The Nucleation of Quartz Under Ambient Conditions: A Microemulsion Approach to Crystallisation

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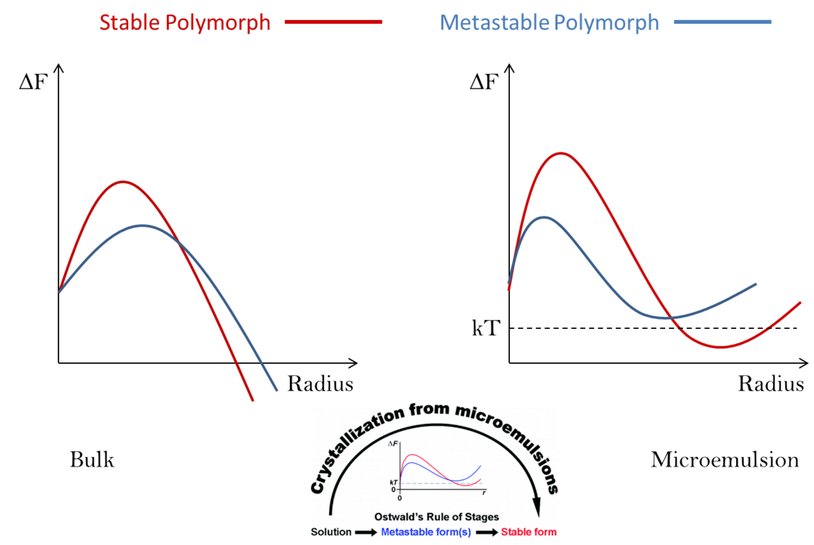
1. Introduction

Quartz crystallisation normally requires harsh conditions; for instance, hydrothermal processes at 200-300 °C and 15-100 bar, where the high growth rate precludes selective formation of nm-sized quartz. Here we show that, remarkably, 2 nm-sized nanoquartz can be produced from microemulsions under ambient conditions. The 2 nm particles are then used to seed controlled hydrothermal syntheses of 5 nm nanoquartz particles under mild conditions of 175 °C and autogenic pressure. Accordingly nanoquartz of varying size and degree of perfection is obtained exclusively for the first time.

2. Background Theory

A minima in the free energy curve is observed when a crystal nuclei in a microemulsion droplet is surrounded by saturated solution. This nuclei can only grow further when it collides with a nucleus-free droplet (with high solute concentration) and forms a transient dimer, thus gaining access to more growth material. Consequently, the ability to form a (near) stable crystal nucleus becomes the determining factor governing whether crystallisation proceeds. The stable polymorph will have the lowest energy minima, since it is the least soluble, and hence most droplets will contain nuclei of this stable form.



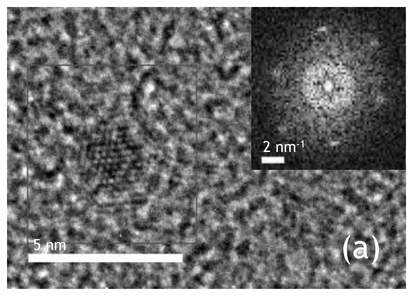
3. Synthesis

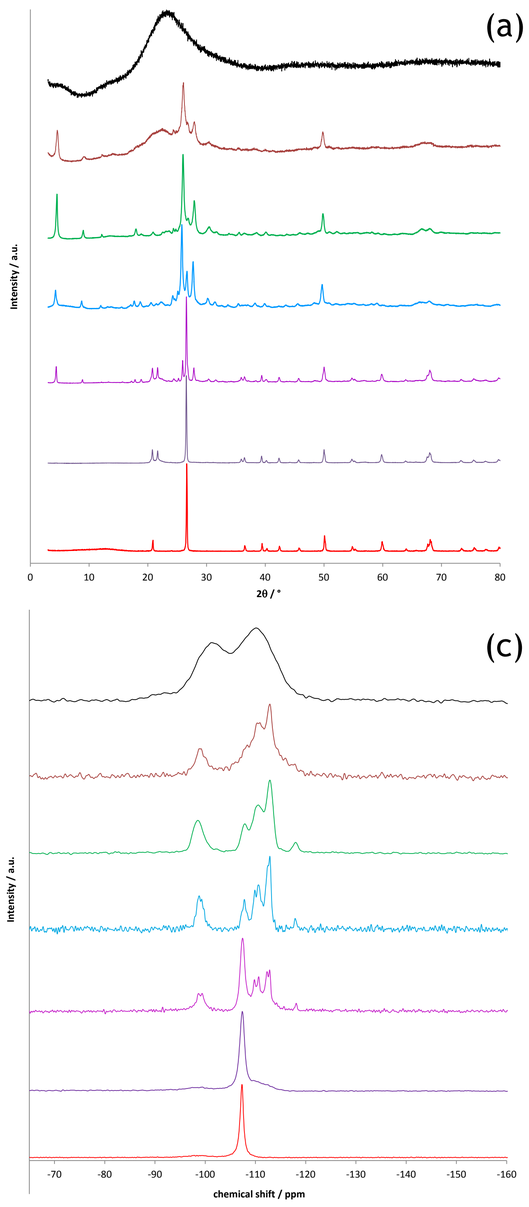
$$Na_2SiO_3 + H_2O \longrightarrow SiO_2 + 2NaOH$$

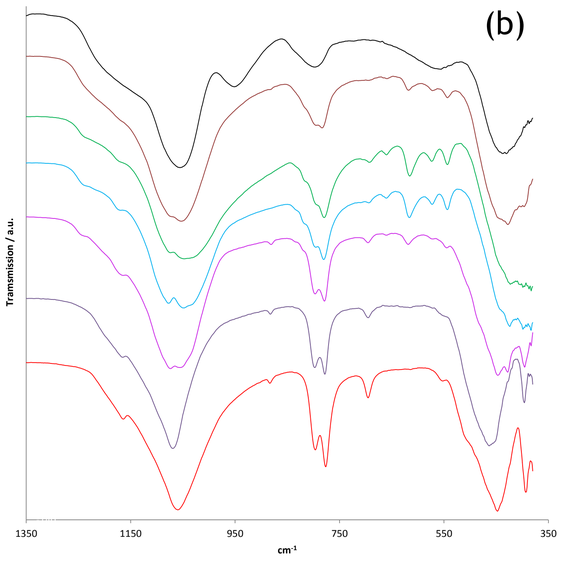
Sodium metasilicate microemulsions were prepared by mixing of the following:

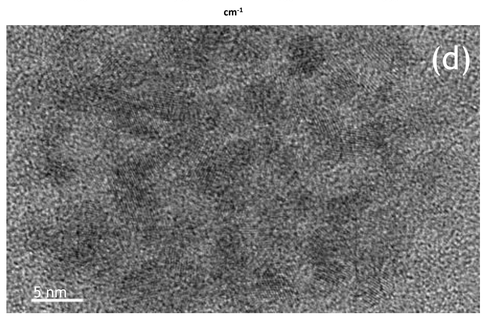
Span® 80	Brij® 30	SMS	H_2O	Heptane
80 g	80 g	0.05 g	1.95 g	240 g

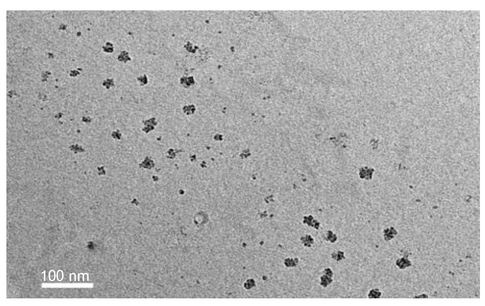
After 14 days at room temperature and pressure a white precipitate was observed (0.022 g), corresponding to quartz nanocrystals of size 2.0 ± 0.7 nm (550 particles sized) (a).











4. Hydrothermal Treatment

The microemulsion nanoquartz product was used as seeds in a hydrothermal treatment. 57.4 mg of nanoquartz was combined with a supersaturated solution of 237.4 mg fumed silica in 20 ml 0.1 M SMS solution in a hydrothermal bomb and left at 175 °C for 1-7 days.

XRD (a), FTIR (b), ^{29}Si ssNMR (c) and TEM (d) was utilised in order to characterise our microemulsion-synthesised nanoquartz (black lines) and the products from 1-day (brown lines), 2-day (green lines), 3-day (blue lines), 5-day (pink lines), 6-day (purple lines) and 7-day (red lines) hydrothermal synthesis at 175 °C

At short hydrothermal run times the nanoquartz exhibits a similar structure to that seen in moganite, with a perturbed structure containing interior defects and differing directional helices. After 7 days, the nanoquartz had perfected with the bulk quartz structure emerging; these perfected crystals having grown to 4.4 ± 0.9 nm (461 particles sized) as shown in micrographs (e).

Note that replacing our microemulsion seeds with fumed silica in the hydrothermal experiments yielded polydisperse micron sized quartz.

5. Conclusions

- Quartz nanocrystals have been produced under ambient conditions *via* a microemulsion-mediated methodology. This is the first non-biological reporting of quartz nucleation under ambient conditions.
- The 2 nm crystals, with their perturbed bulk-quartz structure, were slowly perfected and grown over time using mild hydrothermal conditions. This enabled nanoquartz of varying size and crystal perfection to be obtained exclusively for the first time by simply changing reaction times.
- These nanocrystals, free from contaminants, are ideal for studies aimed at elucidating the harmful role that silica crystallinity plays in inducing lung diseases such as silicosis.

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