



	Experiment title: In situ diffraction studies of the kinetics of the structural evolution of technologically significant sol-gel produced silica-based amorphous materials	Experiment number: ME-673
Beamline: ID15B	Date of experiment: from: 18/02/2004 to: 24/02/2004	Date of report: 1/03/2005
Shifts: 18	Local contact(s): Dr G. Gonzalez-Aviles	<i>Received at ESRF:</i>
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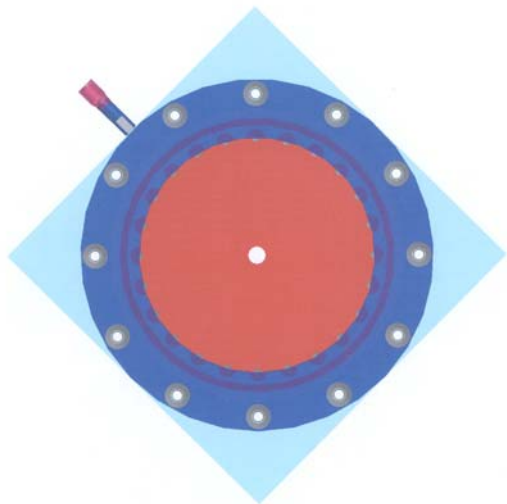
Report:

Overview

The sol-gel method has now been investigated in the preparation of many materials with interesting physical and chemical properties. Multicomponent solids produced by the sol-gel process can have very varied properties depending on physical morphology and the atomic scale disposition of the different elements relative to one another. Their characteristics and hence properties strongly depend on composition and processing, and allows samples with a wide variation of porosity, and hence surface area, and chemical properties to be manufactured. This project used X-ray diffraction on ID15B to see how time-resolved data could be collected during the sol-gel process itself. This project concentrated on the initial gelation process, and was tailored by the nature of the catalysis (e.g. acid concentration). The reaction from the liquid state to the initial gelled mixture (a further experiment examines subsequent structural changes with heat treatment). This has to be followed via amorphous diffraction so requires the use of high energy that allowed the data to be recorded over a large Q range (a significant improvement over the other X-ray sources currently available to us), and hence gives good real space resolution which is important to resolve the different pair correlations, even for these amorphous samples. The large X-ray flux and use of the on-line MAR image plate detector allowed individual data sets to be collected over a very short period of time, whilst retaining a satisfactory signal-to-noise ratio so that good time resolution can be achieved. Hence reaction rates at this stage were varied to allow the time resolution of the diffraction to capture the major structural changes in the gelling process.

Experimental method and results obtained

A new sample cell was constructed (Fig. 1). This cell had two important features for these experiments. There was an entry port (to the upper left in the diagram) that allows the sol-gel precursors to be mixed in the cell while it was situated on the beamline ready to start collecting data immediately after the reaction has started. It also had the capability of mixing the liquid by continuous rotation within the beam. The entry for the X-rays is the small central hole and the X-rays scatter out of the large window to give as wide a Q-range as possible, within the other constraints of the set up. There were kapton windows over both the entry and the exit ports. Using this set-up the samples examined were SiO_2 , $(\text{TiO}_2)_{0.08}(\text{SiO}_2)_{0.92}$, $(\text{TiO}_2)_{0.18}(\text{SiO}_2)_{0.82}$, and $(\text{TiO}_2)_{0.30}(\text{SiO}_2)_{0.70}$. Data sets could be collected with sufficient quality to allow simulation of the r-space data in 1 minute. Data was then continuously collected for several hours, up to 16 hours for some of the slower gelling samples.



Some Q-space (i.e. θ) data is shown in Fig. 2. The data was collected at a range of sample-detector distances (300, 400, 600 and 800mm) corresponding to a Q-range of $0.2\text{--}23\text{\AA}^{-1}$. Increasing the Q-range increases the resolution in r-space, which is a great advantage in trying to fit the resulting peaks in r-space. This was the maximum Q-range that could be achieved, since a further reduction in the sample-detector distance was not possible with the experimental set up. Data sets of sufficient quality could be collected in 60s (=6x10s) which is sufficiently fast that the timescales over which structural changes occur can be picked up. The gel point was recognised when the cell contents were no longer free moving. A range of acid concentrations (as a factor of the traditional concentration used in the normal laboratory based gel formation) was examined to vary the gel time which are summarised as:

mol% TiO ₂	mol% SiO ₂	Acid conc. factor	Gel time (hrs)
8	92	15	3
8	92	20	1.5
8	92	4	No (16)
8	92	10	No (8)
18	82	20	3
30	70	20	5

Table 1. Summary of compositions, acid concentrations and gel times of samples studied.

For all compositions an acid concentration could be found that allowed the samples to gel within the reaction cell on the beamline. The time to gel is shown in the table and if it did not gel the time for which the experiment ran is given. Another sample (TiO₂, 30mol%) where acid was continually added during the data collection until it gelled was examined. To understand these data sets, very careful correction for sample absorption, background scattering and density is having to be made to allow the Fourier transform. However the Q-space data does show changes as the reaction progresses which now need to be understood in terms of the real space structure.

