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Local densification of a single micron sized silica sphere by uniaxial compression

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ABSTRACT

In situ uniaxial compression experiments are performed inside a SEM for compact vitreous SiO_2 microparticles. The local structure of a plastically deformed particle is assessed spatially resolved *ex situ* by micro Raman spectroscopy. By application of a density calibration curve a maximum silica network densification of 11% is found only in zones slightly below the circular contact areas. The particle's inner regions remain unaffected. Conclusions from geometric considerations indicate that the observed plasticity during compression is completely accommodated by local densification.

Commonly, silica glasses are perceived as brittle materials. However, at length scales beneath some microns and under very high pressures, glasses can be permanently deformed [1–3]. Plastic deformation of glasses is associated with volume conservative shear flows and permanent densification of the network [4]. Densification is accommodated, at the expense of the free molar volume, by rearrangements of the glass network on the intermediate structural level (polyamorphic transition) [5]. The free molar volume which varies with the atomic packing density and the Poisson ratio has been identified as a key parameter for the possible maximum densification [6]: highly polymerized structures (open networks with low atomic packing densities and Poisson ratios) can be greatly densified; the overall achievable densification is significantly reduced for depolymerized glasses (higher atomic packing densities and Poisson ratios) [6]. The densification increases gradually with applied pressure between a lower elastic pressure limit and an upper saturation pressure. For the hydrostatic compression of silica the lower threshold is ~10 GPa; saturation occurs at ~25 GPa and at a densification of 21% [7]. Structural compaction can also be induced by irradiation from various sources (including electrons); the maximum densification is limited to 3% [8–12]. The structure of glasses at intermediate length scales can be studied by Raman spectroscopy. Accurate links between the permanent densification from pressure compaction and the corresponding Raman spectra have been established [13,14]. During hydrostatic compression of glasses only structural compaction is observed. For more complex loading situations (e.g. indentation or uniaxial compression) plastic deformation might be accommodated by a combination of volume conservative shear flows and pressure compaction of the silica network. The relative contributions of the aforementioned mechanisms depend on the actual stress in the material. Clearly, the confined volumes encountered e.g. in nanoindentation behave differently than particles with free surface – an example for the deconfinement of particles has recently been given e.g. for silicon [15]. Different (particle) geometries might thus be an ideal testing case for the currently available constituent models describing glass deformation [16,17]. However, mainly the local densification induced by indentation is being studied [13,17,18]. Although well-established e.g. for metallic glasses, pillar testing has hardly been employed for silica glasses. In the studies by Lacroix et al. [19,20] the permanent deformation of compressed silica pillars was completely attributed to shear flows; a direct characterization of the resulting glass structure after compression is not given. Several recent studies evidence a high plasticity of micron sized spherical silica particles [3,21,22]. However, the local structure of the compressed particles has not been characterized and the underlying deformation modes are still unknown.

Within this contribution, we study the local densification of a plastically deformed single vitreous silica microsphere. Uniaxial compression of the single silica particle is performed by a SEM

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supported *in situ* manipulator [23]. After a transfer and alignment procedure, *ex situ* Raman spectroscopy gives access to the local structure of the deformed glass particle [13]: significant densification (about 11%) is found near the deformed contacts; the inner parts of the particle are essentially non-densified. From geometric considerations we conclude that the observed plasticity for the particle is indeed fully accommodated by densification beneath the flattened contact areas.

Vitreous silica spheres were obtained by a heat-treatment (36 h, 1000 °C) of sol–gel Stöber silica (sicastar® plain, micromod Partikeltechnologie): in course of the heat-treatment structurally bound water is removed from the sol–gel particles and cross-linking of the silica network is enhanced – dense vitreous silica particles are thus obtained [2,24]. Particle compression in the SEM supported micromanipulator [23] was performed between a diamond flat punch indenter and a (100) silicon wafer. The displacement rate of the indenter was 200 nm/s; force- and deformation resolutions were 1–10 μN and 5 nm. During compression the electron beam was blanked to exclude effects from electron beam-induced superplasticity [21,22]. For structural characterization a micro Raman setup (LabRAM HR-Evolution, Horiba Scientific, Nd-YAG laser source $\lambda = 532$ nm) was used. Spectra were collected (100–1000 cm^{-1}; resolution 0.5 cm^{-1}) by a 100-fold magnification objective (numerical aperture NA 0.9). The grating was 1800 mm^{-1}, slit and hole were set to 100 μm. Acquisition times per spectrum were 120 s for single particle measurements or 800 s during the line mapping. Laser power in the sample plane was below 2.7 mW. Repetitive measurements ensured that no changes occurred due to the laser power or heating.

Electron irradiation can induce structural changes in silica [8–12]. Accordingly, effects from unavoidable electron irradiation have to be minimized during uniaxial compression. To identify suitable conditions, silica spheres (diameter $x = 1.3$ μm) were exposed to typical SEM imaging conditions whereby the exposure times exceeded the handling times during compression and transfer. *Ex situ* Raman spectra of the irradiated particles are given in Fig. 1. Several features reported for vitreous silica are found in the Raman shift range (100–1000 cm^{-1}) [25–28]: the main band at around 440 cm^{-1} is attributed to symmetric stretching modes of Si–O–Si bonds. Exact band position and shape depend on the distributions of the bond angles and lengths. The bands at 488 cm^{-1} and 602 cm^{-1} ("defect bands" D1 and D2) are symmetric stretching modes of planar 4-fold and 3-fold Si–O rings (relative intensities are linked to their occurrence). The broad band at 800 cm^{-1} is a ω3 mode with little transverse optical–longitudinal optical (TO–LO) splitting. Upon densification (induced by the electron beam or high pressures) the main band narrows and shifts to larger wavenumbers. Moreover, the relative intensity of the D2 band increases. Upon using a non-exposed particle as reference (Fig. 1 (bottom)), it is evident that no structural changes occur at low dose and energy conditions (Fig. 1 (middle), 2 kV, 10 μm aperture). The aforementioned structural changes are clearly noticeable in the Raman spectrum (Fig. 1, top) of the particle irradiated at high energy and dose (10 kV, 30 μm aperture). For the *in situ* compression experiments low dose conditions were assured.

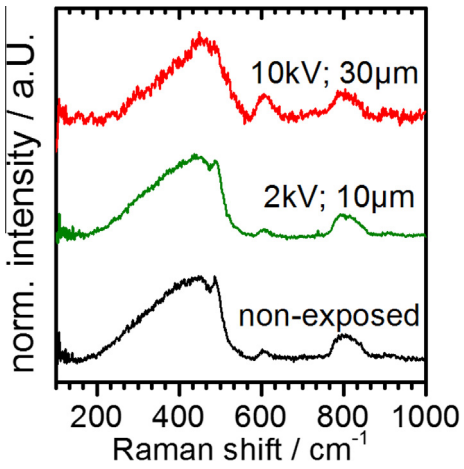

Fig. 1. Raman spectra for individual silica particles ($x = 1.3$ μm) exposed to different SEM imaging conditions; exposure times exceed handling times in the compression experiments. A non-exposed particle is given as reference (bottom).

A schematic drawing of the micromanipulation device is given in Fig. 2A. The device consists of an upper part (Nanomanipulator) and a lower part (Load cell): the Nanomanipulator is a piezoelectric tripod scanner fixed to a coarse positioning stage; it performs all movements of the attached diamond flat punch indenter. By the coarse positioning stage the flat punch can be moved several centimeters in plane of the sample. The piezoelectric scanner is used to perform the compression; strain gauges measure the elongation of the piezoelectric stacks. The sample (single particles on a small piece of silicon) is supported by the Load cell – a spring system of precisely known spring constant. Forces are calculated from spring deflection; sample deformation is the difference between spring deflection and elongation of the piezoelectric stack [23].

In Fig. 2B engineering stress σ (force normalized to initial cross section) vs engineering strain ε (deformation normalized to initial diameter) data from uniaxial compression of a silica microsphere ($x = 4.17$ μm) is given. Conclusions from the data are: firstly, the remaining deformation after unloading (engineering strain around 10%) indicates plastic deformation of the sphere. Secondly, cracking can be excluded due to the smooth curve progression. By applying theoretical models to the loading slope mechanical data can be derived [29]: from Hertzian fitting a Young's modulus of 76 GPa is estimated (5% strain as fitting limit) [30]. From the CEB model applied to the linear elastic–plastic regime a hardness of 13 GPa is obtained [31]. The elastic–plastic-loading index (EPL) is evaluated to 0.48, i.e. half of the introduced mechanical energy is elastically recovered upon unloading [32]. Further experiments indicated that particle fracture occurs at a deformation of 25–30%. Overall, the obtained mechanical data are in excellent agreement with our previously reported results [3]. The compression experiment was performed on mechanically stiff (100) silicon. However, for Raman characterization of the compressed particle silicon is unsuitable due to overlapping spectral features and a significantly higher scattering power.

By a *particle transfer and alignment procedure* the particle is deposited onto a steel foil – meaningful Raman measurements are possible. The procedure is exemplified in Fig. 3 (to minimize electron irradiation, images from transfer of another particle are displayed): after the uniaxial compression experiment (A), the compressed particle is adhered to the side of the diamond flat punch indenter (B). To this end, the particle is carefully contacted from the side. The adhered particle is lifted (C) and transferred to the adjacent steel foil (D). Finally, the particle is deposited (E) and rotated by the tip into a suitable position (F); the contact between tip and particle is loosened by fast tip movements. The exact orientation of the contact zones is obtained from subsequent top view SEM images (Fig. 4A). *Ex situ* micro Raman spectra from the compressed sphere were collected along the arrow indicated in Fig. 4A. Quantification of densification by means of a Raman parameter σ^{Raman} has been proposed for vitreous silica [14]. First, a straight baseline is subtracted between the main band ($\tilde{\nu}_1 = 180\ cm^{-1}$) and the D2 line ($\tilde{\nu}_2 = 680\ cm^{-1}$). The