Zerstörungsfreie Untersuchung der chemischen Verbindungen im Inneren einer (ZEBRA) Batterie – mittels Neutronen

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Was sind ZEBRA Batterien?

Neutronenstreuung - Ergebnisse:

- Radiographie
- Diffraktion

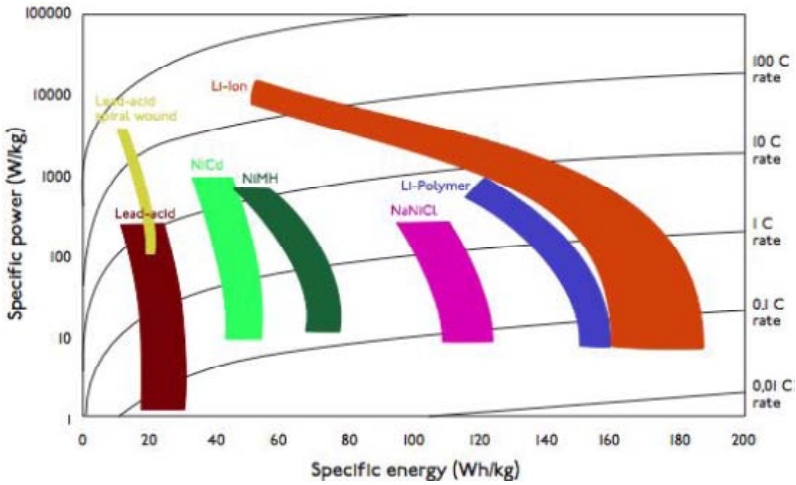
Zusammenfassung

ZEBRA Batterie

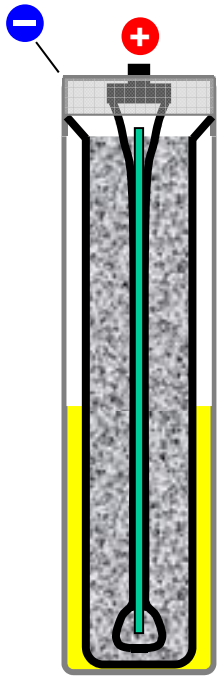
Zeolithe Battery Research Africa

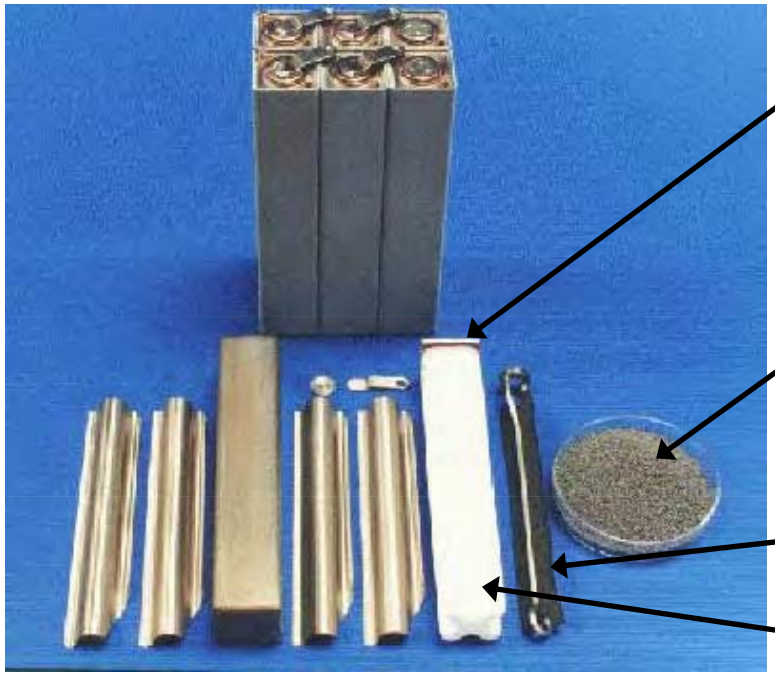
Na/MCl_2

- Hohe Energiedichte
- Lebensdauer > 1000 Zyklen
- Fehlertolerant (Kurzschluss und überladen/-entladen)
- Einsetzbar bei niedrigen und hohen Temperaturen
- Billige Ausgangsmaterialien (Ni, Fe, NaCl)



ZEBRA Batterie





Dichtung zw. β“ - alumina-Rohr und Stahlhülle

Kathode – Fe + NaCl (Pulver)

Kathode Ladungs-kollektor

β“ -alumina Rohr (Na^+ Ionen leitender, fester Elektrolyt)

m1

laden

$$2NaCl + M \rightleftharpoons MCl_2 + 2Na$$

(300°C) entladen

M.H. Vallance et al, *Proc. of the COMSOL Conf.* Boston (2008)

Folie 4

m1 mhofmann; 14.07.2011

ZEBRA Batterie – Zellchemie

Kathode

$Fe\ (s) + 2NaCl\ (s) \rightarrow FeCl_2\ (s) + 2Na^+ + 2e^-$

$NaAlCl_4$ (Elektrolyt)

T ~ 300°C

Anode

$Na^+ + e^- \rightarrow Na\ (l)$

β“ alumina (fester Elektrolyt)

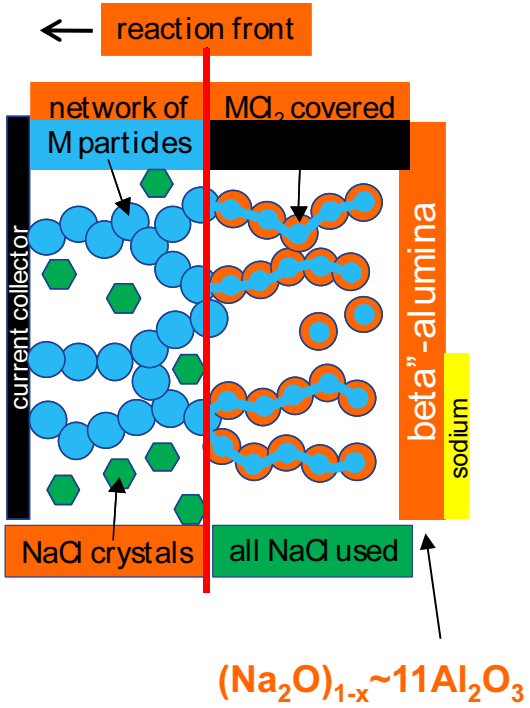
T ~ 300°C

Gesamt

$Fe\ (s) + 2NaCl\ (s) \rightarrow FeCl_2\ (s) + 2Na\ (l)$

T ~ 300°C

Laden



Ni … $E^0 = 2.59$ V

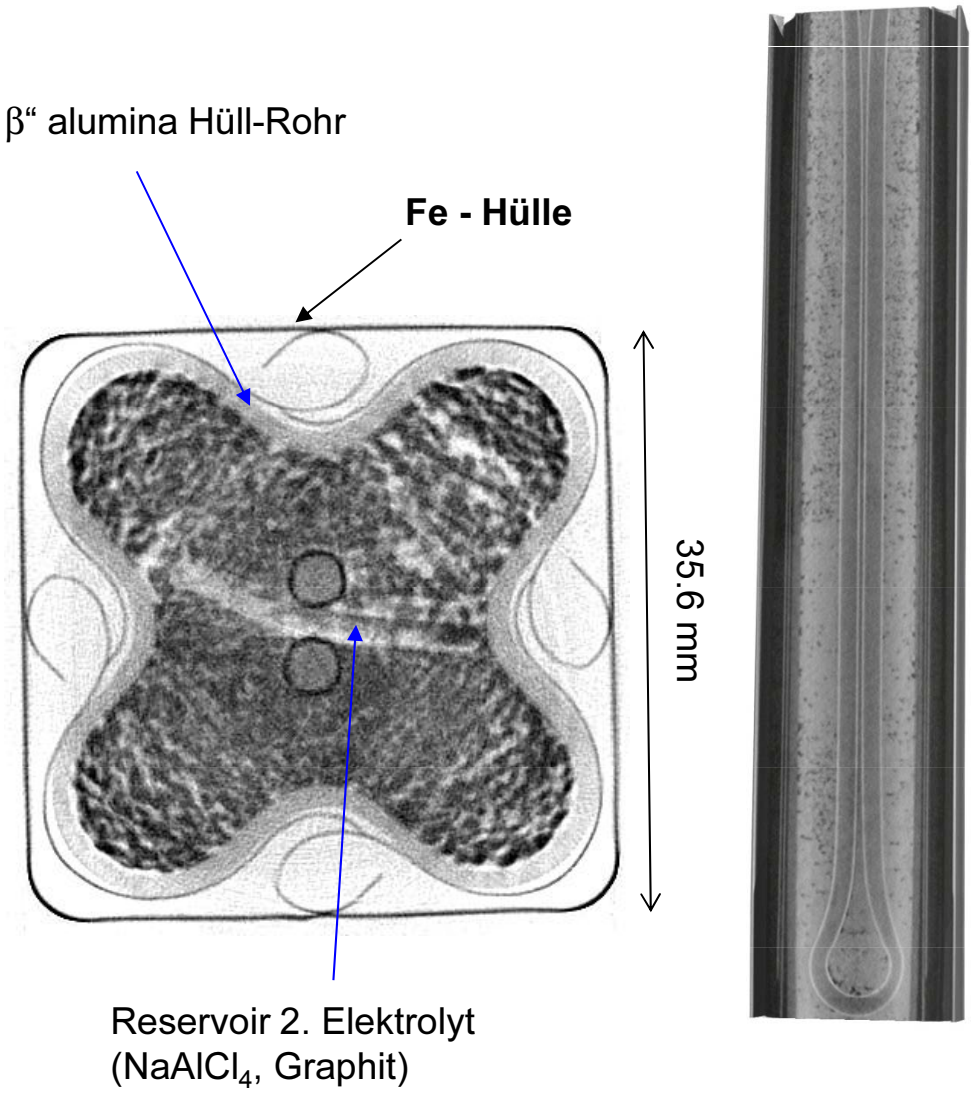
Fe … $E^0 = 2.35$ V

Antares, FRM II -

Tomographie und Radiographie

Neutronenfluß	**2.5×10^{7} $s^{-1}cm^{-2}$**
L/D	**800**
Messfeld	**191mm x 191mm**
Pixelgröße	**93µm x 93µm**
Erreichte Auflösung	**~ 150µm**
Zahl d. Projektionen	**400**
Messzeit für 1 Projektion	**50 s**

2 x $Na/FeCl_2$ Zellen:
w × h = 35.6 mm × 230 mm
- geladen auf 20 Ahr
- entladen

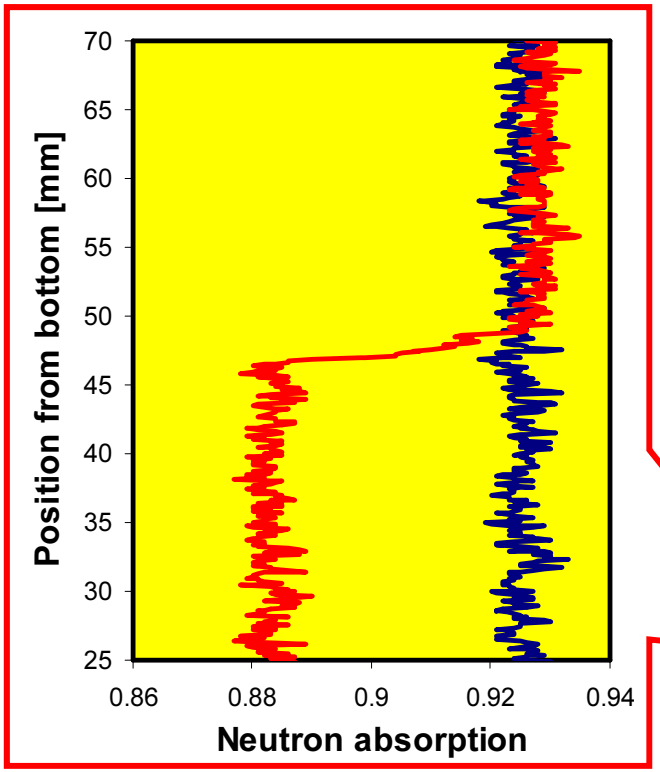


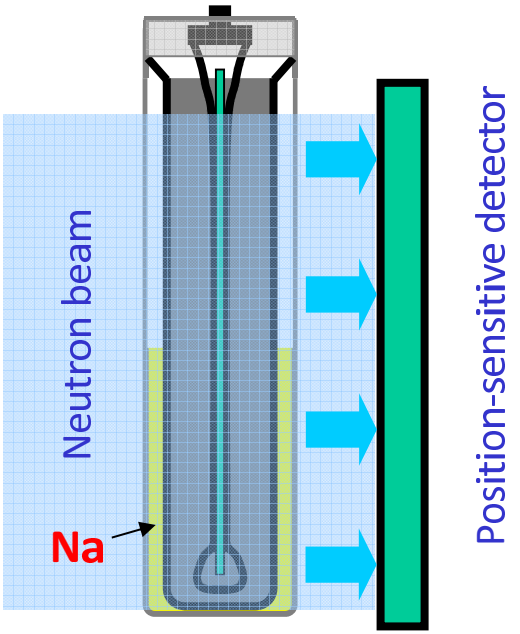
Neutronenradiographie

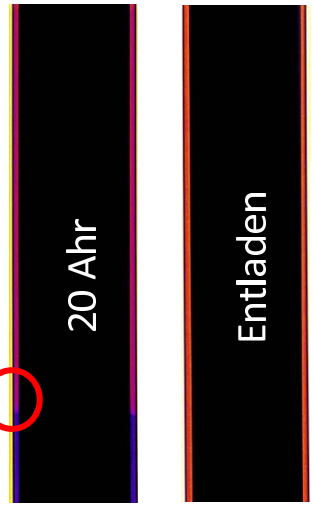
Laden

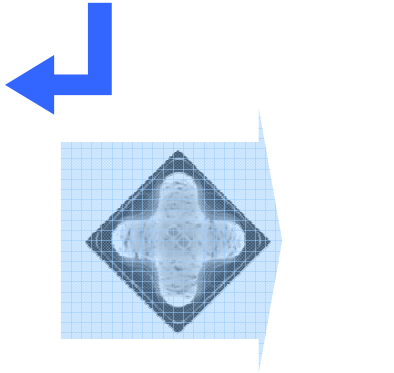
$$2NaCl + M \rightarrow MCl_2 + 2Na$$

Na-Level steigt beim Laden



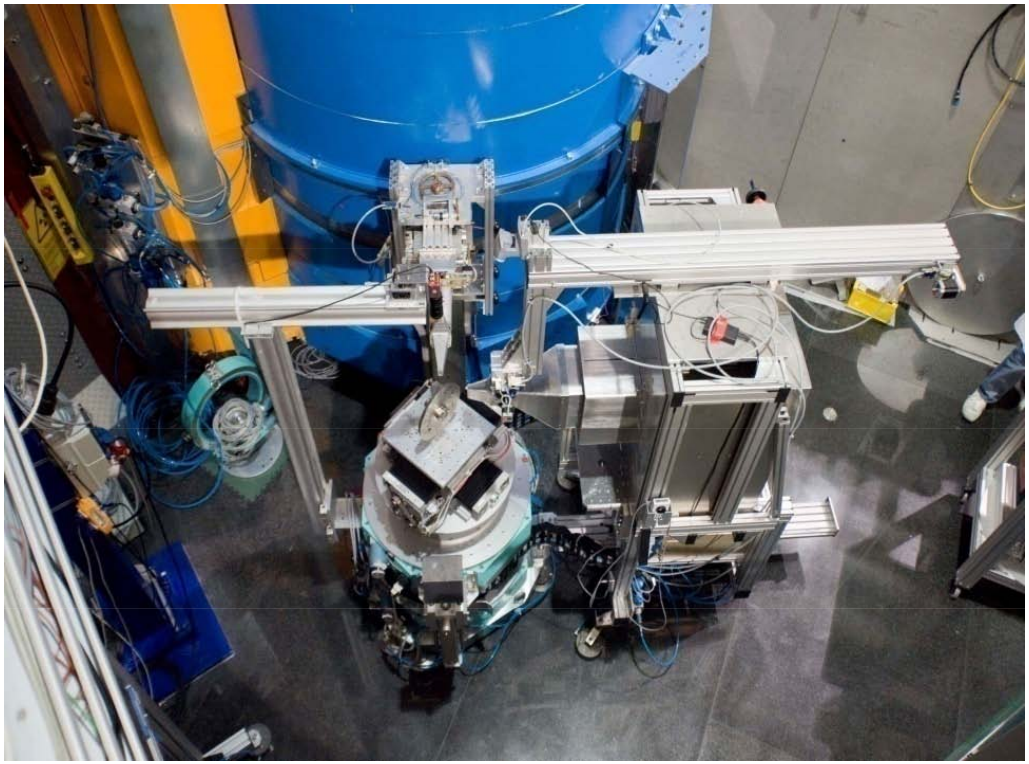






Zellenorientierung

Ortsaufgelöste Neutronendiffraktion



Stress-Spec, FRM II
(Eigenspannungen und Texturen)

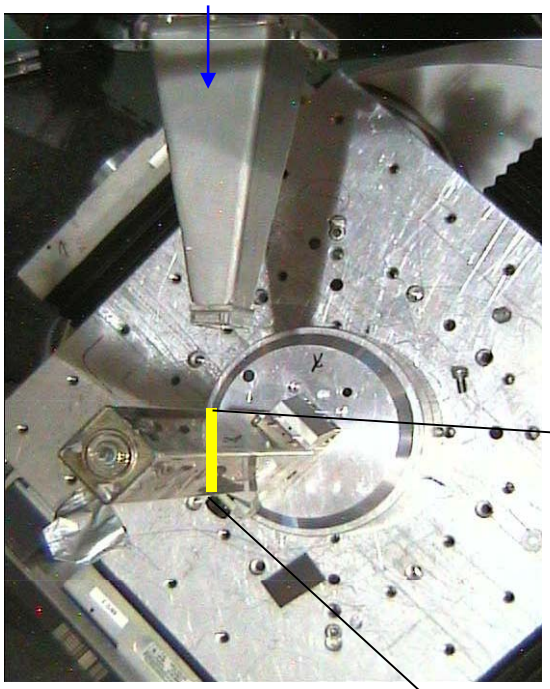
Einfache und flexible
Definition des Messvolumens

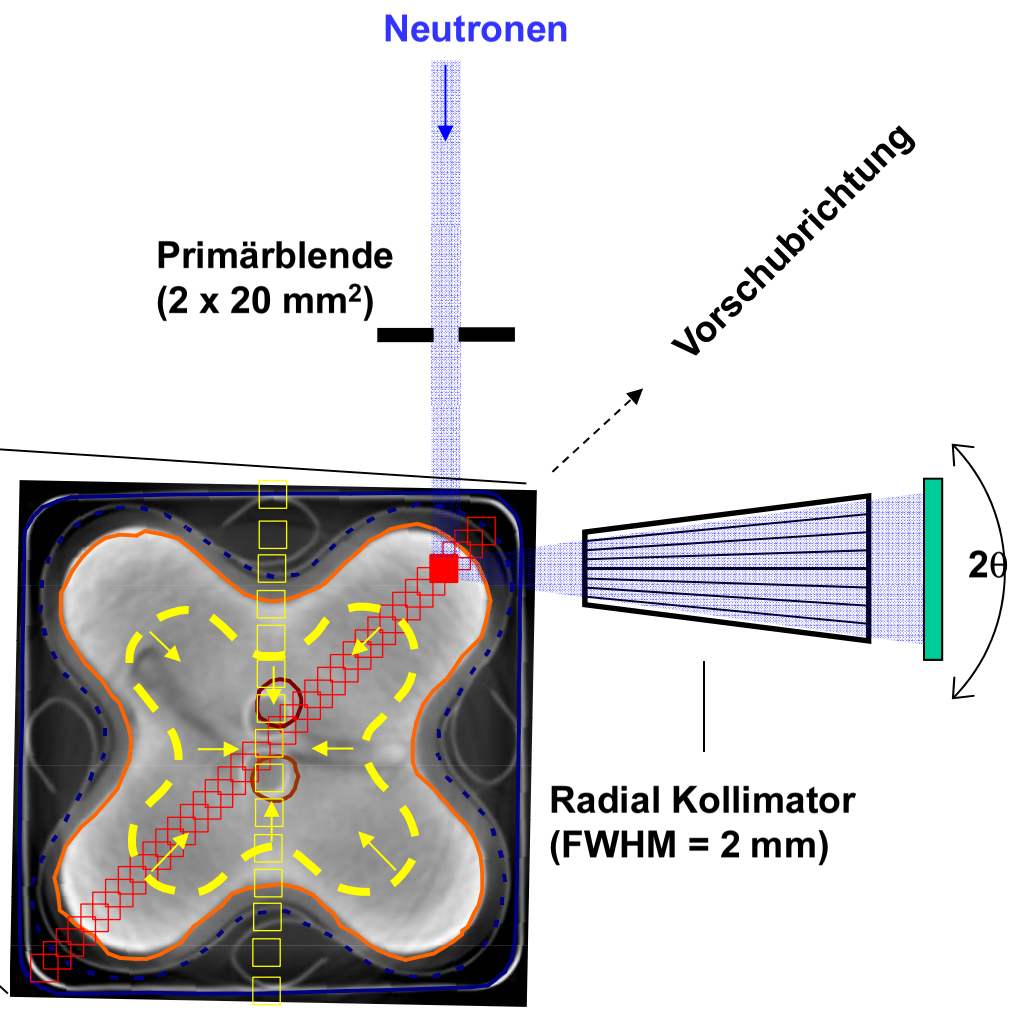
Exakte Probenpositionierung

Variable Wellenlängen-
einstellung

Großer Detektor

Ortsaufgelöste Neutronendiffraktion



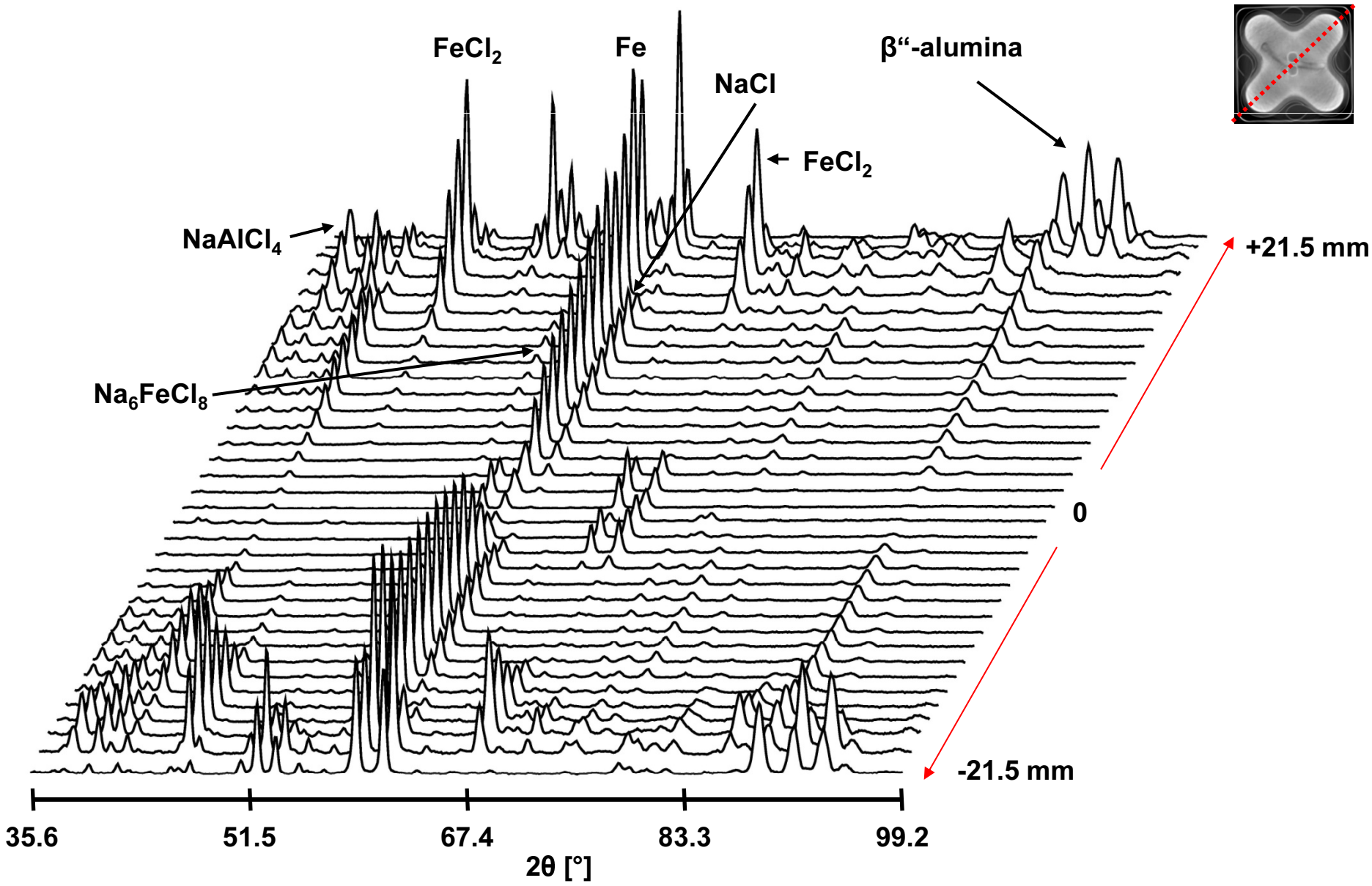


Stress-Spec, FRM II

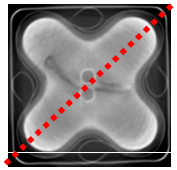
λ = 2.014 Å

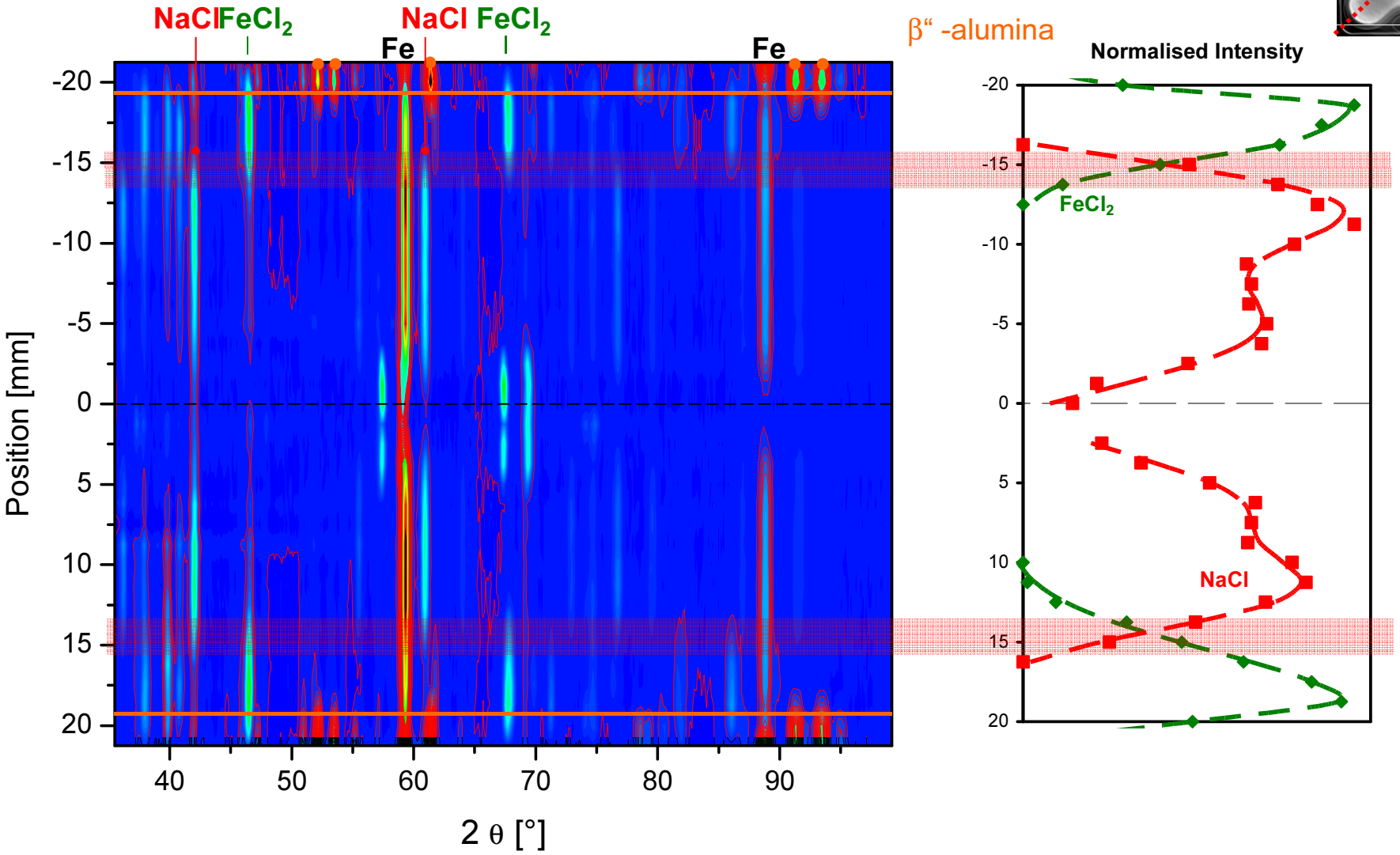
$2\theta_{Bereich}$ = 35 -110°

Messhöhe = 115 mm

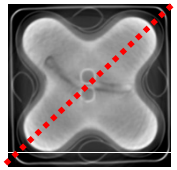

FeCl2
Fe
NaCl
β“-alumina
FeCl2
NaAlCl4
Na6FeCl8
+21.5 mm
0
-21.5 mm
35.6
51.5
67.4
83.3
99.2
2θ [°]

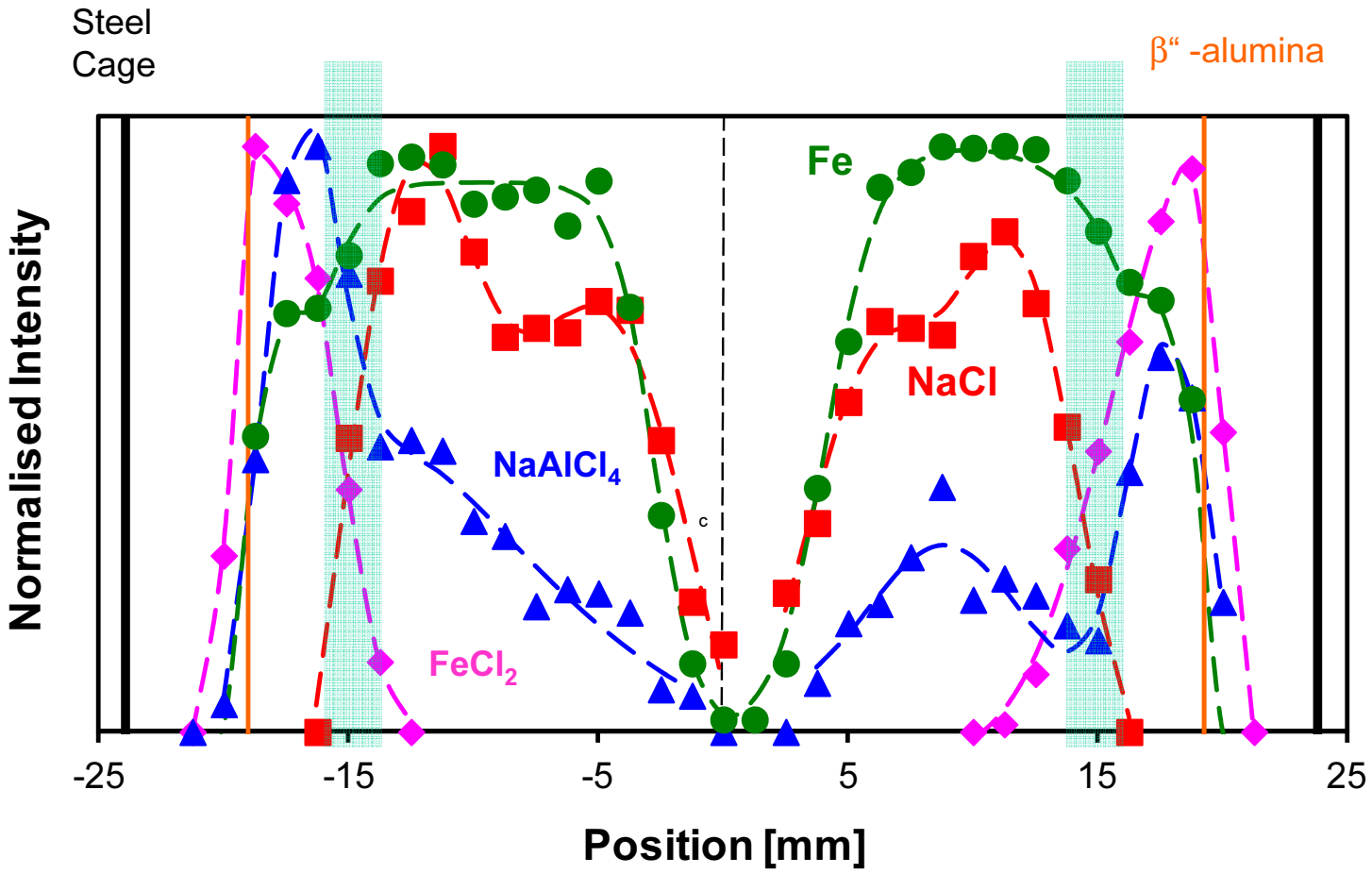
Diagonal-Scan

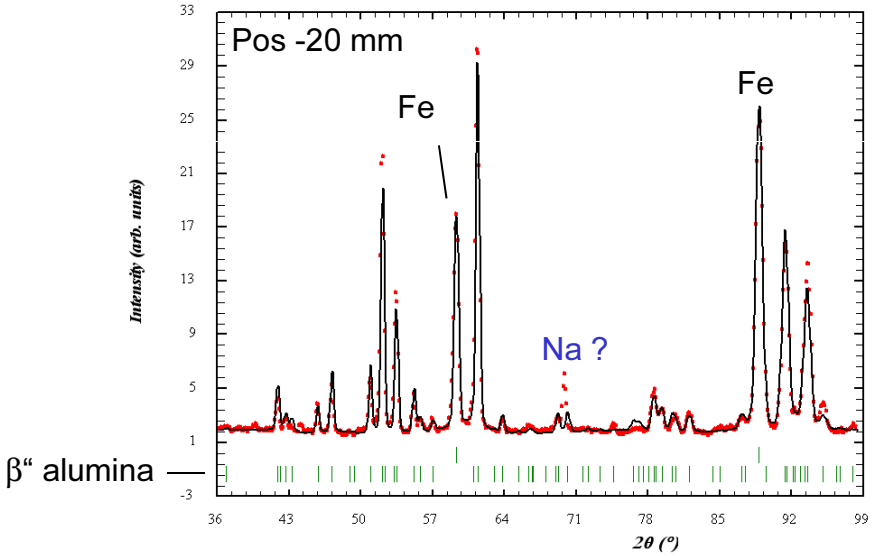


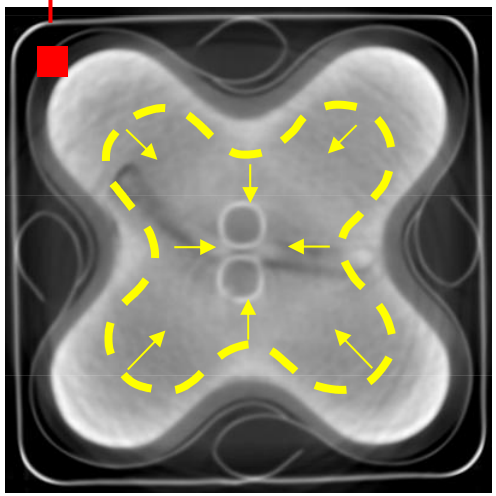


Intensitäten = Phasenverteilung in der Zelle





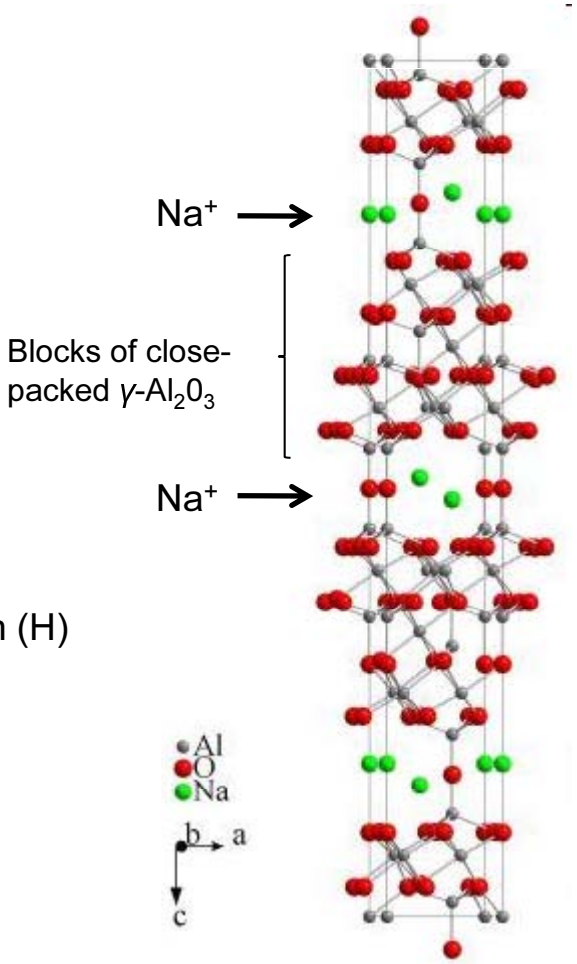


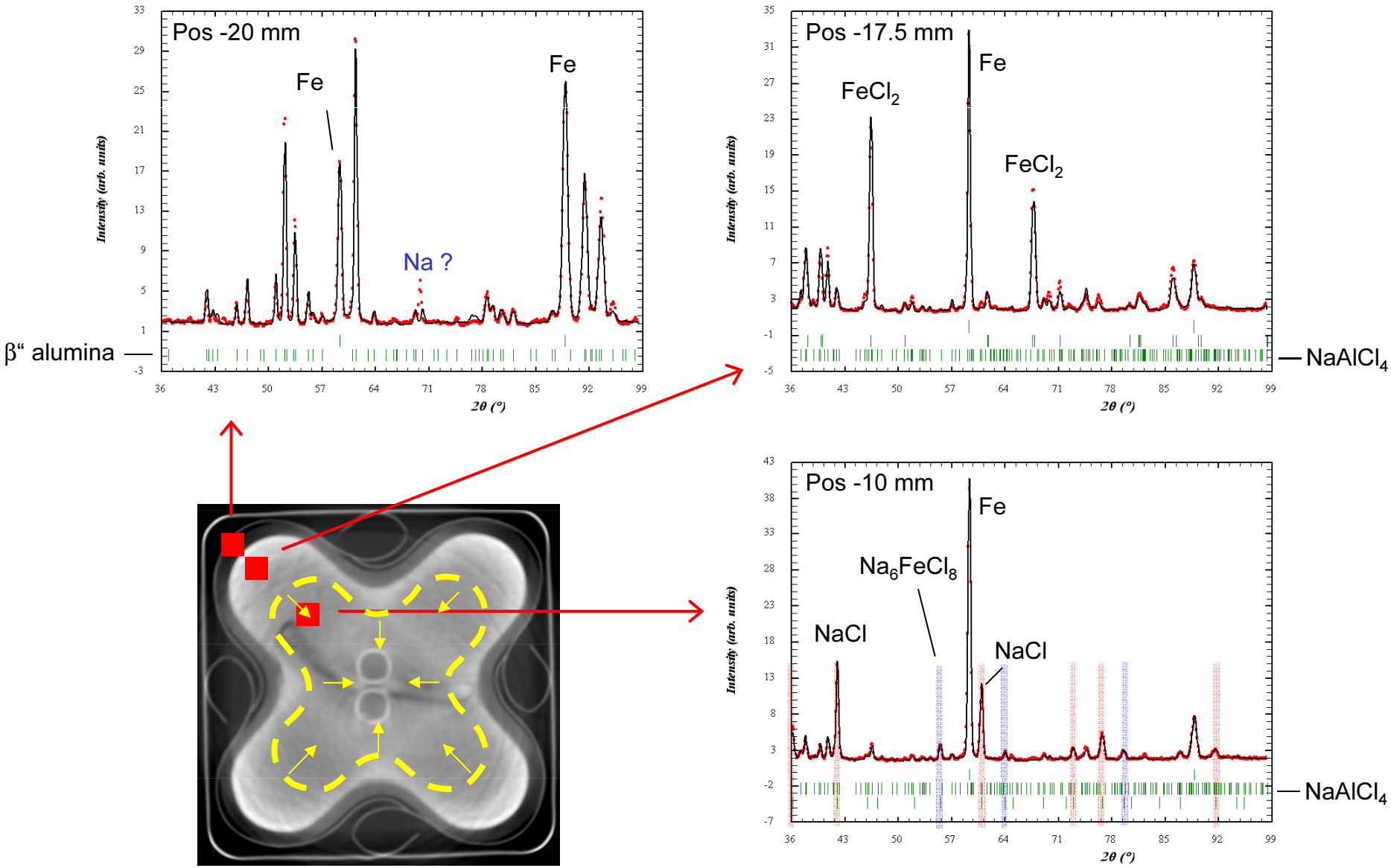


$(Na_2O)_{1-x}$~$11Al_2O_3$

Raumgruppe: R -3 m (H)

a = 5.631(2) Å
c = 33.578(10) Å



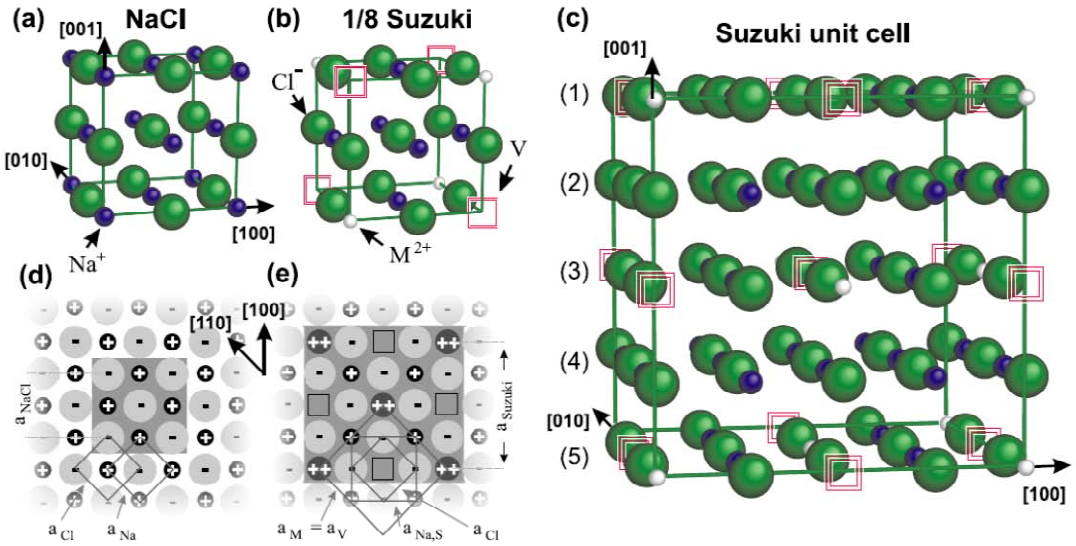

Pos -20 mm
Fe
Fe
Na ?
β“ alumina
Intensity (arb. units)
2θ (°)
Pos -17.5 mm
Fe
FeCl2
FeCl2
NaAlCl4
Pos -10 mm
Fe
Na6FeCl8
NaCl
NaCl
NaAlCl4

$$8\ NaCl + Fe \rightleftharpoons 2\ Na + Na_6FeCl_8$$

$$Na_6FeCl_8 + 3\ Fe \rightleftharpoons 6\ Na + 4\ FeCl_2$$

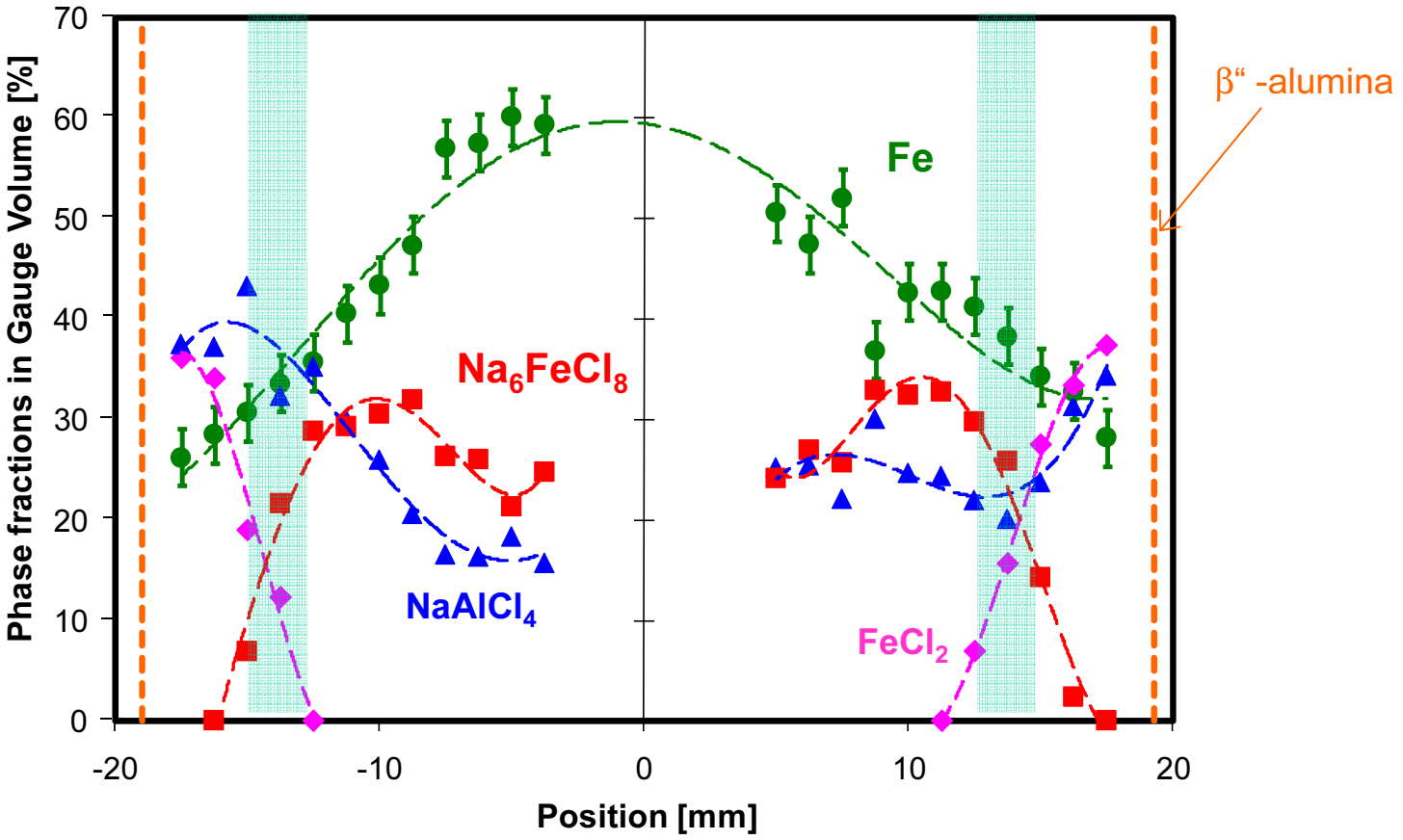
Bei T ~ 250°C / $NaAlCl_4$

$$8\ NaCl + 4\ Fe \rightleftharpoons 8\ Na + 4\ FeCl_2$$



C. Barth, C.R. Henry, *New J. Phys* **11** (2009) 043003

Phasenverteilung im Messvolumen (2x20x2 mm³)



Zusammenfassung:

- Radiographie zeigt Na - Füllstand
- Tomographie erlaubt die innere Struktur und evt. die Porosität zu untersuchen
- Diffraktion:
  - Phasencharakterisierung
  - quantitative Phasenverteilung in der ganzen Zelle

Ausblick:

In-situ Versuche
- Radiographie
- Diffraktion