Supporting information for

Solvothermal flow synthesis of zinc phosphate pigment

Details on Rietveld refinements:

The following parameters were refined: Scale factor, zero point (linear displacement parameter), unit cell parameters and March parameter (the March-Dollase multiaxial function method was used as employed in the FullProf software). The Thompson-Cox-Hastings pseudo-Voigt peak shape function was used with U, X and Y parameters refined. An instrumental resolution file (.IRF, list 2θ, H_G (2θ) & H_L (2θ)) was used in order to correct for instrumental broadening. Background points were chosen manually,

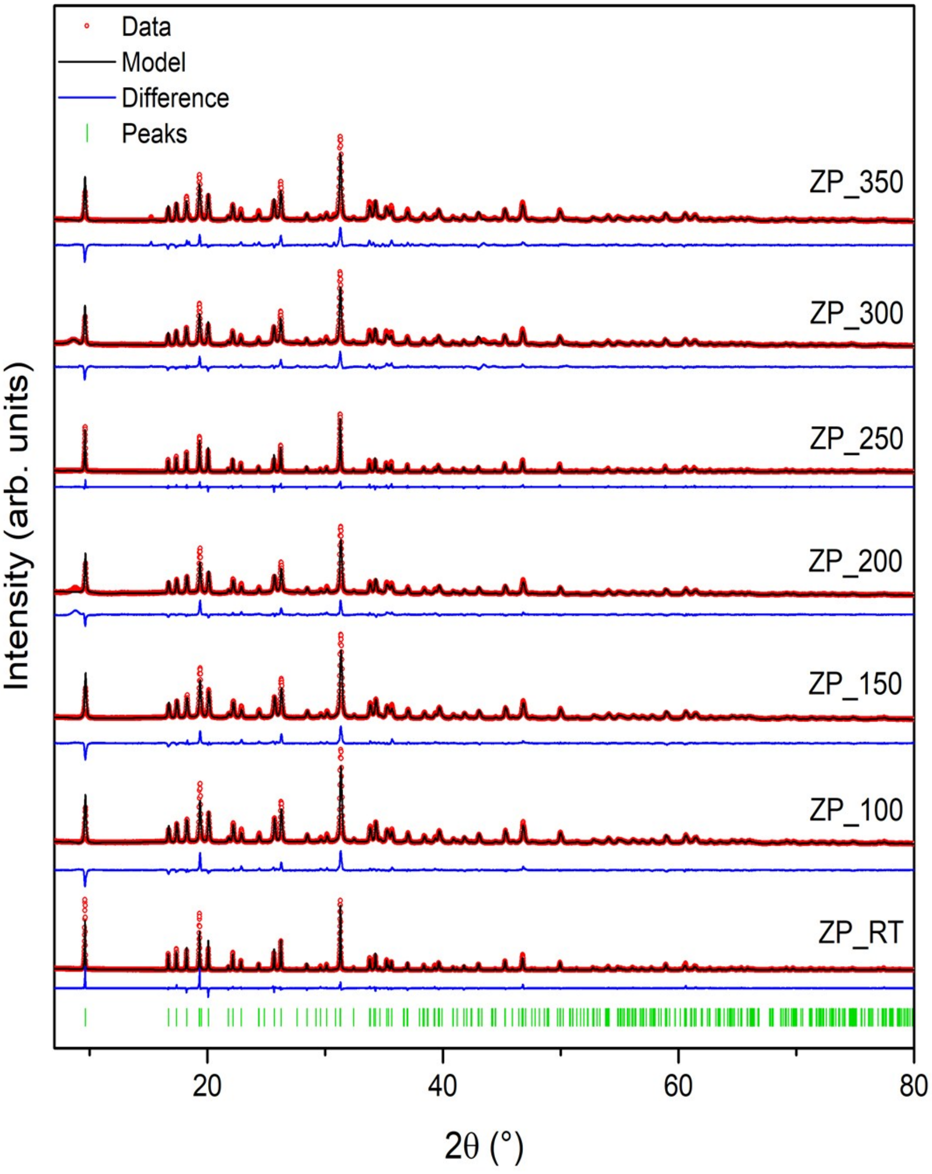


Figure 1: Stacked obs-calc plots of diffraction data; from bottom to top: room temperature to 350 °C. Red circles mark observed data points, black lines mark the refined model. The peak positions of α-hopeite reported by Herschke et al. are plotted in green.

but the heights of these were refined and connected through linear interpolation Convergence was reached for all data sets using the standard stopping criterion for EdPCR (termination when shifts < 0.10 x E.S.D).

Stability of products

PXRD measurements were performed on samples ZP_RT, ZP_100, ZP_150, and ZP_200 after 29 months of storage in vials under ambient conditions. A Rigaku Miniflex diffractometer with Cu Kα_1 & Kα_2 radiation was used to measure the data in Bragg-Brentano geometry. All peaks are found to match hopeite, showing that the product is stable under ambient conditions.

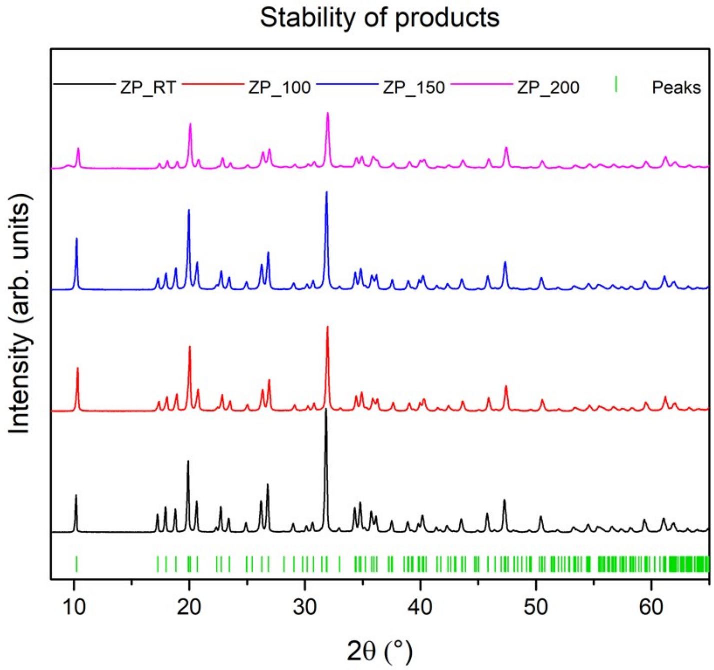


Figure 2: Stacked diffractograms measured after 29 months storage. Peaks positions of α-hopeite by Herschke et al. are marked in green.

Size analysis from PXRD peak broadening:

Only peak shape parameters Y & W were employed in the PXRD crystallite size analysis, meaning that only isotropic size broadening is modelled. All other parameters and settings were maintained from the previously described Rietveld analysis.

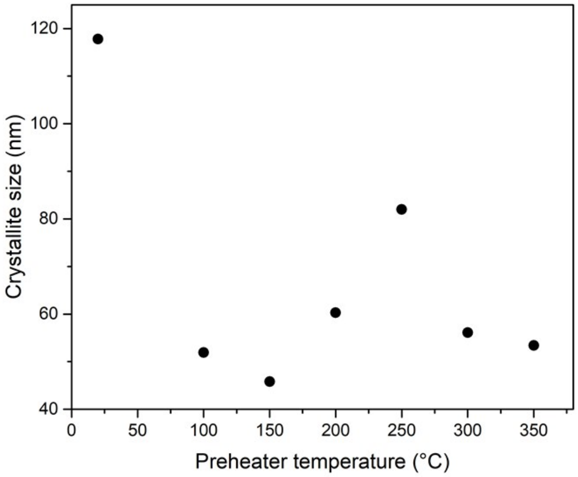
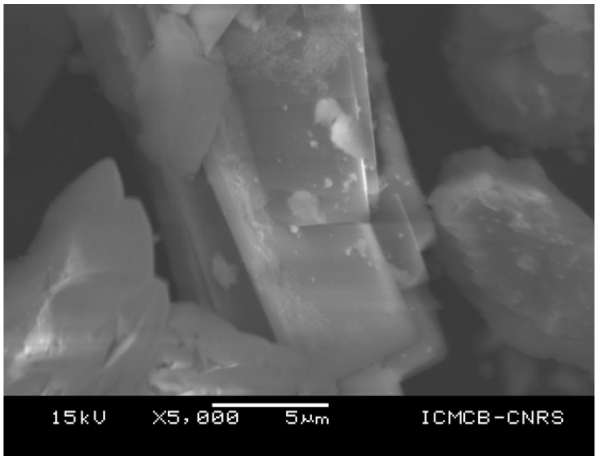


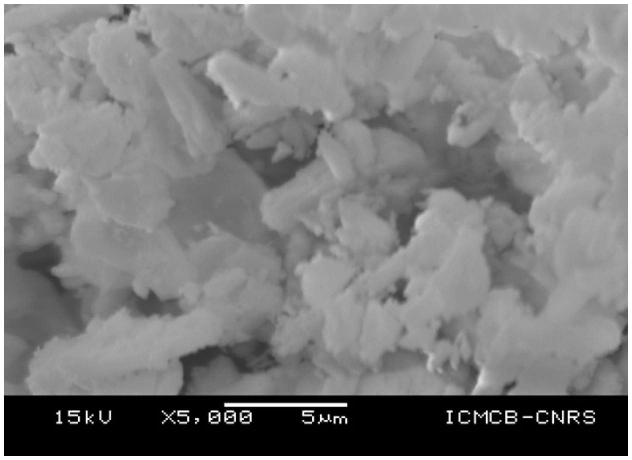
Figure 3: Volume-weighted average crystallite sizes from PXRD peak broadening analysis. Calculated errors are between 0.031 nm and 0.43 nm, which is too small to be seen with the chosen marker. However, the true uncertainty is significantly higher, especially close to the instrumental limit (above 100 nm). The average crystallite size is however found to be significantly higher for the sample prepared at room temperature compared to the samples prepared at elevated reaction temperatures.

Additional SEM images:

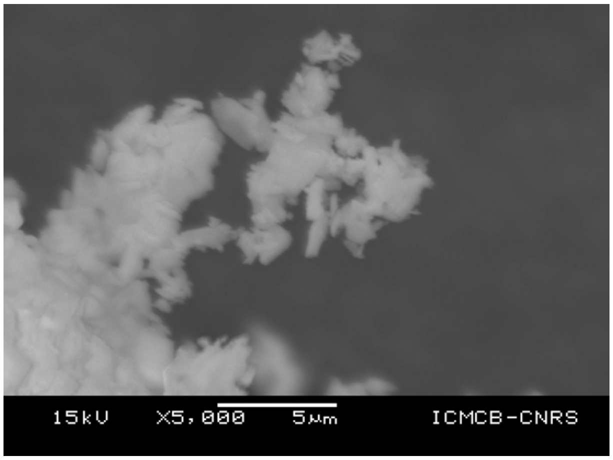
ZP_RT



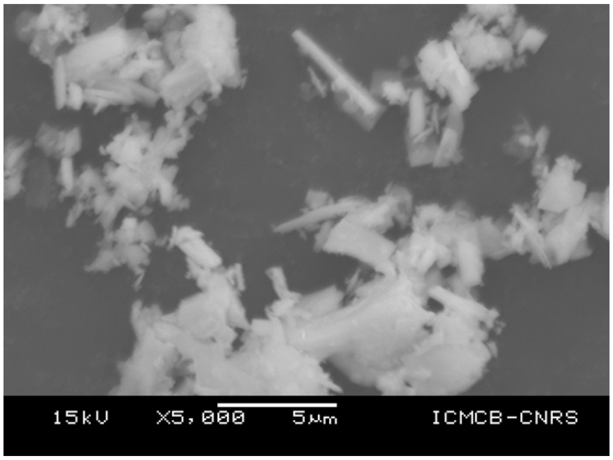
ZP_150

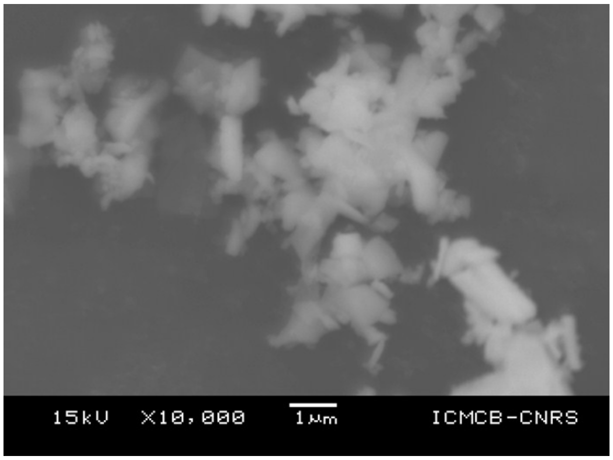


ZP_250



ZP_350 (two images)




15kV
X10,000
1μm
ICMCB-CNRS