
Aging of RDX Crystals investigated by X-ray Diffraction

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Literature: Aging of Crystals

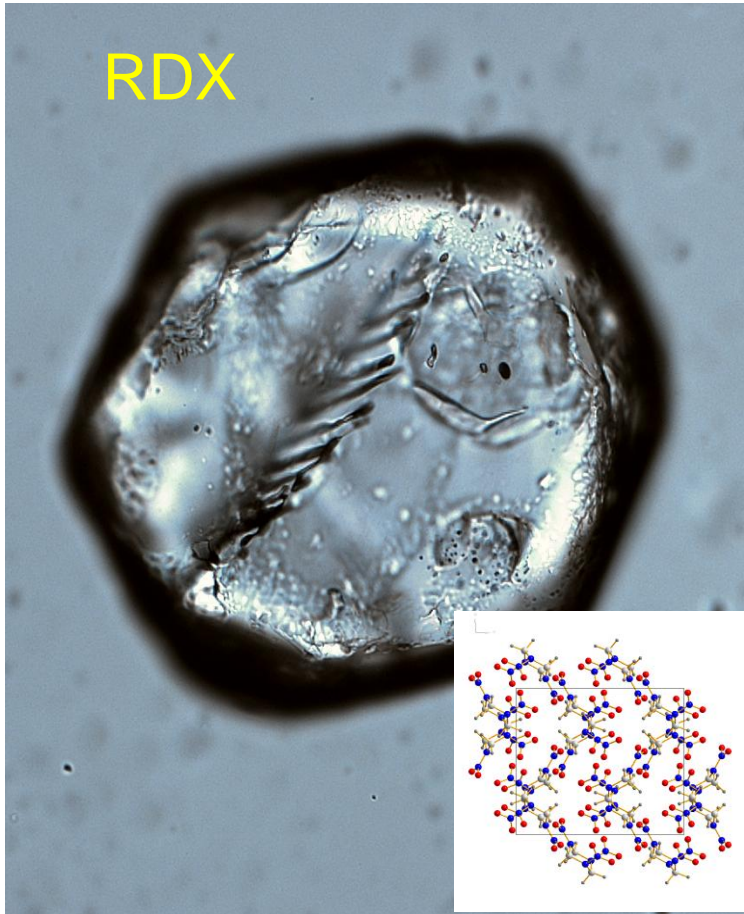
Non-EM

- phase transitions
- crystal growth and morphologic transitions
- frequency shifts of oscillator crystals
- loss of water (e.g. combined with a significant change in color)

Energetic Materials

- release of residual H₂O from HMX
- phase transitions of ammonium nitrate
- significant crystal growth on temperature cycling of AN (Tropicalization)
- no significant changes of the shock sensitivity after aging of PBXN-109 formulations when RS-RDX is included, which *does not seem to be the case for standard RDX produced by the Bachmann process*
- -> *Aging must be affecting the RDX itself (Spyckerelle)*
 - > Microstructure of Crystals

Microstructure of RDX



- **Crystal structure**

$C_3H_6N_6O_6$; orthorhombic; Space group: $Pbca$
 $a = 13.182 \text{ \AA}$; $b = 11.574 \text{ \AA}$; $c = 10.709 \text{ \AA}$;
atom positions....,

- **Size and shape of crystals**

- **Inclusions of solvents**

- **Impurities, e.g. HMX**

- **Lattice defects**

e.g. Dislocations in RDX

Microstructure of RDX

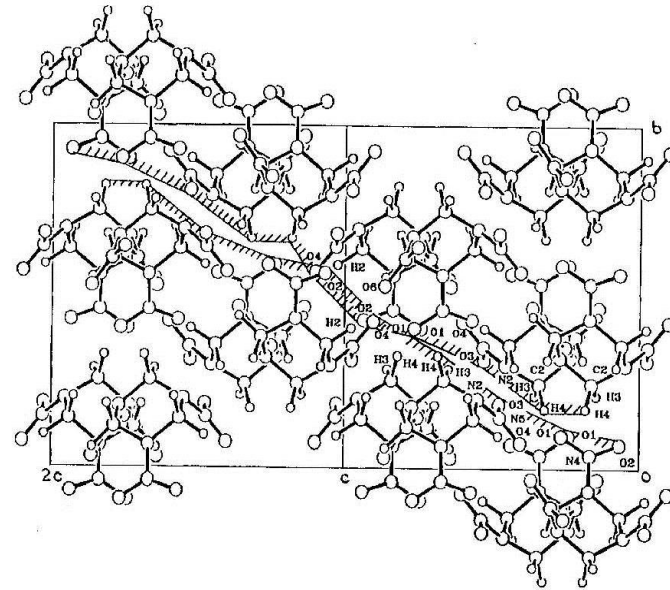
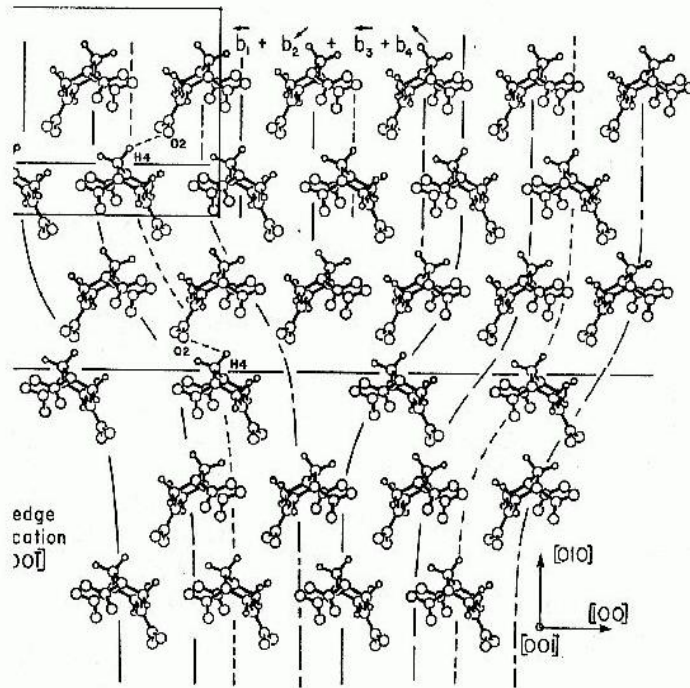


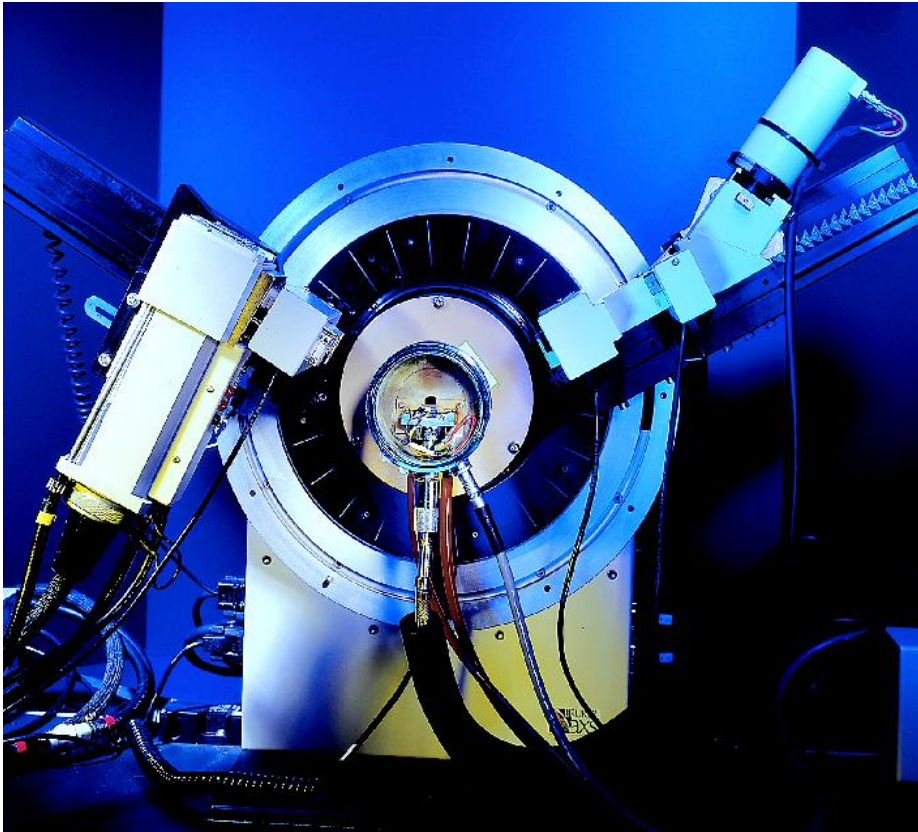
Fig. 3. Dinitroso-related interactions from $[100](02\bar{1})$ slip.

Dislocation Slip Systems
 $(010)[001]$,
 $\{021\}$ and $\{02-1\} [100]$
 (slip plane and Burgers vector)

Gallagher H.G. et al., *Phil. Trans. R. Soc. Lond.*, **1992**, A 339, 293-303

Armstrong R. W. et al., *Proc. Mat. Res. Soc. Symp.*, Vol 296, **1993**, 227-232

X-ray Diffraction (XRD) Techniques for Microstructure

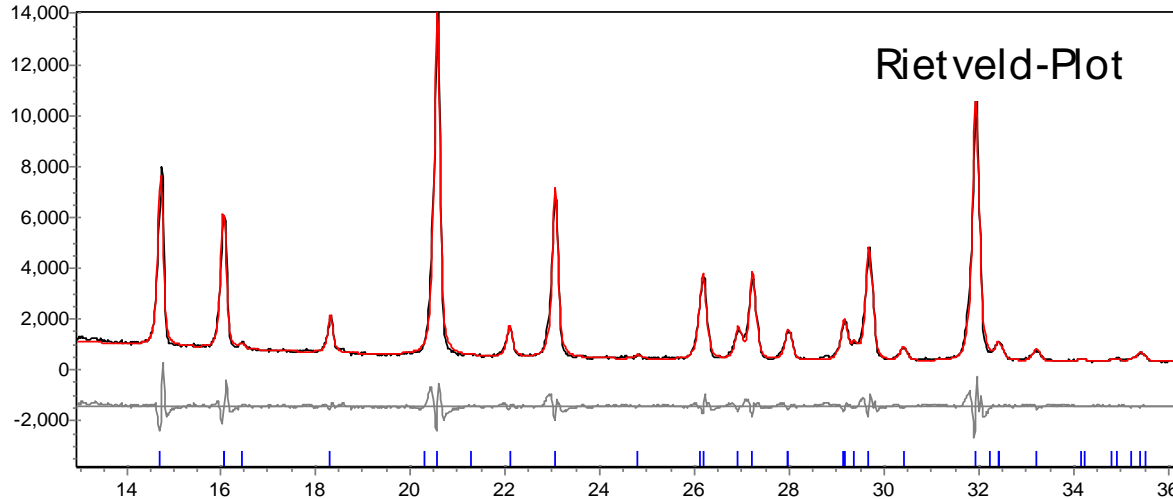
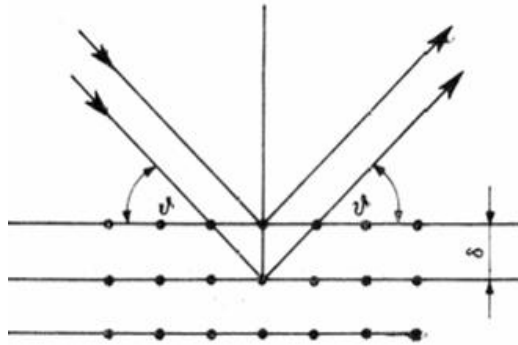


- Non-destructive
- For powders and but also composites as PBX
- Separate information of ingredients
- Benchmarking at the Synchrotron ANKA



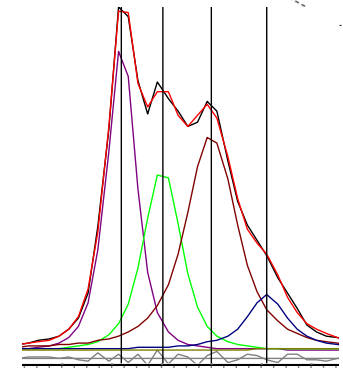
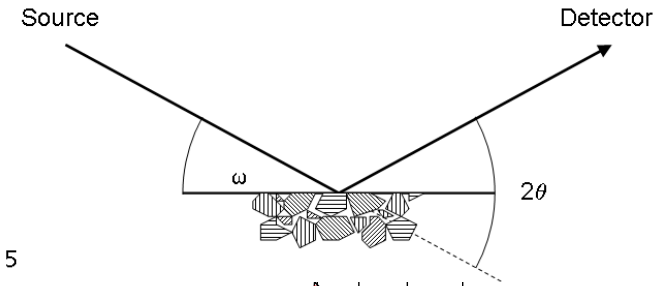
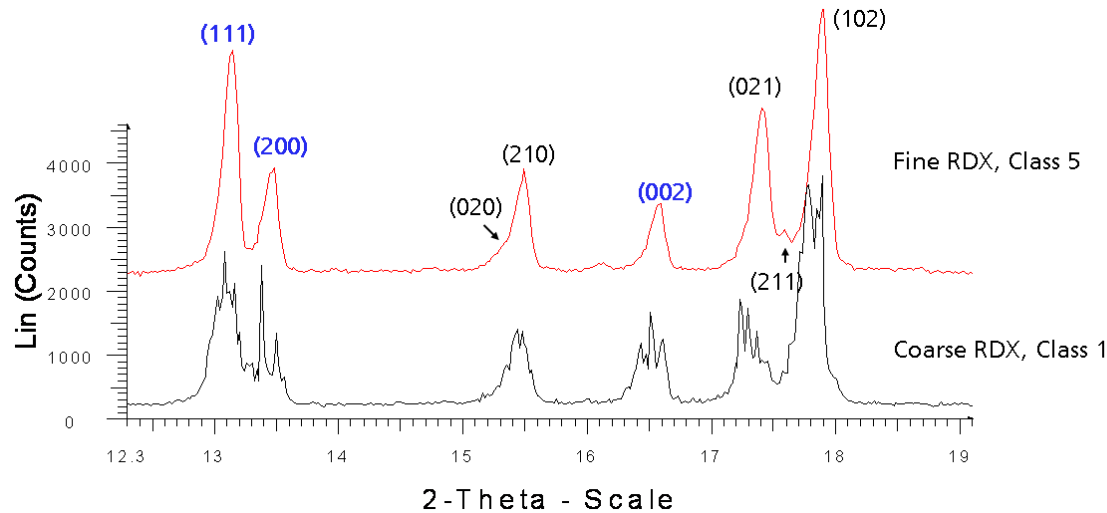
d_{hkl} = lattice plane distance, θ = diffraction angle, λ = wavelength

2θ scans & Rietveld-Analysis (RVA) for fine powders

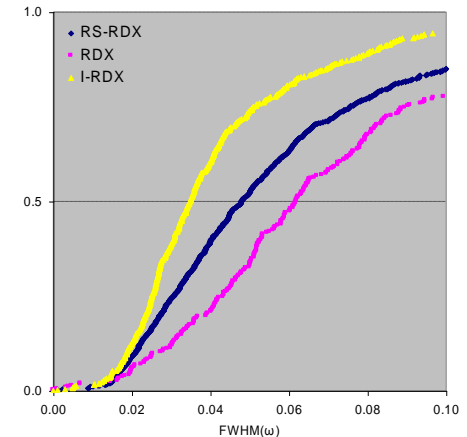


- Peak positions
 - > Lattice parameters (Elementary Cell)
 - > Crystal density
 - > Residual strain
- Profile (width/shape)
 - > Crystallite Size
 - > Microstrain (Double Voigt in RVA)
- Intensity
 - > Concentration (Quantitative Analysis)
 - > Degree of crystallinity

ω -scan for coarse powders (rocking curves)



- Source & Detector fixed in reflection condition
- Information on single coarse crystallites (grain by grain) fine fraction in underground
- Stochastic multi crystallite analysis

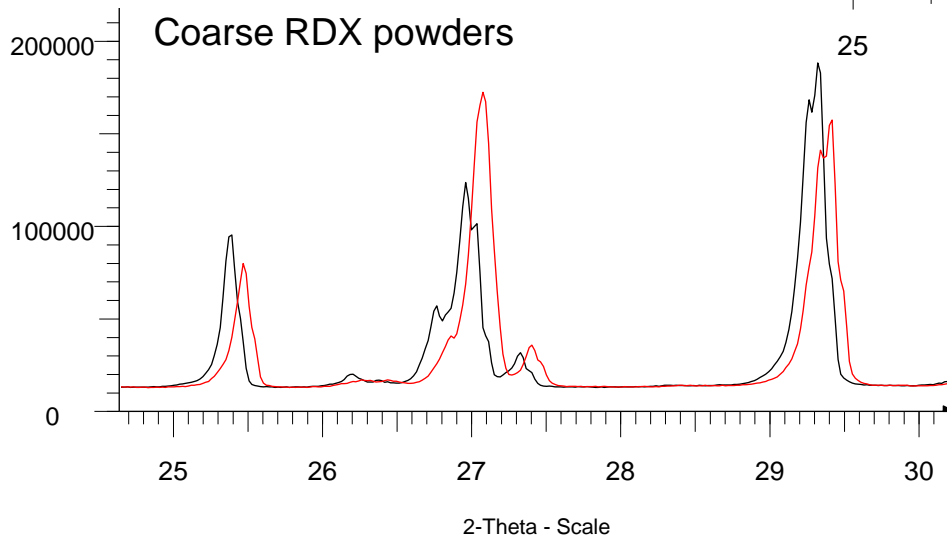
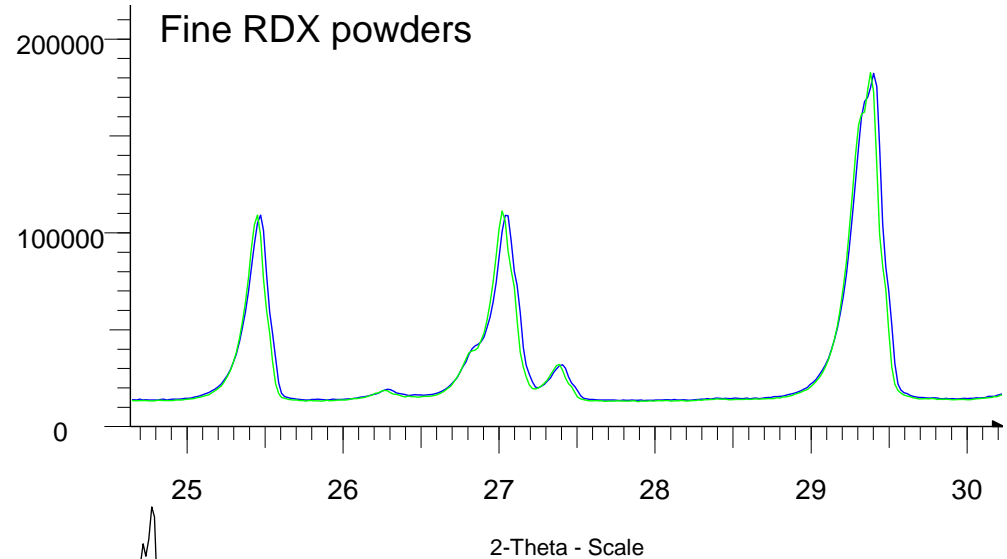


Herrmann, M., Kempa, P.B., Doyle, S., 2007, *Z. Kristallogr. Suppl.* 26, 557.

Samples & Experimental

storage time at 90°C	aged in air*			aged in Ar*	
	0d	15d	30d	15d	30d
2θ scans					
I-RDX, M3C	2 x	1 x	1 x	1 x	1 x
I-RDX, Class 1	2 x	1 x	1 x	1 x	1 x
S-RDX Typ I, Class 5	2 x	1 x	1 x	1 x	1 x
S-RDX Typ I, Class 1	2 x	1 x	1 x	1 x	1 x
ω scans					
I-RDX, Class 1	1 x	1 x	1 x	1 x	1 x
S-RDX Typ I, Class 1	1 x	1 x	1 x	1 x	1 x

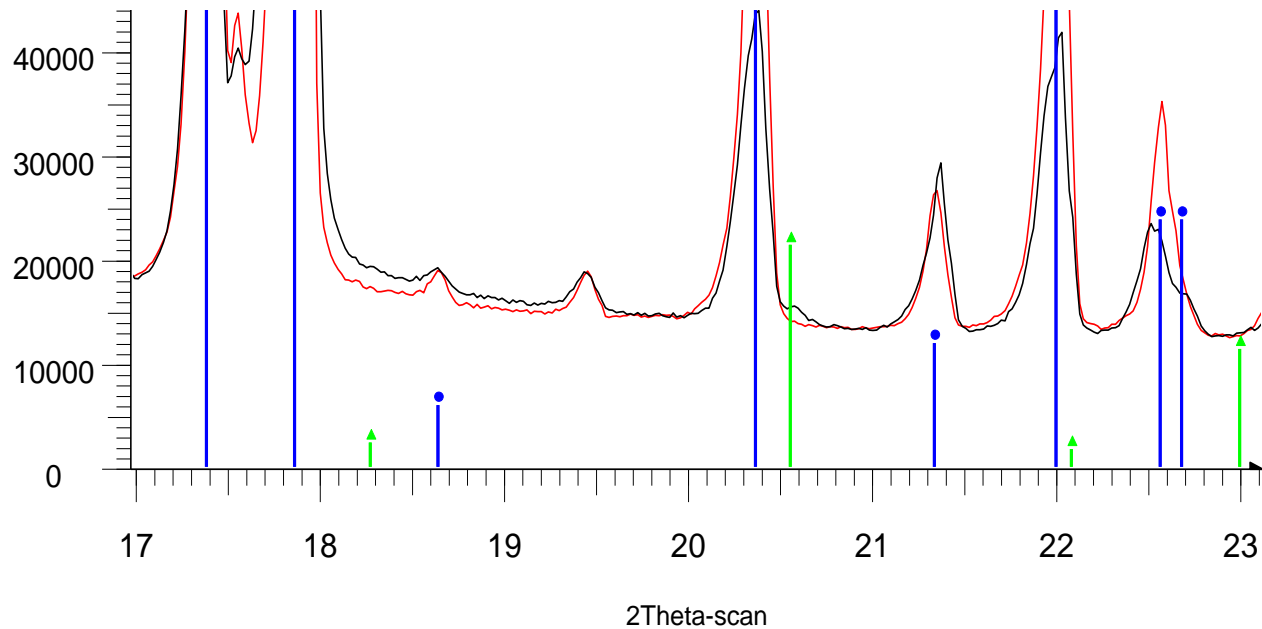
Results: 2 θ scans



- Smooth profiles and reproducible intensities with fine powders
- Ragged profiles in coarse samples -> poor orientation statistics

Results: Impurities

- No significant crystalline HMX in I-RDX but small amount in S-RDX



— pattern of S-RD

— pattern of I-RDX

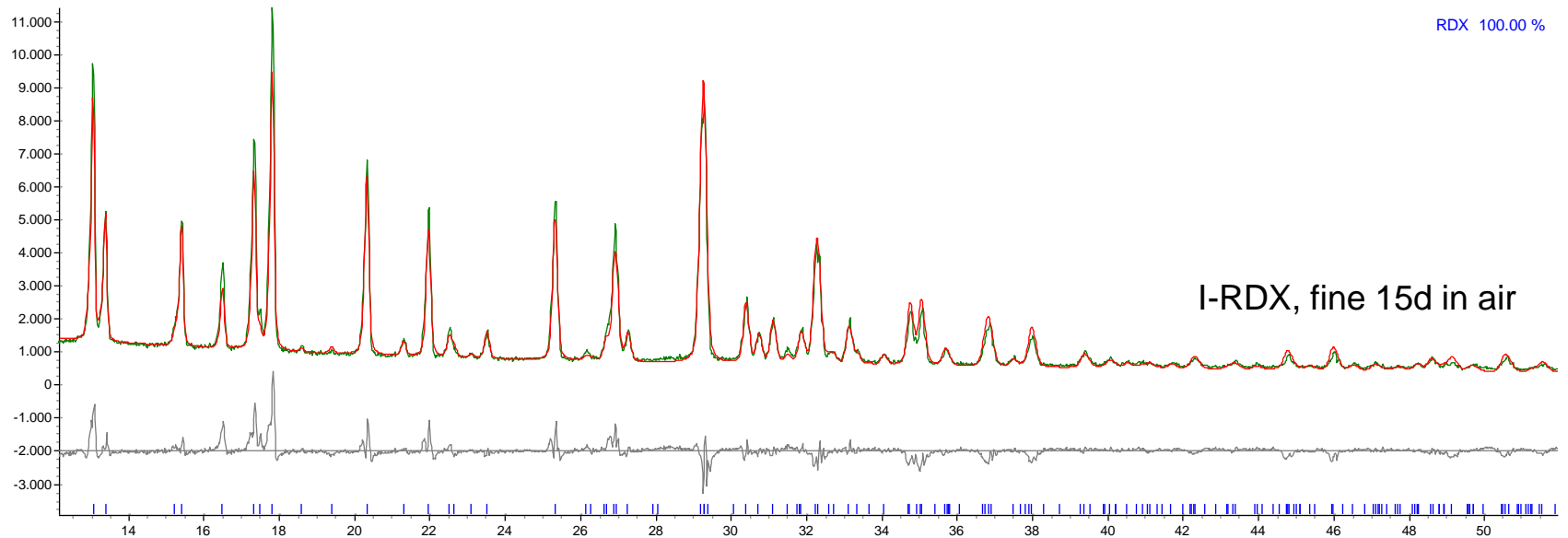
Reference data of the International Centre for Diffraction Data (ICDD)

| PDF-46-1606, RDX

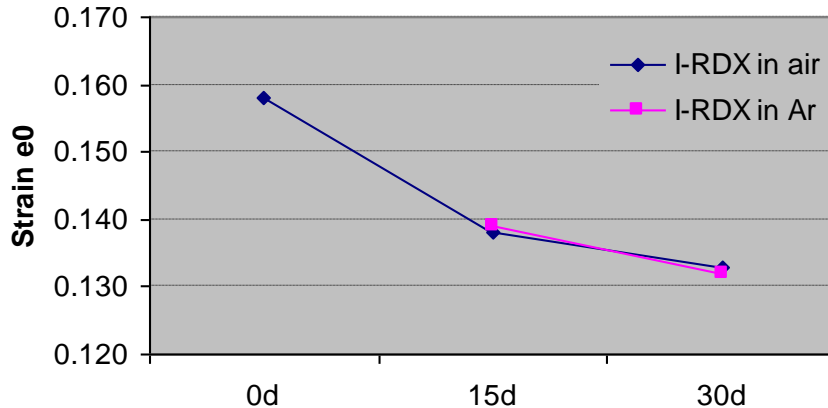
| PDF-45-1539, HMX

Results: Rietveld-Analysis (Double Voigt via TOPAS)

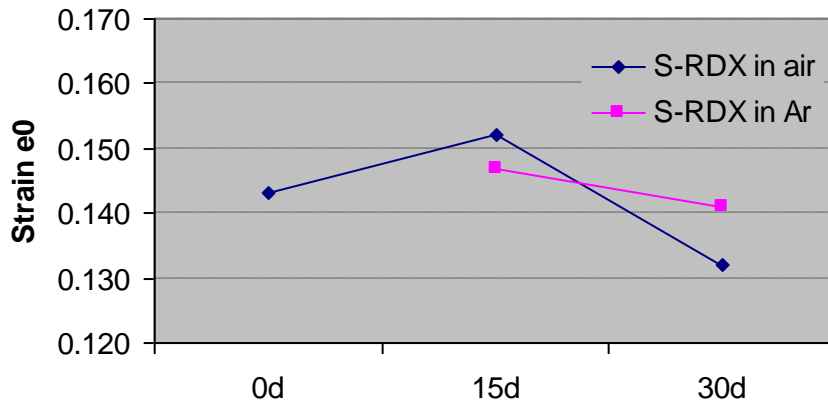
- Structure Data from Literature (Choi et al. 1972)
- No size broadening in RDX (Cry Size L = 10000 = max.)
- Microstrain due to dislocations ($\epsilon_0 = 0.138$)



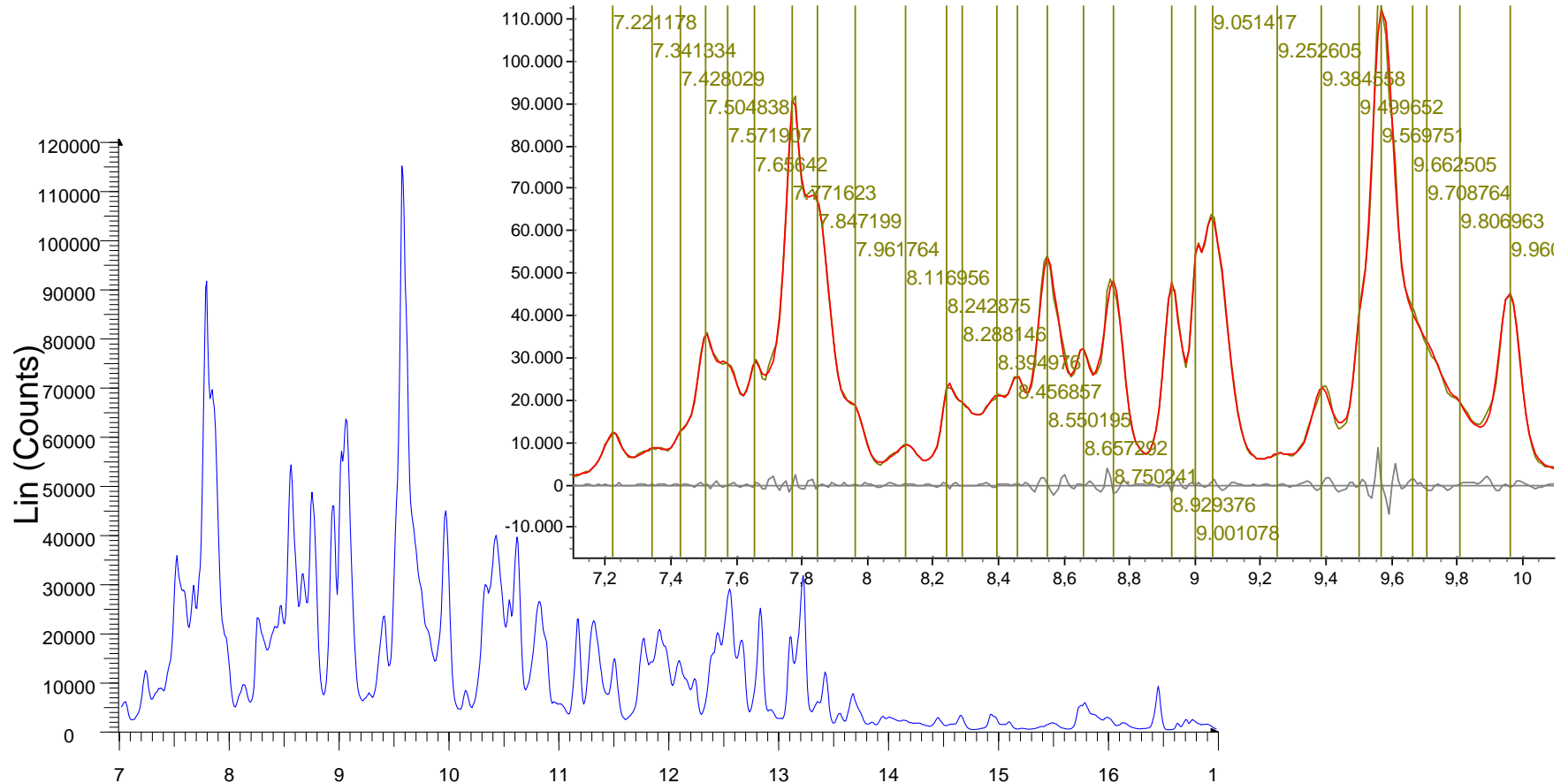
Results: Size/Strain-Analysis



- I-RDX:
Reduced microstrain on aging,
no differences between air and Argon
- S-RDX:
Increased strain after 15 d
but reduced strain after 30 d.
- Different behavior of I-RDX and
S-RDX; significantly higher starting
values of I-RDX but high strain in
S-RDX after 15 d
- Concept of defect healing for
I-RDX and S-RDX beyond 15 d

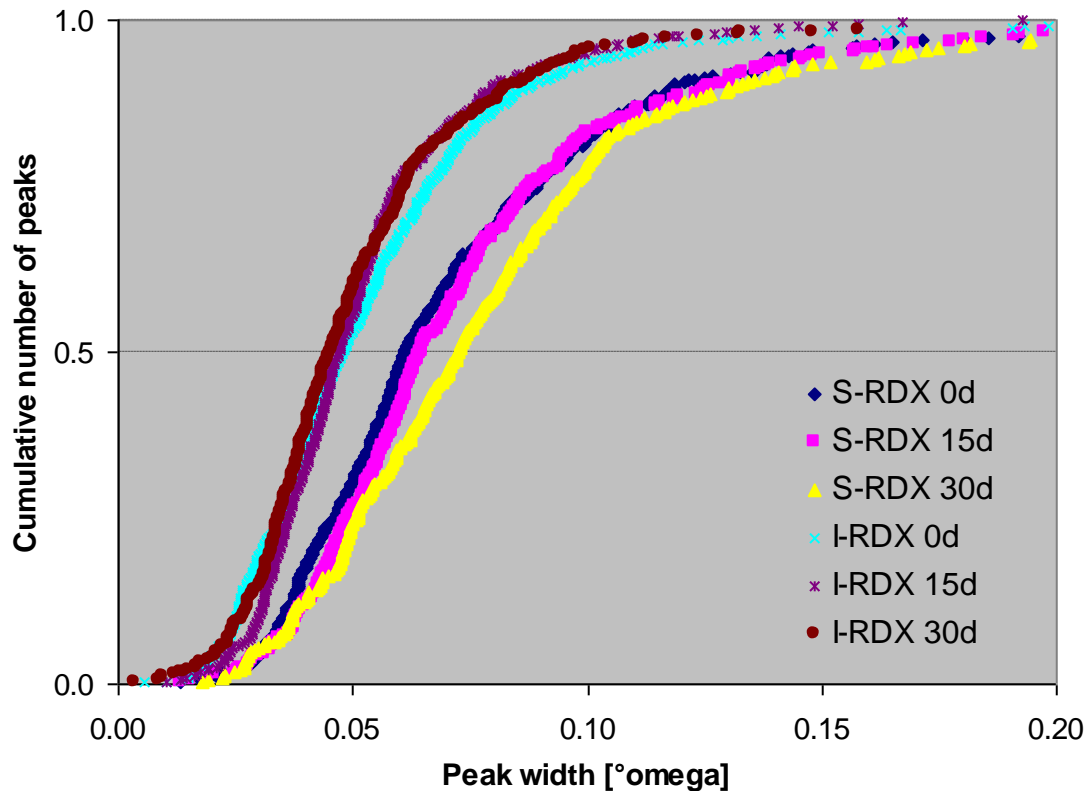


Peak fit of ω -scans



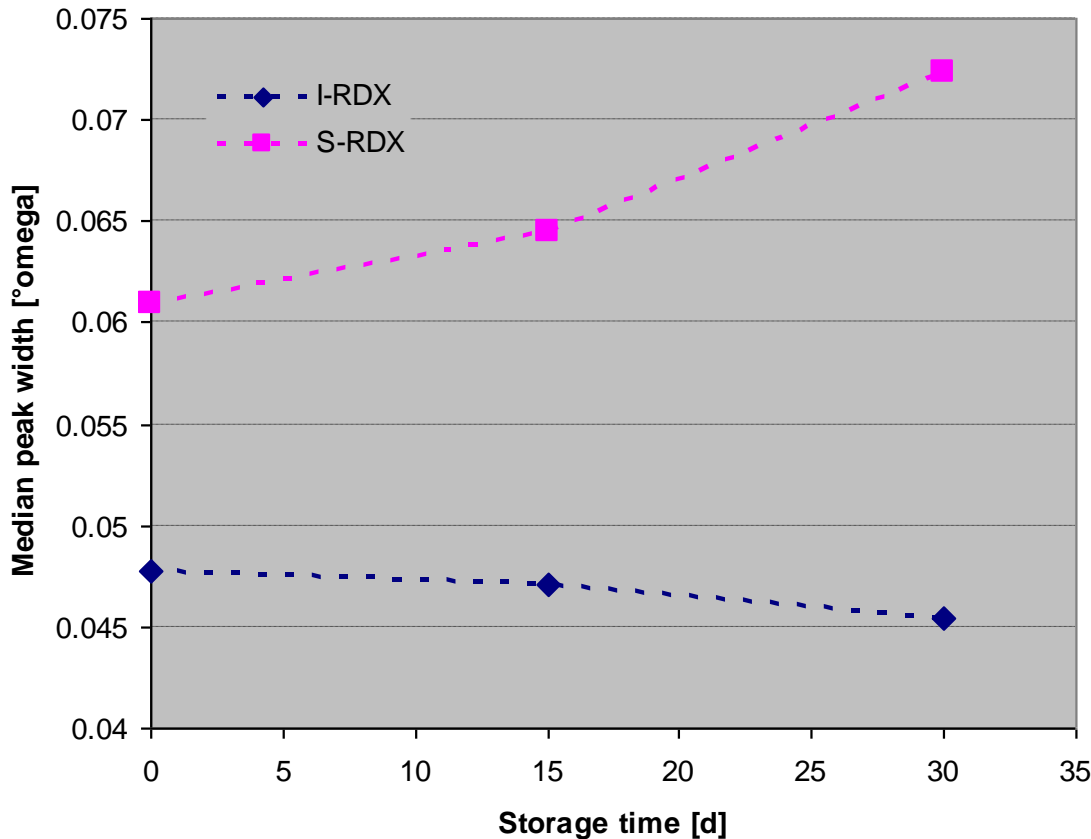
- Evaluation of 7 curves with 340 – 520 peaks per sample
- 2400 peaks...to provide reliable statistical evaluation

Cumulative peak width distribution



- Shift to right means poor quality or high micro strain
- Plot separates I-RDX from S-RDX
- Significant shift of the distribution of S-RDX on aging
- Quantification by median peak widths (X_{50})

Median peak widths / quantification of crystal quality (Coarse grades)



- Significant higher quality of I-RDX compared to S-RDX
- Slight improvement of I-RDX on aging (healing process)
- Significant damage of S-RDX on aging!!
- Effects pronounced within the second aging period (15 – 30d)

Summary and Outlook

- Crystalline HMX impurities in the coarse S-RDX
- No size-broadening but microstrain due to dislocations
- **Different aging mechanisms in I-RDX and S-RDX**
 - strain release / defect healing in I-RDX
 - enhanced strain / crystal damage in S-RDX (crystal damage less clear in fine samples)
- Evaluation of coarse samples aged in argon to be done
- Coarse crystals in the binder should be investigated in future
- Automated evaluation of rocking curves and more detailed evaluation of peak width distribution and quantification of microstrain in future

