

Oxide glass exhibits plasticity without fracture at room temperature

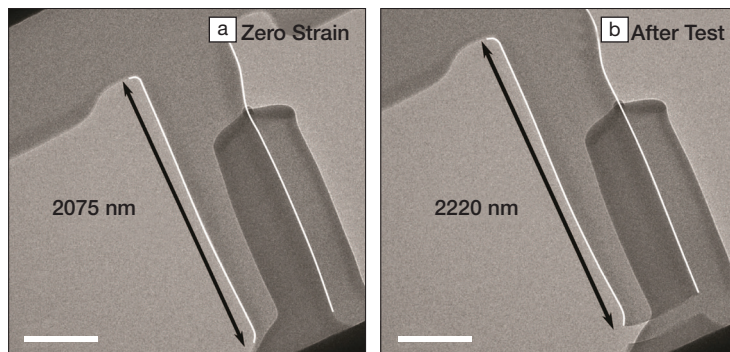
Oxide glasses are well known for their brittle nature, but new experimental research out of an international research consortium has revealed surprisingly high ductility in thin films of amorphous aluminum oxide ($\alpha\text{-Al}_2\text{O}_3$), or alumina, at room temperature. As reported in *Science* (doi:10.1126/science.aav1254), the plasticity is activated when an $\alpha\text{-Al}_2\text{O}_3$ sample free of flaws is subjected to a high stress at varying strain rates.

Inorganic oxide glasses are appealing materials for electronic applications because they can be tailored for many different functional properties. They are chemically and thermally stable and transparent to visible light. However, at room temperature the glasses are prone to sudden, catastrophic failure. This has limited their usefulness.

According to conventional theory, inorganic oxide glasses become ductile only when a high temperature activates a relaxation mechanism such as viscous flow or creep. Viscous flow occurs only above a critical temperature; viscous creep typically requires an external load and a critical temperature. Both viscous flow and viscous creep require a critical temperature well above room temperature so the material is effectively a solid at 300 K.

As a graduate student at Tampere University in Finland, project leader Erkkka Frankberg was studying the boundaries of plastic deformation in ceramics and glasses when preliminary results hinted that it might be possible to create ductile alumina at room temperature. Working with Erkki Levänen at Tampere University, Karine Masenelli-Varlot at the Université de Lyon in France, and Fabio Di Fonzo at the Istituto Italiano de Tecnologia, Frankberg initiated a collaborative effort to experimentally measure the viscosity of flawless $\alpha\text{-Al}_2\text{O}_3$ thin films at room temperature. “We didn’t have exact knowledge that this would be possible, but there was a chance, so we took it,” he explains.

The researchers prepared thin films of defect-free $\alpha\text{-Al}_2\text{O}_3$ by pulsed laser



Transmission electron microscope (TEM) images of a freestanding sample under zero strain (a) and after increasing strain until the point of fracture (b). The change in length is due to tensile stress. The sample is highlighted with a white border; a film can be seen partially overlapping the sample on the bottom right but does not impact the test. Scale bars are 500 nm. Reprinted with permission from Frankberg et al., *Science* **366** (6467), 864 (2019).

deposition, with thicknesses of 40 nm and 60 nm. The samples were probed by a custom micromechanical testing device located inside a transmission electron microscope (TEM) at room temperature. The testing device could apply up to 1 mN of force and had two modes, applying either shear-compressive stress or tensile stress to samples. For each mechanical test, the applied force and sample displacement were measured *in situ* over time and verified by TEM images.

While observing a test through the TEM, Frankberg realized the team could be on to something important. “[The sample] stretched and it stretched,” he recalls. The researchers observed samples elongate by up to 100% under mixed shear/compression loading. Furthermore, the deformation depended on the rate at which the load was applied, implying that a viscous relaxation mechanism had been activated.

Measurements revealed a log-log linear relationship between viscosity and strain rate. As strain rate went to zero, viscosity approached infinity and the material became solid-like. When finite strain was applied, viscosity decreased and the material became plastic. TEM images implied that the Al_2O_3 samples remained amorphous during deformation and could be considered a supercooled liquid.

The researchers ran atomistic simulations to explore the cause of this unusual behavior. The simulations showed initial plastic deformation caused by density changes in $\alpha\text{-Al}_2\text{O}_3$, but this accounted for less than 2% of the permanent elongation of

the axis under tension. The density saturated at around 25% of the total tensile strain and at higher strains the plastic deformation was caused only by viscous creep. In contrast to conventional theory, creep was activated almost solely by the applied load.

According to the simulations, room-temperature plasticity was facilitated by a bond-switching phenomenon well known in amorphous materials. The load prompted individual aluminum atoms to move into open spaces and replace existing oxygen bonds with bonds to neighboring oxygen atoms. As the number of individual bond-switching events accumulated, weaker local atomic groups yielded and enabled flow across the material.

The striking ductility of room-temperature $\alpha\text{-Al}_2\text{O}_3$ challenges the conventional view of what is possible with amorphous oxide materials according to Morten Smedskjær, an expert on oxide glass materials at Aalborg University in Denmark, who was not associated with this research. He notes that it will be interesting to explore whether mechanical activation can induce bond switching, and therefore plasticity, in other disordered oxides.

The atomistic simulations spotlight likely requirements for plasticity in oxide glasses at room temperature. According to the research team, bond switching between neighboring atoms is facilitated by low effective activation energy and high atomic density—both of which hold in $\alpha\text{-Al}_2\text{O}_3$. Furthermore, fractures are often initiated at the locations of defects and cavities, so a flawless material is key.

Frankberg, now a Marie Curie Research Fellow at the Instituto Italiano de Tecnologia, and his collaborators are currently studying this process in detail, working toward a comprehensive theory that would enable researchers to predict which glasses might exhibit plasticity at room temperature. “At this point we still don’t have enough knowledge to make

direct predictions,” Frankberg says. “And that means we don’t have a full theory yet.”

Room-temperature ductile oxide glasses have wide-ranging potential in areas ranging from flexible electronics to batteries and displays, but that requires significant scaling. There are no theoretical restrictions to scaling, according to the researchers. “Instead, the challenge

appears fully technological, given that we lack processing technology that could produce such flaw-free amorphous materials at a macroscopic scale,” the authors wrote. According to Frankberg, tackling this challenge will likely require a community effort that involves academic and industry research teams.

Kendra Redmond

Bio Focus

X-ray polarization reveals the secret to enamel’s toughness

The enamel in adult human teeth needs to be especially tough to last a lifetime. While many animals, such as sharks and crocodiles, constantly replace their teeth and rodents have continuously growing teeth, this is not the case in humans. Even bones in the human body, which are made of the same mineral as enamel, continuously remodel and regrow material over time to repair damage and stay strong. A recent publication in *Nature Communications* (doi:10.1038/s41467-019-12185-7) reported on how the toughness of enamel was a consequence of misorientations of its component crystals, as determined by x-ray polarization-dependent imaging contrast (PIC).

Enamel is the hardest tissue in the human body. Similar to pearl and seashells,

enamel is a kind of hierarchical multiscale nanocomposite; it is made up of multiple materials brought together and structured at different scales. The primary component of enamel is a calcium mineral called hydroxyapatite (HAP). Proteins and water make up about 5% of enamel’s weight. Enamel is made up of enamel rods, which contain multiple long HAP crystals aligned with each other. “We discovered that hydroxyapatite is dichroic, that is, it shows different x-ray absorption spectra when rotating the linear polarization,” says Pupa Gilbert, head of the research group at the University of Wisconsin–Madison.

By using a synchrotron as an x-ray source with a photoemission electron microscope, “you can rotate the polarization and reconstruct the orientation of each crystal in a sample,” Gilbert says. She and her colleagues used her polarization-dependent imaging contrast to make maps showing the orientations of the individual HAP crystals in enamel and made an important discovery: the crystals within a single enamel rod have different orientations that differ by at least 30°, but that can go up to 90°, as determined by the orientations of the crystalline *c*-axes.

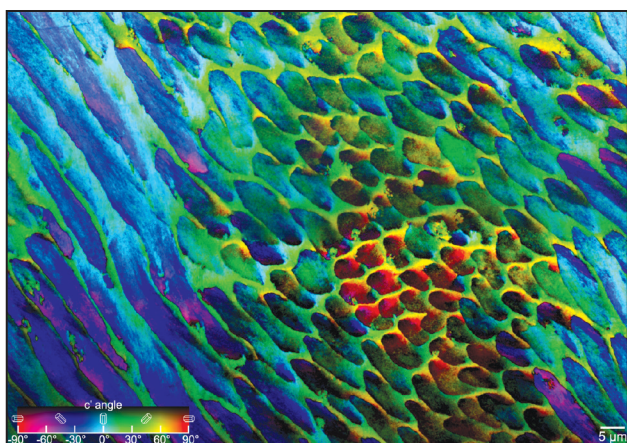
Gilbert thought these mis-orientations might have a purpose, and reached out to her colleague Markus J. Buehler, of the

Department of Civil and Environmental Engineering at the Massachusetts Institute of Technology, to further explore this. Buehler’s research group carried out molecular dynamics simulations of HAP crystals under stresses similar to those involved in chewing food. The simulations showed that when the atoms are perfectly aligned across crystals, cracks easily propagate through the crystal grain boundaries. However, when the atoms in adjacent crystals are only slightly misoriented (less than 30° off), a growing crack is deflected by the boundary and stops. Smaller mis-orientation angles actually stop crack growth better than larger angles.

Cayla Stifler, a graduate student in Gilbert’s group, developed software to determine how much crystals in the teeth they imaged were misoriented relative to adjacent crystals. Gilbert says this analysis “found that the enamel in our mouth has only small misorientation angles, between 1° and 30°. Very likely we evolved to have such small misorientation angles because they are the best at deflecting cracks, so our tooth enamel breaks all the time, but only at the nanoscale, so cracks can’t travel far.”

The team is interested in looking at enamel in other animals with the polarization imaging technique to analyze their crystals’ orientations. “The greatest force our jaw can apply is about 700 Newtons, but T. Rex was capable of 60,000 Newtons. That makes me want to look at its enamel as soon as I have more beamtime,” Gilbert says. Studying orientation, along with other structural properties like the size and shape of crystals in enamel and other biominerals, could also yield new ways to design tougher biomimetic materials.

Matthew Diasio



The map shows a pattern of different enamel rods crossing each other in the inner enamel of the human tooth, with three groups of rods exposed on the polished surface: in longitudinal (left), transverse (right of center), and oblique (center, right) cross sections. Credit: *Nature Communications*.