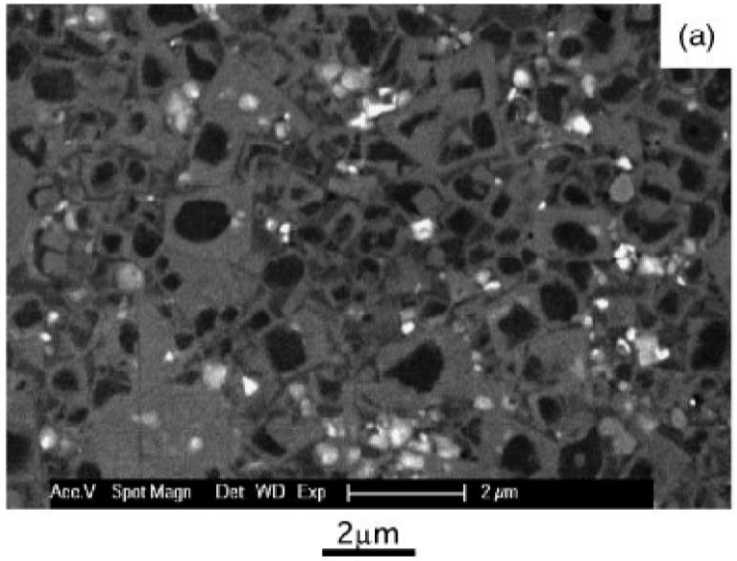
MOTIVATING EXAMPLES – CHEMICAL INHOMOGENEITY

$BiFeO_3$
(n=2: Bi_2O_3 and Fe_2O_3)



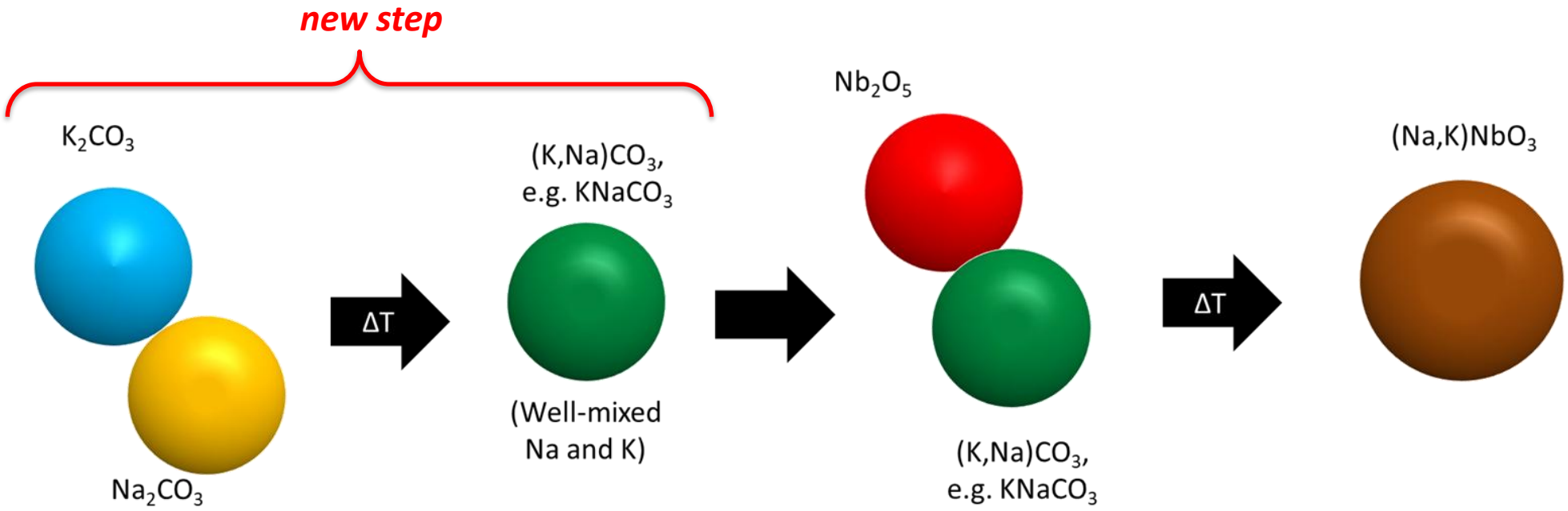
Rojac, Bencan, Malic, Tutuncu, Jones, Daniels, and Damjanovic, JACERS 97, 1993 (2014)

$Na_{0.5}K_{0.5}NbO_3$
(n=3: K_2CO_3, Na_2CO_3, Nb_2O_5)



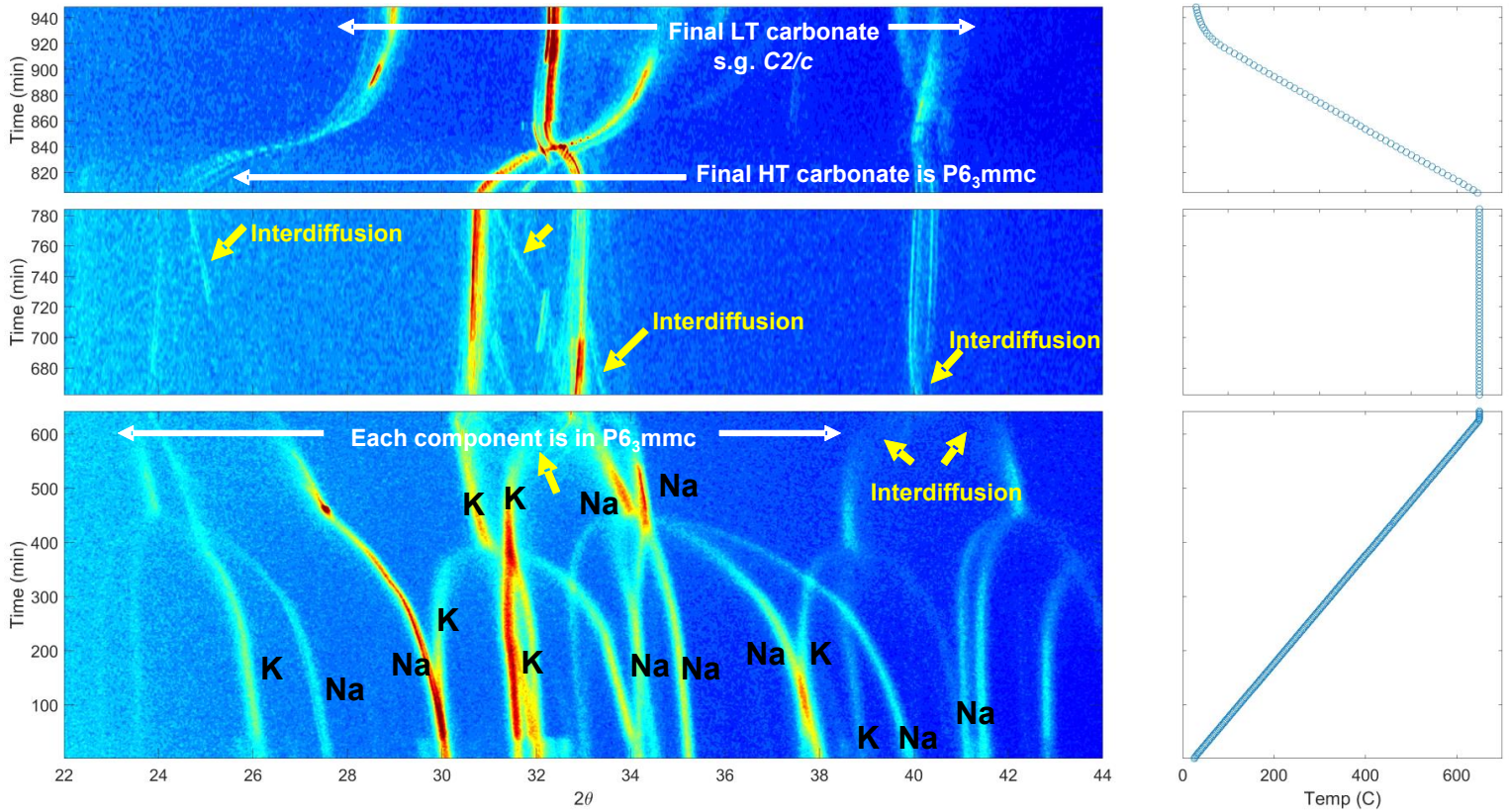
Wang, Damjanovic, Klein, Hollenstein, and Setter, JACERS 90, 3485 (2007)

Our Hypothesis: Reducing the number of unique precursors (n) will increase chemical homogeneity of the product due to more uniform incorporation of the metal cations.



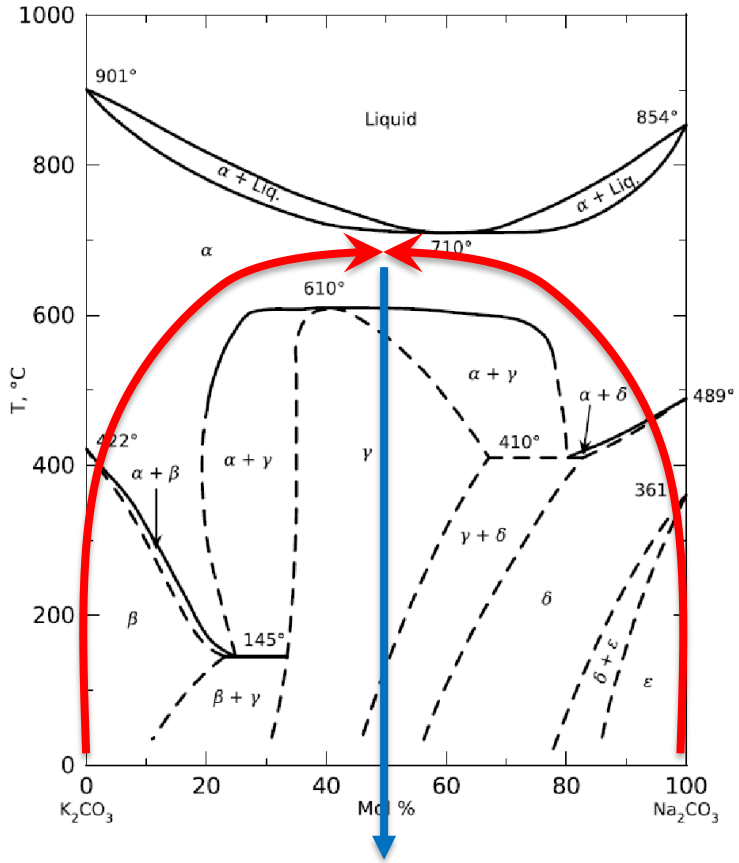
$Na_2CO_3 + K_2CO_3 \rightarrow KNaCO_3$

Na_2CO_3 and K_2CO_3 heated together



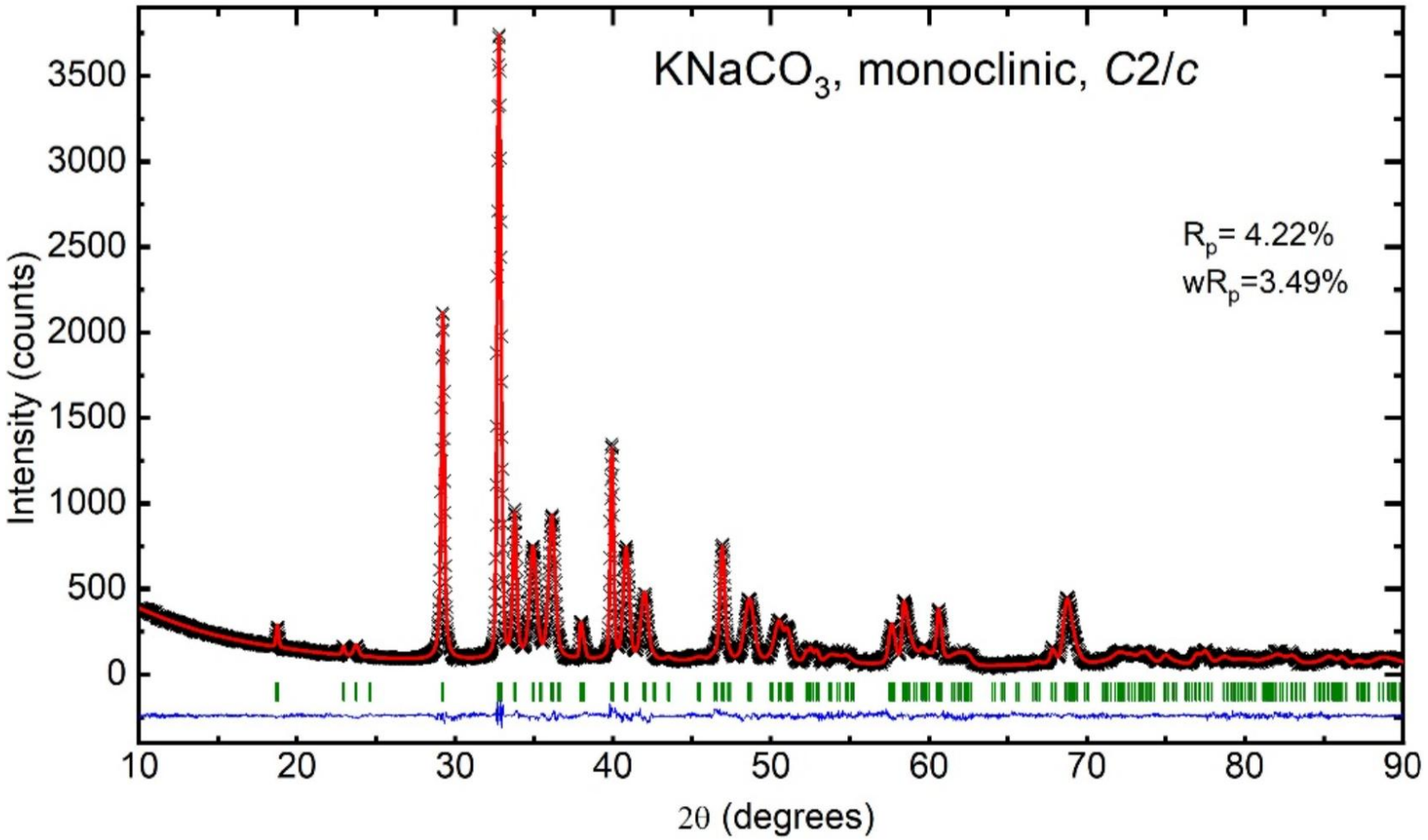
K_2CO_3 and Na_2CO_3 reflections marked as simply "K" and "Na" for clarity

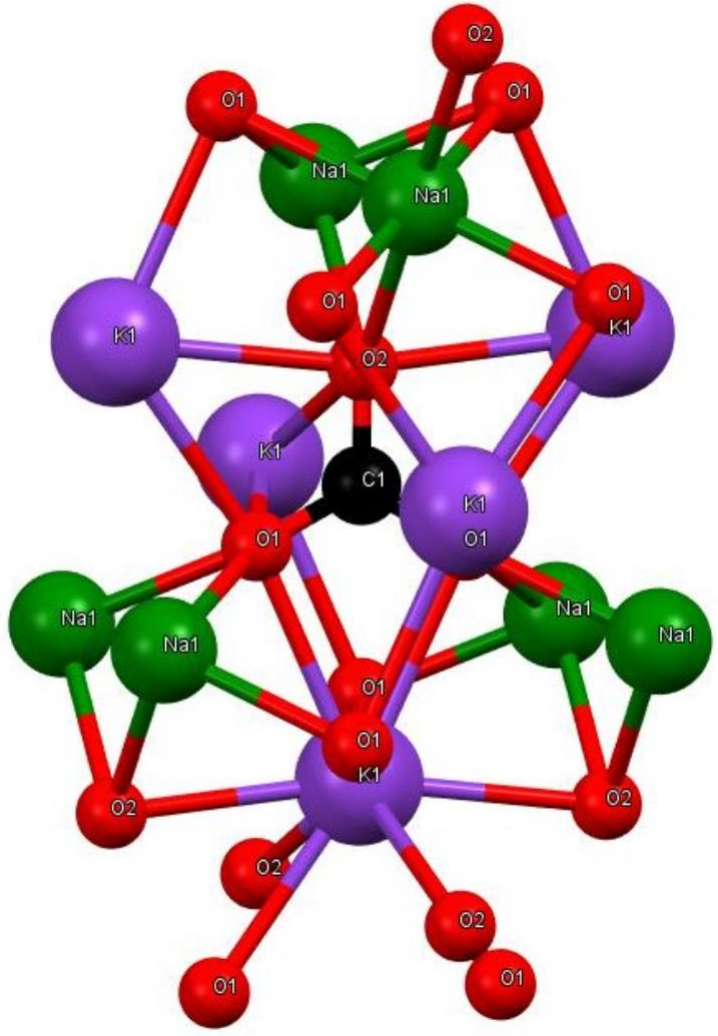
Fig. 01008 in the ACerS/NIST phase equilibria database; System K_2CO_3-Na_2CO_3 by A. Reisman, J. Am. Chem. Soc., 81 [4] 807-811 (1959).



$KNaCO_3$

We refined the structure of $KNaCO_3$ using both powder and single crystal diffraction

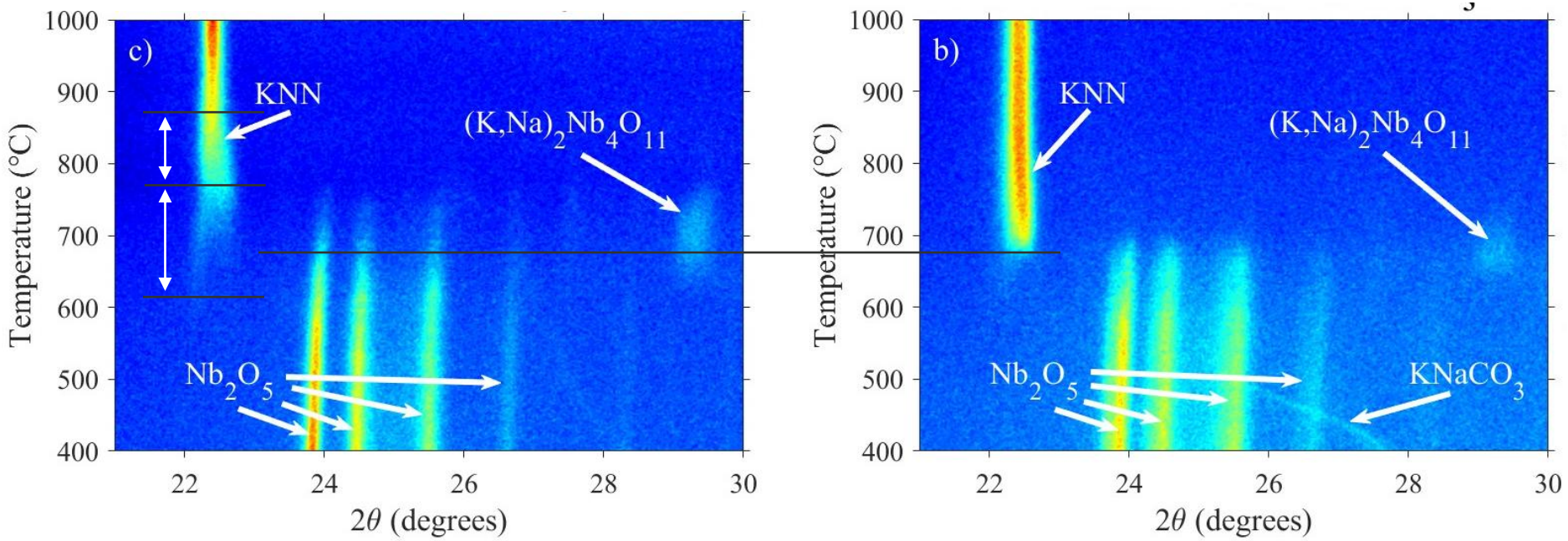




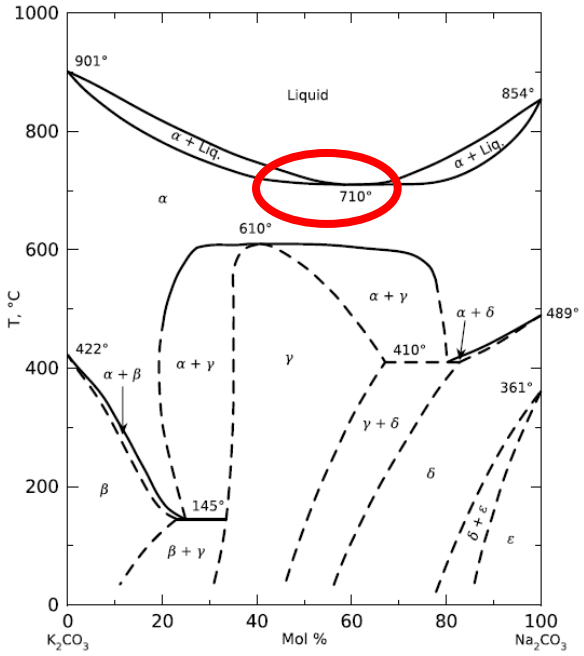
Synthesizing KNN from Carbonates

Forming KNN from **original carbonates**, Na_2CO_3 and K_2CO_3

Forming KNN from **pre-reacted carbonates**, i.e. $KNaCO_3$

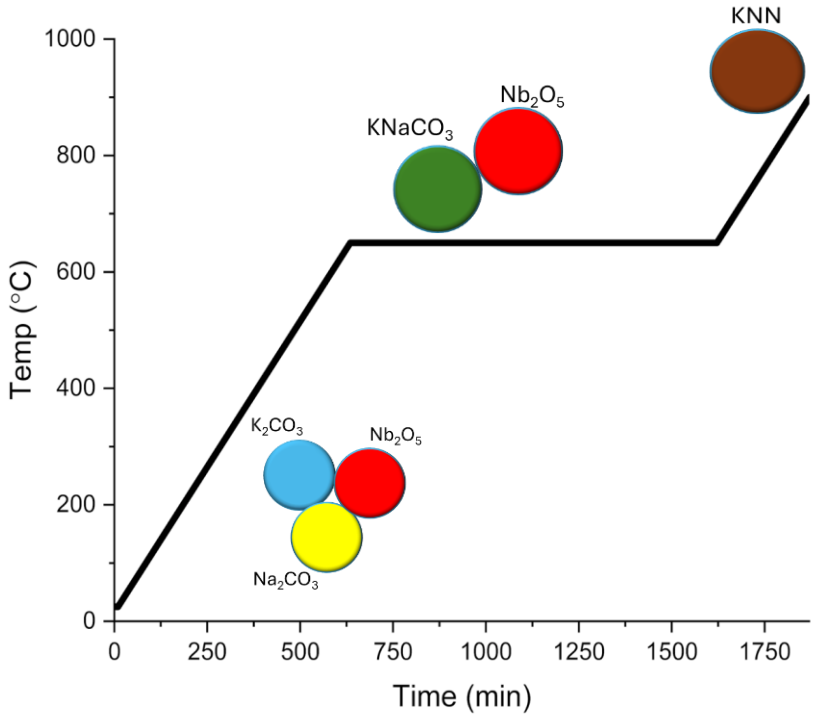


$KNaCO_3$ melts at the lowest temperature of 710°C, lowering the formation temperature of the perovskite.

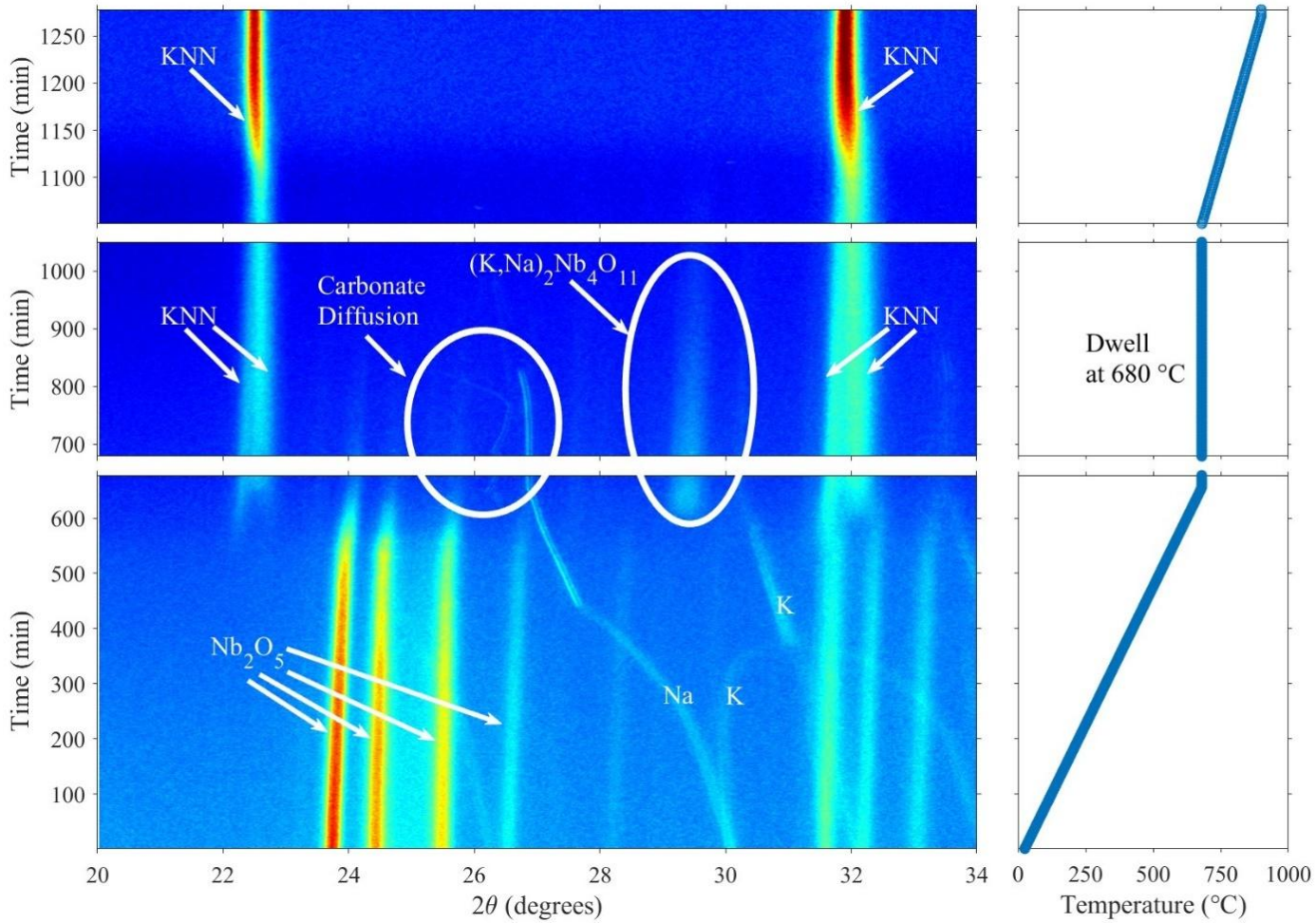


The use of pre-reacted enables a more uniform formation of KNN, and at a lower temperature.

Could $KNaCO_3$ be reacted *in situ* during a traditional (single batch) process?

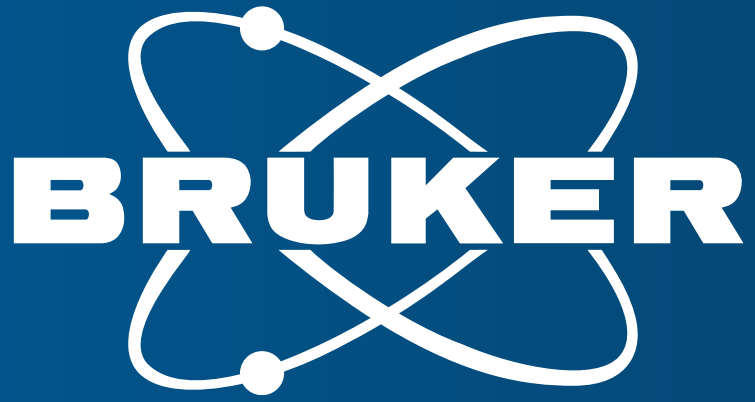


Intermediate dwell temperature of **680°C**



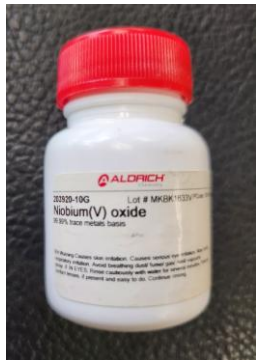
Thank you!

Tom Rowe
Thomas.Rowe@Bruker.com



Innovation with Integrity

Three Comparative Routes to Perovskite Synthesis



control

Dried K_2CO_3 from supplier

Dried Na_2CO_3 from supplier

+ Nb_2O_5 → KNN

“from starting carbonates”

control

K_2CO_3 by itself

Na_2CO_3 by itself

+ Nb_2O_5 → KNN

“from annealed carbonates”

new process

$Na_2CO_3 + K_2CO_3$ → $KNaCO_3$

+ Nb_2O_5 → KNN

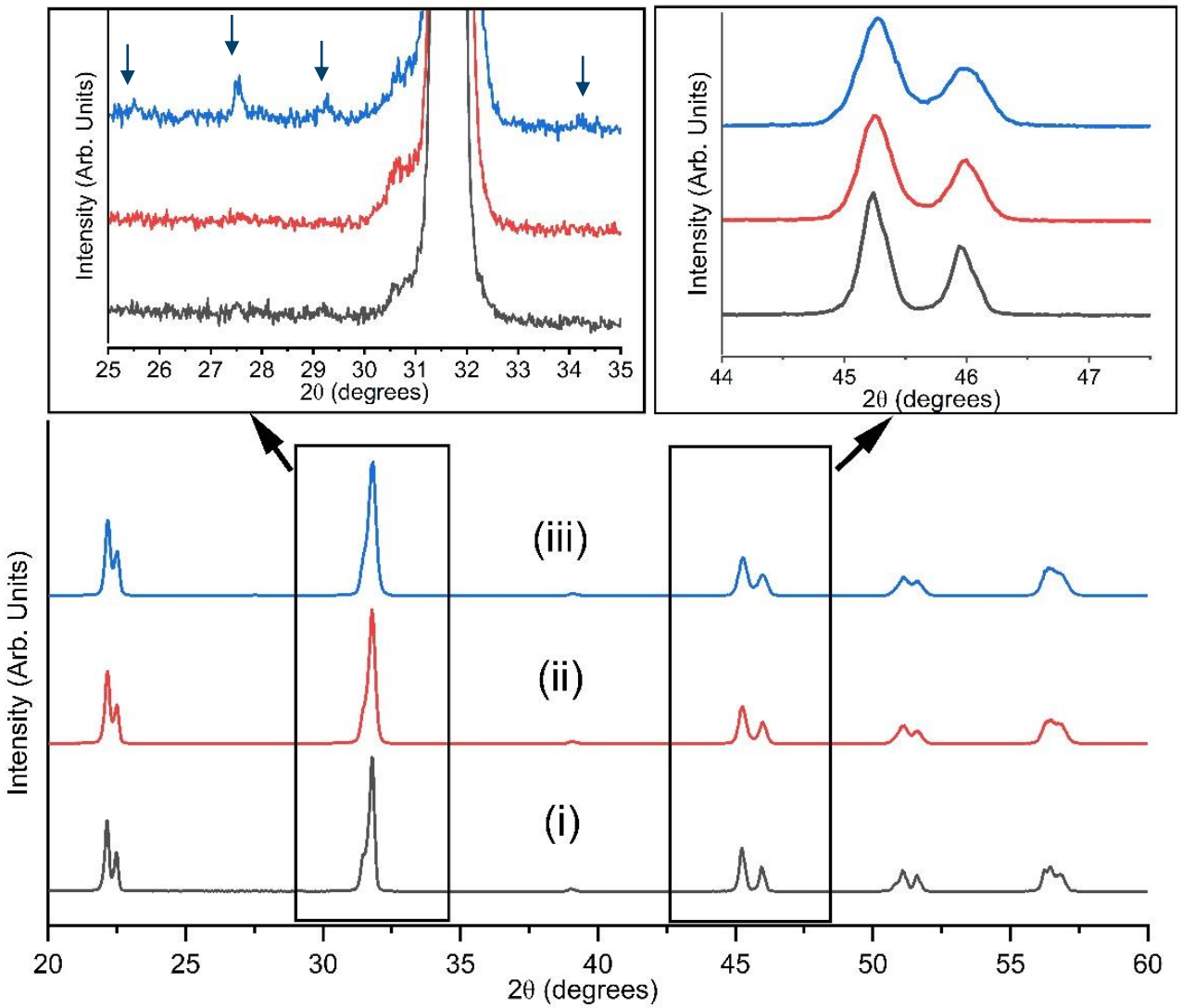
“from pre-reacted carbonates”

Heat at 1 °C/min to 680 °C, hold 2 hours, cool

Heat at 1 °C/min to 950 °C, hold 2 hours, cool

- Representative XRD diffractograms after synthesizing KNN using a muffle furnace

→ $(K,Na)_6Nb_{10}O_{30}$, Tetragonal Tungsten Bronze (TTB)



“from annealed carbonates”

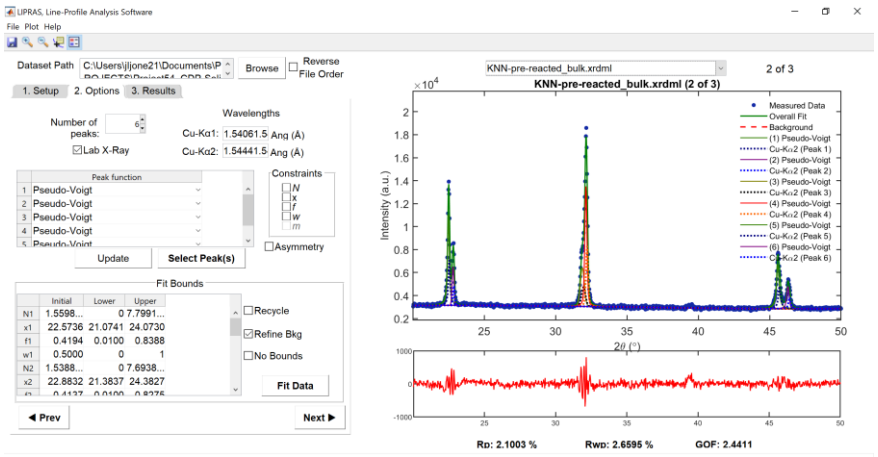
“from starting materials”

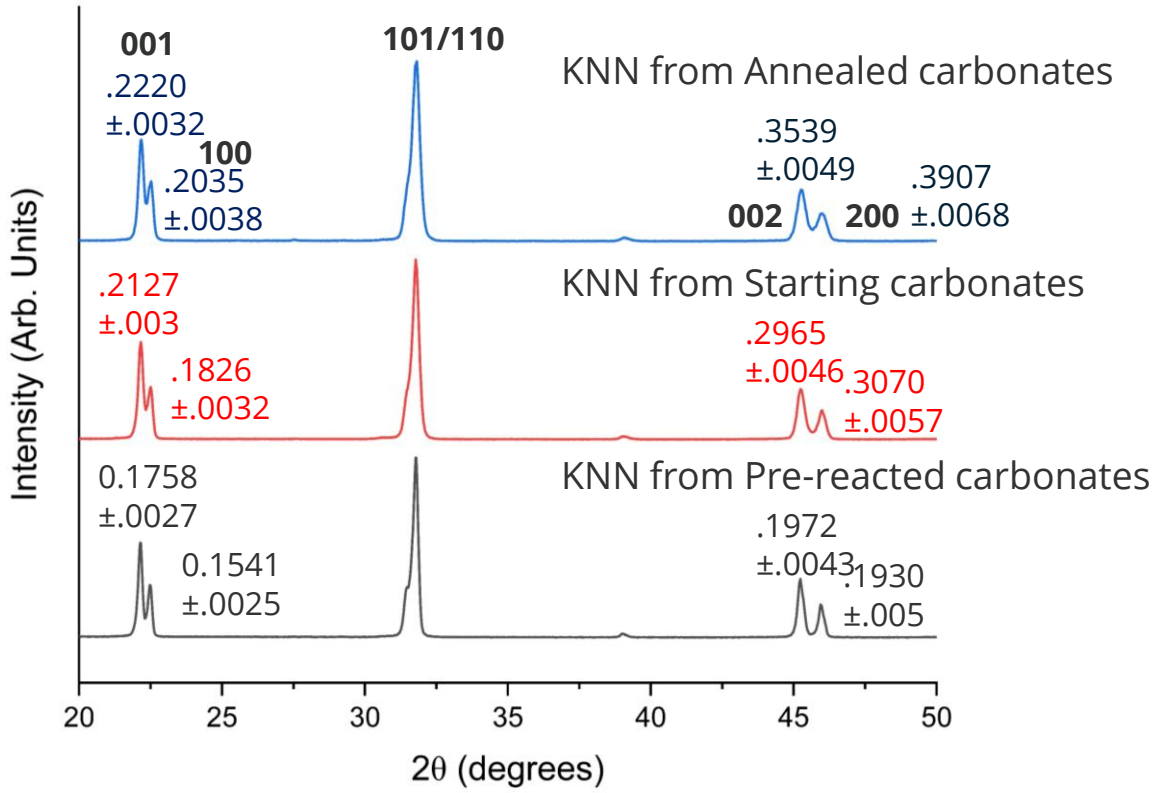
“from pre-reacted carbonates”

Quantifying Peak Widths and Microstrain

The 001, 100, 002, and 200 peaks were fit using LIPRAS

(Since the orthorhombic peak splitting is small, we treat the structure as pseudo-tetragonal)





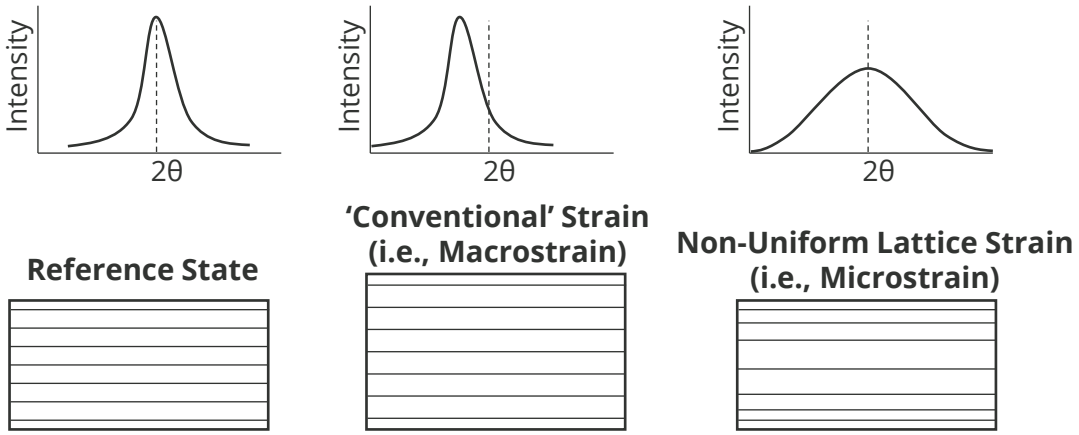
When using $KNaCO_3$ as a source, the KNN peaks are finer, indicating better 'crystallinity'.

Quantifying Peak Widths and Microstrain

Stokes and Wilson (1944) showed that **microstrain** contributes to broadening of the profile

Origins could include:

- Non-uniform lattice distortions (shown below)
- Antiphase boundaries
- Dislocations
- Faulting
- **Clustering in Solid Solutions**



Williamson-Hall analysis can separate crystallite size vs. microstrain contributions to peak broadening (e.g., FWHM)

Scherrer equation: $D = \frac{K\lambda}{\beta \cos\theta}$ *Microstrain equation:* $\varepsilon = \frac{\beta}{4 \tan\theta}$

Total broadening: $\beta_{total} = \frac{K\lambda}{D \cos\theta} + 4\varepsilon \tan\theta$

Remove Instrument broadening: $\beta_{sample} = \sqrt{(\beta_{total})^2 - (\beta_{instrument})^2}$

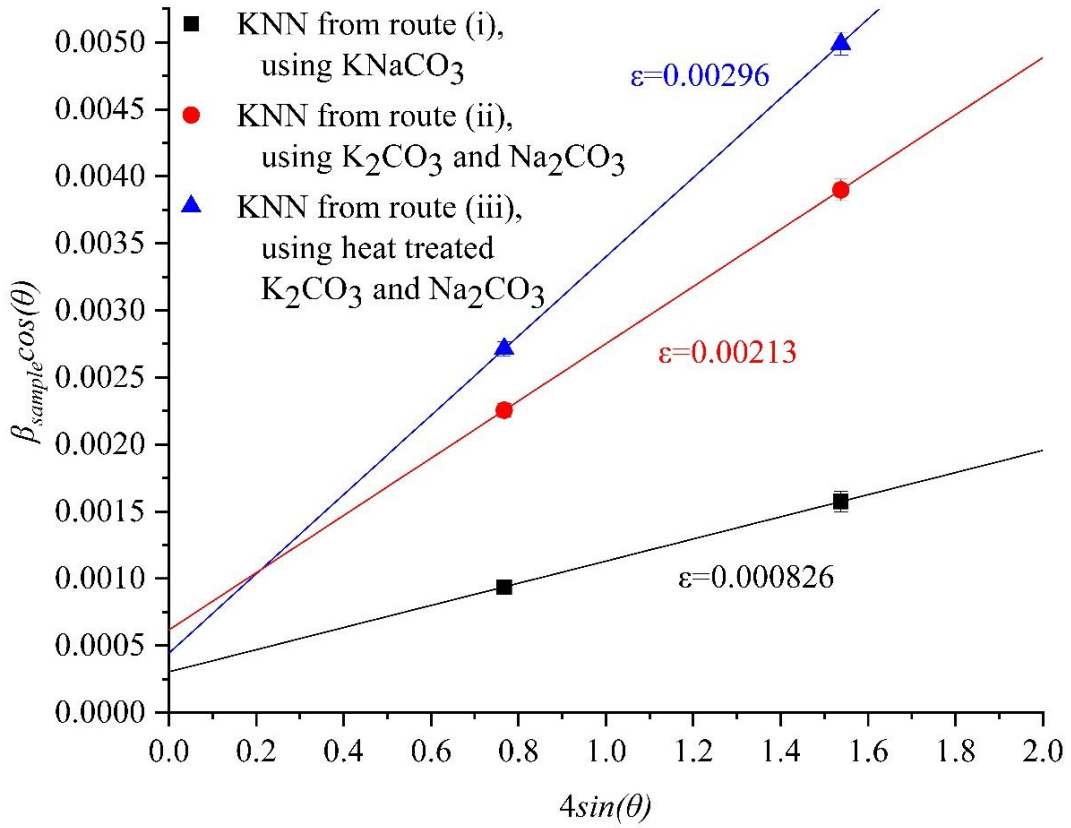
Rewritten: $(\beta_{sample} \cos\theta) = \varepsilon(4\sin\theta) + \frac{K\lambda}{D}$

Forms a line: $(y) = m(x) + b$

Slope is microstrain ***Intercept is size***

Quantifying Peak Widths and Microstrain

(Reminder that slope correlates to microstrain; ***lower slope = less microstrain = less chemical clustering****)*



The use of $KNaCO_3$ substantially reduces the microstrain contribution to broadening (*factor of 2.6*) in KNN, consistent with improved chemical homogeneity in KNN.