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Towards damage resistant Al_2O_3 – SiO_2 glasses with structural and chemical heterogeneities through consolidation of glassy nanoparticles

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ABSTRACT

Al_2O_3 – SiO_2 binary glasses with structural and chemical heterogeneities were prepared by consolidating glassy nanoparticles with different compositions using classical molecular dynamics simulations. Consolidated glasses show both excellent ductility and enhanced flow strength. It was found that the structural heterogeneities such as over-coordinated network formers and neighboring oxygen induced during consolidation serve as plasticity carriers to increase the ductility. On the other hand, the enhanced yield strength in consolidated glasses is due to the chemical heterogeneity inherited from the starting glassy nanoparticles, which does not compromise the ductility. Furthermore, apparent work hardening behavior appears upon cold work in the consolidated glasses, with an increase in yield strength from ~3.3 to ~6.4 GPa after 40% cold work. Consolidation with glassy nanoparticles could be a viable way to synthesize strong, damage resistant and transparent oxide glasses that cannot be obtained through the traditional melt-quench process.

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1. Introduction

Oxide glasses are widely used in energy, electronic and engineering applications (e.g., solar panels, optical fibers, automobile and building windows), thanks to their superior optical, thermal and chemical properties [1–3]. However, oxide glasses are generally brittle due to their high resistance to shear flow and low resistance to crack propagation [4,5]. Consequently, the damage resistance and practical strength of oxide glasses are usually very low [6]. Particularly, the fracture toughness (K_{IC}) and failure strength of oxide glasses are typically much lower than high-strength metallic alloys [7,8]. Such brittleness is one of the most serious limitations for the current commercial application of oxide glasses. Hence, there is a pressing need to toughen oxide glasses. As the elastic moduli of oxide glasses are generally comparable to high-strength metallic alloys, damage resistant oxide glasses would have the potential to serve as load-bearing structural materials.

Many efforts have been made to increase the damage resistance of oxide glasses. The most widely used strategy is surface strengthening, which can inhibit crack propagation with a pre-built compressive stress near glass surface layer. However, such surface treatments may not be universally applicable, in addition to the undesired potential failure induced by the pre-built interior tensile

stress. For example, thermal tempering [9,10] cannot be applied to oxide glasses with low thermal expansion coefficients; chemical tempering [11–13] is restricted to glasses containing mobile alkali ions. More importantly, tempering does not enhance the intrinsic resistance of glass to crack propagation, as the fracture toughness of chemically tempered Gorilla glass [14] is still less than $1 \text{ MPa}\cdot\text{m}^{1/2}$.

Apart from surface strengthening methods, damage resistant oxide glasses can be obtained through composition design and optimization [15,16]. Recently, new glass systems like lithium/sodium/cesium aluminoborate, binary aluminosilicate and pure alumina glasses [15,17–21] have been reported to possess intrinsically high ductility. For instance, amorphous alumina was found to deform via viscous creep at room temperature, which leads to exceptional ductility up to 100% and fracture toughness over $3 \text{ MPa}\cdot\text{m}^{1/2}$ [19]. However, the glass forming ability of ductile amorphous oxides such as binary aluminosilicate and pure alumina is usually low, making it difficult to synthesize them via the traditional melt-quenching process. Even with special levitation techniques [22,23], the size of the obtained glass sample is still restricted to millimeters in diameter. On the other hand, the chemical durability of alkali aluminoborate glasses is generally poor due to the high content of hygroscopic B_2O_3 [24].

Another strategy to toughen oxide glasses is to introduce a second phase via microstructure tuning [25–28], creating composite materials with a glassy matrix [3,29–31]. Recently, Jiang et al. [32] reported a record high fracture toughness of $\sim 6.6 \text{ MPa}\cdot\text{m}^{1/2}$

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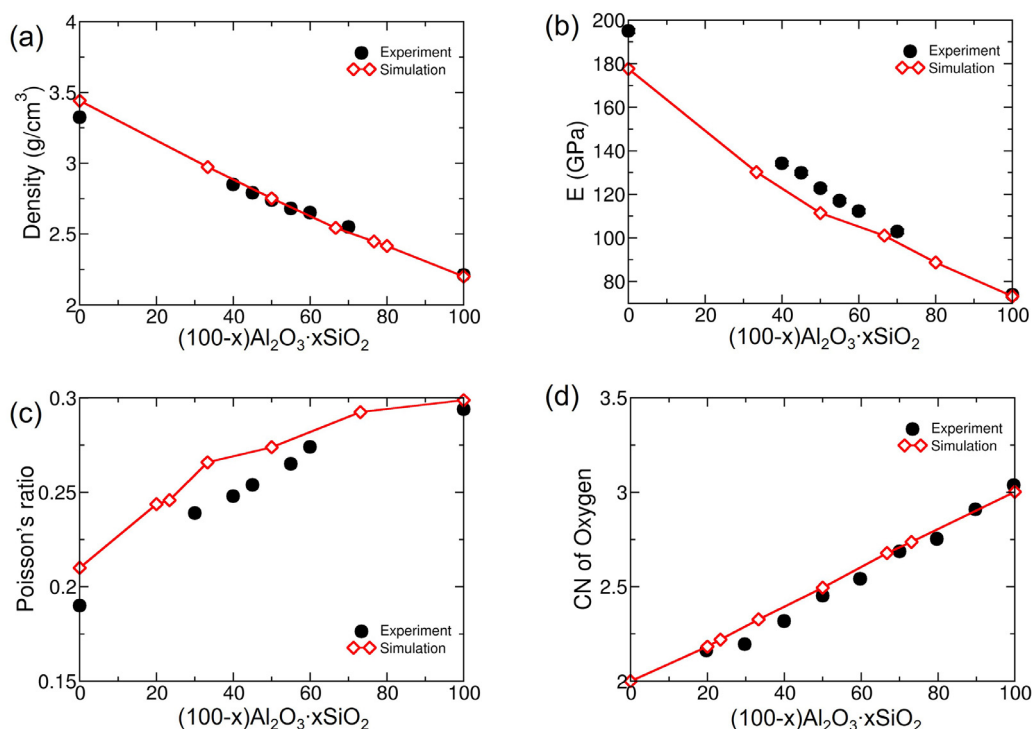


Fig. 1. (a) Density, (b) the Young's modulus and (c) the Poisson's ratio of $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses as a function of composition at ambient conditions. (d) Coordination number (CN) of oxygen as a function of composition for $\text{Al}_2\text{O}_3\text{-SiO}_2$ liquids at 2250 K and ambient pressure. Experimental measurements of density, the Young's modulus and the Poisson's ratio are taken from Refs. [18,19]. Experimental measurements of CN of oxygen are taken from Ref. [66].

in $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ glass with well distributed SiC nanoparticles in the glass matrix. The exceptional crack resistance originates from a collection of extrinsic toughening mechanisms [33–35], including crack deflection [6,36], branching and bridging [37,38]. However, it is extremely difficult to disperse the second-phase nanoparticles in liquid/glass matrix with the traditional processing technique. In addition, most second-phase nanoparticles used for toughening are crystalline materials, which may reduce the transparency of oxide glasses [39].

Up to now, to meet the escalating demands of strong and damage resistant oxide glasses in many technological important areas, more effective and generally applicable toughening strategies to increase their intrinsic ductility and practical strength are still in great need. To this end, tailoring structural heterogeneity has recently been shown very effective in improving intrinsic toughness of glasses [40–45]. Particularly, following the concept of nanoglass in metallic glasses [46–53], Zhang et al. [54] prepared tough silica glass by consolidating glassy nanoparticles with relatively low pressure. The brittle to ductile transition in consolidated silica glass is due to the formation of over-coordinated cations (e.g., five-fold silicon atoms) near glassy nanoparticle surfaces, which give rise to structural heterogeneity and serve as plasticity carriers in the resulting glass [55,56]. A straightforward extension of this toughening strategy is to simultaneously introduce structural heterogeneity and chemical heterogeneity (composition fluctuations across different length scales), which showed great potentials in strengthening and toughening high entropy alloy systems [57,58]. Note that the introduction of chemical heterogeneity via traditional melting quenching technique in oxide glasses is very challenging since the entropy effects favor chemical homogeneity. Even in systems with phase separation [59], the chemical heterogeneity is hard to be controlled to obtain desirable properties. Therefore, the role of chemical heterogeneity, especially the synergistic effect of structural and chemical heterogeneities on toughening oxide glasses remains elusive. Herein, using molecular dynam-

ics simulations, we systematically investigated the effect of both structural and chemical heterogeneities on the mechanical properties of $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses consolidated from glassy nanoparticles. By selecting the starting nanoparticles with different chemical compositions and tuning consolidation pressure, chemical and structural heterogeneities can be easily controlled via the consolidation technique. Our studies demonstrated that the structural and chemical heterogeneities in consolidated $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses substantially increase their damage resistance. Interestingly, apparent work hardening was also observed in consolidated glasses, with yield strength increasing substantially after cold work. We rationalized the toughening and hardening mechanism by constructing the structure-property relationships in consolidated glasses. The consolidation method described here may present a universal and feasible means to simultaneously introduce structural and chemical heterogeneities in oxide glasses to increase their damage resistance.

1.1. Simulation methodology

Force field Classical MD simulations were carried out in LAMMPS package [60] (<https://lammps.sandia.gov/>). The equations of motion were integrated by Velocity-Verlet algorithm with a time step of 0.8 fs. Nose-Hoover barostat and thermostat [61,62] were used to control pressure and temperature of the system. To model the behavior of aluminosilicate glasses, we slightly modified the original SHIK potential [63]. Particularly, the attraction parameter ($C_{\text{Al-Al}}$) for the Al-Al pair was increased from 100 to 160. The short-range cutoff was set as 0.8 nm. The long-range Coulombic interaction was calculated via the Wolf summation method [64,65] with a cutoff of 1.0 nm to increase the computational efficiency. This modified pairwise potential can accurately reproduce the structure and properties of $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses measured in experiments [18,19,66] over a wide composition range as shown in Fig. 1. As seen in Fig. S1, it can also reproduce the brittle to ductile transi-

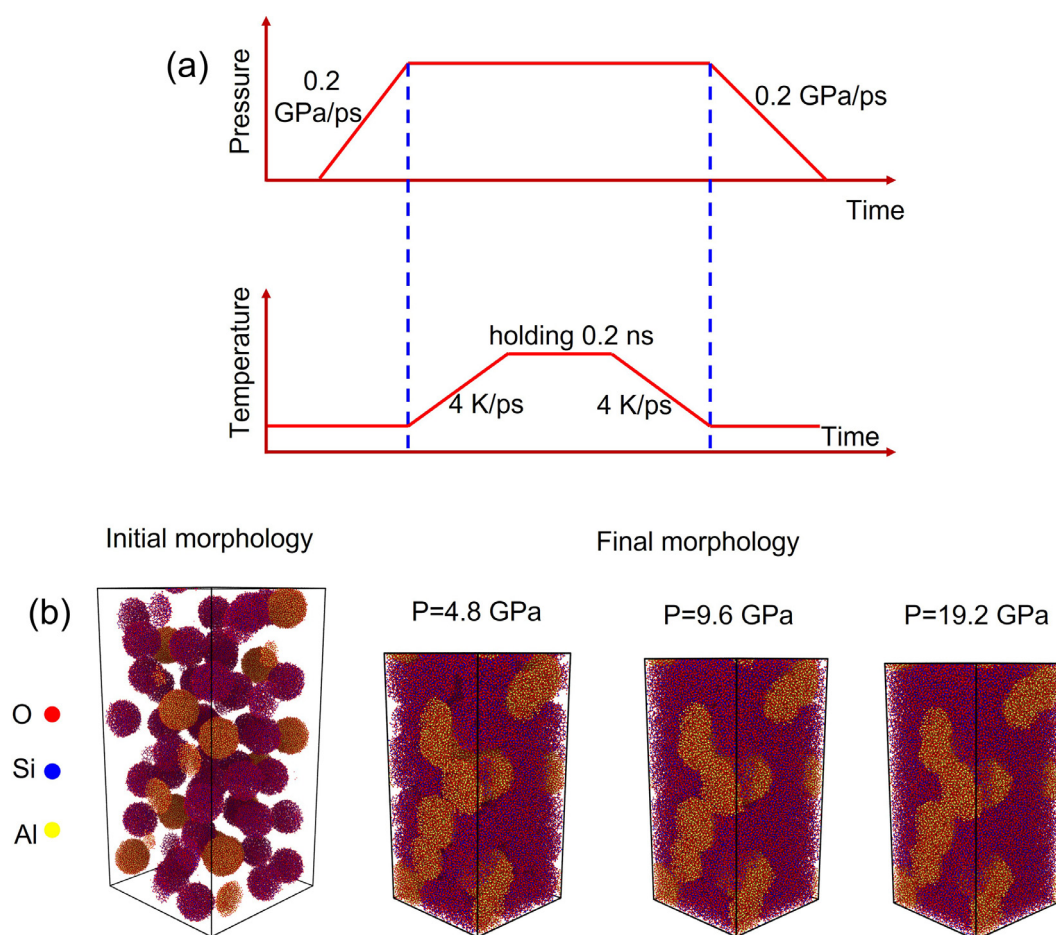


Fig. 2. (a) Temperature and pressure profile used to prepare consolidated glasses. Consolidation process can be carried out at different temperatures (300 K to 1500 K) and pressures (0 GPa to 19.2 GPa). Note that the heating and cooling rate is fixed at ~ 4 K/ps, and pressure ramping and releasing rate is fixed at 0.2 GPa/ps. (b) Illustration of starting nanoparticles with diameter of 5 nm and final morphologies of glass consolidated at three representative pressures. The resulting nominal composition is $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$. Red, blue and yellow particles represent oxygen, silicon and aluminum atoms, respectively. The samples shown in the final morphology were relaxed back to zero pressure and 300 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tion in Al_2O_3 - SiO_2 glass with increasing Al_2O_3 content as observed in previous experiments [18,19].

Sample preparation Bulk samples with varying compositions were quenched from well-equilibrated liquids from high temperature (3600 K) to room temperature (300 K) with a rate ~ 4 K/ps under zero pressure. Nanoparticles with uniform sizes were then carved from the bulk glassy samples. Charge balance was maintained by selectively deleting certain surface atoms on the nanoparticles.

The size of nanoparticles might be slightly adjusted to maintain the same nominal composition. Relaxation of nanoparticles was conducted at room temperature under constant volume for ~ 1 ns, followed by a thermomechanical consolidation route as shown in Fig. 2(a). For starting nanoparticle diameter ranging from 1 to 8 nm, the size of the resulting glassy sample after consolidation is around 10 nm by 10 nm by 20 nm ($\sim 200,000$ atoms). The sample size is around 20 nm by 20 nm by 20 nm (~ 1 million atoms) when the starting nanoparticle diameter is above 8 nm. To introduce nanoscale chemical heterogeneity, a mixture of glassy nanoparticles with two different compositions are used for consolidation. In this regard, the molar fraction of the starting nanoparticles is carefully adjusted to maintain the desired nominal composition. The degree and distribution of chemical heterogeneity can be tuned in a systematic manner by changing the size and composition of the starting nanoparticles. Fig. 2(b) illustrates the initial morphology of

glassy nanoparticles as well as the final morphologies of glass consolidated under different pressures. In the rest of this work, samples consolidated with binary nanoparticles of different chemical compositions are called binary consolidated glasses (BCS). Glasses quenched from high temperature liquids are called as-quenched glasses (AQ) and used for comparison. Glasses compressed from AQ samples that are free of chemical heterogeneities are called compressed glasses (CP).

Mechanical tests Uniaxial tension tests with an engineering strain rate of 1.25 ns^{-1} were carried out at room temperature to investigate the mechanical properties of thus-obtained oxide glasses. The mechanical response of both brittle and ductile sample is not sensitive to the strain rate in the range tested as seen in Fig. S2. Periodic boundary conditions were applied in all three directions. These samples are sufficiently long but not slender enough to trigger any known size/shape effect [67,68]. For ductile oxide glasses, the flow stress is averaged over the strains ranging from 30 to 65%. The visualization software OVITO [69] was used to generate simulation snapshots. Local atomic strain was calculated by using the method proposed by Falk and Langer [70].

2. Results

Toughening in low alumina containing BCS samples First, we systematically investigated the mechanical properties of AQ, CP and BCS glasses with the same nominal composition of

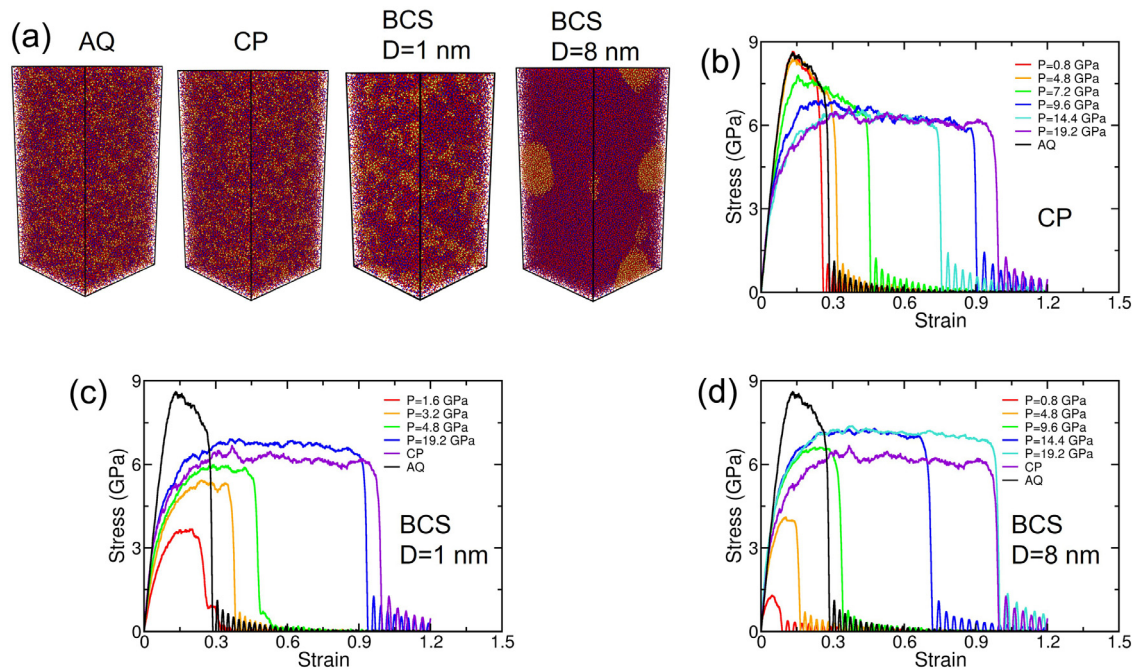


Fig. 3. (a) Final morphologies of $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$ glasses prepared from different routes. AQ is the as-quenched glass. CP is compressed with the bulk as-quenched glass at 19.2 GPa and 300 K. BCS is consolidated with a mixture of alumina and silica nanoparticles at 19.2 GPa and 300 K. Red, blue and yellow particles represent oxygen, silicon and aluminum atoms, respectively. (b) Stress-strain curves of CP glasses compressed at different pressures and 300 K, in comparison with that of AQ sample. (c) Stress-strain curves of BCS glasses consolidated with 1 nm glassy silica and alumina nanoparticles at different pressures and 300 K. (d) Stress-strain curves of BCS glasses consolidated with 8 nm glassy silica and alumina nanoparticles at different pressures and 300 K. Stress-strain curves of AQ and CP ($P=19.2$ GPa) are included in (c) and (d) for easy comparison. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$, a typical low alumina containing glass. Fig. S3 shows that density of these samples gradually increases as the consolidation pressure increases, due to the pore-closing as well as permanent densification. The AQ glass exhibits a typical brittle behavior as shown in Fig. 3(b). As the compression pressure increases, the obtained CP samples display an apparent brittle to ductile (BTD) transition when the pressure exceeds 7 GPa. Below this critical pressure, the deformation and fracture behavior of CP sample is very similar to the AQ sample, exhibiting a brittle behavior (cleavage). As the applied pressure reaches 19.2 GPa, the CP sample exhibits extensive ductility and apparent roughness in the fracture surface (see Fig. 4).

Unlike the chemically homogeneous AQ and CP samples, the BCS glasses consolidated with ~ 1 nm of glassy alumina and silica nanoparticles possess apparent chemical heterogeneity. Despite the existence of pores inside, improved ductility can be achieved in BCS samples consolidated with ~ 3 GPa pressure (Fig. 3(c)), much lower than over 7 GPa needed for compressing bulk samples. The critical pressure observed here is slightly higher than that needed for consolidating pure silica nanoparticles (2.4 GPa) [54], which might originate from the inhibition of pore healing due to the high elastic moduli of amorphous alumina (see Fig. 1(b)). As the consolidation pressure increases, the ductility of BCS increases, reaching $\sim 100\%$ failure strain when $P = 19.2$ GPa. Interestingly, by introducing nanoscale chemical heterogeneity, the flow strength of pore-free BCS prepared from 1 nm glassy particles appears to be higher than the CP sample by ~ 0.5 GPa.

We then increased the diameter of silica and alumina glassy nanoparticles from 1 nm to 8 nm for consolidation, so that the spatial distribution of chemical heterogeneity across the samples is increased. With low consolidation pressure (~ 5 GPa), BCS glass displays weakened strength and ductility as seen in Fig. 3(d), presumably due to the fact that large pores in the sample need higher pressure to be healed. As the consolidation pressure increases, the

BCS glass exhibits an apparent BTD transition with a critical pressure of ~ 10 GPa. For the ductile BCS prepared with 19.2 GPa pressure at 300 K, both glassy alumina and silica nanoparticles inside are severely deformed as seen in Fig. 4, indicating high intrinsic ductility. In addition, prior to the fracture, the propagated crack is apparently bridged by glassy alumina particle due to their relatively high elastic modulus, thus providing additional energy dissipation mechanism and contributing to high crack resistance. In contrast, the crack bridging mechanism displayed here is not observed in the ductile CP glass and in the BCS glass with $d = 1$ nm as seen in Fig. 4. Note that the flow strength of consolidated glass is further enhanced to 7.2 GPa as the starting nanoparticle size increases to 8 nm. Such substantial improvement in strength appears not at the expense of ductility as shown in Fig. 3(d), which is of vital importance for toughness optimization. The mechanism for enhanced strength in the chemically heterogeneous BCS glasses will be discussed later.

Toughening in high alumina containing BCS samples Using the same consolidation technique, we further prepared high alumina containing $73.1\text{Al}_2\text{O}_3 \cdot 26.9\text{SiO}_2$ glass (nominal composition), which was known to exhibit very low glass forming ability in experiments [18]. Density of final samples can be found in Fig. S4, while the final morphologies of representative CP and BCS samples can be seen in Fig. 5(a) that shows obvious chemical heterogeneity in the BCS sample. As shown in Fig. 5(b), the AQ sample exhibits high intrinsic ductility under uniaxial tension. However, the stress overshooting followed by flow strength reduction indicates strain localization, work softening or possible shear banding, similar to behaviors observed in many metallic glass systems [71–73].

Fig. 5(b) shows that, with the increase of compression pressure, the apparent yielding and stress overshoot of the AQ glass start to diminish when pressure is ~ 10 GPa, and disappear when $P = 19.2$ GPa. For BCS glasses consolidated with a mixture of 2 nm glassy alumina and silica nanoparticles at 300 K, the critical pressure to

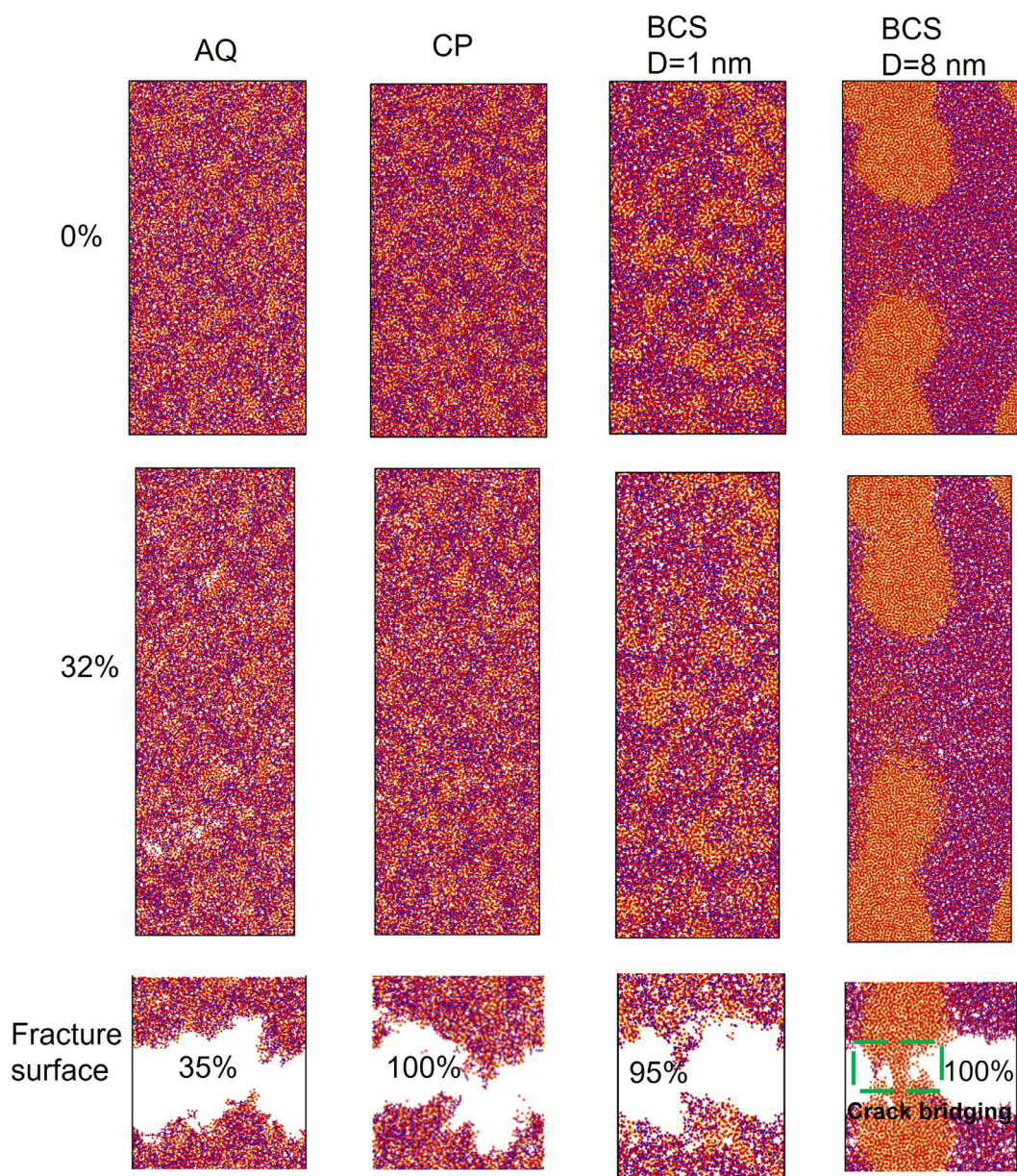


Fig. 4. Deformation snapshots of AQ, CP and BCS ($D=1$ and 8 nm) at different stages of uniaxial tension tests. The fracture surfaces as well as the fracture strain values are shown in the bottom row. The nominal composition is $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$, CP and BCS were compressed/consolidated at 19.2 GPa and 300 K. For clarity, a 2 -nm thick slice is shown here. Red, blue and yellow particles represent oxygen, silicon and aluminum atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

obtain sufficient ductility is ~ 3 GPa despite the existence of pores as shown in Fig. 5(c) and Fig. 6. The ductility and strength increase as the consolidation pressure increases, mainly due to the closing of pores as shown in Fig. 6. In addition, the deformation in BCS is more homogeneously distributed compared to the AQ sample. Meanwhile, the pore-free BCS exhibits slightly enhanced flow strength as compared to both CP and AQ samples (Fig. 5(c)), which will be carefully investigated later.

Temperature effect in consolidation In an effort to further reduce the critical pressure for obtaining tough oxide glasses, we increased the temperature during consolidation. Given the low glass forming ability of high alumina containing glasses, we only prepared and tested low alumina containing glasses with the nominal composition of $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$ to investigate the effect of consolidation temperature. Note that the consolidation pressure is

fixed at 3.2 GPa. When subjecting to higher consolidation temperatures, CP glasses first exhibit marginally enhanced ductility, then return back to brittle behavior. The highest ductility is reached at the consolidation temperature of 900 K as seen in Fig. 7(a). In contrast, BCS samples display both improved ductility and strength when consolidation temperature increases to 900 K, mainly due to the closing of pores (see Fig. S3(b)). Alternatively, the enhancement in both strength and ductility indicates a reduction of the critical pressure in triggering the BTB transition as the consolidation temperature increases. Therefore, this finding opens the possibility in preparing tough oxide glasses with consolidation pressure and temperature feasible in experiments. When the consolidation temperature is above 900 K, the yield strength keeps increasing with almost constant failure strain as seen in Fig. 7(b), suggesting the reduction of population of plasticity carriers [54]. We will iden-

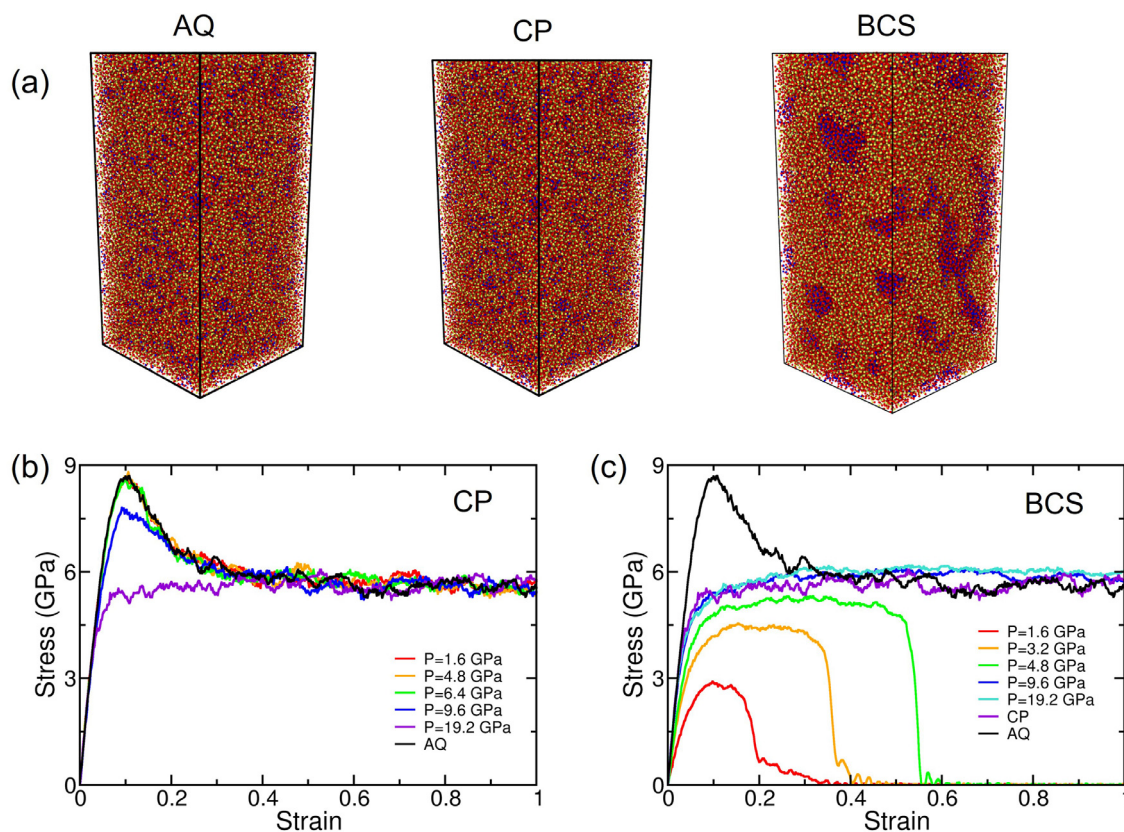


Fig 5. (a) Final morphologies of $73.1\text{Al}_2\text{O}_3\cdot 26.9\text{SiO}_2$ glasses prepared with different processing routes. The CP and BCS are prepared with a bulk sample and a mixture of 2 nm glassy alumina and silica nanoparticles at 19.2 GPa and 300 K, respectively. Red, blue and yellow particles represent oxygen, silicon and aluminum atoms, respectively. (b) Stress-strain curves of CP glasses compressed at different pressures and 300 K, in comparison with that of the AQ sample. (c) Stress-strain curves of BCS glasses consolidated at different pressures and 300 K, in comparison with that of the CP ($P=19.2$ GPa) and AQ sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tify the plasticity carriers in $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses and understand the role of consolidation temperature and pressure in forming such carriers later.

Work hardening ability Apparent hardening was observed in the CP and BCS samples with a nominal composition of $23.4\text{Al}_2\text{O}_3\cdot 76.6\text{SiO}_2$ by conducting loading-unloading-reloading uniaxial tests, as seen in Fig. 8. For ductile CP sample, the yield strength of the original sample is ~ 3 GPa as seen in Fig. 8(a), which increases to ~ 4.2 , 5.4 and 5.8 GPa after cold worked with 8, 20 and 40% strain, correspondingly. In contrast, BCS prepared with 8 nm glassy alumina and silica nanoparticles originally yields at ~ 3.3 GPa as seen in Fig. 8(b), then at 4.9, 6.2 and 6.4 GPa after cold worked at 8%, 20% and 40% strain, respectively. Interestingly, by introducing chemical heterogeneity through consolidation of glassy nanoparticles, BCS glass obviously displays a higher work hardening ability. The substantial increase in yield strength after 40% cold work in CP and BCS sample is rarely reported in oxide glasses, its structural origin will be illustrated in the following section. Encouragingly, compression-induced work hardening behavior was recently reported in metallic glasses by Pan et al. [74]. Our observations in MD simulations may stimulate studies of work hardening behavior in consolidated $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses and other oxide glasses in experiments.

3. Discussions

Plasticity carriers It is well known that over-coordinated atoms appear after pressure treatment [41,75] and are found to be responsible for enhanced ductility in silica glass [54,56]. Here, the

population of over-coordinated Si and Al atoms (see Fig. S5(a)) inside CP samples (nominal composition of $23.4\text{Al}_2\text{O}_3\cdot 76.6\text{SiO}_2$) start to increase when the applied pressure exceeds ~ 5 GPa as seen in Fig. S5(b). Meanwhile, the population of over-coordinated cations increases dramatically for AQ samples with increasing Al_2O_3 content as seen in Fig. S5(c). Similar observations of over-coordinated cations in $\text{Al}_2\text{O}_3\text{-SiO}_2$ were also reported in experiments recently [76,77]. Therefore, we speculate that these over-coordinated cations together with neighboring oxygen atoms are the plasticity carriers for $\text{Al}_2\text{O}_3\text{-SiO}_2$ glasses, which are responsible for both the composition induced (see Fig. S1) and pressure induced (see Figs. 3, 8) BTD transition. To prove this, we first analyzed the correlation between plasticity and population of over-coordinated atoms. Fig. 9(a) shows that the plasticity of CP and BCS samples increases with the population of oxygen atoms bonded with over-coordinated cations, regardless of composition and processing routes. The critical population for the BTD transition is found to be $\sim 15\%$ of the total number of oxygen atoms.

Theoretically, plastic deformation is realized by the incremental bond switching events. Hence, we further examined the shear deformation propensity of oxygen atoms with different coordination environments during plastic deformation. Following our previous method [45,54], the sample was first loaded above the yielding point ($\sim 5\%$) and then unloaded to zero stress, so that $\sim 1.5\%$ plastic strain remains. Then the corresponding atomic shear deformation of oxygen atoms with different coordination environments was calculated and averaged. As shown in Fig. 9(b), the oxygen atoms bonded with over-coordinated cations ($\text{CN} \geq 5$) dis-

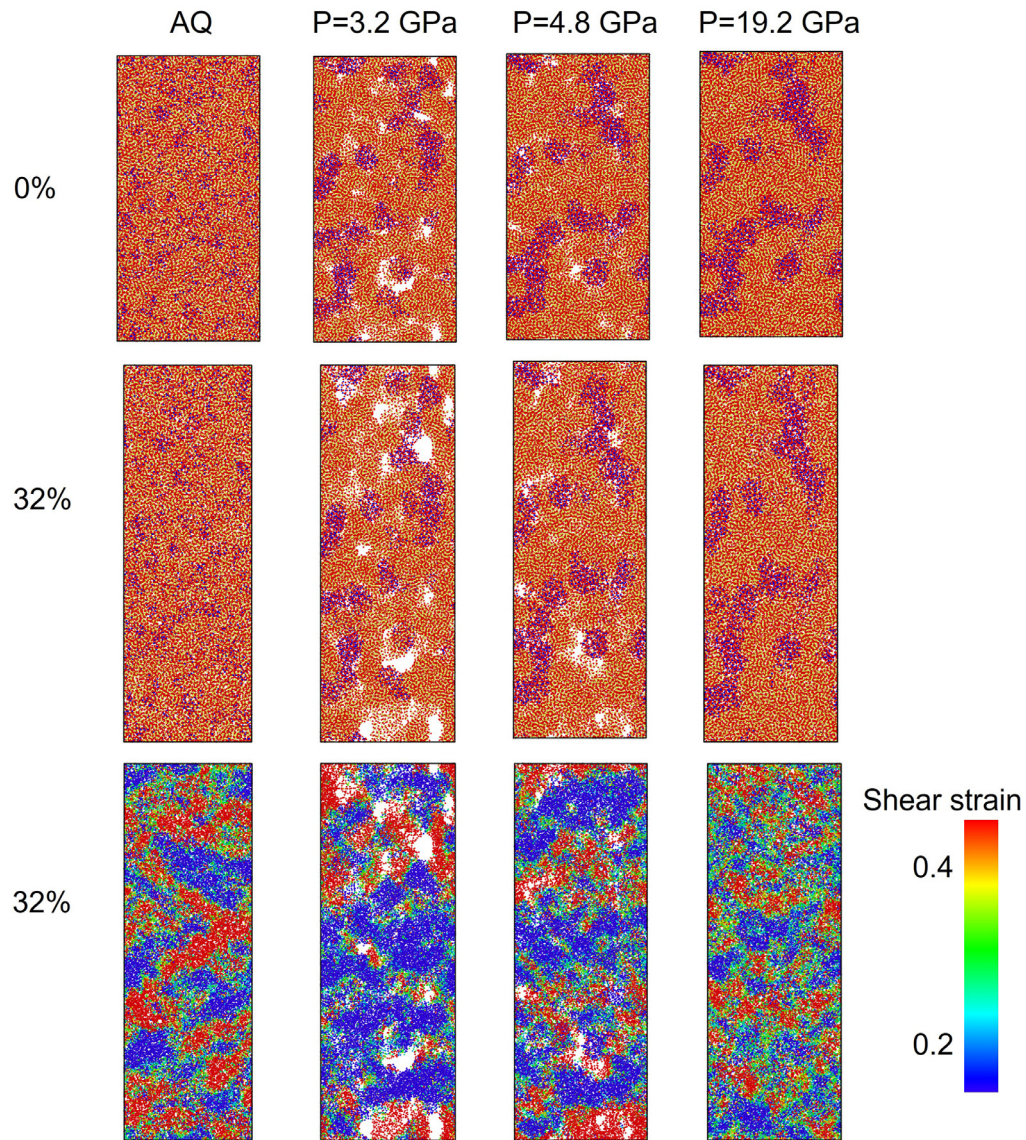


Fig. 6. Deformation snapshots of AQ and BCS glasses (prepared under different pressures at 300 K) at different stages of uniaxial tension tests. For clarity, a 2-nm thick slice is shown here. The nominal composition is $73.1\text{Al}_2\text{O}_3 \cdot 26.9\text{SiO}_2$. For the first two rows, red, blue and yellow particles represent oxygen, silicon and aluminum atoms, respectively. The third row shows the deformation distribution at 32% strain, which is color coded by the local shear strain. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

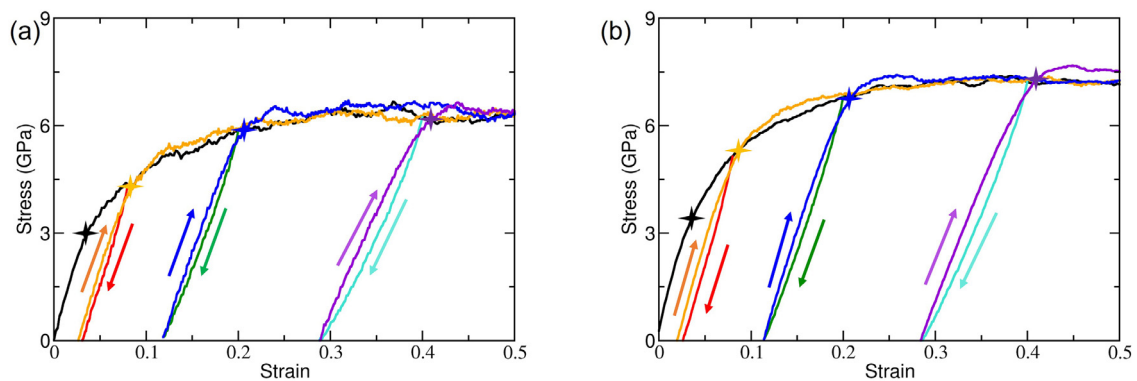


Fig. 7. Stress-strain curves of (a) CP and (b) BCS glasses consolidated under 3.2 GPa at different temperatures, in comparison with that of AQ. CP glasses are compressed with bulk as-quenched sample. BCS glasses are consolidated with a mixture of 1 nm silica and alumina nanoparticles. The nominal composition is $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$ for both CP and BCS samples. The uniaxial tension tests are conducted at 300 K.

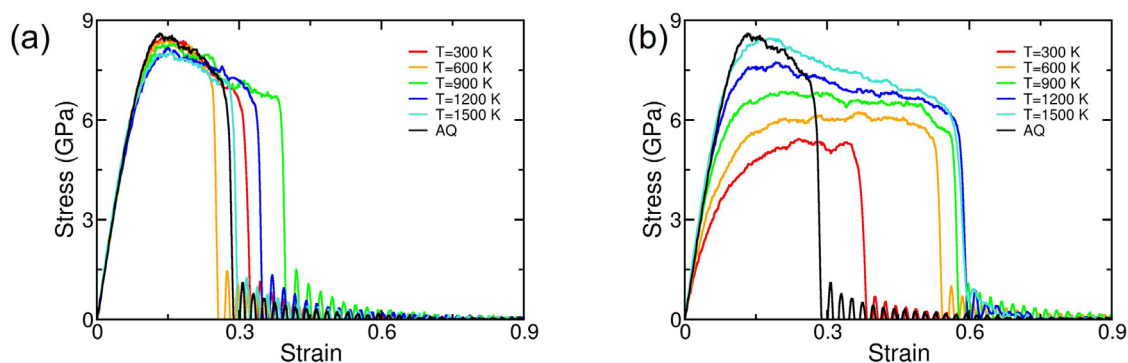


Fig. 8. Stress-strain curves of (a) CP and (b) BCS with a nominal composition of $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$ during initial loading, unloading and reloading of uniaxial tension test. BCS is prepared with 8 nm glassy silica and alumina nanoparticles. Both BCS and CP are prepared at 19.2 GPa and 300 K. The stars indicate the yield strength during the initial loading and reloading after unloading from different strains.

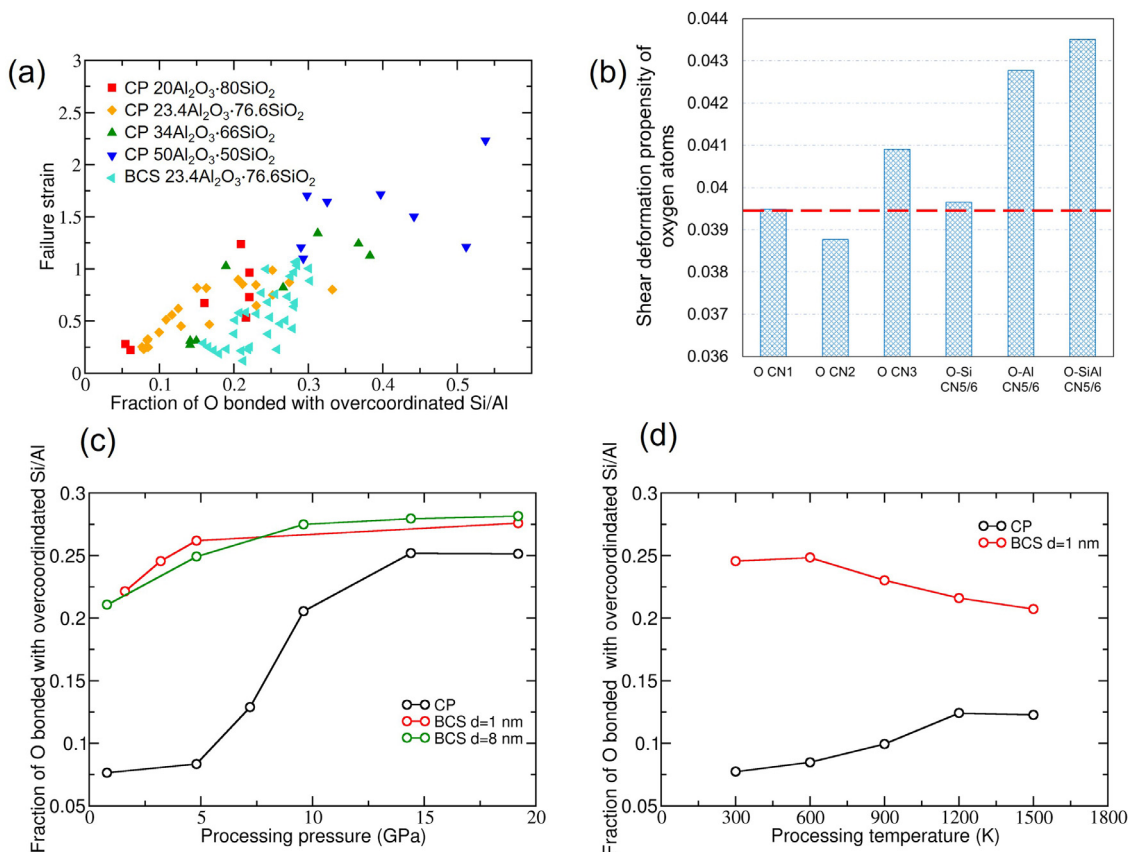


Fig. 9. (a) Correlation between failure strain and population of oxygen atoms bonded with over-coordinated Si/Al in CP and BCS samples. BCS glasses are prepared with a mixture of glassy silica and alumina nanoparticles ($d=1, 2, 5, 8$ nm). Both BCS and CP are prepared at different temperatures and pressures. (b) The shear deformation propensity of oxygen atoms with different bonding environments. Here we calculate the shear deformation propensity of 1-fold, 2-fold and 3-fold coordinated oxygen atoms, oxygen atoms bonded with overcoordinated Si, overcoordinated Al, as well as both overcoordinated Si and Al. The red dash indicates the overall shear deformation propensity of all oxygen atoms. (c) Population of oxygen atoms bonded with overcoordinated Si/Al in CP and BCS with a nominal composition of $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$ prepared under different pressures at 300 K. (d) Population of oxygen atoms bonded with over-coordinated Si/Al in CP and BCS with nominal composition of $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$ prepared under 3.2 GPa and at different temperatures.

play over 10% higher shear deformation propensity. Therefore, the over-coordinated cations and their neighboring oxygen atoms act as plasticity carriers during plastic deformation. Since the population of over-coordinated cations and their bonded oxygen atoms are closely related, we use the population of oxygen atoms bonded with over-coordinated cations to represent the plasticity carriers thereafter. By consolidating binary nanoparticles, a larger population of plasticity carriers is generated at relatively lower applied pressure as seen in Fig. 9(c). Here two factors contribute to a high population of plasticity carriers: (1) both the dangling bonds near

the surface of glassy nanoparticles and the shear stress induced at contact areas between nanoparticles during consolidation reduce the activation energy barrier for plasticity carrier formation [54]; (2) starting glassy alumina possesses substantial amount of plasticity carriers as seen in Fig. S6. Therefore, the BTD transition is triggered with a lower pressure by consolidating binary nanoparticles than compressing bulk samples. By increasing the consolidation temperature under relatively low consolidation pressure (3.2 GPa), the population of plasticity carriers in CP is not apparently enhanced (still below 15%) as seen in Fig. 9(d). As a result, the CP

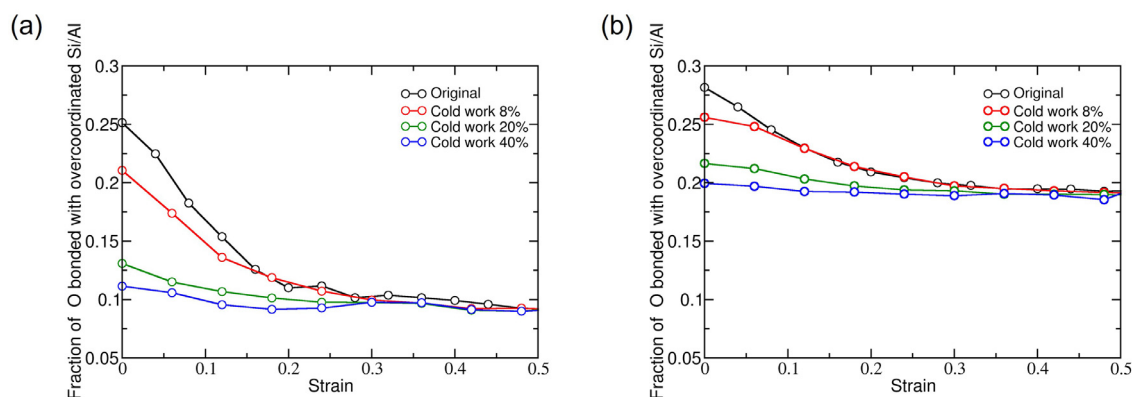


Fig. 10. (a) Population of oxygen atoms bonded with over-coordinated cations as a function of strain in the original CP glass (prepared under 19.2 GPa at 300 K) and cold worked samples. (b) Population of oxygen atoms bonded with over-coordinated cations as a function of strain in the original BCS glass and cold worked samples. The BCS glass is consolidated with 8 nm glassy silica and alumina nanoparticles at 19.2 GPa and 300 K. In both (a) and (b) the nominal composition is $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$.

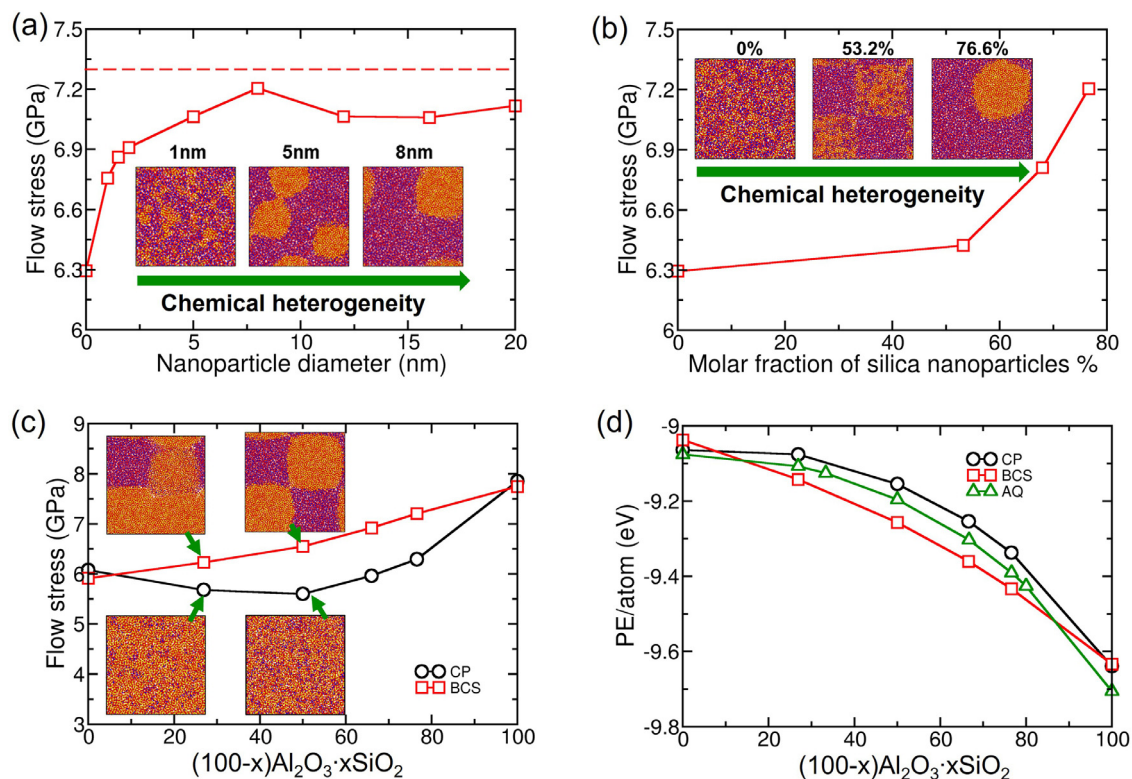


Fig. 11. (a) Flow stress versus starting nanoparticle size for BCS with a nominal composition of $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$. The dash line indicates the theoretical flow stress calculated from the mixing rule of composites. These BCS samples are prepared with a mixture of glassy silica and alumina nanoparticles. (b) Flow stress versus molar fraction of silica nanoparticle. The microstructures of BCS within a 2-nm thick slice are shown as insets. Red, blue and yellow particles represent oxygen, silicon and aluminum atoms, respectively. These BCS samples are prepared with a mixture of 8 nm glassy silica and aluminosilicate nanoparticles such that the nominal composition is fixed at $23.4\text{Al}_2\text{O}_3 \cdot 76.6\text{SiO}_2$. (c) Flow stress versus nominal compositions for BCS and CP glasses. BCS are consolidated with 8 nm glassy silica and alumina nanoparticles. Insets show the microstructures of BCS and CP samples with nominal compositions of $73.1\text{Al}_2\text{O}_3 \cdot 26.9\text{SiO}_2$ and $50\text{Al}_2\text{O}_3 \cdot 50\text{SiO}_2$. The flow stress in (a–c) is averaged from 30–65% strain. (d) The potential energy (PE) per atom versus nominal compositions of CP, BCS and AQ samples. BCS and CP are consolidated/compressed under 19.2 GPa at 300 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

samples do not exhibit an apparent BTB transition as the consolidation temperature increases. In contrast, the population of plasticity carrier in BCS is gradually reduced as the consolidation temperature increases. This is due to the relaxation of plasticity carriers back to lower energy states under the influence of temperature. However, in the consolidation temperature range studied here, the population of remaining plasticity carriers is still above the critical population, so the prepared BCS glasses remain ductile as seen in Fig. 7(b). Thus, the temperature acts as a double-edged sword in consolidating glassy nanoparticles. Particularly, increasing consolidation temperature can facilitate the generation of plasticity carriers

and healing of pores, improving toughness; at the same time high temperature can relax some of the plasticity carriers, resulting in brittleness.

Interestingly, the surprising work hardening ability observed in ductile CP and BCS samples is also closely related with the population of plasticity carriers. In particular, the work hardening behavior can be understood by the relaxation of plasticity carriers under applied stress as seen in Fig. 10. Before loading, the population of plasticity carriers is ~25% in the CP sample. It is reduced to 21%, 13% and 11% after cold worked with a strain of 8%, 20% and 40%, respectively. Similarly, the population of plasticity carriers is 28% in

the original BCS sample. After cold worked with a strain of 8%, 20% and 40%, it is reduced to 25%, 22% and 20%, respectively. Therefore, the stress facilitated relaxation of plasticity carriers is the origin for the observed work hardening behavior, which is similar to the behavior of consolidated silica glass [40,54] and rejuvenated metallic glasses via compression [74].

Heterogeneity-strength correlation Apart from the ductile behavior discussed above, we also observed enhanced strength in BCS glasses, by varying the size and distribution of chemical heterogeneity. Using $23.4\text{Al}_2\text{O}_3\cdot 76.6\text{SiO}_2$ glass as an example, we systematically investigated the effect of chemical heterogeneity on the strength of consolidated glasses. Here we first checked the effect of nanoparticle size without changing the starting nanoparticle compositions. When consolidating with glassy alumina and silica nanoparticles, the flow strength of $23.4\text{Al}_2\text{O}_3\cdot 76.6\text{SiO}_2$ glass first increases with the starting nanoparticle size, then reaches a plateau as the size exceeds 8 nm, as seen in Fig. 11(a). This plateau value (~ 7.2 GPa) is very close to the theoretical flow strength (~ 7.3 GPa) of glass composited with amorphous silica and alumina. We then investigated the effect of starting nanoparticle composition on the strength of BCS glasses without changing the overall nominal composition of the resulting glass. To do this, we used pure silica as one type of starting nanoparticles and replaced glassy alumina with a certain composition of aluminosilicate nanoparticles (e.g., $23.4\text{Al}_2\text{O}_3\cdot 76.6\text{SiO}_2$, $50\text{Al}_2\text{O}_3\cdot 50\text{SiO}_2$ or $73.1\text{Al}_2\text{O}_3\cdot 26.9\text{SiO}_2$). We maintained the same nominal composition by carefully adjusting the molar fraction of glassy silica. Note that the size of both starting nanoparticles are fixed at 8 nm. The flow strength is found to increase with the molar fraction of silica nanoparticles, since silica glass display a higher flow strength (~ 8 GPa) as compared to amorphous alumina (see Fig. 11(b)). Therefore, we can enhance the strength of aluminosilicate glasses by increasing the degree of chemical heterogeneity through either increasing the nanoparticle size or the composition contrasts. Finally, BCS glasses over a wide range of nominal compositions by using 8 nm glassy alumina and silica nanoparticles were prepared under 19.2 GPa at 300 K, whose microstructure can be found in Fig. 11(c). Compared with CP sample, the enhancement in flow strength is obtained in BCS over a large nominal composition range, 1 GPa increase is seen in $50\text{Al}_2\text{O}_3\cdot 50\text{SiO}_2$ glass in Fig. 11(c). We attribute the enhanced strength to the unique stable bonding in BCS glasses, which is confirmed by their lower potential energy as seen in Fig. 11(d). Those stable bonds are inherited from the starting silica nanoparticles and are mostly preserved in the consolidation process. Note that such bonding cannot be obtained in the traditional melt-quenching process since it is considerably deteriorated due to the entropic effect, which is confirmed by the higher potential energy of AQ samples than that of BCS samples of binary aluminosilicates in Fig. 11(d). Consequently, by introducing both structural and chemical heterogeneities across the samples, both strength and ductility can be simultaneously increased in oxide glasses consolidated from glassy nanoparticles.

4. Conclusions

Consolidation with glassy nanoparticles enables optimization of both structural and chemical heterogeneity, which lead to simultaneous enhancement in strength and ductility of $\text{Al}_2\text{O}_3\text{-SiO}_2$ binary glass. Substantial ductility can be obtained by consolidating nanoparticles at relatively low pressure (~ 3 GPa), while over 7 GPa is required for compressing bulk samples to trigger the BTD transition. Over-coordinated cations and their neighboring oxygen atoms are identified as the plasticity carriers due to their high shear deformation propensity under stress. The introduction of chemical heterogeneity results in up to 20% higher flow strength due to the stable bonds preserved in the starting silica nanoparticles. Ductile

tile glasses exhibit apparent work hardening ability, which is more pronounced in samples with chemical heterogeneity. The consolidation technique demonstrated in this work can open the door to design strong and damage resistant oxide glasses that cannot be obtained in the traditional melt-quench process, paving the way for their potential use in load bearing applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.actamat.2021.117016.

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