

**Experiment title:**

Time resolved powder diffraction;
in-situ studies of hydrothermal syntheses

Experiment**number:**

CH136

Beamline:

BM16

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Report:

In the last years a number of studies have shown that in-situ powder diffraction using synchrotrons X-ray radiation is a very powerful tool for studying e.g. crystallization and chemical reactions involving crystalline material (e.g. 1-4). Use of intense synchrotrons X-ray radiation combined with position sensitive detectors enables studies of even quite fast chemical reactions, and allows real-time structural information to be extracted@-7).

The aim of the present experiments was to study, in-situ, the high temperature hydrothermal synthesis of α -eucryptite, LiAlSiO_4 . α -Eucryptite is a high temperature hydrothermal phase forming above 350°C, and can be prepared by hydrothermal conversion of zeolite Li-A(BW), $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$ in an aqueous solution of LiCl (8).

For in-situ powder diffraction studies of hydrothermal syntheses we usually use quartz glass capillaries. However, 50 atm. is about the maximum pressure it is possible to apply to these capillaries. To maintain hydrothermal conditions at temperatures above 350° a pressure of more than 170 atm. must be applied. Also the reactivity of aqueous solutions increases considerably at high temperatures, and it is therefore necessary to use e.g. stainless steel containers for the hydrothermal syntheses. By modifying our equipment slightly it was possible to perform the hydrothermal syntheses in 1.6mm steel tubes with wall thickness of ca. 0.3mm. The reaction cell is shown schematically in Fig. 1. The T-piece was connected to a hand operated hydraulic pump using a steel tube, and a water pressure of 2-300 atm was applied. The sample was heated using a hot air blower. In order to penetrate the steel tube 35keV X-rays ($\lambda = 0.3570\text{\AA}$) was used. The detector was a Translating Imaging Plate (TIP) system developed especially for time, temperature and wavelength dependent powder diffraction (2,9).

Fig. 2 shows the diffraction patterns during hydrothermal conversion of anhydrous Li-ABW, $\text{LiAlSi}_4\text{O}_{14}$ in a ca. 4M solution of NaNO_3 . The diffraction peaks from the steel capillary have been truncated for clarity. The diffraction patterns are well resolved with FWHM's (Full Width at Half Maximum) of ca. 0.05° in 2θ . The starting material (Fig. 2a) is hydrothermally hydrated to zeolite Li-A(BW), Figs. 2b-c, and is finally transformed into a another phase, Fig. 2d. (Marked reflections belong to zeolite Li-A(BW)). This phase could be indexed based on a cubic unit cell, $a = 9.024(2)\text{\AA}$, indicating a sodalite type material.

Using zeolite Li-A(BW) as a starting material hydrothermal conversion to α -eucryptite using aqueous LiCl (~4M) was studied. Upon heating formation of the α -eucryptite phase was observed, and Fig. 3 shows a part of powder diffraction rings of the starting material and the formed α -eucryptite. In Fig. 3a the pattern was obtained using no oscillation of the sample, and a clear difference is seen between the diffraction lines. The starting material has very small crystallite, and consequently the Debye-Scherrer ring is uniform and smooth. The product α -eucryptite grows as larger crystals, and the result is Debye-Scherrer rings which consists of a number of sharp reflections. Integrated intensities of diffraction lines are used to estimate the amount of crystalline material, and it is very important to obtain good averaging. By oscillation of the sample $160''$ a significant improvement in the averaging is obtained, as seen from figure 3b.

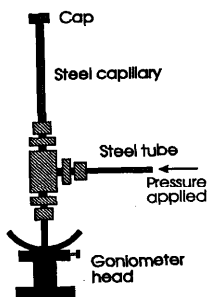


Fig. 1. Sketch of the steel capillary mounted on a goniometer head.

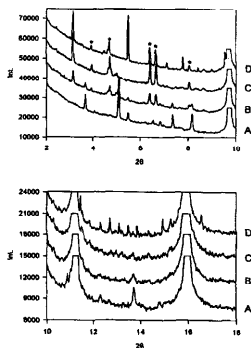


Fig. 2. Powder diffraction profiles during hydrothermal conversion of anhydrous Li-ABW in ~4M $\text{NaNO}_3(\text{aq})$

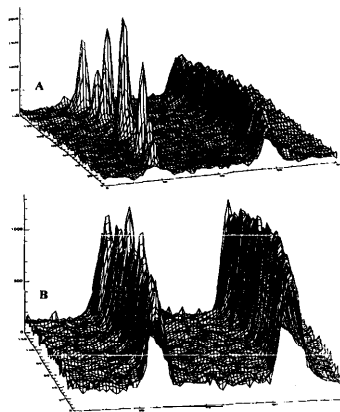


Fig. 3. Part of the Debye Scherrer powder diffraction rings of a partially converted sample, A) No oscillation. B) $160''$ osc.

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