Sintering of nanoscaled sodium-silicate glass ceramic

Rudolf Winter, Edgar R van Hoek, Malcolm P Coleman, Aled R Jones
Department of Physics, University of Wales Aberystwyth, Penglais, Aberystwyth SY23 3BZ, Wales, UK

Ball milling of polycrystalline quartz leads to structural disorder on both the atomic and the nanometre scale in a two-stage process depending on the milling time. In the first stage, cracks in the grains lead to the formation of wide-angle grain boundaries, increasing the fraction of the material located in disordered interface sites. In a second step, the nanocrystallites are progressively shock-amorphised, forming a glassy structure comparable to that found usually in glass quenched under high pressure. The effect of the first stage is reversible by annealing at moderate temperature, while the amorphisation is irreversible at temperatures below the glass transition temperature.

The combination of NMR spectroscopy, diffraction, and small-angle scattering allows to monitor both the atomic structure (connectivity of SiO_4 tetrahedra revealed by NMR), granularity (size of crystallites as seen by diffraction) and agglomeration (small-angle scattering from aggregates of grains independent of their atomic structure).

The sintering behaviour of the nanocrystalline silica samples with Na_2O is compared with that of normal polycrystalline glass batches of the same composition. The preference of Na ions in attacking the amorphised intergranular regions is shown by NMR. In the initial stage of the reaction, agglomeration of silica grains (both in nanocrystalline and in nanoscaled amorphised samples) is facilitated by surface reaction with the modifier, leading to an increase of the agglomerate particle size as extracted from small-angle data. At the same time, local ordering and the precipitation of sodium silicates is observed in ^{23}Na and ^{29}Si NMR spectra.

Introduction

The response to mechanical stresses of nanocrstalline materials is governed by their structure on various length scales. Ordered, crystalline grains are embedded in a disordered matrix. The matrix itself can be an inhomogeneous arrangement of atoms, *e.g.* a gradient structure[1] or an entirely amorphous phase. The interface structure determines how strong grains are bonded together and hence how stress is distributed and relieved in the ceramic. This is of particular importance to the mechanism of crack propagation.

Experimental

Coarse-grained polycrystalline quartz was ground in a double SPEX 8000 high-energy ball-mill for up to 128 hours. Corundum vials and one 8mm corundum ball were used to prepare approximately 2g of nanoscaled silica per batch. The weight of the sample and ball were recorded before and after each run. There is no indication that noticeable amounts of container or ball material are abraded and mixed into the samples; no alumina reflections are found in the diffractograms either. Ex-situ annealing and reactive sintering experiments were carried out in a Carbolite vertical tube furnace. For reactive sintering, either coarse-grained Na_2O (Aldrich) or micron-sized Na_2CO_3 was used.

^{29}Si magic-angle spinning (MAS) NMR spectra were obtained on a Bruker Avance DSX 400 spectrometer with a Bruker 9.4T cryomagnet. The sample powder was placed inside standard 4mm ZrO_2 MAS rotors which were spun at a rate of 5kHz in a standard Bruker MAS probe. While the $\pi/2$ pulse length is 1.4μs, a pulse angle of approximately 30° was typically used, with a spectral width of typically 780kHz, while 4096 data points were

recorded per free induction decay. The recycling delay was 400s since the absence of paramagnetic centres accounts for an unusually long relaxation time. 140 scans were needed to achieve the signal-to-noise ratio sufficient for the analysis undertaken in this study.

In-situ x-ray diffraction experiments were carried out on an Enraf Nonius Cu rotating anode diffractometer at the Materials Support Laboratory at Daresbury. This diffractometer operates in transmission geometry and records a scattering angular range from ~5°(2θ) to ~80°(2θ) simultaneously using a linear detector. The samples were free-standing pellets of 13mm diameter and approximately 250μm thickness. These were prepared with a uniaxial die press at a load of 3 metric tons. Typically, 2min scans were recorded while the temperature was increased at a rate of 2K/min. Angle-dependent background arising from the transmission geometry was subtracted prior to analysis.

Results

The size of crystalline regions with undistorted crystal structure can be derived from the broadening of a diffraction line. The Scherrer formula[2] relates the width of the broadened line with the instrumental line width and the Bragg angle. For ball-milled quartz, we have shown that the diffraction line broadens after 128 hours of milling to such an extent that no crystalline domains can be identified any longer[3]. In this contribution, an intermediate sample (prepared by 32 hours of ball-milling) and the final 128-hour product are studied.

A ^{29}Si NMR spectrum of the 32-hour sample is shown in Fig.1, along with a coarse-grained and a conventional amorphous reference. The line consists of two superimposed Gaussian contributions with different width and centre frequency. The chemical shift of the narrower component corresponds to the shift of both the coarse-grained and the amorphous reference materials. The line width of this component is 4.1ppm, *i.e.* between the amorphous (16ppm) and the coarse-grained (0.6ppm) components. Other intermediate samples with grinding times of at least 8 hours show the same splitting, with the relative contribution of the broad component successively increasing[3]. In the 128-hour sample, the narrow component has entirely vanished, and only one shifted, broad component persists.

In-situ x-ray diffraction experiments were carried out in order to establish whether the structural changes incurred by ball milling are reversible. Four scans obtained during a heating run at room temperature, ~240°C, ~450°C, and 1025°C are compared in Fig. 2. While there is little change between ambient and 240°C or between 450°C and 1025°C, the structure becomes more dynamic in the intermediate range. The shoulder near the quartz (101) line increases in intensity and narrows sufficiently to be identifiable as a diffraction line. The broad amorphous background narrows slightly also and shifts to smaller angles. Even after 2 hours at 1025°C, no further change is observed, and no crystalline diffraction pattern is restored.

The reactive sintering of the amorphised 128-hour sample with Na_2O was traced by ^{29}Si NMR (not shown owing to limited space). Spectra recorded after heating up to 300°C are identical, showing only the characteristic shifted broad silica line described earlier. Spectra taken after annealing at 350°C or higher, on the other hand, contain two additional broad lines centred at -70ppm and -80.5ppm, respectively. There are no further changes to the spectrum at temperatures up to 550°C. On the other hand, the spectrum of a coarse-grained

batch after reactive sintering at 850°C has no remaining SiO_2 contribution, a narrow crystalline sodium silicate line, and a small, broad, amorphous component near the foot of the crystalline sodium silicate line.

Discussion

The broadening of the NMR line with progressive grinding time indicates that the local order at the atomic level is decreased. This is due to the increased fraction of atoms in disordered sites near the surface of grains and in wide-angle grain boundaries. A narrow spike, which is attributed to the bulk atoms, persists in the spectra even at long milling times. After more than 8 hours of grinding, a shifted, broad component appears and increases in relative intensity as grinding progresses. This is identified as pressure-amorphised interface material, since its chemical shift corresponds well with literature data of glass quenched under pressure[4]. After 128 hours of milling, the sample is almost completely amorphised. The diffractograms allow to distinguish the nanocrystalline and amorphous components as a broadened quartz (101) Bragg line and a broad amorphous background. The amorphised components remain amorphous, but relax slightly between 240°C and 450°C. At the same time, the (101) peak increases slightly, indicating that the crystalline order of the nanocrystalline component is retained. The reactive sintering experiments show that the pressure-amorphised samples react much faster and at considerably lower temperature (below 350°C) than coarse-grained batches[5], and that disordered modifications of both sodium metasilicate and sodium disilicate are formed as can be seen from the two broadened NMR lines around 70 and 80ppm.

Conclusion

With ^{29}Si MAS NMR and diffraction, we have shown that the mechanical stress induced in quartz by ball milling causes a two-stage structural disintegration. Initially, grains are split into smaller grains leading to a nanocrystalline structure with a non-crystalline interface component. Subsequently, the grains undergo pressure-induced amorphisation. The second stage is irreversible by annealing up to 1025°C. The reactivity with Na_2O is of pressure-amorphised nanoscaled silica is considerably enhanced compared with its coarse-grained counterpart, and the amorphised fraction of the material reacts completely at temperatures below 350°C.

Acknowledgement. We would like to thank Ray Jones, Materials Support Laboratory, CLRC Daresbury Laboratory, for the opportunity to use their diffractometers. Financial support from the Engineering and Physical Sciences Research Council, the University of Wales Research Fund, and Pilkington plc is also acknowledged.

Fig.1: ^{29}Si MAS NMR spectra of ball-milled (32 hours) silica particles. The broken lines indicate the two components of a double-Gaussian fit (thin line). For comparison, spectra of amorphous silica (top, with single-Gaussian fit) and of coarse-grained quartz (not ground, bottom) are shown.

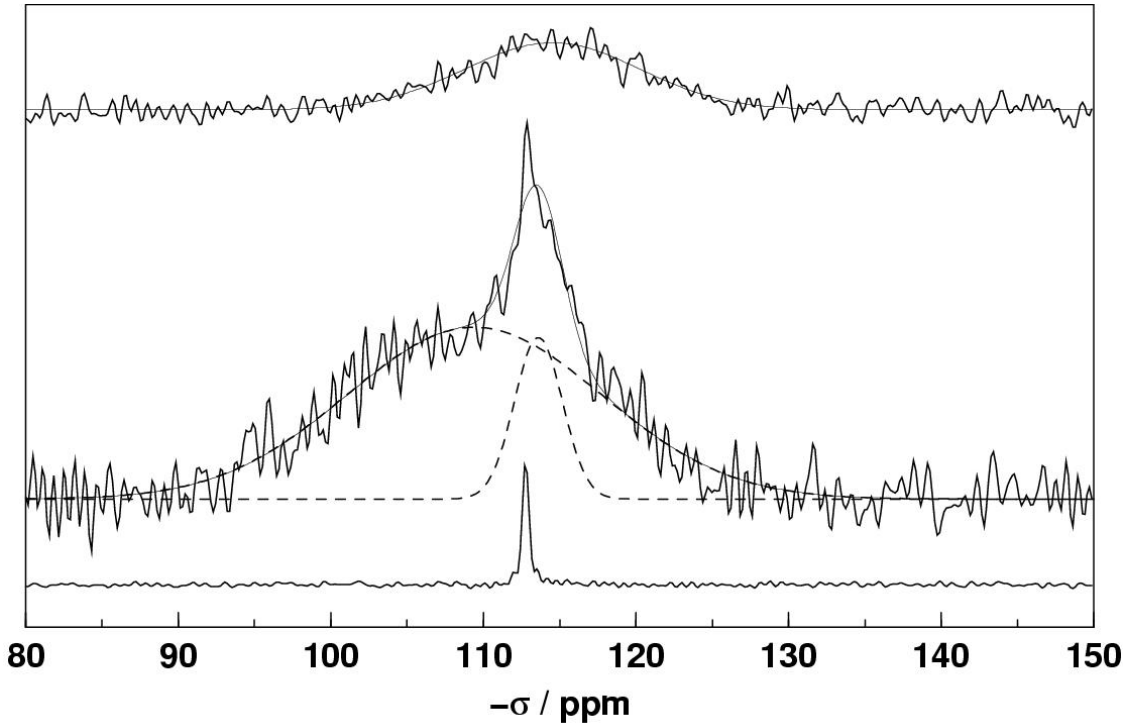
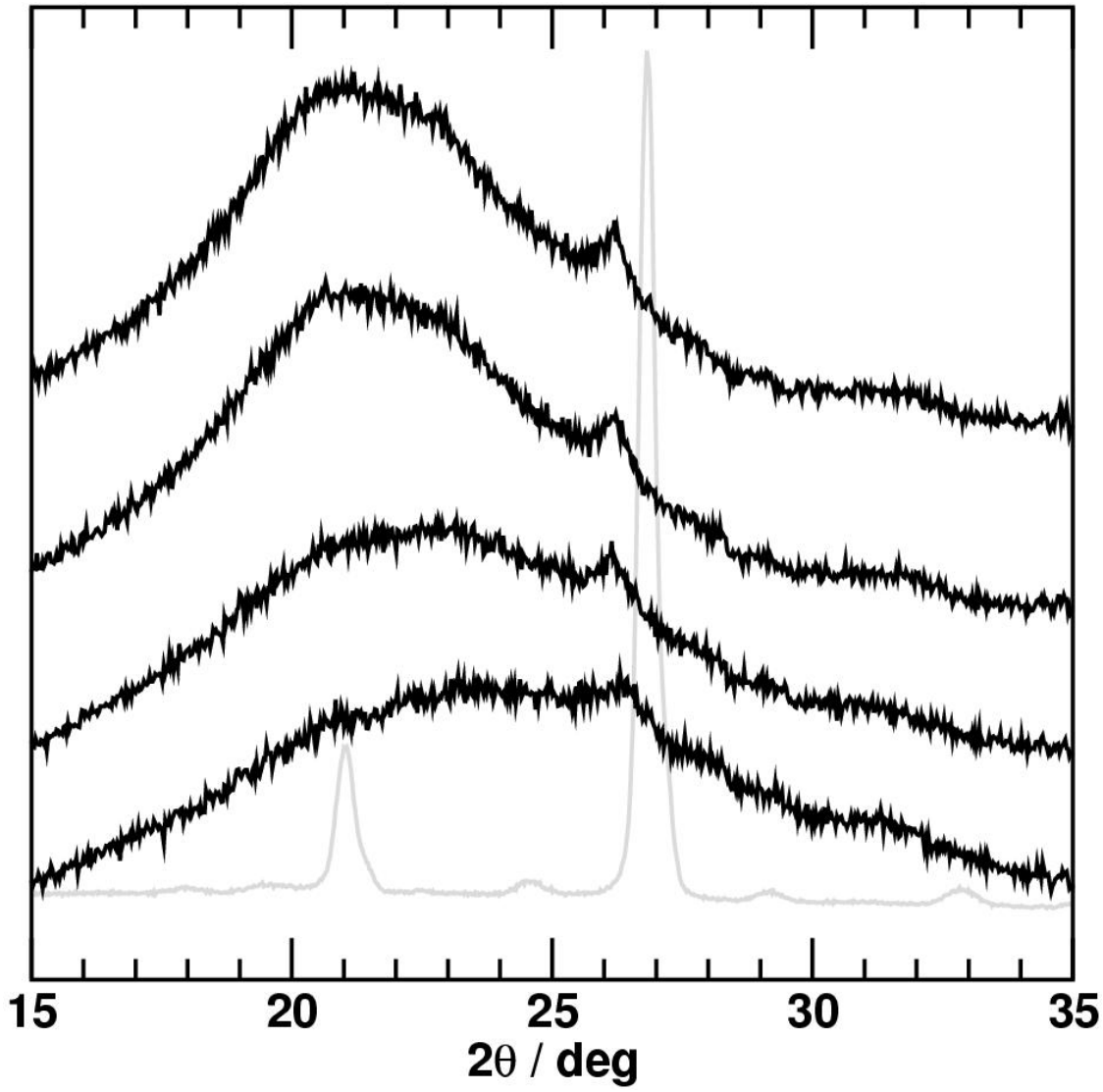


Fig.2: Diffractograms of ball-milled (128 hours) silica after heat treatment at a rate of 15K/min. Bottom to top: before annealing, at ~240°C, at ~450°C, and at 1025°C. The grey curve displayed in the background is the diffractogram of coarse-grained quartz with its (100) and (101) reflections, for comparison.



---

[1] R Winter and P Heitjans, J Phys Chem B **105**, p. 6108 (2001).

[2] HP Klug, LP Alexander, *X-ray Diffraction Procedures* (Wiley, New York, 1974).

[3] ER van Hoek and R Winter, Phys Chem Glass. (In press)

[4] PS Fiske, WJ Nellis, Z Xu and JF Stebbins, Am Mineral **83**, p. 1285 (1998).

[5] AR Jones, R Winter, GN Greaves, IH Smith in *these proceedings*.