

Formation of monatomic metallic glasses through ultrafast liquid quenching

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It has long been conjectured that any metallic liquid can be vitrified into a glassy state provided that the cooling rate is sufficiently high¹⁻⁴. Experimentally, however, vitrification of single-element metallic liquids is notoriously difficult⁵. True laboratory demonstration of the formation of monatomic metallic glass has been lacking. Here we report an experimental approach to the vitrification of monatomic metallic liquids by achieving an unprecedentedly high liquid-quenching rate of 10¹⁴ K s⁻¹. Under such a high cooling rate, melts of pure refractory body-centred cubic (bcc) metals, such as liquid tantalum and vanadium, are successfully vitrified to form metallic glasses suitable for property interrogations. Combining in situ transmission electron microscopy observation and atoms-to-continuum modelling, we investigated the formation condition and thermal stability of the monatomic metallic glasses as obtained. The availability of monatomic metallic glasses, being the simplest glass formers, offers unique possibilities for studying the structure and property relationships of glasses. Our technique also shows great control over the reversible vitrification-crystallization processes, suggesting its potential in micro-electromechanical applications. The ultrahigh cooling rate, approaching the highest liquid-quenching rate attainable in the

experiment, makes it possible to explore the fast kinetics and structural behaviour of supercooled metallic liquids within the nanosecond to picosecond regimes.

Since the first discovery of metallic glass (MG) in the 1960s (ref. 1), the search for new types of MG has not stopped^{2,6,7}. To date, most MG formers are known to consist of two or more elements with distinct atomic sizes and chemical affinities^{2,8}, usually formed by quenching the liquids with techniques varying from conventional die casting⁶ $(10^{1}-10^{3} \text{ K s}^{-1})$, melt spinning² ($10^5 - 10^6$ K s⁻¹), liquid splat-quenching⁹ ($\sim 10^9 - 10^{10}$ K s⁻¹) to pulsed laser quenching¹⁰ ($\sim 10^{12} - 10^{13}$ K s⁻¹). New techniques such as nanocalorimetry¹¹ $(10^{4} - 10^{6} \text{ K s}^{-1})$ have also emerged, vying for high heating and cooling rates. Unfortunately, these solidification techniques can hardly be applied to the production of monatomic MGs, mainly because of the extremely low glass-forming ability of monatomic metallic liquids, resulting from their fast nucleation and crystal growth kinetics at deep undercoolings^{4,12–14}. Thus, vitrification of pure monatomic MGs requires extremely high critical cooling rates, far above the experimentally accessible level, to suppress crystal growth. The monatomic MG may also be confronted with the thermal stability issue at room temperature, at which spontaneous crystallization seems inevitable¹⁴.



Figure 1 | Illustration of an ultrafast liquidquenching approach. a-c, Schematic drawing of the experimental configuration. Two protruded nano-tips are brought into contact with each other (a) and are melted by the application of a short square electric pulse with a duration of \sim 3.7 ns and a voltage in the range 0.5-3 V (b). Heat dissipates rapidly through the two bulk substrates (indicated by two red arrows), vitrifying the melting zone to form monatomic MGs (c). d, e, High-resolution TEM images showing two contacting Ta nano-tips (d) forming a Ta MG (e) after the application of a 0.8-V, 3.6-ns electric pulse. The GCIs are denoted by yellow dotted curves. f-h, Fast Fourier transformations confirming a fully vitrified region 20 nm long and 15 nm thick (g) bounded by two crystalline substrates viewed along the $\langle 100 \rangle$ (f) and $\langle 110 \rangle$ (h) crystallographic orientations, respectively.

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Figure 2 | **Structure and thermal stability of Ta MG. a**, TEM morphology of a typical Ta MG with length of ~90 nm and diameter of ~60 nm. The GCIs are indicated by yellow dotted curves. **b**, Electron diffraction of Ta MG, as quenched (left) and after relaxation for ~8 h (right). **c**, Comparison of the structure factors of the Ta MGs as formed (pink line), after relaxation for 8 h (green line) and simulated (orange circles). All three curves show very similar peak positions, including well-separated second (q_2) and third (q_3) peaks (indicated by cyan arrows). The ratios of peak positions are the same for the relaxed and simulated structures: $q_2/q_1 = 1.68$ and $q_3/q_1 = 1.99$.

Consequently, except for a few special circumstances (for example at very thin edges of a splat-quenched nickel foil⁹), monatomic MGs have not been found to form from pure metal melts by vitrification.

More recently, pure metallic germanium liquid was reported to vitrify under hydrostatic pressure above 7.9 GPa (ref. 5). However, on releasing pressure to ambient condition, germanium MG quickly transforms to a non-metallic low-density amorphous phase, in which case the tendency and mechanism of liquid vitrification are largely different from those of most d-block transition metals. Other non-vitrification methods (such as vapour deposition¹⁵ and chemical synthesis¹⁶) have been attempted to produce monatomic amorphous samples, which are often in geometrically confined forms (such as substrate-supported thin films and nanosized powders) and are plagued with either purity¹⁶ or stability¹⁷ problems, offering limited potential for broader applications. Therefore advanced techniques to fabricate high-purity monatomic MGs with controllable geometries are highly appealing. By building an in situ Joule heating nanodevice inside a transmission electron microscope (TEM), we present a unique ultrafast liquid-quenching system for vitrifying monatomic metallic liquids. This technique exploits the excellent thermal conductivity of the metals and maximizes the heat conduction rate of the cooling system.

Our ultrafast quenching technique is illustrated in Fig. 1a–c (see Methods). First, two protruded nano-tips with clean surfaces (Extended Data Fig. 1a, b) are brought into contact with each other (Fig. 1a) under an ultrahigh vacuum condition inside the TEM. A short square electric pulse, typically 0.5–3 V in amplitude and within 3.7 ns in duration, imposes local Joule heating on the joined tips, causing melting of the extrusion tips and the formation of a melting zone in the middle (Fig. 1b). On instantaneous cessation of the electric pulse and, consequently, local Joule heating, heat dissipates rapidly through the solidifying piece and the conductive heat reservoir, creating an extremely high cooling rate sufficient to vitrify the melt into a glassy state (Fig. 1c). In Fig. 1d, e we demonstrate that a 0.8-V, 3.6-ns electric pulse on two connecting crystalline



Figure 3 | Dynamic vitrification process in liquid Ta revealed by AtC computer simulation. a, Atomic configuration showing a liquid zone of Ta 35 nm in length after Joule heating (at t = 0 ps). The atoms are coloured on the basis of their degree of disorder represented by local bond-orientational order parameter q_6 (ref. 29). The red colour corresponds to liquid Ta after Joule heating. b, Atomic configuration showing the formation of a Ta MG segment 30 nm in length after quenching (t = 150 ps). The average temperature of the Ta nanowire is close to room temperature at t = 150 ps. The inset highlights the interface structure between amorphous and bcc Ta. c, A time-temperature-transformation diagram derived from isothermal MD simulations, outlining approximately the formation condition of Ta MG. The crystal zone is estimated from the crystal growth rates of the (100) plane (cyan circles) and the (110) plane (orange squares). The red solid line indicates the temperature evolution of the moving LCI (and later on GCI) during cooling.

Ta nano-tips (Fig. 1d) led to the formation of a Ta MG 15 nm wide and 20 nm long (Fig. 1e). Structural characterization of the MG is presented below. The dimensions of the MGs can be controlled by tuning electric pulse parameters while engaging *in situ* tensile or compressive loading. In this way, Ta MGs with dimensions of 100 nm in diameter or an aspect ratio of \sim 4 are obtainable (Extended Data Fig. 1c, d). The formation of even larger Ta MGs, which are not electron transparent, was not pursued in this work. Applying this method, we have systematically tested the vitrification capability of transition metals and successfully obtained Ta, V, W and Mo monatomic MGs; their morphologies are provided in Extended Data Figs 2–4. The materials systems that have been vitrified are typically early transition bcc metals with high melting points and excellent thermal conductivities.



Figure 4 | **Reversible crystallization–vitrification phase changes of Ta MG. a**, Formation of a Ta MG 40 nm thick and 50 nm long under a 3.6-ns, 1.26-V electric pulse. The two GCIs are indicated by yellow dotted curves and are labelled A and B, respectively. **b**, **c**, Controlled gradual crystallization under a series of pulses 3.6 ns in duration and 0.90 V in amplitude. Crystallization proceeded with crystal growth at GCI B (indicated by a yellow arrow) and

The amorphous nature of the MG as obtained was confirmed by TEM diffraction patterns. As a first check, the diffusive diffraction halos in the fast Fourier transformation (Fig. 1g) of the area bounded by two glasscrystal interfaces (GCIs) are characteristic of amorphous structure, contrasting the bright diffraction spots of the Ta substrates with a well-defined bcc structure (Fig. 1f, h). To confirm the glassy structure and the thermal stability of Ta MG, a sample 60 nm in diameter and 90 nm in length was relaxed in high vacuum at room temperature for 8 h (Fig. 2a). Electron diffraction patterns of the Ta MGs as quenched (Fig. 2b, left) and after relaxation (Fig. 2b, right) showed similar features characterized by diffuse halos typical of amorphous structure. The corresponding integrated and optimized one-dimensional static structure factors¹⁸ S(q) (Fig. 2c) showed similarities in their shape and peak positions, indicating that no major structural changes occurred in Ta MG after 8 h. The slight shift to the right in the main peak positions of S(q) may be attributed to structural relaxation in the glass, as expected. The main peak positions of the relaxed Ta MG were measured to be 2.63 \AA^{-1} , 4.42 \AA^{-1} and 5.23 Å⁻¹, corresponding to $q_2/q_1 = 1.68$ and $q_3/q_1 = 1.99$, which are almost identical to the simulated structure factor (orange circles in Fig. 2c) derived by quenching liquid Ta at a cooling rate of $\sim 10^{13}$ K s⁻¹ on the computer. The observed S(q) of Ta MG also agrees well with theoretical works on monatomic systems¹⁹⁻²², as well as with previous experimental results on amorphous cobalt²³ and iron²⁴, for which $q_2/q_1 = 1.69$ and $q_3/$ $q_1 = 1.97.$

To understand the vitrification process of the liquid and estimate the cooling rate, atoms-to-continuum (AtC) simulations²⁵ have been performed, where the molecular dynamics (MD) system is coupled to an additional electron temperature field that implements the two-temperature model (TTM)²⁵ for heat transport (see Methods). The present experimental approach is capable of vitrifying monatomic metallic liquids on temporal and spatial scales commensurate with those in MD modelling, permitting a direct comparison between experiment and MD simulation and enabling accurate interpretation of the multiphysics of the cooling process. Quenching of liquid Ta starts at the moment when external

completed after six crystallization pulses (inset in c). d, A second vitrification pulse resulted in the formation of a Ta MG similar to that shown in **a**. **e**, **f**, Close-up views of the atomically rough and diffuse GCIs during a phase-change cycle. A schematic drawing with cyan dotted lines along one set of the (110) planes shows the gradual breakdown of the long-range order across the GCI.

Joule heating is turned off (Extended Data Fig. 5a), during which the temperature evolution in the nanowire depends on rapid heat dissipation through the massive crystalline substrates kept at room temperature. As a result of the large temperature gradient, excellent heat conductivity and small specimen size, ultrafast cooling is achieved, as demonstrated by the evolution of the temperature distribution in the Ta nanowire (Extended Data Fig. 5b). The computed cooling rate of the liquid zone (Extended Data Fig. 5c) reaches as high as 10^{14} K s⁻¹ at 4,200 K and decreases slightly to 5×10^{13} K s⁻¹ at the glass transition temperature $T_{\rm g}$ of liquid Ta, which is estimated to be ~1,650 K (Extended Data Fig. 6).

Accompanying the rapid quenching process, the real-time dynamics of the atomic system was revealed by MD simulations, indicating that whether a MG can eventually form is determined by the competition between the liquid-quenching rate and the crystal growth rate from the melt. Under the given experimental condition, a large portion of the original liquid Ta zone 35 nm in length was vitrified after Joule heating was cut off (Fig. 3a, b), demarcated by atomically rough GCIs (Fig. 3b inset), corroborating our experimental observations. More generally, the time needed for complete crystallization due to crystal growth at the (100) (cyan circles) and the (110) (orange squares) interfaces of the pre-existing crystals (that is, the crystalline substrates) at different temperatures is computed and plotted in the time-temperature-transformation diagram for Ta (Fig. 3c), based on the growth rates of these two liquidcrystal interfaces (LCIs) from the melt (Extended Data Fig. 5d). In the AtC simulation shown in Fig. 3a, b, the temperature evolution of the LCI (and later on the GCI) of the system follows the red curve in Fig. 3c, which trends into the glass-forming region (that is, the left side of the time-temperature-transformation curves) and corresponds to a quenching rate one order of magnitude higher than the critical cooling rate of \sim 5 \times 10¹² K s⁻¹ estimated from the dimensional consideration (described in Methods), justifying the formation of Ta MG under the present experimental configuration. The effect of a trailing edge in the applied electric pulses is taken into account by modelling liquid quenching under a heat flux terminated within 0.4 ns in a ramp function rather than instantly.

As shown in Extended Data Fig. 7a, b, 18 nm of the 35-nm Ta liquid was successfully vitrified into MG under a cooling rate varying between 3×10^{13} and 10^{13} K s⁻¹ (Extended Data Fig. 7c).

The thermal stability of Ta MG is rationalized by our computation, showing that the crystal growth of low-index faces of bcc Ta is a thermally activated process at room temperature, with infinitesimally small growth rates at the GCIs (based on Extended Data Fig. 5d). It should be pointed out that the 'slow' growth rate of Ta crystals is distinctly different from that of face-centred cubic (fcc) metals, in which the growth of crystal interfaces is expected to be spontaneous and fast even at zero temperature¹⁴. Indeed, we have tried but failed to produce any monatomic MGs from fcc metals (for example gold, silver, copper, palladium, aluminium, rhodium and iridium) using the very same approach.

The competition between vitrification and crystal growth can be controlled experimentally, leading to a novel phase-change phenomenon in the MG. Figure 4 illustrates a vitrification-crystallization cycle in a Ta sample controlled by alternately applying two kinds of electric pulse with the same duration (3.6 ns) but different voltages. With the assistance of in situ TEM observation, the structural and morphological evolutions of the sample can be monitored on the fly. As shown in Fig. 4a, a Ta MG 40 nm in thickness and 50 nm in length obtained with a high-voltage (1.26-V) electric pulse (that is, the vitrification pulse) reverted to its original crystalline state after the application of a series of low-voltage (0.90-V) electric pulses (that is, the crystallization pulses), with each pulse reducing the size of the sandwiched amorphous zone (Fig. 4b, c). The GCIs were identified as being atomically rough and diffuse during both vitrification (Fig. 4e) and crystallization (Fig. 4f). After complete crystallization of the Ta MG (Fig. 4c and inset), another vitrification pulse again generated a glassy zone of Ta (Fig. 4d) with almost identical dimensions and morphology to that shown in Fig. 4a, demonstrating that a reversible glass-crystal phase-change process is achievable by our approach. Another example of controlled phase changes in Ta MG is presented in Supplementary Video 1. This reversible phase-change behaviour of Ta, bearing a resemblance to those in chalcogenide glasses^{26,27}, indicates the potential of the present methodology for employing marginal glass formers with extremely fast crystallization kinetics for applications in phase-change-based nano-devices^{26,27}.

The vitrification of pure metallic liquids reported here should not be attributed to the enhanced glass-forming ability associated with impurities in the original materials (Extended Data Table 1) and/or oxygen contamination during experimental procedures (see Methods and Extended Data Fig. 8). The successful formation of monatomic MGs opens up new opportunities for studying the structural dependence of rheological, thermal, electrical and mechanical properties of MGs, in which complications due to chemical effects in multicomponent MGs can be shielded. For instance, we have conducted tensile tests on the monatomic Ta MG as synthesized (Extended Data Fig. 9 and Supplementary Video 2). The insight gained from the mechanical testing experiment is beyond the scope of the present paper and will be presented later. Last, we stress that the ultrafast quenching rate (${\sim}10^{14}\,{\rm K\,s}^{-1}$) achieved in this technique is high enough to freeze the atoms within a fraction of a nanosecond. With such a high cooling rate to reach deep quench, the inherent structure of liquids²⁸ can be accessed, enabling investigations to be made of the fast kinetics of supercooled liquids and the mechanisms for the formation of metastable materials under conditions far from equilibrium.

Online Content Methods, along with any additional Extended Data display items and Source Data, are available in the online version of the paper; references unique to these sections appear only in the online paper.

Received 6 April; accepted 25 June 2014. Published online 6 August 2014.

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Supplementary Information is available in the online version of the paper.

Acknowledgements We thank A. J. Coley and Y. Liu for their assistance in designing the electrical circuit for our experiment, and Y. He for performing the liquid-quenching experiment on iridium and rhodium. H.W.S. acknowledges helpful discussions with L. V. Zhigilei. S.X.M. acknowledges National Science Foundation (NSF) grant CMMI 0928517 through the support of the University of Pittsburgh. Work at George Mason University was supported by the US NSF under grant no. DMR-0907325. This work was performed in part at the Center for Integrated Nanotechnologies (CINT), an Office of Science User Facility operated for the US Department of Energy (DDE) Office of Science. The computational work was conducted on the SR10000-K1/52 supercomputing facilities of the Institute for Materials Research, Tohoku University.

Author Contributions L.Z. and J.W.W. carried out the TEM experiments under the direction of S.X.M. S.X.M. created the experimental protocols. H.W.S. performed the computer simulation. L.Z., H.W.S. and S.X.M. performed the experimental data analysis. All the authors (L.Z., J.W.W., H.W.S., Z.Z. and S.X.M.) contributed to the discussion of the results. L.Z., S.X.M. and H.W.S. wrote the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to S.X.M. (sxm2@pitt.edu) or H.W.S. (hsheng@gmu.edu).

METHODS

Specimen preparation. All materials studied in the present work, with purities listed in Extended Data Table 1, were provided by ESPI Metals. During specimen preparation, one end of a metal rod was flattened by a punch to form a substrate, which was then notched by a tungsten carbide cutter and torn apart with two clamps. This strategy generated many triangular nano-tips at the fracture edge of the metal pieces (Extended Data Fig. 1a), serving as specimens for the liquid-quenching experiment. Two such metal pieces with nano-tips were mounted on a Nanofactory scanning tunnelling microscope (STM) TEM holder, with one at the fixed end and the other at the piezo-manipulator.

Minimization of possible contamination. Some materials studied, such as Ta, are reactive with the atmosphere, especially oxygen. Here we made a special effort to minimize possible contamination by performing our experiment under helium or high vacuum and by deoxidation before the liquid-quenching experiment.

First, specimen preparation and loading procedures were conducted inside a glove box filled with helium (the content of O_2 and H_2O was below 1 p.p.m.). The STM holder, together with the samples, was then quickly transferred to the TEM while being kept in an air-proof environment. The time of exposure to air was less than 2 s. During such a short period, oxygen contamination was limited to surface adsorption, as shown by the lack of an amorphous oxidation layer on the specimen surface (Extended Data Fig. 1b). Oxygen absorption on clean Ta surfaces at room temperature has been reported to be a self-limiting process in which the absorption rate drops exponentially with respect to increasing oxygen coverage³⁰. It is therefore expected that a limited amount of oxygen was absorbed by our specimen during specimen preparation and transfer.

Once the specimens were inside the TEM column ($\sim 10^{-5}$ Pa), oxidation became negligible, as demonstrated by the following estimation. Assuming the sticking probability of oxygen molecules to be 1.0 (that is, oxygen molecules attach to the surface as soon as they hit the specimen), the oxygen adsorption rate can be obtained by calculating the collision frequency between oxygen molecules and the specimen surface. Under the high vacuum inside the TEM column, the oxygen partial pressure is as low as 2×10^{-6} Pa, in which case the interactions between oxygen molecules, k_B is the Boltzmann constant and *T* is absolute temperature, the oxygen molecule density inside the TEM column can be represented as

$$n = p/k_{\rm B}T \tag{1}$$

According to the Maxwell-Boltzmann distribution theory, the mean speed of oxygen molecules is $\langle v \rangle = \sqrt{\frac{8RT}{\pi M}}$, where *R* is the gas constant and *M* is the molar mass of oxygen molecules. In the scenario where collisions occur between oxygen molecules and a flat surface, only the speed along the normal direction of the surface (v_N) should be considered. Therefore the mean speed should be recast as

$$\langle v_{\rm N} \rangle = \frac{2}{\pi} \sqrt{\frac{8RT}{\pi M}} \tag{2}$$

Because oxygen molecules have an equal possibility of travelling along all directions, only half of them move towards the surface. Hence the collision frequency Z on a unit surface area can be calculated as

$$Z = \frac{1}{2} n \langle v_{\rm N} \rangle \tag{3}$$

Replacing *n* and $\langle v_N \rangle$ with equations (1) and (2), we obtain

$$Z = \frac{p}{k_{\rm B}T\pi} \sqrt{\frac{8RT}{\pi M}} \tag{4}$$

Under a partial pressure of 2×10^{-6} Pa and at a temperature of 300 K, $Z = 2.16 \times 10^{15}$ collisions s⁻¹ m⁻². With such a collision rate and a dimension of 85 nm $\times 40.8$ nm $\times 13.6$ nm (the size of the Ta nanowire in our computer simulation), ~ 20 collisions take place per second, corresponding to an increase in the oxygen content by 1.4 p.p.m. (weight percentage). In the real experiment, the sticking probability for each collision is less than 1.0, which makes oxidation even more trivial. During our ultrafast quenching experiment on the nanosecond scale, oxygen contamination of the specimens inside the TEM was deemed negligible.

Before the melt-quenching experiment, the joined nano-tips (specimens) were Joule-heated by applying a current on the order of 100 μ A to a temperature close to the melting point for half an hour. Such heating in high vacuum expels oxygen from Ta, which serves as an effective method to obtain Ta free of oxygen^{31,32}. Although in some cases the complete removal of oxygen was reported to be difficult, the remaining proportion of oxygen is rather small³³. This is confirmed by the EELS spectrum, in which the oxygen K-edge is invisible (cyan curve in Extended Data Fig. 8), indicating that the oxygen concentration in the current specimen was below the detection limit of EELS⁴⁹ (that is, below 10³ p.p.m. in atomic ratio).

Liquid-quenching and tensile experiments. All *in situ* experiments were conducted inside an FEI Tecnai F30 TEM operating at an acceleration voltage of 300 kV. We preferred longer tips with low-index zone axes (that is, $\langle 111 \rangle$, $\langle 001 \rangle$ and $\langle 110 \rangle$) parallel to the incident electron beam, which can be easily found in our samples. The two chosen nano-tips were brought into contact by the piezo-manipulator of the STM holder. After deoxidation by Joule heating, the liquid-quenching experiment started with the application of a transient square electric pulse by a Keithley pulse generator, creating a melting zone at the nano-tips, followed by ultrafast quenching via rapid heat dissipation through the substrates, leading to the formation of monatomic MGs. Tensile tests on the Ta MG as formed were performed by gradually retracting the substrate mounted on the piezo-manipulator. The strain rate can be controlled by adjusting the speed at which the substrate is retracted; in the present study it was controlled to be $\sim 10^{-3} \text{ s}^{-1}$.

Development of a new embedded-atom-method (EAM) potential for Ta. A realistic interatomic potential^{34,35} has been developed for the large-scale simulation of Ta. The potential, in the EAM formalism, was developed through fitting the potential energy landscape of Ta established through extensive *ab initio* calculations based on the density functional theory. The interatomic potential was developed in a tabulated form and is publicly available from https://sites.google.com/site/eampotentials/Ta.

More than 600 reference configurations (96–128 atoms in each configuration) of Ta were used in the potential fitting process, including equations of state of relevant crystal structures, liquid phases, point and interfacial defects, liquid inherent structures, and MGs quenched at various cooling rates, with a special emphasis on the liquid states and phase behaviour of Ta. Phonon frequencies and experimental elastic constants of the crystals selected were also taken into account in the fitting. High-precision *ab initio* calculations were conducted for each selected atomic configuration, using the plane-wave method and pseudopotential implemented in the Vienna *Ab-initio* Simulation Package (VASP)^{36–38}. The projector augmented-waves method and the generalized-gradient approximation were employed in all the VASP calculations, and sampling of the Brillouin zone was performed with $3 \times 3 \times 3$ Monkhorst–Pack *k*-point grids. The valence electron configuration of Ta in the density functional theory calculation is $5d^36s^2$.

The EAM potential was optimized with the force-matching method³⁵ implemented in the potfit package³⁹. Through a recursive method, the generated parameters of EAM were further refined until self-consistent conditions were achieved. Similar techniques have been successfully employed to generate highly optimized EAM potentials for fcc elements and multi-component metallic systems⁴⁰. The Ta EAM potential as developed accurately predicts the melting temperature of bcc Ta, the liquid density of Ta, the formation of the β -Ta phase and many other properties of Ta. More details on the validation of the newly developed EAM potential of Ta will be presented elsewhere.

AtC simulation of the heat transport. The two-temperature model was used for the AtC computer simulation²⁵. Because heat dissipation is conducted through phonon and electron transport, classic MD is incapable of simulating the electron transport process that dominates heat transfer in the current setup. In the TTM, the atomistic system, which runs MD simulation, is coupled to an additional electronic system described by the finite-element method. To model the coupling between the electronic system and the atomic system, the following two governing equations are used:

$$\rho_{\rm p} c_{\rm p} \dot{T}_{\rm p} = \kappa_{\rm p} \nabla^2 T_{\rm p} - g_{\rm e-p} (T_{\rm e} - T_{\rm p}) + \rho_{\rm p} r_{\rm p}$$
⁽⁵⁾

$$\rho_e c_e \dot{T}_e = \kappa_e \nabla^2 T_e - g_{e-p} (T_e - T_p) + \rho_e r_e \tag{6}$$

where ρ , *c*, *T* and κ are the density, specific heat, temperature field and thermal conductivity of phonons (with subscript p) or electrons (with subscript e), respectively; g_{e-p} denotes the electron–phonon coupling parameter, and *r* is a mass normalized source term originated from all the energy exchange events induced by external sources (for example the effects of Peltier cooling/heating, laser heating and Joule heating). Five parameters are needed to implement the AtC model to simulate the vitrification process of Ta. Following the approach of ref. 25, the five parameters are set as follows.

The phonon heat capacity $\rho_p c_p$. The phonon heat capacity per volume in the classic limit is provided by the Dulong–Petit law⁴¹:

$$\rho_{\rm p}c_{\rm p} = 3k_{\rm B}/V_a \tag{7}$$

where $k_{\rm B}$ is the Boltzmann constant and V_{α} is the atomic volume of Ta at a given temperature. For Ta at 3,000 K, the Dulong–Petit law yields a value of $2.1 \times 10^6 \, {\rm J \, m^{-3} \, K^{-1}}$ for $\rho_{\rm p} c_{\rm p}$.



The phonon thermal conductivity κ_p . The thermal conductivity of the phonon system is obtained by conducting classic MD simulation of Ta at desired temperatures (by both the Green–Kubo method and a direct method employing Fourier's law⁴²). At 3,000 K, the thermal conductivity of Ta due to phonons is estimated to be $3.5 \text{ W m}^{-1} \text{ K}^{-1}$, which is trivial in comparison with the experimental thermal conductivity of Ta crystal near its melting point at 3,200 K (67 W m⁻¹ K⁻¹) (ref. 43). Note that the electron thermal conductivity is about 20-fold the phonon conductivity. The electron heat capacity $\rho_e c_e$. The electron heat capacity per volume is evaluated from the free electron density. Considering that the free electrons behave similarly to a kinetic gas:

$$\rho_{\rm e}c_{\rm e} = \frac{\pi^2}{2} \frac{n_{\rm e}k_{\rm B}}{E_{\rm F}} T_{\rm e} = \gamma(n_{\rm e})T_{\rm e} \tag{8}$$

where n_e is the valence electron number and E_F is the Fermi level. Within the temperature range of interest, $\rho_e c_e$ is assumed to have a constant value of $5.0 \times 10^5 \text{ J m}^{-3} \text{ K}^{-1}$. The experimental value of the electron heat capacity coefficient γ is measured to be 541 J m⁻³ K⁻² (ref. 44).

The electron thermal conductivity κ_e . The estimation of the electron thermal conductivity of Ta is based on the Franz–Wiedemann law:

$$\kappa_{\rm e} = L\sigma T_{\rm e} = \kappa_0 \frac{T_{\rm e}}{T_{\rm p}} \tag{9}$$

where σ is the electrical conductivity, and *L*, the Lorentz constant, is $2.443 \times 10^{-8} \text{ W} \Omega \text{ K}^{-2}$. At 300 K, the electrical conductivity of Ta is about $8.0 \times 10^6 \Omega^{-1} \text{ m}^{-1}$, and $\kappa_0 = 58.6 \text{ W} \text{ m}^{-1} \text{ K}^{-1}$, which corresponds to the electron thermal conductivity when the atomic temperature is equal to the electron temperature at equilibrium (that is, when $T_{\rm e} = T_{\rm p}$).

The electron-phonon coupling coefficient g_{e-p} . The electron-phonon coupling coefficient is assumed to have a linear relationship to temperature⁴⁵. For Ta, the coupling coefficient is set at 3.0×10^{17} J m⁻³ K⁻¹ s⁻¹, comparable with the experimental electron-phonon coupling parameters for other transition metals⁴⁶.

Thermal conductivity of Ta crystal at 3,000 K by the TTM-MD method. The thermal conductivity is obtained from the Fourier heat law:

$$\kappa = \frac{-q}{\nabla T} \tag{10}$$

where \dot{q} is the heat flux density. With the parameters prescribed above, the thermal conductivity of Ta at 3,000 K is estimated as 62.6 W m⁻¹ K⁻¹, which agrees well with the experimental value⁴³.

Formation of Ta MG by rapid liquid quenching. The AtC method was used to simulate the cooling process of an $85 \times 40.8 \times 13.6$ nm³ Ta nanowire containing 2,457,600 atoms, without applying periodic boundary conditions. Both ends of the nanowire along the *x* axis are connected to heat reservoirs by fixing temperatures (both the atomic temperature and the electronic temperature) at 300 K. Joule heating is simulated by injecting electron heat flux into the system, creating a temperature distribution along the nanowire as shown in Extended Data Fig. 5a. Quenching processes in scenarios where the heat flux is terminated instantly and within 0.4 ns in a ramp function were simulated. The cooling process starts instantly after Joule heating is zeroed out, which proceeds at a quenching rate on the order of 10^{13} – 10^{14} K s⁻¹ (Extended Data Figs 5c and 7c). Such an ultrafast cooling rate strongly favours vitrification over crystal growth, leading to the formation of Ta MG.

Estimation of the critical cooling rate. The critical cooling rate \dot{T}_c required for vitrifying liquid Ta is estimated from dimensional considerations:

$$\dot{T}_c \approx T_L \nu / L$$
 (11)

where $T_{\rm L}$ is the temperature of the liquid, ν is the average moving velocity of the liquid-crystal interface, which is estimated to be $\sim 50 \,\mathrm{m \, s^{-1}}$ from Extended Data Fig. 5d, and *L* is the length of the melting zone. The critical cooling rate is derived by considering the temperature drop ΔT , which is the temperature interval between $T_{\rm L}$ and the glass transition temperature $T_{\rm g}$, divided by the time *t* required for complete crystallization. As shown in Fig. 3c and Extended Data Fig. 6, $T_{\rm g}$ is approximately half of $T_{\rm L}$, leading to $\Delta T \approx 0.5T_{\rm L}$. Assuming that complete crystallization is signified by two GCIs merging in the middle of the melting zone, each interface travels a length of 0.5L, leading to $t = 0.5L/\nu$. Hence, we have $\dot{T}_c = \frac{\Delta T}{t} \approx \frac{0.5T_{\rm L}}{(0.5L/\nu)} = \frac{T_{\rm L}\nu}{L}$. Under the simulation geometry in which *L* is about 30 nm, the estimated critical cooling rate is $\sim 5 \times 10^{12} \,\mathrm{K \, s^{-1}}$.

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Extended Data Figure 1 | Ta nano-tips and Ta MG obtained by liquid quenching. a, Triangular nano-tips derived by pulling a metal substrate apart. b, High-resolution TEM image of a Ta nano-tip viewed along the (001) zone axis with no oxidation layer identified at the surface. c, Controllable size by tuning the electric pulse. A Ta MG with diameter close to 100 nm is obtainable

under an electric pulse with voltage above 2 V. **d**, Tunable aspect ratio by coupling with tensile or compressive stress. A nanowire with an aspect ratio of 4 was formed by applying tensile loading during liquid quenching. The glass–crystal interfaces (GCIs) are indicated by yellow dotted curves.



Extended Data Figure 2 | Formation and room-temperature stability of V MG. a, TEM image of two crystalline V nano-tips in contact with each other. b, Formation of a V MG 75 nm long and 80 nm thick under a 1.2-V, 3.6-ns electric pulse. The V MG as formed was sandwiched by two crystalline substrates with two GCIs (denoted by yellow dotted curves). c, d, Thermal stability of V MG at room temperature. Amorphous V was found stable after relaxation for 6 h (c) and even 56 h (d). To protect V from oxidation, an

amorphous carbon layer 5 nm thick was coated on the surface of the V MG. The reduced length of the V MG in **d** is due to a slight change in the viewing angle. **e**, High-resolution image of the V MG relaxed for 56 h, showing typical amorphous characteristics. **f**, Electron diffraction pattern of V MG, showing diffusive amorphous halos and a diffusive background. The bright diffraction spots originate from bcc V because the aperture was not small enough to exclude the neighbouring crystalline V substrate.

Extended Data Figure 3 | **Formation of Mo MG by ultrafast quenching. a**, TEM image of two contacting Mo nano-tips with a well-defined bcc structure viewed along the (111) zone axis (inset in **a**). **b**, Formation of Mo MG under the first vitrification pulse. The GCIs are indicated by yellow dotted curves. **c-e**, Growth of the Mo MG under subsequent vitrification pulses. The GCIs

moved one step away from each other (denoted by two yellow arrows in **b**) after the second (**c**), third (**d**) and fourth (**e**) pulse, respectively, resulting in the growth of the Mo MG. The amorphous structure is corroborated by the diffuse halos in the fast Fourier transformation (inset in **e**).

Extended Data Figure 4 | Formation and spontaneous crystallization of W MG. a, High-resolution TEM image of the original crystalline W nano-tip viewed along the $\langle 100 \rangle$ zone axis. b, Formation of W MG in the W nano-tip under a vitrification pulse. An atomically rough and diffuse GCI was identified, where the transition zone from amorphous to bcc W was about 1–2 nm thick

(the region between the two dotted yellow curves). **c**–**e**, Time-lapse images of spontaneous crystallization of W MG. W MG is unstable at room temperature, undergoing spontaneous crystal growth at the GCI to a well-defined bcc structure.

Extended Data Figure 5 Cooling rate and crystal growth rate estimated by AtC computer simulation. a, Atomic temperature distribution of a Ta nanowire with dimensions $85 \times 40.8 \times 13.6$ nm³ at time zero when Joule heating is stopped instantly. The $32 \times 12 \times 6$ finite-element meshes were used to simulate the electron temperature field in the TTM. The electron temperature on both sides of the nanowire was kept constant at 300 K. **b**, Evolution of atomic temperature distribution along the *x* direction of the Ta

nanowire during the cooling process. **c**, Cooling rate as a function of temperature in liquid Ta (the middle section within 5 nm along the *x* direction). The highest cooling rate at the initial stage of quenching reaches as high as 10^{14} K s⁻¹. **d**, Crystal growth rate at the LCIs of the (100) (cyan circles) and (110) (orange squares) crystallographic planes, on the basis of classic MD simulation. The simulation details for crystal growth from the melt are similar to those in ref. 47.

Extended Data Figure 6 | Glass transition temperature $T_{\rm g}$ of Ta from MD simulation. Both the enthalpy change and the volume change as a function of

temperature indicate that $T_{\rm g}$ is close to 1,650 K, which is in good agreement with other theoretical work $^{\rm 48}$

Extended Data Figure 7 | **Vitrification of liquid Ta under a heating flux terminated within 0.4 ns by AtC computer simulation. a**, Atomic configuration of the Ta nanowire after Joule heating. A melting zone 35 nm long was formed before quenching (atoms coloured with red). **b**, An 18-nm

region in the middle of the melting zone is vitrified to a glassy state after being quenched to room temperature. c, Cooling rate as a function of temperature in the middle region of the melting zone during quenching. The cooling rate varied between 3×10^{13} K s⁻¹ at 4,200 K and 10^{13} K s⁻¹ at T_g.

Extended Data Figure 8 | Electron energy-loss spectroscopy (EELS) spectra of oxygen in Ta. An oxygen K-edge was identified at about 530 eV energy loss from Ta that had been exposed to air for ~10 min (red curve). In contrast, no oxygen K-edge was detected in both Ta MG and crystal (cyan curve) when the Ta nano-tips were processed in a helium-protected environment and

deoxidized by Joule heating before the liquid-quenching experiment, indicating that the oxygen concentration in the Ta MG was below the detection limit of EELS, which is \sim 1,000 p.p.m. in atomic ratio⁴⁹ (that is, \sim 100 p.p.m. in weight percentage).

Extended Data Figure 9 | **Tensile mechanical test on Ta MG.** (See also Supplementary Video 2.) **a**, A hybrid Ta nanowire: the left half is Ta MG and the right half is bcc Ta. This hybrid nanowire was fabricated by forming a Ta MG nanowire at first, followed by controlled gradual crystallization to move one of the GCIs (outlined by yellow dotted curves) to the middle of the

nanowire. **b**, Deformation of Ta MG along a major shear band, which began shortly after tensile loading. No plasticity was observed in bcc Ta on the right. The major shear proceeded along $\sim\!52^\circ$ off the tensile loading direction, as denoted by two dark red arrows.

Extended Data Table 1 | Purities of the bcc metals studied here

	Impurity concentration (ppm)			
Impurities	Ta (99.98%)	V (99.9%)	W (99.98%)	Mo (99.98%)
Cr	10	50	10	< 20
Nb	10			
Si	10	150		
W	40			
Zr	10			
Мо	10	130		
Mg	10			
Sn	10	< 30		
Fe	15	200	20	< 50
Ni	15	< 50	130	< 50
Ti	10	150		
V	10			
Cu	10	< 50	< 20	< 10
Mn	10			
Al	10	50		
Co	10			
Са		< 50		
к			< 20	< 30

The purities of Ta, V, W and Mo were 99.98%, 99.9%, 99.98% and 99.98%, respectively. The listed impurity concentrations (in parts per million) of the four bcc metals can be found from the table of ESPI elements at http://www.espimetals.com/index.php/online-catalog.