CHEMICAL SCIENCE

A Novel Form of Topologically Ordered Amorphous Silica obtained from Collapsed Silicalite at High Pressure

Pressure-induced amorphization of open-structured solids provides a distinct way to synthesize amorphous materials with respect to glass formation by standard temperature quenching of liquids. This opens the route to prepare new amorphous forms with different entropies and intermediate range structures along with novel physical and mechanical properties (i.e. lower fragility etc.) [1]. Aluminosilicate and siliceous zeolites, built up of corner-sharing Si(Al)O$_4$ tetrahedra, are examples of such low-density, porous, open-structured materials, which undergo pressure-induced amorphization. The large volume collapse during the amorphization of these materials may be of considerable interest for new applications in shock wave absorption [2]. The present study focuses on the determination of the structure of the new form of amorphous silica obtained from the pressure-induced amorphization of the essentially pure SiO$_2$ zeolite, silicalite-1-F by Reverse Monte Carlo (RMC) refinement of total X-ray scattering data.

Calcined silicalite-1-F (SOMEZ, France) was compressed to 20 GPa in a Walker-type multi-anvil apparatus in order to prepare the amorphous form [3]. High energy total X-ray scattering data from the recovered amorphous sample (Fig. 1), were obtained using the two axis diffractometer and 61.6 keV X-rays at beamline **BL04B2** [4] and correspond to a characteristic broad-featured pattern of an amorphous material. The pair distribution function was obtained in the form of the total correlation function $T(r)$ (Fig. 2) by direct Fourier transformation of the total scattering data. Based on these data, the Si-O bond length of 1.62 Å is only slightly greater than that of normal silica glass [5]. It can be noted that in amorphous silicalite-1-F, the Si-Si correlation is very broad and is

characterized by a double peak. This is an indication of strong local distortions of the intertetrahedral Si-O-Si bond angles.

RMC modeling was used to determine the structure of amorphous silicalite-1-F (Fig. 3). The starting RMC model was obtained by progressively reducing the volume of a 2×2×4 orthorhombic supercell of the silicalite structure while randomly moving atoms to maintain local tetrahedral geometry and network topology. Once the model had attained the measured pressure amorphized sample density (model size 35.344 × 34.726 × 46.244 Å^3), the model was further refined using RMC protocols by minimizing the difference between the $S(Q)$ calculated from the model and the experimental $S(Q)$ (Fig. 1). The model $S(Q)$ shows no Bragg peaks with no long-range oscillations in the partial radial distribution functions, $g_{ij}(r)$ [3], showing that the model is truly amorphous, despite originating from the low-pressure crystal structure.

It can be seen from the RMC models that the amorphization and the attendant loss of periodicity is linked to the collapse of the pores in the silicalite structure, which occurs through large random local changes in Si-O-Si bond angles based on the strong broadening of the Si-Si correlation. The strong reduction in Si-Si-Si and Si-O-Si bond angles with respect to silica glass [3,5] and the presence of a double peak in the Si-Si correlation (Fig. 2) are indicative of highly strained configurations on different length scales, respectively; in the ring edges and locally in the Si-O-Si angles around the oxygen atoms. This intertetrahedral Si-O-Si angle distribution in amorphized silicalite-1-F is centered around 125° rather than 145-150° and is much broader than in silica glass [3,5].
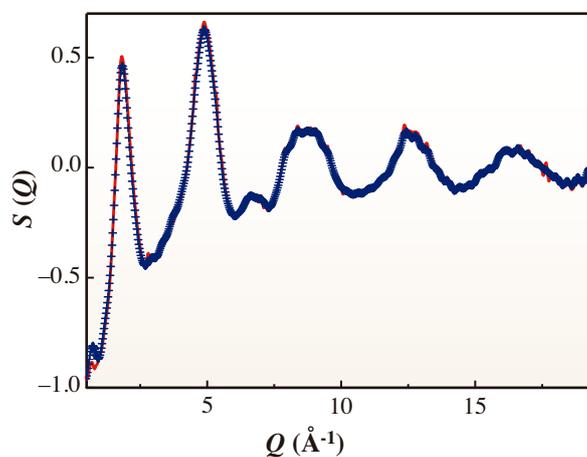

Fig. 1. X-ray total structure factor $S(Q)$ of pressure-amorphized silicalite-1-F (+) and calculated $S(Q)$ from the RMC refined model (red solid line).

There are small voids corresponding in particular to the collapsed 5, 6 and 10 membered rings (MRs) of the initial crystalline structure. The present experimental results and RMC model indicate that the amorphization can take place while still retaining remnant periodicity and without a major change in ring statistics. The ring statistics in pressure-amorphized silicalite-1-F found in Fig. 3 can be explained by an extraordinary "topologically ordered" structure (i.e. still retaining the initial chemical bonds and connectivity); amorphous materials usually exhibit "topologically disordered" structures, in which ring statistics are very broad and very different from the corresponding crystal phase. Inspection of the silica glass model (Fig. 3) shows that voids are also present, but distributed in a random manner, more a characteristic of a quenched liquid.

In conclusion, the present results based on the total X-ray scattering study of a novel form of silica recovered from high-pressure conditions emphasizes the difference between the structural topology of amorphous silica obtained by temperature-induced vitrification and that obtained by pressure-induced amorphization of a crystalline material, the siliceous zeolite silicalite-1-F. The latter is shown to retain the basic topology (i.e. chemical bonds and connectivity) of the initial crystalline phase, but with strong geometrical distortions. The same process in more complex aluminosilicate zeolites will, in addition, also conserve the chemical order of the crystal leading to an amorphous material, which is topologically and chemically ordered. This opens the route to prepare new amorphous materials with different intermediate-range structures, a lower entropy with respect to a standard glass, distinct physical and mechanical properties, eventually approaching those of an "ordered" or "perfect" glass. The structural collapse, in particular around the empty pores, in this material leads to a high degree of densification providing a mechanism for shock wave absorption.
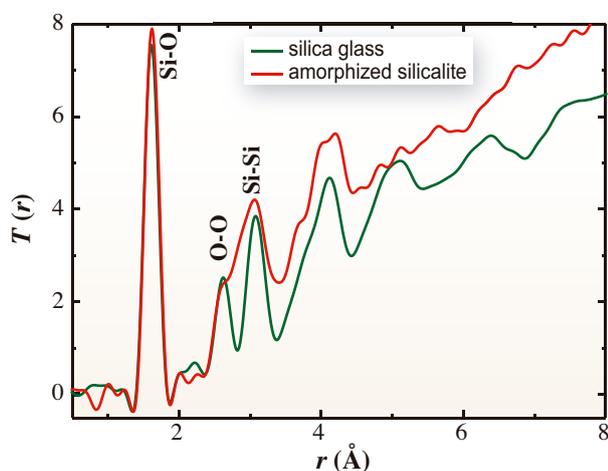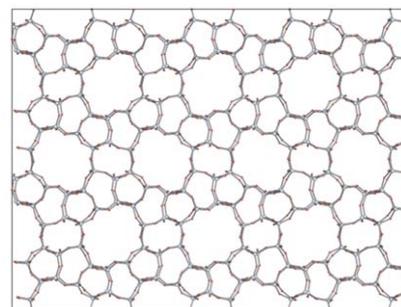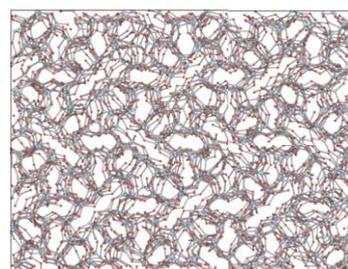

Silicalite-1-F

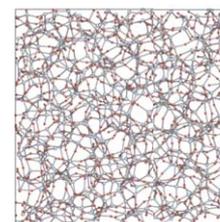**Pressure-Amorphized Silicalite-1-F**

Silica Glass

Fig. 3. The structure of silicalite-1-F projected along the [010] direction and RMC models of pressure amorphized silicalite-1-F and silica glass [5].

Fig. 2. Total correlation functions $T(r)$ of pressure-amorphized silicalite and silica glass.

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