Long-Range Topological Order in Metallic Glass

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Glass lacks the long-range periodic order that characterizes a crystal. In the $Ce_{75}Al_{25}$ metallic glass (MG), however, we discovered a long-range topological order corresponding to a single crystal of indefinite length. Structural examinations confirm that the MG is truly amorphous, isotropic, and unstrained, yet under 25 gigapascals hydrostatic pressures, every segment of a centimeter-length MG ribbon devitrifies independently into a face-centered cubic (fcc) crystal with the identical orientation. By using molecular dynamics simulations and synchrotron x-ray techniques, we elucidate that the mismatch between the large Ce and small Al atoms frustrates the crystallization and causes amorphization, but a long-range fcc topological order still exists. Pressure induces electronic transition in Ce, which eliminates the mismatch and manifests the topological order by the formation of a single crystal.

A crystalline structure is composed of a unit cell that repeats by translational periodicity. In contrast, an amorphous material has far more degrees of freedom and complex configurations [for example, (*1*–*6*)]. It has been established that nominally "disordered" glass structure may still have short-range order (SRO) of the nearest-neighbor atoms (*7*–*9*) that can be visualized by atomic-scale, high-resolution transmission electron microscopy (HRTEM); quantified by radial distribution function using electron (ED), x-ray (XRD), and neutron (ND) diffractions; and analyzed by theoretical simulations. Substantial progress has been made recently in detecting and defining medium-range order (MRO) on length scale longer than the nearest neighbor to several nm [for example, (*6*, *10*–*17*)]. The bond lengths and angles of the clusters in glass may deform, shorten, stretch, and twist relative to their crystalline equivalent, while the topological relationship and connectivity of atoms are conserved (*13*). The SRO and MRO clusters in glass are thus often presented as topologically equivalent to a nanoscale portion (up to nm scale) of a crystal without its rigorous crystalline atomic spacings and bonding angles (*8*, *10*, *13*, *14*, *16*). Whether a glass can have long-range structural order (LRO) close to a crystal, that is, the "perfect glass state" (*16*), has been pursued extensively in open framework glasses, such as ice, silica, and amorphized zeolite (*2*–*4*, *6*, *16*, *18*–*20*), via the route of polyamorphic densification (which is transition between two different amorphous states) resulting from cage collapses. These recent efforts have revealed topological MRO of nm length (*13*) but have not yet discovered LRO.

We have taken an alternative route of studying a close-packed metallic glass (MG) and its polyamorphic densification because of 4f electron delocalization (*21*, *22*). By using single-roller melt-spinning method (*23*), we produced a $Ce_{75}Al_{25}$ MG ribbon with about 1 cm in length (hereafter referred as the *X* direction), 1 mm in width (*Y*), and 20 μm in thickness (*Z*). The amorphous structure of the as-prepared sample was

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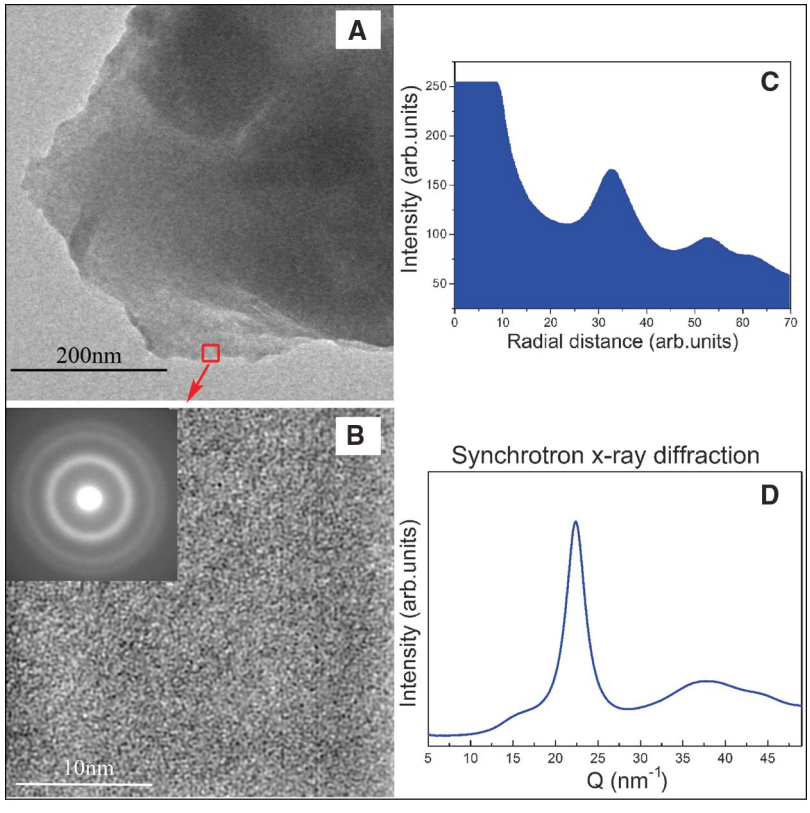

Fig. 1. Structure characterization of the as-prepared $Ce_{75}Al_{25}$ MG ribbon. (**A**) TEM image taken at the Electron Microscopy Center for Materials Research, ANL. (**B**) HRTEM image of the selected thin-edge area shown in the red square of (A). (Inset) ED pattern of the selected area. (**C**) The azimuthal integration of the ED pattern. (**D**) The synchrotron XRD pattern showing the same feature as (C). Diffractions can cover the entire sample but cannot see individual unit cells, whereas HRTEM is capable of resolving unit-cell–sized crystals but can only cover a minute portion of the sample. We searched over 20 randomly picked HRTEM points in the MG to assure a statistically representative imaging. Combination of these diagnostic probes shows that the sample is homogeneous and amorphous. We searched but did not find any microcrystals. Sample preparation for electron microscopy was as follows: The sample was thinned by the mechanical cracking method without any high-energy damaging process as in traditional ion milling and electrical polishing. A thin sliver was scratched off the MG ribbon and dropped into liquid nitrogen. Low temperature embrittled and cracked the sliver into very small flakes, which were dispersed in liquid alcohol and picked up by a copper net for HRTEM analysis.

investigated and confirmed by HRTEM imaging, ED, and XRD analyses (Fig. 1). The MG ribbon was cut into specimens about 50 μm by 40 μm by 15 μm in size. To ensure that we were looking at the internal bulk properties, all six surfaces of the rectangular specimen were recut or polished. A specimen was loaded in a diamond-anvil cell (DAC) along with ruby as the pressure calibrant and helium as the hydrostatic pressure-transmitting medium. In-situ XRD patterns of the $Ce_{75}Al_{25}$ MG at various pressures were collected at synchrotron beamline 16ID-B of the High Pressure Collaborative Access Team (HPCAT), Advanced Photon Source (APS), Argonne National Laboratory (ANL). The sample displayed broad amorphous XRD pattern below 24.4 GPa (Fig. 2). With a slight pressure increment to 25 GPa, the XRD image abruptly and completely transformed to a characteristic spotty zone axis pattern (*24*) of an face-centered cubic (fcc) (*25*) single crystal whose [111] direction coincides with the ribbon length (*X*), and [1$\bar{1}$0], with the ribbon thickness (*Z*). The single crystal (*26*) was preserved after decompressed to the ambient pressure (Fig. 3). Detailed XRD images during compression and decompression are shown in fig. S1.

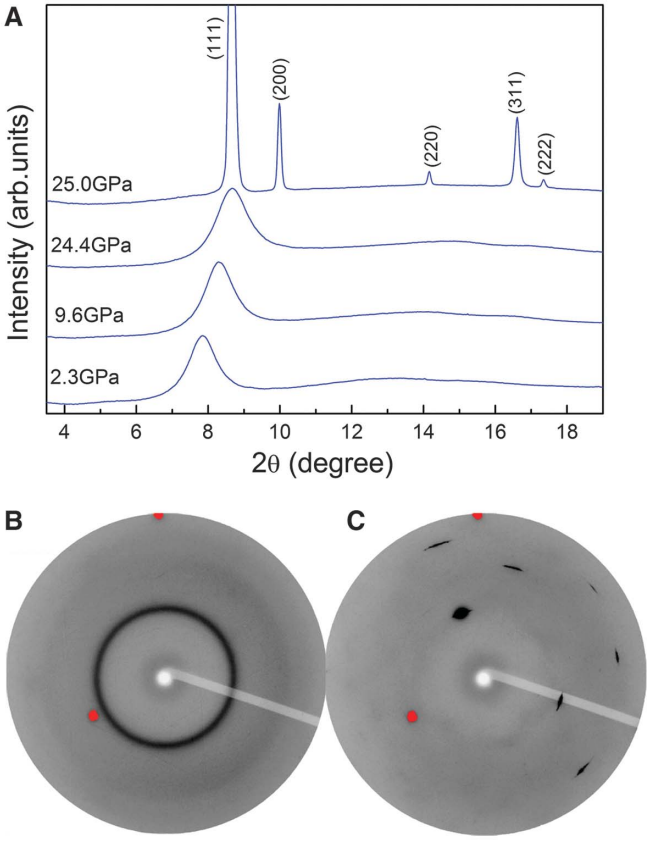

Fig. 2. In-situ high-pressure XRD of $Ce_{75}Al_{25}$ MG in a DAC. (**A**) Integrated XRD patterns, (**B**) two-dimensional (2D) XRD image below 24.4 GPa showing typical glass pattern, and (**C**) 2D XRD image at 25.0 GPa showing typical single-crystal zone-axis pattern (*24*). A focused (15 μm by 15 μm) monochromatic x-ray (wavelength, 0.36806 Å) through the DAC axis without rotation was used for (B) and (C). Red spots are masks of diamond single-crystal XRD spots.

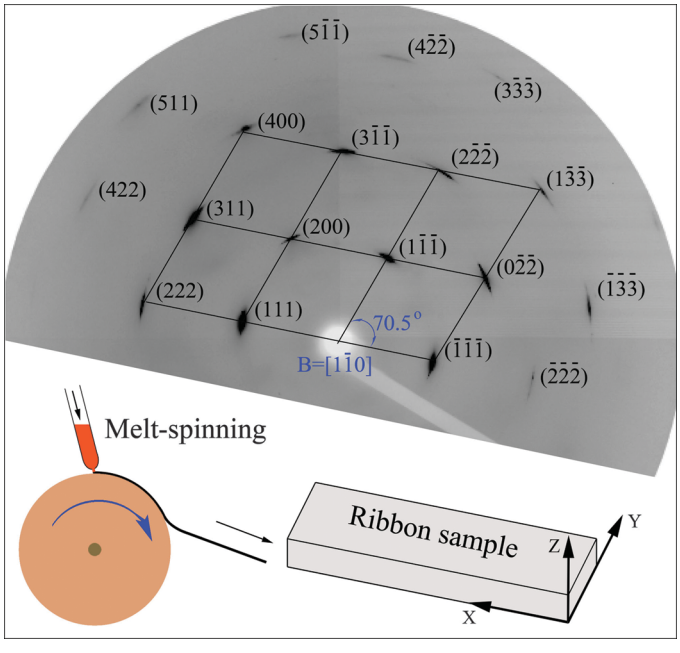

Fig. 3. The 2D XRD image of the fcc single crystal quenched to ambient pressure. The image is indexed as a *Z*-[1$\bar{1}$0] zone-axis pattern with ±5° rotation of the ω axis. The relationship between the crystallographic orientation and ribbon geometry is shown in the schematic illustration.

We observed an invariable orientational relation that the [111] crystallographic direction always formed along the ribbon *X* direction, and [1$\bar{1}$0], along the ribbon *Z* direction over a very long range throughout the entire MG ribbon. We ruled out the possibility of rapid crystal growth originated from a single seed by repeating the experiment with eight different specimens randomly selected from different parts of the same ribbon (fig. S2). Specimens were cut with different surface angles relative to the *X*-*Y*-*Z* axes to test for possible effects of the sample-pressure medium (He) interface and were tilted in the DAC to test for effects of compression direction on crystallization orientation. The strain-free state of the MG was verified (fig. S3), and the stress effect was tested (fig. S4). All tests invariably show the *X* [111]-*Z*[1$\bar{1}$0] relationship upon devitrification in every random unstressed fragment of the MG ribbon. Our observation indicates a topological LRO relationship between structures of the MG and the fcc crystal, without which the nucleation and growth would produce polycrystals of random orientations. At ambient pressure, the stable crystalline phase of $Ce_{75}Al_{25}$ (α phase) has the hexagonal structure that is topologically different from fcc. Indeed, when we devitrified the MG at ambient pressure at 200°C, the product was randomly oriented hexagonal polycrystals. A single crystal is only obtained within the fcc stability field above 25 GPa, demonstrating that the LRO in the MG is uniquely fcc.

The MG must have acquired its LRO during its formation. Both pure Ce and Al crystallize in the fcc structure and have a tendency to produce preferred orientation. The tendency may persist in the random mixture of Ce and Al during the melt-quenching, roller-spinning process. At ambient pressure, the atomic volume of Ce is twice that of Al, and its electronegativity 0.5 lower than that of Al. The extreme mismatch of Ce and Al atoms prevents the formation of a crystalline alloy and results in a glass that shares the common long-range topological relationship with the fcc crystal, but without its long-range spatial periodicity. Such topological LRO will not produce sharp peaks in ED and XRD, which depend on the presence of periodic atomic spacings. This is consistent with the cluster-packing model (*11*, *15*, *21*), which established the fcc symmetry as one of the possible topological MROs in MG. Extension of the topological MRO of the MG to a longer range of many clusters beyond several nm, however, is difficult to quantify by diffraction (fig. S6).

The present observation provides a fresh approach to connect the MRO and LRO through devitrification. Under compression, the Ce atomic volume collapsed because of the 4f electron

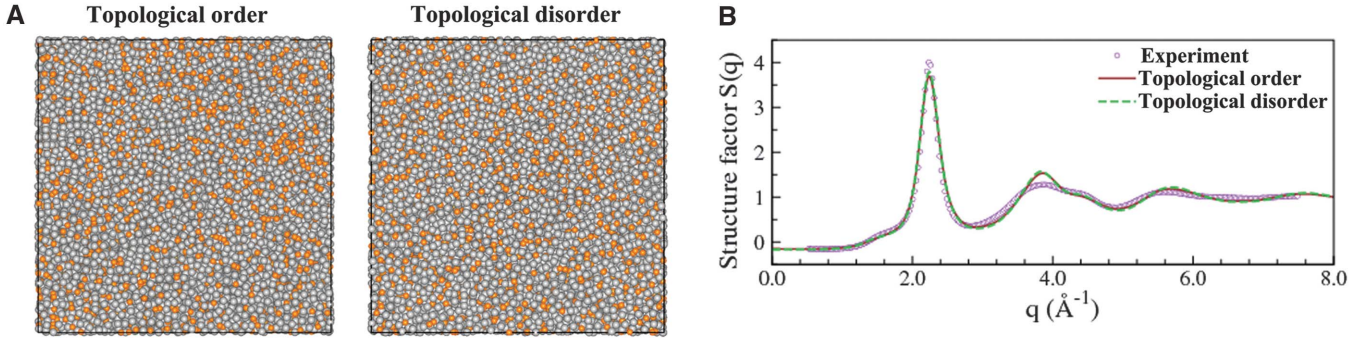

Fig. 4. Computational simulation of $Ce_{75}Al_{25}$ MG structure and XRD patterns at 300 K and ambient pressure. (**A**) Structures of randomly distributed, 3:1 mixtures of Ce (gray spheres) and Al (orange spheres) obtained through two different calculation paths. (**B**) Calculated XRD patterns of the topologically ordered and disordered MGs in comparison to experimentally measured XRD pattern. **q** is the vector of reciprocal space.

delocalization (*21*, *22*, *27*). As the differences of atomic volume and electronegativity between compressed Ce and Al diminish, the Hume-Rothery criteria for crystallization of fcc solid solution are satisfied (*25*). The hidden LRO is then manifested by the pressure-induced devitrification into a single crystal. Although the Ce and its electronic transition provide an unusual opportunity for revelation of the LRO, they are by no means a necessary condition for the LRO itself. $Ce_{75}Al_{25}$ MG does not stand out in the solvent-solute cluster-packing model (*11*, *28*, *29*) among many other MGs that may also have similar topological LRO. In-depth understanding of the $Ce_{75}Al_{25}$ MG case may provide clues for revealing topological LRO in other glasses without the help of Ce.

Is it possible to show explicitly the atomic arrangement of the MG with topological LRO? Is it distinguishable from a MG without the LRO? How could the LRO escape detection by diagnostic probes, for example, HRTEM, ED, and XRD? To address these questions quantitatively, we applied the theoretical methodology (*24*) that has proven successful for other MG systems (*15*, *21*, *30*). We used classical molecular dynamics (MD) calculations using high-fidelity *n*-body interatomic potentials acquired from extensive ab initio calculations (*30*) to simulate the amorphous structure and its evolution through pressure, temperature, and electronic changes. We started by distributing 24,000 Ce and 8000 Al atoms randomly on an fcc lattice at ambient pressure to reflect the tendency of preferred orientation of the quenched melt on the spinning roller. Then we relaxed the lattice constraint and let the simulation proceed. Because of the extreme mismatch between Ce and Al, the atomic positions, coordination numbers, and bonding angles of the fcc alloy automatically deformed, stretched, and twisted, but the topology was basically intact. Finally the fcc lattice was frustrated and transformed to a MG as shown at Fig. 4A, left. This MG, however, still kept hidden memory of the original fcc topology. When the simulation proceeded to high pressures, where the 4f localized Ce transformed to 4f delocalized, the MG became unstable and reverted through a discontinuous transition back to the fcc lattice of the original orientation.

For comparison, we also generated a MG without LRO by quenching a melt directly from 1500 K to 300 K without the fcc constraining step, and the result is shown in Fig. 4A, right. These two structures are practically indistinguishable from each other down to atomic-level resolution, comparable to what would be seen in a HRTEM image. XRD patterns of ordered and disordered MGs were also computed by using MD atomic configurations (Fig. 4B). They show the broad glass patterns indistinguishable from each other and agree with our experimental XRD pattern in peak positions, peak widths, and intensities, reflecting their similarity in SRO and MRO and their absence of long-range spacing periodicity. Diffractions (ED, XRD, and ND) are powerful probes for atomic spacing but are insensitive to topological LRO in glass.

In summary, we observed a pressure-induced devitrification where every portion of a cm-sized $Ce_{75}Al_{25}$ MG ribbon crystallizes independently to the identical orientation, in effect, forming a giant fcc single crystal. We deduced the presence of incipient topological LRO in the glass. Because of the drastic pressure-induced volume collapse of Ce, Ce-Al MG represents an exceptionally favorable system for discovery of the long-sought perfect glass (*1*, *6*, *16*, *19*), which may also exist in other glasses, including many MGs with the similar atomic size disparity and Hume-Rothery frustration as the Ce-Al MG.

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Supporting Online Material

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Materials and Methods
Figs. S1 to S6
Table S1
References (*31*–*40*)

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