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In situ mechanical quenching of nanoscale silica spheres in the transmission electron microscope

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ABSTRACT

A novel approach for *in situ* mechanical quenching experiments of nanoscale silica spheres inside the transmission electron microscope is presented. Electron irradiation is used to mimic temperature by mediating plastic flow. Quenching under load is achieved by switching-off the electron beam. This is employed in different loading scenarios. Complementary finite element method simulations underline a change of Young's modulus, which strongly depends on the interplay of electron irradiation and mechanical load. We attribute the reduction in Young's modulus to compression-induced structural anisotropy which is frozen-in by rapid quenching and propose a model on how structural anisotropy develops in nanoscale silica.

The mechanical and physical properties of glasses depend on both, the nature of the bonding and their topology, including the near, intermediate and long range order [1]. Traditionally, the structure of glasses is modified through changes in the chemical composition [2]. It is, however, also well-known that the application of mechanical loads during cooling of melts can lead to changes in network topology and, subsequently, in the properties of glasses [3–5]. In particular, quenching under uniaxial load can lead to anisotropic features, a phenomenon which has been attributed to flow-induced anisotropy. The existence of deformation-induced structural anisotropy has been shown experimentally after uniaxial compression of silica [6], borosilicate [7], aluminoborosilicate [8], alkali silicate [9], as well as bulk metallic glasses (BMG) [10–12]. Tensile deformation was shown to lead to structural anisotropy in silica glass fibers [13] and various metaphosphate glasses [14,15]. Furthermore, molecular dynamics simulations point to the possibility that structural anisotropy can also be introduced in amorphous silica at room temperature (RT) by plastic deformation under shear [16]. Although increases in the tensile strengths and Young's moduli (E) of glass fibers have been attributed to structural anisotropy [17,18], and compression experiments on BMG showed that structural anisotropy leads to anisotropic elastic constants [12], a detailed analysis of the influence of structural anisotropy on mechanical properties of amorphous materials is currently missing.

Here we present a novel approach to perform athermal mechanical quenching experiments in a transmission electron microscope (TEM) and analyze its influence on the mechanical properties. We use the compression of nanoscale silica spheres as an example, since prior studies have demonstrated that electron beam (e-beam) irradiation can be exploited to induce ductility and superplasticity in these spheres [19–23]. E-beam induced plastic flow has also been shown in silica wires [19,24]. The proposed *in situ* TEM mechanical quenching process is therefore expected to be applicable also to other silica glass nanostructures, and probably oxide glasses in general. A simple mechanistic model based on the development of structural anisotropy is suggested to explain the changes in the elastic response after mechanical quenching.

In situ compression experiments on monodisperse silica spheres (Stöber-Fink-Bohn (SFB)-type silica [25,26]) were performed in the TEM under displacement control by using the PI95 TEM Picoindenter® (Hysitron Inc., USA) [27], equipped with a 1.5 μm wide diamond flat punch. The Picoindenter was used inside of a Philips CM30 TWIN/STEM (FEI Company, Netherlands), which is equipped with a LaB_6 filament and operated at 300 kV acceleration voltage. Since the e-beam irradiation has a strong impact on the mechanical behavior of silica spheres in the TEM, a proper calibration and knowledge of the e-beam current density inside the TEM is required (see more details in Ref. [21]). Finite element method (FEM) simulations have been used to translate the load–displacement (L–D) curves into intrinsic material properties according to our previous approach [21]. This type of

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approach using complementing experiments with FEM simulations was reported previously for nanoindentation of amorphous silica [28], amorphous silica micropillar compression [29,30] and indentation of window glass [31]. In the present work the software Abaqus 6.13 [32] was used to account for the concurrent elastic and plastic deformation and the resulting geometrical bounds in a FEM model, in which the material is simplified to follow an elastic/ideally plastic behavior yielding three material parameters: E, Poisson ratio (ν) and yield stress (σ_{yield}). For simplicity, our FEM model does not consider effects such as densification and/or friction, which occur during the experiments. More details on FEM simulations are provided in supporting information S1.

In the present work three types of *in situ* compression experiments were performed in the TEM, which are shown in Fig. 1 for three representative silica spheres with a comparable initial size. In addition, *in situ* compression experiments on silica spheres were conducted under e-beam irradiation, since this data is needed for FEM modeling (see supporting information S1 and the related *in situ* movie M1). Prior to all *in situ* compression experiments the silica spheres have been irradiated with an identical beam current density of 9×10^{-2} A cm^{-2} for 60 s (e-beam treatment). After this e-beam treatment the silica spheres exhibited a shrinkage of 15–18% [21]. In experiment (A) the silica sphere was loaded and unloaded at beam-off conditions. This experiment was published in our previous work [21] and is shown here again for direct comparison. In experiment (B), which we refer to as quenching under load, the silica sphere was compressed under e-beam irradiation, while the e-beam was switched-off at half of the loading ramp. In a classical quenching experiment, the specimen is first heated up to a high temperature (in the case of glasses well above the glass transition temperature) and quenched rapidly down to RT, while the final glass network structure is dictated by the quenching rate [4]. In our approach the term "quenching" is used in a different manner: the silica sphere is first irradiated with electrons (while staying at/near RT [19]), after which the e-beam is switched off (quenching point) during loading and the pre-stressed, plastically deforming silica network structure is instantaneously "frozen-in". Further loading and unloading of the sphere was then performed at beam-off conditions. In experiment (C), which we refer to as quenching after relaxation, the silica sphere was first compressed under e-beam irradiation, followed by a holding segment, allowing for relaxation of stresses. At half of the holding segment the e-beam is switched off. After completion of the holding segment the silica sphere is loaded and unloaded at beam-off conditions. For experiments (B) and (C) *in situ* movies M2 and M3 are provided in the supporting information, respectively.

As can be seen in the L–D response, the silica sphere from experiment (A) exhibits an elastic-plastic deformation behavior, while it did not fracture during and/or after compression. The amount of plastic deformation is, however, less pronounced in comparison to the beam-on compression experiment (see supporting information S1 and *in situ* movie M1). This is not surprising, as the e-beam is well-known to support plasticity of nanoscale silica [19–23]. However, even without e-beam support, plasticity was reported to occur in amorphous silica on macroscopic scale [33], microscale amorphous silica pillars [29], and nanoscale silica spheres [19–21,34,35] and wires [36], which agrees well with the observations in experiment (A). In experiment (B), first, a continuous increase of the load with gradual compression of the silica sphere was observed. Starting from the quenching point the slope of the load signal drastically increased and followed a linear trend. During the unloading segment of the L–D curve the load followed this path until reaching a value of zero, confirming pure elastic behavior of the silica sphere starting from the quenching point until the end of the experiment. In experiment (C) the silica sphere exhibits a similar deformation behavior during beam-on compression in comparison to the sphere

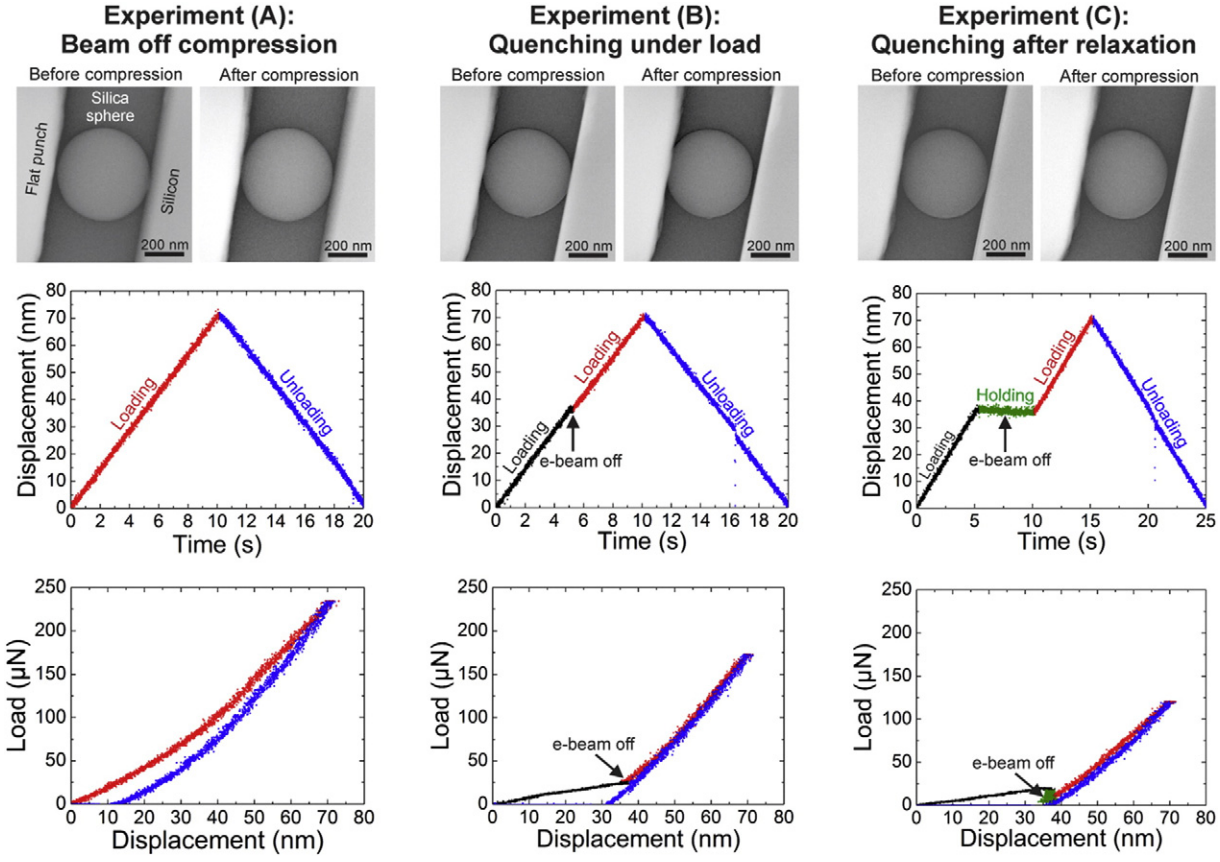

Fig. 1. *In situ* nanomechanical data of nanoscale silica spheres compressed in the TEM. In experiment (A) the silica sphere was compressed at beam-off conditions (taken and adapted from our previous work [21]). Experiment (B) shows the quenching under load approach, while experiment (C) shows the quenching after relaxation approach achieved in the TEM.