# Phase transformations in a promising Na-rich cathode material for sodium-ion batteries

*Ponomareva O.Yu., Vasin R.N., Sumnikov S.V., Korneeva E.A., Samoylova N.Yu.*

Joint Institute for Nuclear Research, Dubna, Russia

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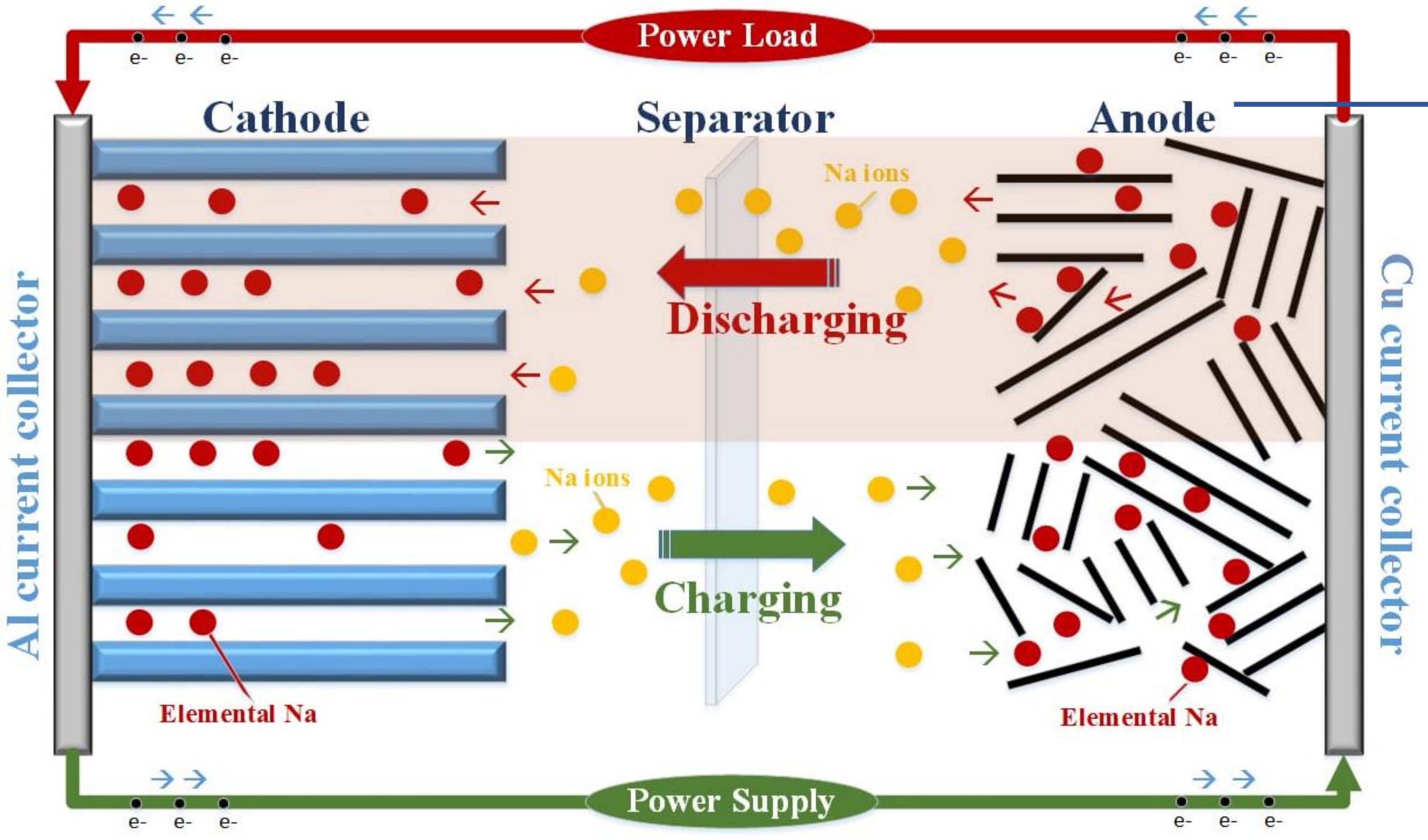
## SIB operation diagram

Sodium-ion batteries (SIB) are promising electrochemical devices due to the sodium availability compared to lithium.

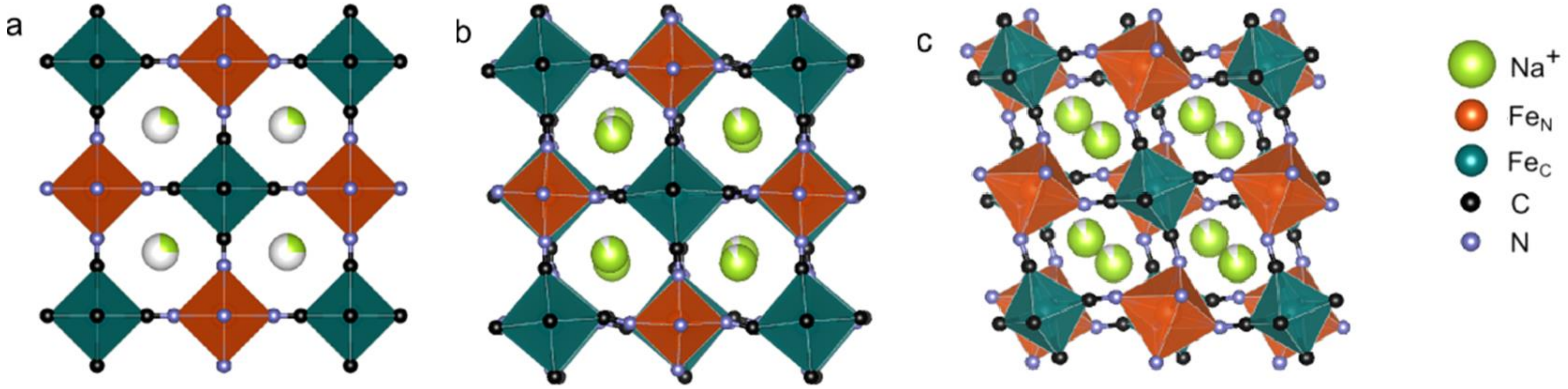



It may be Na-metal or carbon material (hard carbon )

Developing efficient cathode materials is very important task for the wide distribution of SIB.

# Sodium iron (II) hexacyanoferrate (II) materials

One of the perspective cathode materials for SIB are hexacyanoferrates $Na_xM[Fe(CN)_6]\cdot nH_2O$ (Prussian blue analogues, where M are transition metal cations), which have open framework structure and low-temperature synthesis.




*Local structures of a) cubic (Cub), b) monoclinic (M) and c) rhombohedral (R) Prussian blue analogues.* ***M is Fe***

**It is believed that the electrochemical capacity of the rhombohedral phase is maximal.**

[W. Brant et al. // Chem. Mater. 2019, 31, 7203−7211]

## Problem:

$Na_xFe[Fe(CN)_6]\cdot nH_2O$ contains structured and adsorbed water. During battery operation, water causes capacity decrease.

## Decision:

Drying.
Not so simple: heat treatment can destroy the cathode material.

## Our task:

Study of the influence of morphology on phase transitions during dehydration

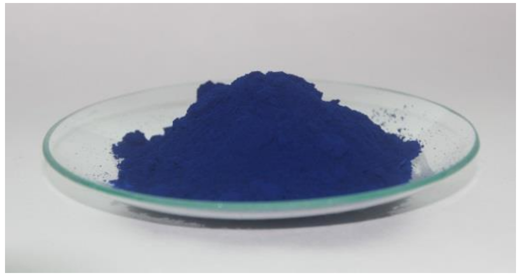
## For this

We investigated the phase transitions in the commercial and self-synthesized powders with different morphology during their heating

# Synthesis of $Na_xM[Fe(CN)_6]\cdot nH_2O$

1. For the synthesis of Prussian Blue analogue (PB) the reaction of acid decomposition of sodium ferrocyanide in saturated aqueous solution of sodium ions was used.

$$Na_4Fe(CN)_6 \xrightarrow[\text{NaCl}_{\text{(saturated water solution)}},\ 60^\circ\text{C}]{\text{HCl}} Na_{1+x}Fe[Fe(CN)_6]\cdot nH_2O$$



*Dark blue powder, Prussian blue* ***(PB)***

Ideal composition for high SIB capacity is $Na_2Fe[Fe(CN)_6]\cdot nH_2O$.

*Prussian white* ***(PW)***

In scientific research model batteries a sodium metal anode is often used. In this case the active cathode material can be electrochemically brought to $Na_2Fe[Fe(CN)_6]\cdot nH_2O$ after first charge-discharge cycle of the battery. Real SIBs are manufactured with hard carbon as an anode. It becomes impossible to enrich electrochemically the cathode material with sodium. Therefore, it is necessary to initially synthesize the Na-rich material.

# Synthesis of $Na_xM[Fe(CN)_6]\cdot nH_2O$

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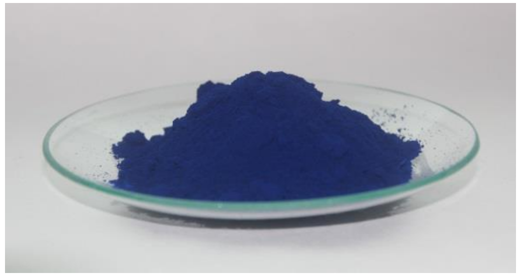


*Dark blue powder, Prussian blue **(PB)***

2. The enrichment of sodium content using saturated solution of a reducing agent containing sodium in dry solvent under inert conditions.

$$Na_{1+x}Fe[Fe(CN)_6]\cdot nH_2O \xrightarrow[Acetone_{(dry)},\ \text{solution was bubbled with Argon}]{NaI_{(saturated\ water\ solution)}} Na_{2-y}Fe[Fe(CN)_6]\cdot mH_2O$$

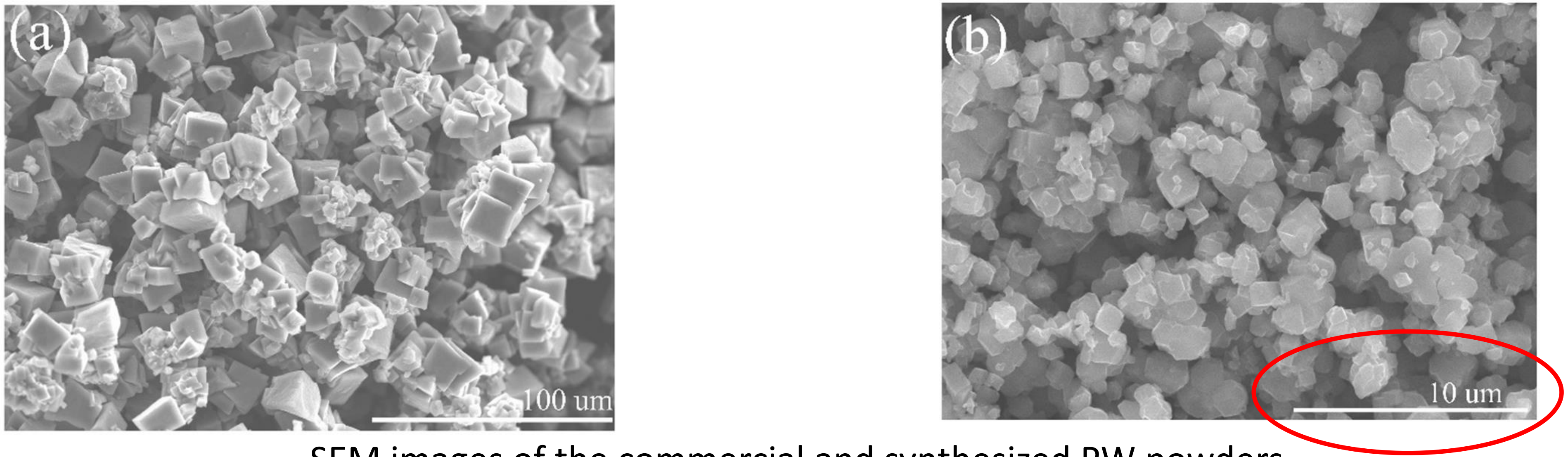
*Light blue powder, Prussian white **(PW)***

## The commercial Prussian White powder

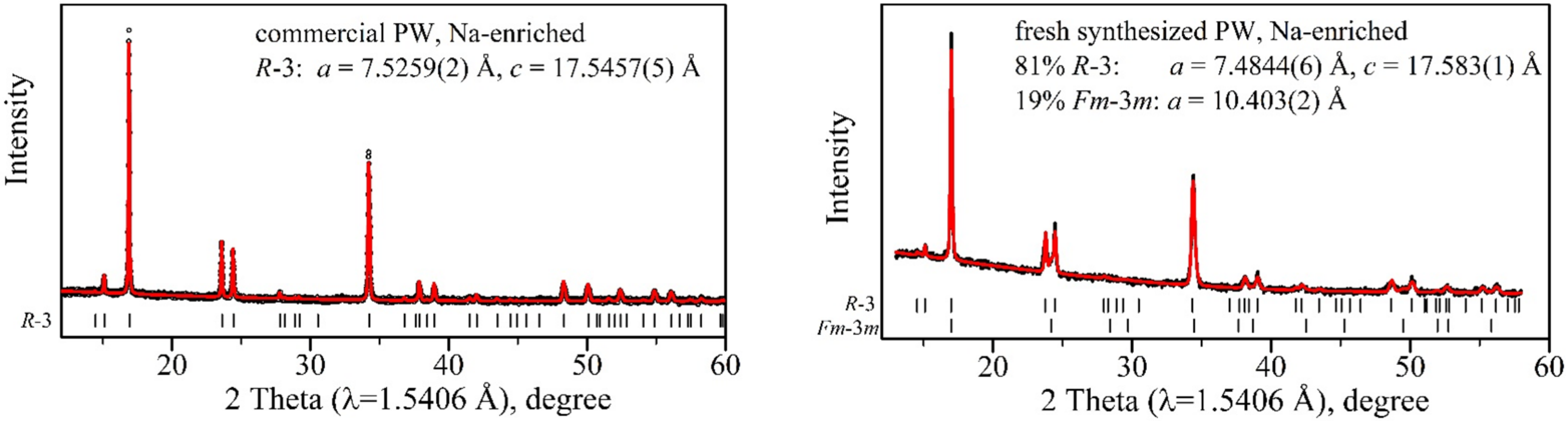
with a declared formula $Na_{1.82}Fe[Fe(CN)_6]\cdot 2.2H_2O$ was purchased from Altris AB (Sweden).

It was enriched with sodium in the same way as synthesized PB.

# Morphology and structure of the commercial and self-synthesized powders

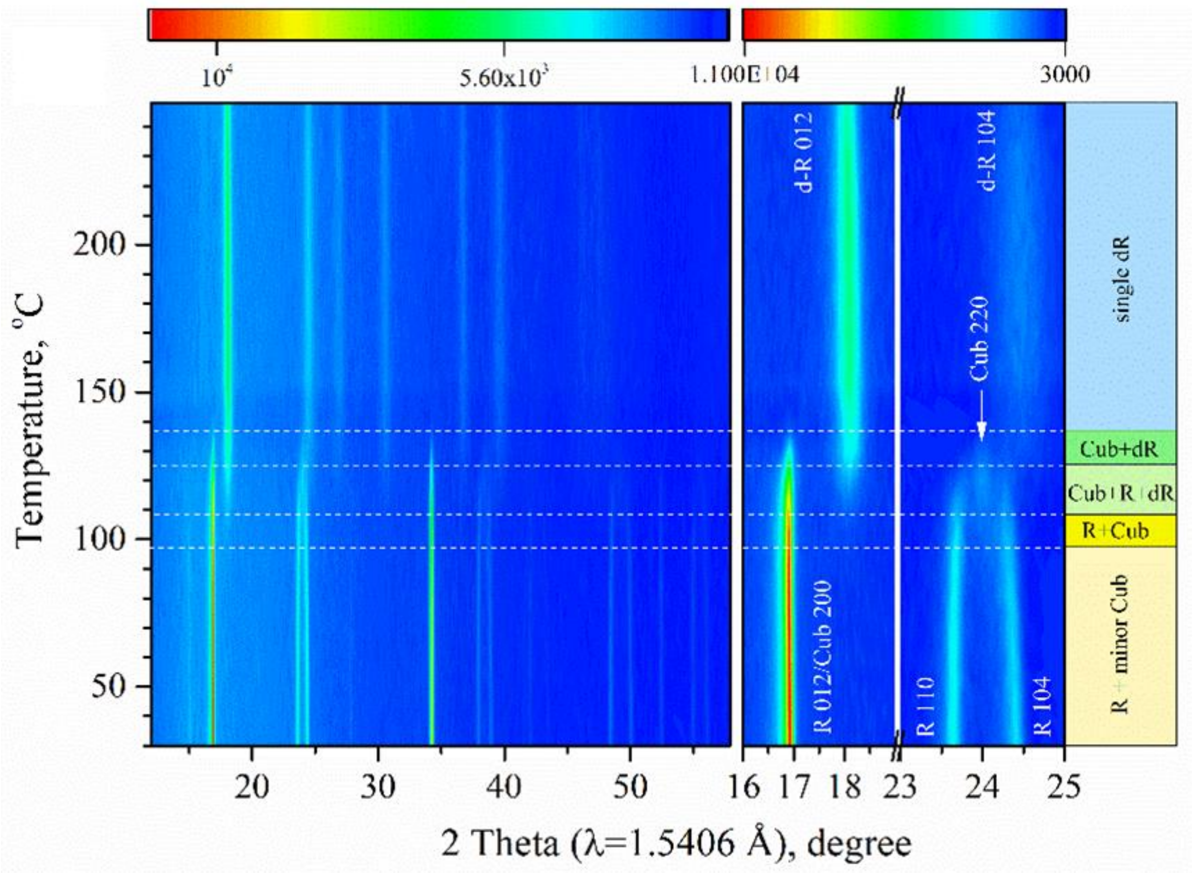



SEM images of the commercial and synthesized PW powders.

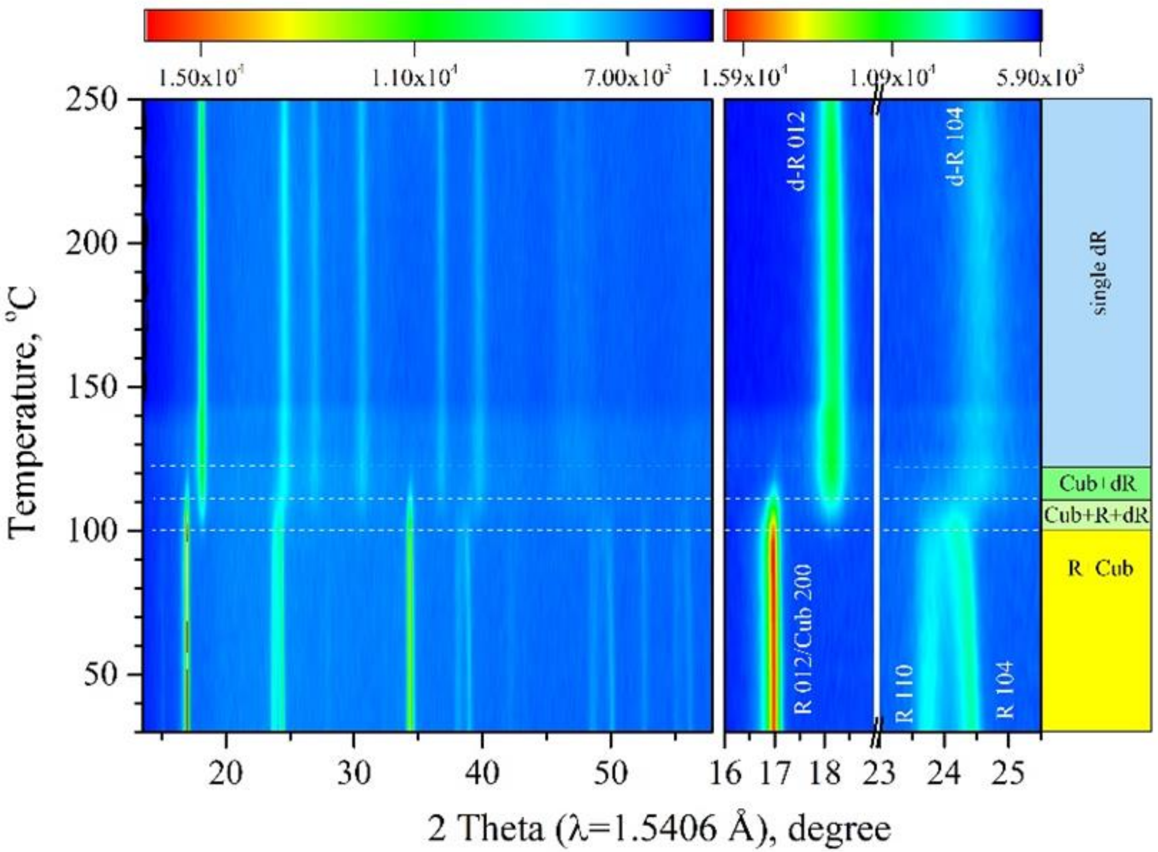



XRD patterns of the commercial and synthesized PW powders.

# 2D map of the XRD patterns measured in situ during heating up 250°C.




XRD patterns of **commercial** PW powder




XRD patterns of **synthesized** PW powder

# Conclusions

The structural phase transitions in the commercial PW powder enriched with sodium, as well as in a similar synthesized $Na_{2-y}Fe[Fe(CN)_6]\cdot nH_2O$ powder during heating up to 250°C were investigated using X-ray diffraction.

A reduction in particle size of PW powder leads to more efficient dehydration: phase transitions during PW heating are shifted to lower temperatures.

Drying at lower temperature will not lead to material degradation. Therefore, an increase of the PW capacity is expected.

The effect of morphology of PW material on its electrochemical performance is under investigation.

*This work was supported the Russian Science Foundation, project No. 21-12-00261 (2021-2023)*

# Thank you very much for your attention!