SUPPORTING MATERIAL

for

In Situ Synchrotron X-ray Powder Diffraction Study of Formation and Growth of Yttrium and Ytterbium Aluminum Garnet Nanoparticles in Sub- and Supercritical Water

Peter Nørby, Kirsten M. Ø. Jensen, Nina Lock, Mogens Christensen, Bo B. Iversen*

Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University,

Langelandsgade 140, DK-8000 Aarhus C, Denmark

Sequential Rietveld refinement

The sequential Rietveld refinements were performed in the *FullProf Suite* program package.[1] The refinement was performed in reverse order with refinement of the unit cell parameters, scale factor(s), and background. The background was modeled using linear interpolation. Thermal parameters (*B*-values), for the atoms in the garnet phase were fixed to 1, and the *B*-values in possible additional phases were set to 0. The exact *B*-values do not significantly affect the conclusions about the size evolution of the nanoparticles. The position of the atoms was fixed to the coordinates from the ICSD (Inorganic crystal structure database) *i.e.* YAG and YbAG were based on the ICSD database pdf no. 01-070-7794 and 01-073-3186, respectively. All atomic sites were assumed to be fully occupied, and the zero point was fixed. The peak profiles were described by the Thompson-Cox-Hastings pseudo-Voigt function.[2] The effect of instrumental peak broadening was corrected for by performing a LeBail refinement of data on a strain-free micrometer-sized LaB_6

standard sample. Two profile parameters were refined for the garnet phase, I_G (Gaussian) and Y (Lorentzian). Scale factors, unit cell parameters and background points were also refined.

The refined diffraction profile parameters were used to calculate the peak Full Width Half Maximum (FWHM) values by applying an approximation described in the literature, consisting of a series expansion derived from a set of computer-generated convolutions.[2] The FWHM of the Gaussian (Γ_G) and Lorentzian (Γ_L) components of the peak profile vary with angle as:

$$\Gamma_G{}^2 = U \cdot \tan^2\theta + U \cdot \tan\theta + W + \frac{I_G}{\cos^2\theta}$$

$$\Gamma_L = X \cdot \tan\theta + \frac{Y}{\cos\theta}$$

The numerical approximation provided by Thompson-Cox-Hastings gives that the FWHM (Γ) can be calculated as:

$$\Gamma^5 = \Gamma_G{}^5 + 2.69269\Gamma_L\Gamma_G{}^4 + 2.42843\Gamma_L{}^2\Gamma_G{}^3 + 4.47163\Gamma_L{}^3\Gamma_G{}^2 + 0.07842\Gamma_L{}^4\Gamma_G + \Gamma_L{}^5$$

From the calculated FWHM the volume-weighted average size can be calculated using the Scherrer formula.

$$\langle D \rangle = \frac{0.94 \cdot \lambda}{\Gamma \cdot \cos\theta}$$

where <D> is the volume-weighted average size.

In the refinements done in this paper the above equations reduces to:

$$\Gamma_G = \frac{I_G{}^{1/2}}{\cos\theta}$$

$$\Gamma_L = \frac{Y}{\cos\theta}$$

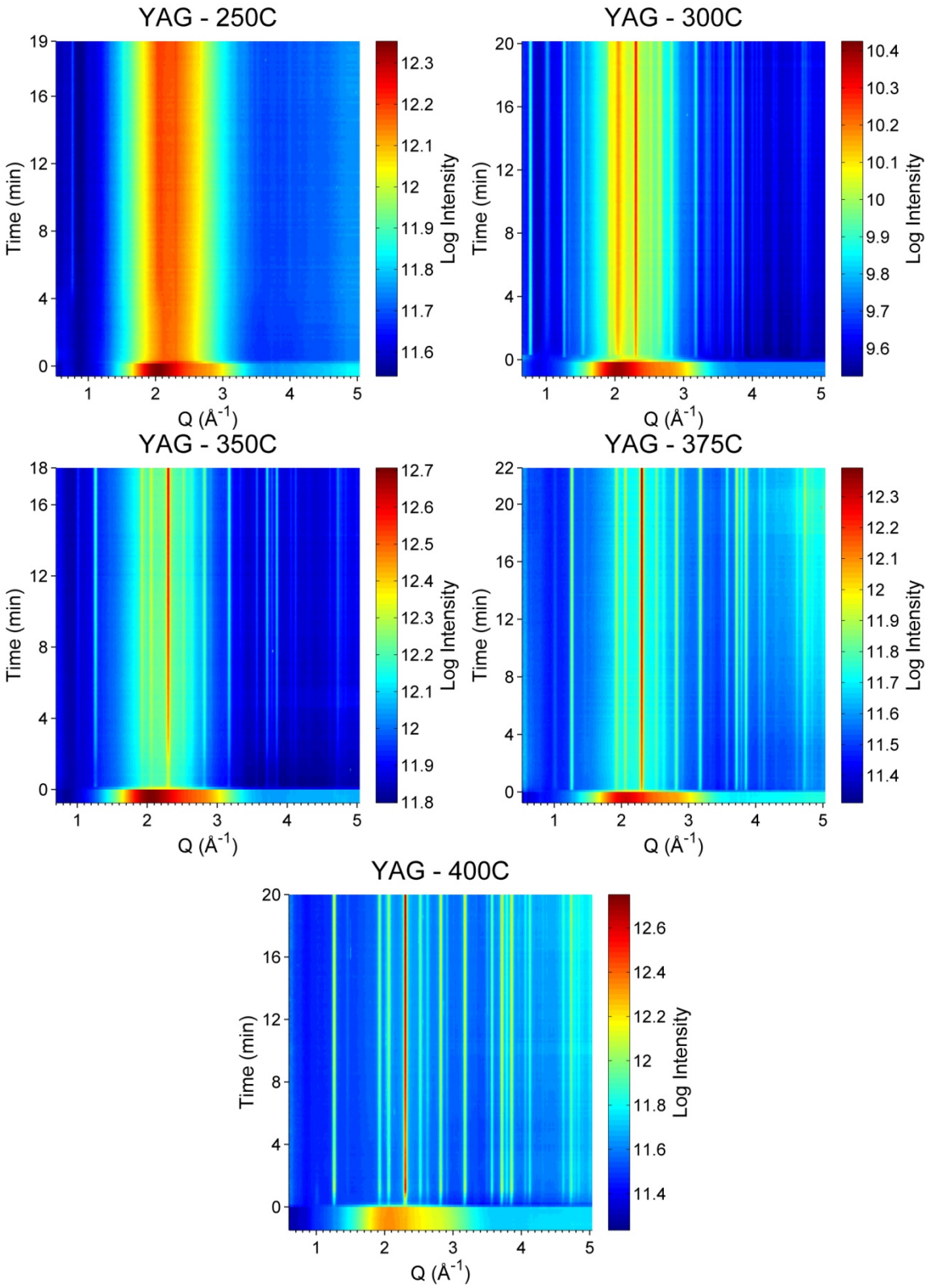
And the FWHM can be expressed by the refined parameters Y and I_G.

$$\frac{\Gamma}{\cos\theta} = \left(I_G{}^{5/2} + aYI_G{}^{2} + bY^2I_G{}^{3/2} + cY^3I_G + dY^4I_G{}^{1/2} + Y^5\right)^{1/5}$$

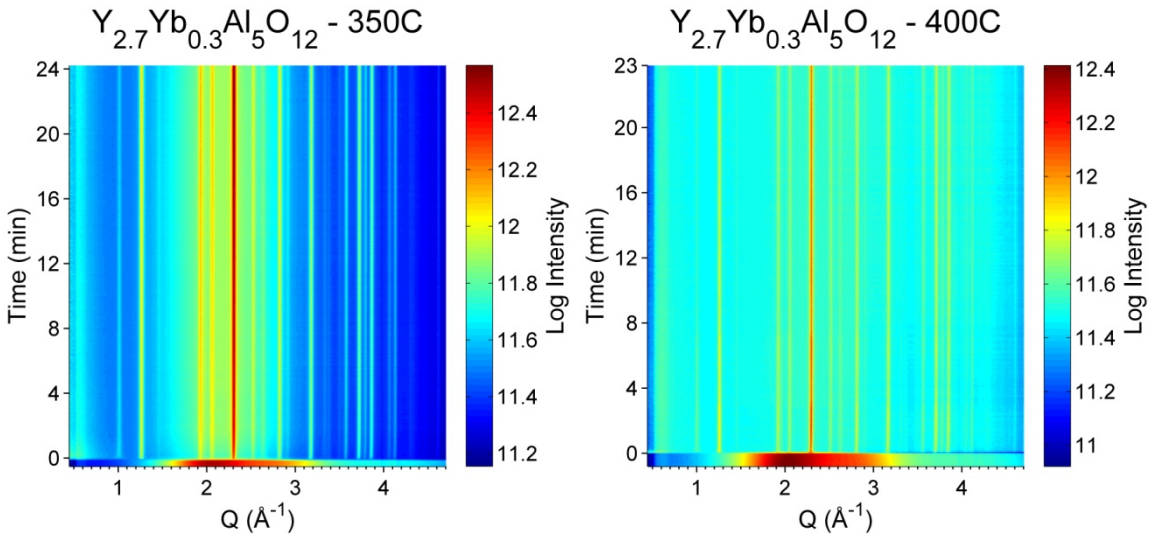
This shows that the volume-weighted average size is independent on the diffraction angle, when only Y and I_G is refined:

$$\langle D\rangle = \frac{0.94\cdot\lambda}{\left(I_G{}^{5/2} + aYI_G{}^{2} + bY^2I_G{}^{3/2} + cY^3I_G + dY^4I_G{}^{1/2} + Y^5\right)^{1/5}}$$

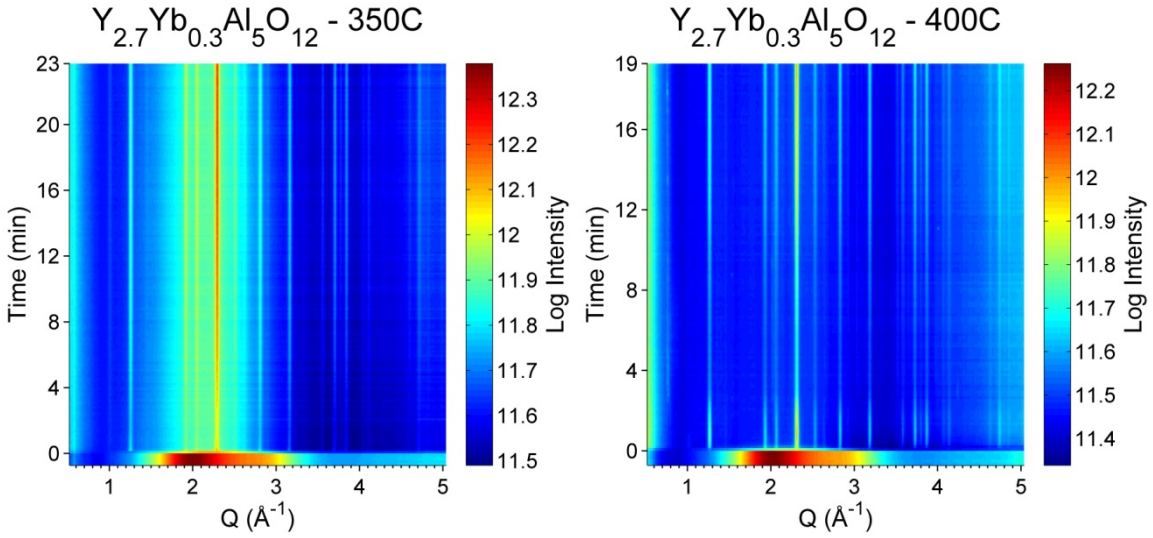
Two dimensional PXRD raw data plot for YAG



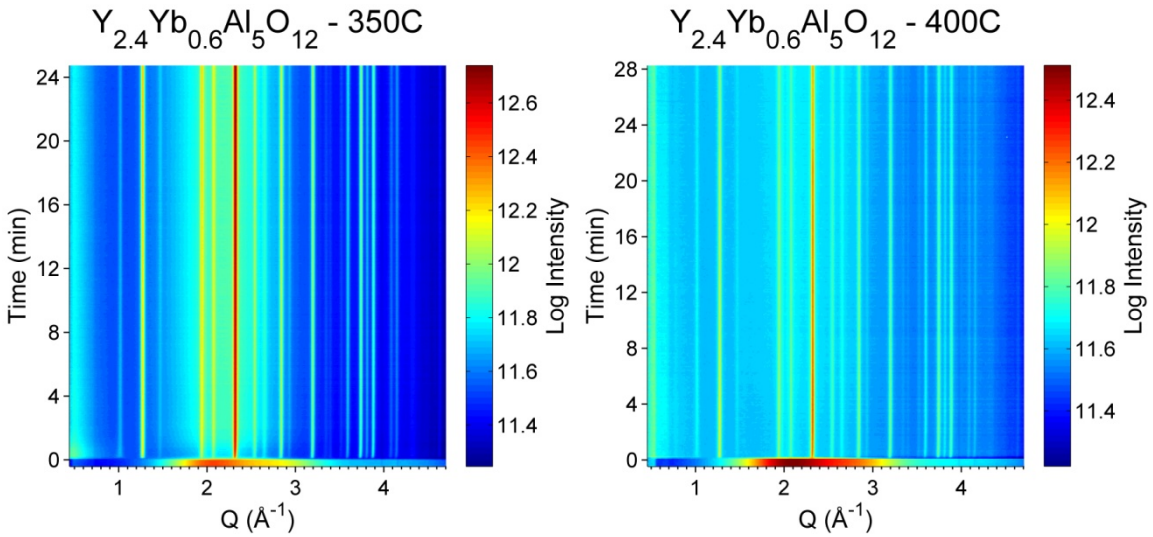
Two dimensional PXRD raw data plot for $Y_{2.7}Yb_{0.3}Al_5O_{12}$ (NO_3^--precursor)



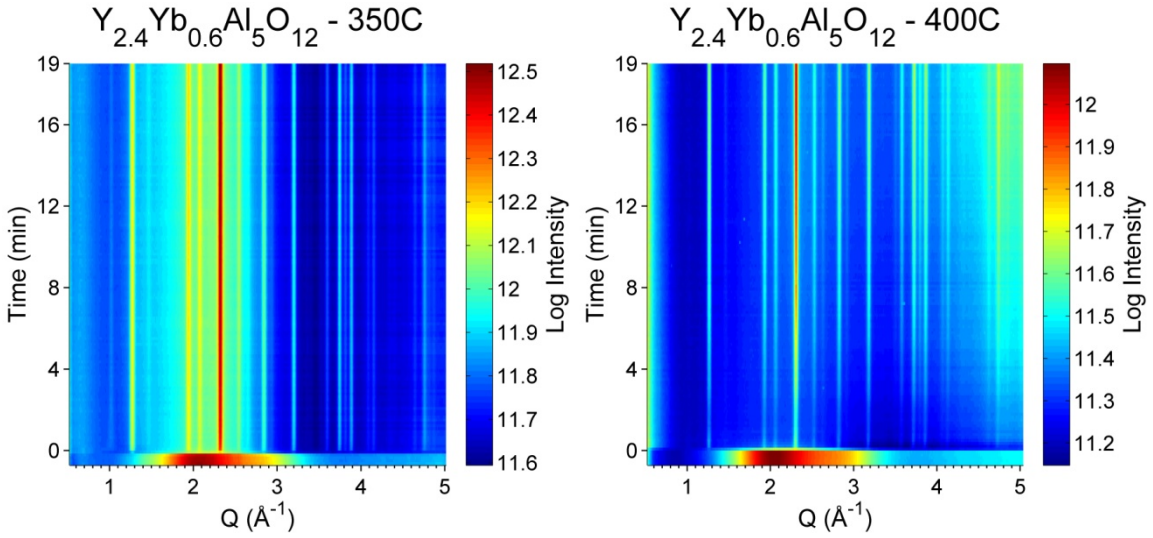
Two dimensional PXRD raw data plot for $Y_{2.7}Yb_{0.3}Al_5O_{12}$ (Cl^--precursor)



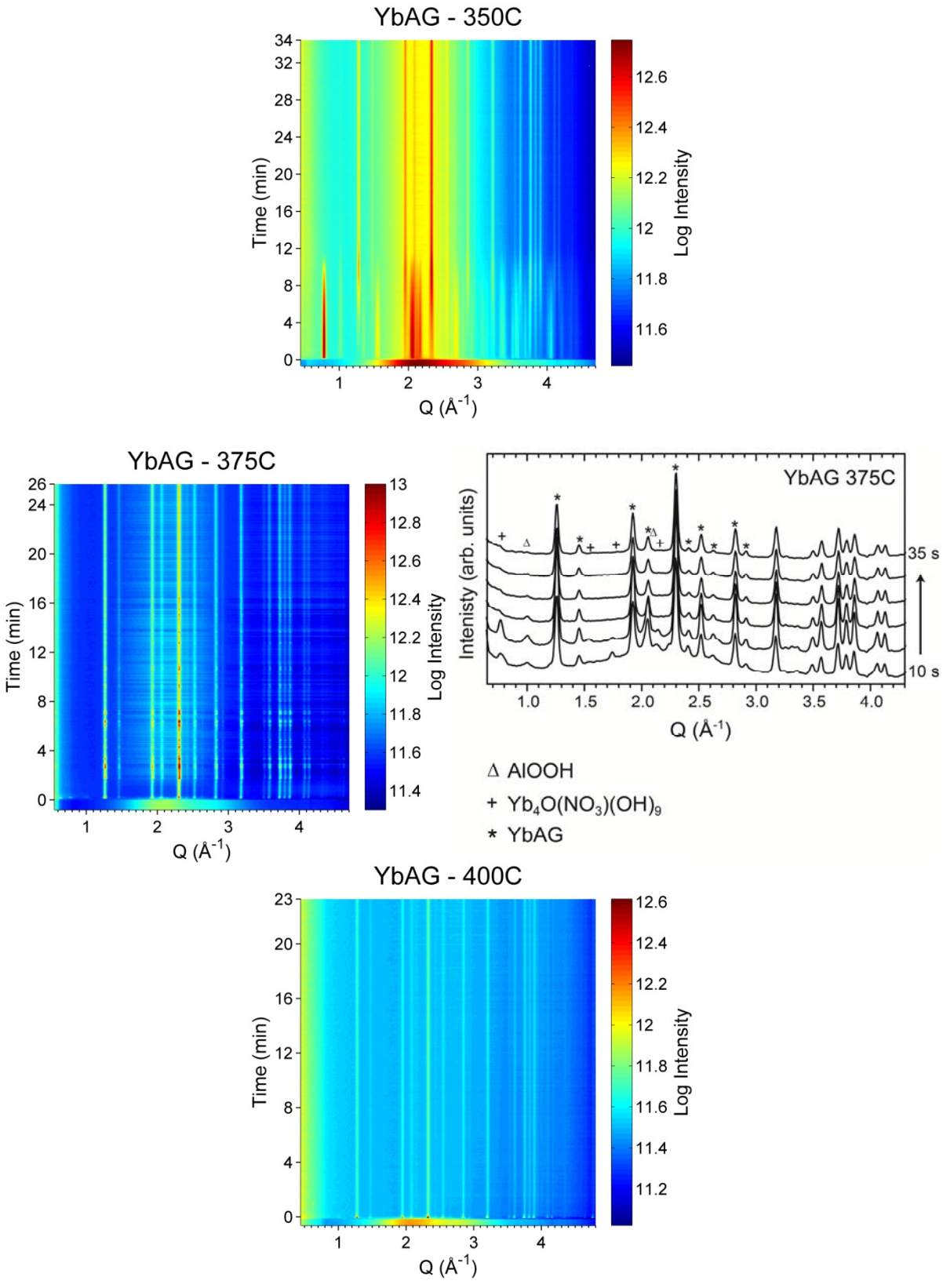
Two dimensional PXRD raw data plot for $Y_{2.4}Yb_{0.6}Al_5O_{12}$ (NO_3^--precursor)



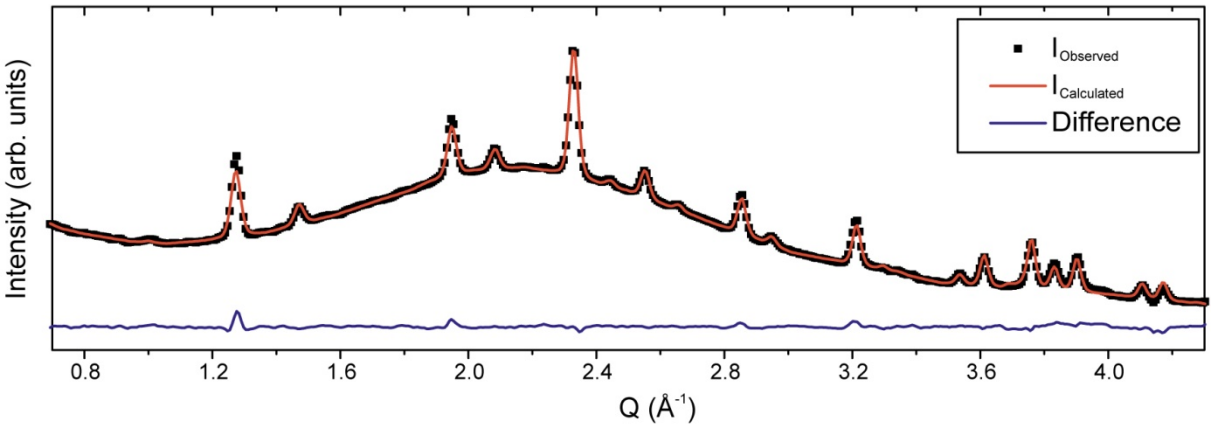
Two dimensional PXRD raw data plot for $Y_{2.4}Yb_{0.6}Al_5O_{12}$ (Cl^--precursor)



Two dimensional PXRD raw data plot for YbAG

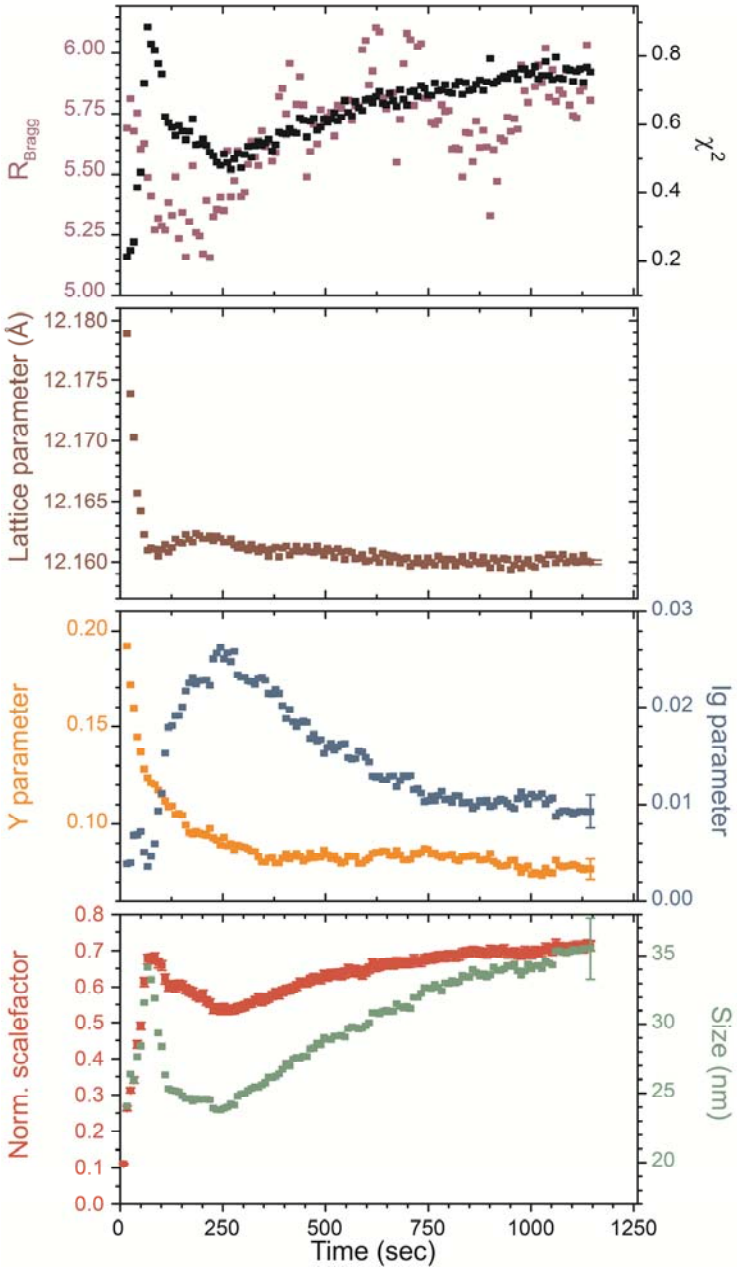


Example of Rietveld refinement



YbAG, 350°C, 34 minutes (last frame)		
Wavelength	1.000 Å	
Q range	0.7 – 4.3 $Å^{-1}$	
Number of points	609	
Number of refined background points	28	
Phase	AlOOH	YbAG
Number of parameters (not including background points)	4	4
R_{Bragg}	24 %	6.5 %
Weight fraction	13(3) %	87(3) %
Scale factor	0.004(1)	$9.3(2)\cdot10^{-5}$
A	2.865(5) Å	12.0366(2) Å
B	12.48(3) Å	
C	3.744(4) Å	
Y		0.00788(4)
I_G		0.014(2)

R-value, Chi square, lattice parameter, Y and I_G, scale factor and size for YAG synthesised at 400°C as a function of time



References

1. Rodriguezcarvajal, J., *Physica B-Condensed Matter* **1993,** *192*, 55-69.

2. Thompson, P.; Cox, D. E.; Hastings, J. B., *Journal of Applied Crystallography* **1987,** *20*, 79-83.