

The development of monodispersed alumino-chromate spinel nanoparticles in doped cordierite glass, studied by in situ X-ray small and wide angle scattering, and chromium X-ray spectroscopy

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Received 24 September 2004; received in revised form 26 May 2005

Available online 7 July 2005

Abstract

The crystallization mechanism in cordierite glass ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) doped with 0.34 mol% Cr_2O_3 has been studied in detail with in situ small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) and ex situ Cr X-ray absorption fine structure (XAFS). The crystalline component comprises an alumino-chromate spinel precipitating within the bulk together with an independent silica-rich stuffed quartz phase that appears to nucleate from the specimen surface. By employing a double heat treatment close to the glass transition, finely dispersed spherical crystallites of a alumino-chromate spinel are grown from Cr nucleating sites. The total crystallized volume of around 4% and the composition of the spinel, $\text{MgCr}_{0.18}\text{Al}_{1.82}\text{O}_4$, are directly related to the Cr content in the starting glass. Moreover, the alumino-chromate particles are found to be closely monodispersed partway through the crystallization process, growing from rough crystallites to smooth particles of radius $210 \pm 20 \text{ \AA}$, with a final bulk particle density of $1.21 \pm 0.4 \times 10^{15} \text{ cm}^{-3}$. Growth is limited by diffusion in the soft glass and is complete when all the available Cr is exhausted. The advantages of in situ combined scattering, diffraction and spectroscopy for probing the nanostructure, crystallography and local atomic structure in the formation of ceramics, the order in which events take place and the insights this gives in the underlying physical processes are stressed.

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PACS: 61.43.Fs; 61.46.+w; 81.05.Je; 81.10.Jt; 82.80.Ej; 61.10.Eq; 61.43.Hv; 64.70.Kb

1. Introduction

The growth of crystalline phases in an amorphous glass matrix can be either homogeneously nucleated, in which case the crystals are formed in a supersaturated

solution without the addition of nucleating agents, or, alternatively, heterogeneously nucleated from impurities like ZrO_2 , Cr_2O_3 , etc. previously dissolved into the quenched glass. Where homogeneous nucleation tends to produce coarse devitrification, heterogeneous nucleation will often result in optically transparent finely dispersed ceramics. Both the formation of nucleation sites as well as the subsequent crystal growth rate are temperature dependent. However, the optimum temperatures for these two processes are generally not the same and

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therefore many glass ceramic processes of commercial interest involve two or more temperature steps, where heat treatment close to the glass transition temperature, T_g , is used to generate nucleation sites and where subsequent treatment above T_g allows for crystalline growth [1]. If the nucleating sites are numerous the production of nanocrystals is likely. The solid state reaction kinetics of glass ceramic formation, however, is complicated by the interplay between a relatively large number of parameters (molecular vibration frequencies, interfacial energy, diffusion coefficients, etc.), most of which have either not been investigated comprehensively to date or their accuracy is insufficient for theoretical prediction. Therefore, the duration of heat treatment and the temperatures employed are mainly still empirically determined. The method most often adopted to study the morphology, is to subject glasses to a given heat treatment and to rapidly quench, in an effort to freeze in the ceramic structure without introducing any changes. The quenched material can then be studied ex situ by electron microscopy, optical spectroscopy, nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), etc. as well as by X-ray or neutron scattering techniques. As we will show in this work the development of crystalline structure after the nucleation stage and the accompanying microstructure, are ideally studied by in situ X-ray scattering techniques.

Cordierite ($Mg_2Al_4Si_5O_{18}$) ceramics – with their low average thermal expansion coefficient, high resistance to thermal shock, excellent chemical stability, low dielectric constant and optical transparency – find many applications. For instance as the honeycomb support for exhaust catalysts and there are promising new applications as substrates in electronic packaging and in the development of tunable lasers and solar concentrators [2–10]. A variety of preparation methodologies have been directed at synthesizing cordierite ceramics. These range from controlled devitrification [3,4,11–14] and low temperature sol–gel processes [15–17] to exotic techniques like colloidal reaction [5] and high temperature combustion sintering [18]. In this paper we comprehensively examine the synthesis of glass ceramics from solid specimens of cordierite glass, employing combinations of synchrotron radiation techniques [19–22]. These include in situ SAXS and WAXS and ex situ XAFS spectroscopy.

Previous experiments on powdered cordierite glass samples using differential scanning calorimetry (DSC) and Differential Thermal Analysis (DTA) showed that the crystallization kinetics depend on the particle size [27]. For glass particles <200 μm in size two crystallization exotherms were observed beyond the glass transition temperature of 805 °C, the first of which was identified with a metastable μ -cordierite (or stuffed quartz) phase and the second with an α -cordierite (or

spinel) phase. Avrami analysis techniques suggested that crystallization was mainly initiated by surface effects. On the other hand small angle neutron scattering (SANS) experiments on solid, non-powder samples doped with Cr as a nucleating agent indicated that the crystallites that initially precipitate in the amorphous cordierite matrix closely follow the behavior expected for spherical particle growth [14].

In the work described here monolithic Cr-doped cordierite glass has been the starting material. Preliminary results have established qualitatively the development of crystallization in the Cr environment using XAFS, identified the co-precipitation of a spinel and a stuffed quartz phase using in situ WAXS and establishing in parallel SAXS measurements the broad changes in microstructure from the annealed to the devitrified glass [23–26]. In this paper, we present new results of XAFS experiments on Cr-doped cordierite glass employing a double heat treatment and directly compare these with results from a range of alumino-chromate spinels. Earlier SAXS/WAXS results have been augmented with intermediate temperature heat treatments and the analysis reveals evidence for particle shape and monodispersity. Moreover, the crystalline volume fraction has been deduced from SAXS and can be directly related to that obtained from XAFS data. In particular, we are now able to report quantitative details of nucleation and growth at each stage of development of these fine-grained cordierite glass ceramics – the nature of the nucleating site, the size and shape of crystallites that are precipitated and their density and composition.

2. Experimental method

$Mg_2Al_4Si_5O_{18}$ cordierite glasses were produced by ball-milling reagent grade MgO , Al_2O_3 and SiO_2 together with 0.34 mol% Cr_2O_3 (0.8 wt%). The batch was melted at 1680 °C for 12 h, cast at 500 °C, re-melted for 4 h and finally recast and annealed at 700 °C for 2 h. The glass was dark green, indicative of dissolved Cr^{3+} . Monolithic specimens were cut and polished for in situ SAXS/WAXS measurements which were using an adapted Linkam THM1500 furnace heating element [28]. The small physical dimensions of this element allowed us to incorporate it in the vacuum chamber of our SAXS/WAXS camera. We estimate that temperature gradients at 1200 °C were not more than 40 °C over the whole sample. This was reduced considerably at lower temperatures. All samples were mounted in the furnace and given a pre-heat treatment at 875 °C for 4 h before the temperature was raised to the temperature at which the isothermal crystallization experiments were performed: 920, 940, 970 and 1040 °C. Ex situ room temperature XAFS measurements were made from bulk

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