ESRF	**Experiment title:** In situ diffraction studies of the kinetics of the initial gelation and high temperature phase separation of technologically significant sol-gel produced silica-based amorphous materials	**Experiment number**: HS-2392
Beamline: ID15B	**Date of experiment**: From: 30/06/2004 to: 06/07/2004	**Date of report**: 1/03/2005
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Report:

Overview

This project built on the time-resolved X-ray diffraction data collected on ID15B through ME-673 of the kinetics and structural evolution of the initial gelation stages of the sol-gel process. The aim of this particular experiment was to follow the structural evolution within the gel in the high temperature regime (up to 750^{o}C). This means that the loss of loosely adsorbed water occurs first, after which structural hydroxyls are driven off and the connectivity of the largely silicate network begins to change. Multicomponent solids produced by the sol-gel process can have very varied properties depending on physical morphology, the atomic scale disposition of the different elements relative to one another and the connectivity of the underlying network. 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. The structural evolution here 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 X-ray sources currently available to us), and hence give good real space resolution which is important to resolve the different 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. The system studied here was the oxide mixture TiO_2-SiO_2 for which we have a lot of other data (e.g. solid state NMR, FTIR, XAFS, etc.).

Experimental method and results obtained

The experiments were carried out using a high temperature furnace that allowed pressed pellets to be held in the hot zone. The furnace was capable of temperatures up to ~1200^{o}C, but was used here up to only 750^{o}C. Samples were heated at a rate of 1^{o}C per minute and held for 15 minutes at 125, 200, 210, 220, 225, 230, 240, 250, 400, 500, 600 and 750^{o}C. It was constructed to allow a wide escape for the X-rays so that the maximum Q-range could be captured. This furnace was constructed by the Royal Institution, London.[†] A sample to detector distance of 300mm was used corresponding to a Q-range of 0.8-23 Å^{-1}. Data sets of sufficient quality could be collected in 60s which is sufficiently fast that the timescales over which

structural changes occur can be picked up. The samples looked at covered a range of composition that had been studied previously up to the gel point on ID15B.

The actual samples studied were TiO_2, SiO_2, $(TiO_2)_{0.08}(SiO_2)_{0.92}$, $(TiO_2)_{0.18}(SiO_2)_{0.82}$, $(TiO_2)_{0.30}(SiO_2)_{0.70}$, $(Nb_2O_5)_{0.30}(SiO_2)_{0.70}$, $(Nb_2O_5)_{0.0375}(TiO_2)_{0.075}(SiO_2)_{0.8875}$. During this experiment 8 *ex-situ* samples were also run $(Nb_2O_5)_{0.0375}(TiO_2)_{0.075}(SiO_2)_{0.8875}$ (NHT, 250, 500 and 750°C) and $(Nb_2O_5)_{0.0175}(TiO_2)_{0.035}(SiO_2)_{0.9475}$ (NHT, 250, 500 and 750°C). The range of oxides studied were the component oxides, the main binary mixtures of TiO_2 and SiO_2 and then a comparison with an Nb_2O_5 binary and the effect in a ternary composition. The samples with TiO_2 span the composition range where TiO_2 will form a homogeneous sample and where phase separation occurs.

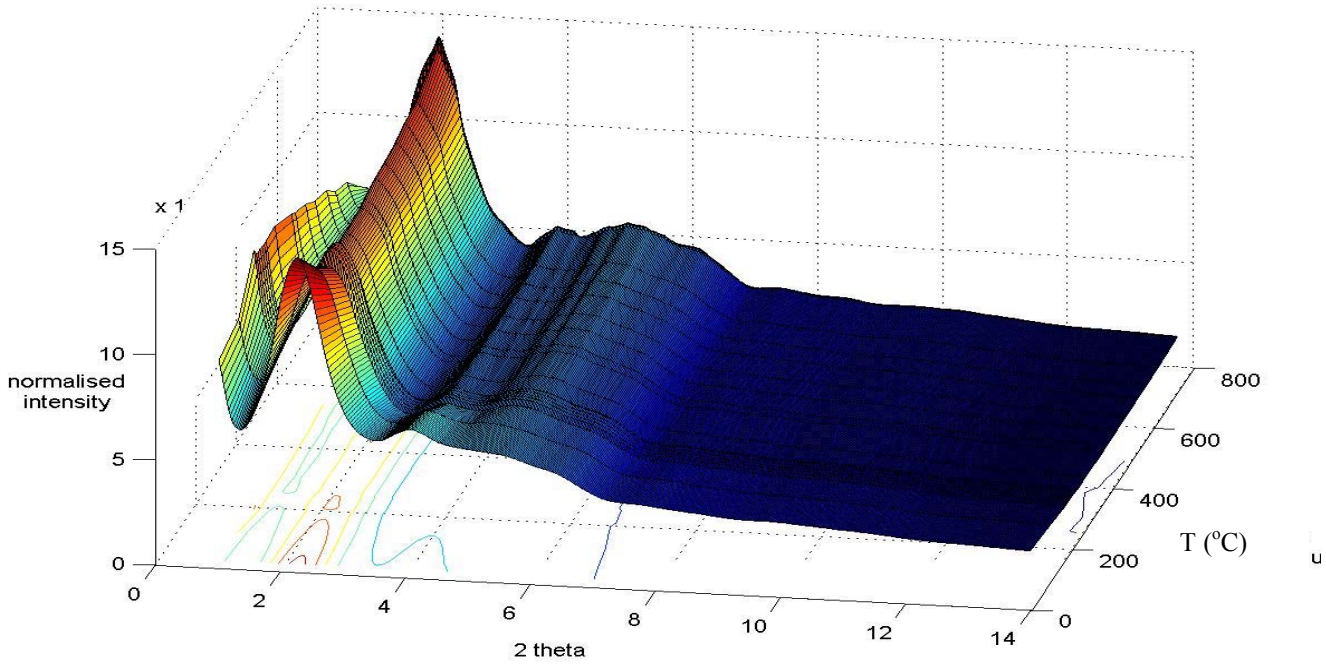

Figure 1. In situ diffraction pattern from $(TiO_2)_{0.3}(SiO_2)_{0.7}$ heated up to 750°C.

Some typical Q-space data is shown in Fig. 1 for a 30mol% TiO_2 sample. Although no detailed analysis has been carried out, the Q-space data showed that in the amorphous gels there were clear differences between the simple oxides and the binary mixtures, as well as the different binary mixtures. In the $(TiO_2)_{0.30}(SiO_2)_{0.70}$ which contains phase separated TiO_2, the crystallisation of this phase was readily picked up through the Bragg peaks formed. The data clearly then evolved with heat treatment. 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. Complete analysis will reveal some new insight into the structural evolution of these materials with temperature.

† Prof. G. Sankar, The Royal Institution, London is thanked for the loan of the furnace and his help in setting this experiment up.