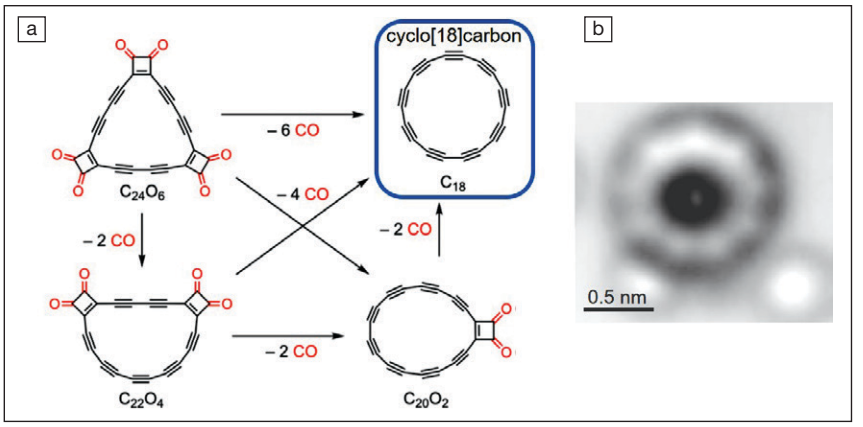
## The carbon allotrope family welcomes a new member

Following fullerenes, carbon nanotubes, graphene, and graphdiyne, a new carbon molecule—cyclo[18]carbon—has recently joined the carbon allotrope family. This new allotrope consists of 18 *sp*-hybridized carbon atoms interconnected in a ring form. Due to their high reactivity, purely *sp*-hybridized cyclo-carbons had never been isolated before, leading to past controversy over their existence and structures. A joint research team led by Leo Gross of IBM Research–Zürich, as well as Przemyslaw Gawel and Harry L. Anderson of the University of Oxford, has settled the dispute. They successfully synthesized and revealed the molecular structure of cyclo[18]carbon. This work was published recently in *Science* (doi:10.1126/science.aay1914).

The collaboration was initiated three years ago when the Anderson team approached Gross about making cyclo-carbons by leveraging IBM's expertise for atom manipulation. "The route that was successful in the end seemed like a long shot to me, and I was happily surprised that it worked," Gross says.

The researchers adopted a voltage-pulse decarbonylation strategy to prepare cyclo[18]carbon. They first synthesized cyclocarbon oxide $C_{24}O_6$ (a precursor) and sublimed it onto a Cu(111) surface partially coated with NaCl bilayers. The substrate was kept at 10 K to stabilize the oxide and loaded into a combined scanning tunneling microscope/atomic force microscope (STM/AFM) instrument. Owing to the atomic resolution of the STM/AFM, the researchers were able to trigger chemical reactions with one precursor molecule at a time by applying 3 V voltage between the STM probe and the precursor molecule for a few seconds. This process eliminated the CO moieties of $C_{24}O_6$ and successfully synthesized cyclo[18]carbon after detaching all six CO moieties. By analyzing the contrast of the AFM images, the researchers concluded that cyclo[18]carbon consists of alternating triple and single carbon–carbon bonds, in contrast to a ring merely composed of double bonds. The synthesized carbon rings have not been separated from the copper substrate due to the high reactivity of cyclocarbons. "It cannot be stable at room temperature in the presence of potential reaction partners," Gross says.




(a) The voltage-pulse decarbonylation process converted cyclocarbon oxides ($C_{24}O_6$, $C_{22}O_4$, and $C_{20}O_2$) to cyclo[18]carbon. (b) Atomic force microscope image of cyclo[18]carbon. The two bright lopes at the lower part are individual CO molecules. Credit: *Science*.

Changshui Huang of the Chinese Academy of Sciences, whose research group studies graphene and graphdiyne, says this work offers a powerful tool to address the challenge of high reactivity of cyclocarbons. "Low-temperature atom manipulation is a viable strategy to study active molecules. It could open up new opportunities to create and characterize transient and elusive cyclocarbon structures," Huang says. He was not involved in this study.

The researchers plan to continue collaborations associated with the new carbon allotrope. For example, they have observed that at suitable positions and given sufficient energy, multiple carbon rings can fuse on the NaCl surfaces. Gross says, "With this approach, we hope to create other carbon-rich materials and study them. Possibly we could use these networks as electronic devices, for example, for neuromorphic computing."

**Tianyu Liu**

## Designed crack-resistant cesium aluminoborate glass heals under hydration

Oxide glasses are disordered molecular structures and typically show poor intrinsic ductility. As a consequence, these materials are brittle. Although it is possible to toughen glasses using additives or heat-treatment methods, their resistance to crack formation and propagation remains very low. To address this long-standing challenge, one strategy is to look at the molecular design of the glass and to tune its composition. By enabling the formation of weak ionic bonds, it has been possible to develop glass compositions that exhibit high crack resistance through the plasticity of their molecular network.

One of these compositions, $Cs_2O$-$Al_2O_3$-$B_2O_3$, contains $Cs^+$ ions that can form multiple weak ionic bonds with oxygen anions. Under stress, those bonds break and dissipate energy. Also, in the presence of water, new bonds can be formed. Morten M. Smedskjaer, his team and collaborators from Aalborg University and the Technical University of Denmark, and the University of California, Los Angeles, used this rationale to determine this glass composition, and are studying its cracking and healing behavior.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Their results were published in *Advanced Science* (doi:10.1002/advs.201901281).

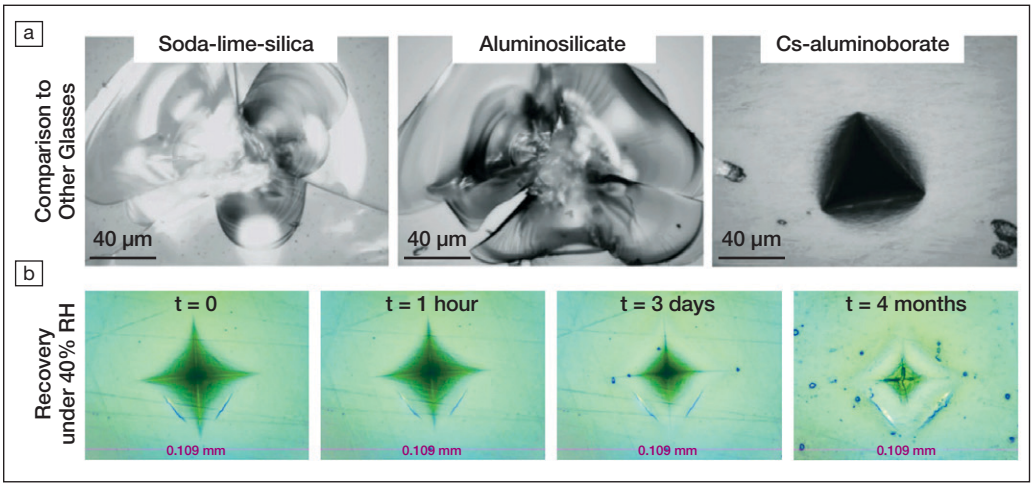
Although cesium aluminoborate glass has poorer chemical stability, hardness, and strength compared to other glasses with only 2.0 GPa hardness and 20 GPa Young's modulus, it exhibits a high Poisson's ratio of 0.32 and an ultrahigh resistance to crack formation (**Figure a**). The interpretation for these results lies in the ability of the Cs–O bonds to break easily and to induce *micro-ductility* in the glass network. Microscale shear deformation induced during the indentation experiment could be responsible for preventing crack formation and propagation.

Another unusual feature of cesium aluminoborate glass is its volume recovery under humid conditions over time. The researchers observed that an indentation made under a load of ~1 N recovered 44% of its volume after only 4 hours at room temperature at ~40% humidity. **Figure b** shows another striking example of recovery after indentation at 5 N. This recovery, or healing, is the result of structural changes in the glass network due to hydrolysis. Raman spectroscopy revealed that water molecules diffuse inside the glass and hydrolyze the borates, increasing their reactivity to form new bonds.

This study demonstrates how molecular and compositional designs in glass can be used to create new properties, such as crack resistance and healing. Yet, more work is needed to obtain a more comprehensive understanding of the mechanical deformations at the atomic level. Smedskjaer says, "We wish to investigate further at the medium range order how the glassy network connectivity responds to indentation and hydration. Also, we want to understand the composition dependence of the observed effect of humid aging and if this could be applicable to other more durable glasses."

This work on oxide glasses also finds resonance in other fields. Yakai Zhao, a research fellow working on metallic glasses from Nanyang Technological University, Singapore, and who did not take part in the study, says, "The findings of the paper not only present record-breaking crack resistance in oxide glasses, but also enlighten us with new avenues for designing crack-resistant materials through careful design of their chemical composition. It is astonishing to see the excessive volume recovery upon long-term surface aging. I am looking forward to understanding more how to manipulate this environment-assisted recovery to design damage-healable materials."

**Hortense Le Ferrand**




(a) Optical images showing the indentation marks left by a cube corner indenter at 5 N on soda-lime silica, aluminosilicate, and Cs-aluminoborate (this study) glasses. (b) Recovery with time under 40% room temperature relative humidity (RH) of the Cs-aluminoborate glass after Vickers indentation at 5 N. Credit: *Advanced Science*.





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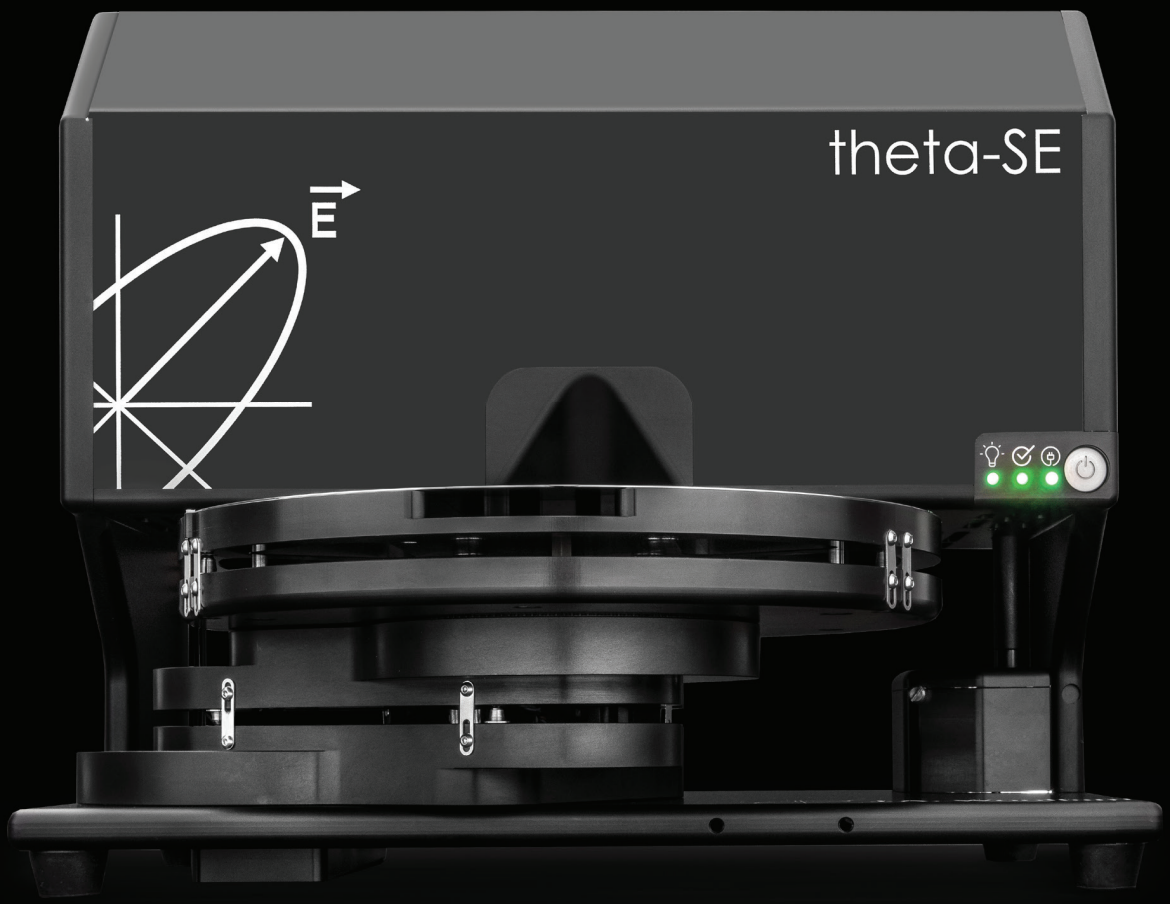


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