SAXS WAXS Studies on Ceramics Glasses

G.N. Greaves[a], W. Bras[b], M. Oversluizen[b] and S.M. Clark[c]

[a]Department of Physics, University of Wales, Aberystwyth SY23 3BZ, United Kingdom

[b]DUBBLE CRG / ESRF, Netherlands Organisation for Scientific Research (NWO), PO Box 220, F38043 Grenoble Cedex France

[c]Synchrotron Radiation Source, Daresbury, Warrington, WA4 4AD, UK

New Cr X-ray Absorption Fine Structure (XAFS) data has been combined with the results of Small Angle X-ray Scattering (SAXS) and Wide Angle X-ray Scattering (WAXS) experiments to probe in detail the crystallisation mechanism in cordierite ($Mg_2Al_4Si_5O_{18}$) glass doped with 0.34 mol% Cr_2O_3. By direct comparison with chromo-aluminate spinels ($MgCr_{2x}Al_{2(1-x)}O_4$) Cr XAFS is used to determine the composition of the devitrified Cr species. This is identified as $MgCr_{0.18}Al_{1.82}O_4$, which can be directly related to the Cr content in the starting glass and as a result the total crystalline volume in the fully developed ceramic is predicted to be 4%. *In situ* WAXS also reveals the presence the spinel phase but in addition a silica-rich stuffed quartz phase. This grows independently of the spinel and is probably nucleated from the glass surface. From our knowledge of the compositions of both crystalline phases we are able to deduce that the SAXS contrast between the surrounding glass and the spinel crystallites is 30 times greater than that between the quartz crystallites and the glass matrix, and therefore dominates the measured scattered intensity and the SAXS invariant that is derived from it. As a consequence we are able to show that the spinel crystalline volume fraction inherent in the SAXS is in close agreement with the 4% value obtained from the Cr XAFS. Furthermore *in situ* SAXS reveals the gradual development of the spinel particle size and shape during heat treatment. This is conducted in the super-cooled region just above the glass transition temperature, T_g. By employing a two step annealing process nucleation can be separated from growth and from time-resolved SAXS measurements the alumino-chromate nanocrystals are found to be closely monodispersed. Over a total time course of 600min they grow from rough crystallites to smooth spherical particles of radius 21+/- 2nm, with a final density of 1.2 +/-0.4 10^{21} m^{-3}. As the process of ceramic formation takes place in the viscous melt, growth is indeed found to be limited by diffusion and is complete when all the Cr is exhausted. We use this comprehensive *in situ* study of crystallisation in cordierite glass to demonstrate the advantages of combining SAXS, WAXS and XAFS for probing the time-resolved chemistry - the microstructure and its development from nucleation sites – that underpins the processing of nanoparticle ceramics.