

Ultrafast Heating Unveils Hidden Liquid–Liquid Phase Separation

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Article

Keywords: Liquid–liquid phase separation, Phase transitions, Nucleation and crystallization, Supercooled liquids, Ultrafast calorimetry

Posted Date: March 24th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-9020514/v1>

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Additional Declarations: There is **NO** Competing Interest.

Abstract

In supercooled liquids, phase selection is governed by competing transformation timescales, yet crystallization typically pre-empts access to metastable liquid states. Liquid–liquid phase separation (LLPS) has long been proposed as a fundamental source of mesoscale heterogeneity, yet direct experimental access to heating-induced LLPS has remained elusive. Here we demonstrate that ultrafast heating opens a kinetic window in which crystallization and liquid–liquid demixing become temporally separable. Using a model supercooled metallic liquid, we directly resolve the emergence and growth of coexisting liquid populations on millisecond timescales by correlating ultrafast calorimetry with nanoscale real-space imaging and reciprocal-space structural probes. We show that subtle endothermic signatures in the supercooled regime—previously attributed to relaxation phenomena—constitute thermodynamic fingerprints of LLPS. The resulting chemical partitioning preconfigures subsequent crystallization pathways, revealing how competing timescales govern access to hidden regions of the liquid free-energy landscape. Our results establish kinetic control as a general route to reveal metastable liquid–liquid coexistence that is otherwise masked by crystallization, providing a framework for understanding non-equilibrium phase selection in supercooled liquids.

Introduction

Liquids are often regarded as structurally homogeneous states of matter, yet increasing theoretical and experimental evidence indicates that many liquids harbor latent instabilities toward *liquid–liquid phase separation* (LLPS). Such instabilities have been linked to polyamorphism and anomalous thermodynamic behavior in supercooled liquids.^{1, 2, 3, 4, 5, 6, 7, 8} Despite its conceptual importance, direct experimental access to LLPS has remains challenging because crystallization typically intervenes before phase separation can fully develop, particularly upon heating where restored atomic mobility rapidly activates competing solidification pathways.^{9, 10}

Phase selection in supercooled liquids is governed by competing transformation timescales that can kinetically suppress access to metastable states.^{11, 12} When crystallization outpaces alternative instabilities, thermodynamically allowed liquid states remain experimentally inaccessible. LLPS represents a prototypical example of such kinetically hidden behavior. Whether deliberate separation of these competing timescales can reveal otherwise inaccessible liquid states remains an open question in non-equilibrium condensed-matter physics.¹³

Rare precedents for heating-accessed LLPS span diverse materials systems, including water–glycerol mixtures¹⁴ and supercooled water¹⁵, underscoring that this phenomenon is not restricted to a single class of liquids. However, such observations remain exceptional, reflecting the narrow kinetic window in which phase separation can emerge before crystallization dominates. It therefore remains unclear whether LLPS can be systematically accessed upon heating and, more broadly, whether kinetic control provides a general route to hidden regions of the liquid free-energy landscape.

Metallic glasses (MGs) provide a uniquely controllable experimental platform in which deeply supercooled liquid states can be accessed over well-defined temperature windows while suppressing crystallization sufficiently to allow competing liquid-state instabilities to emerge.^{9, 16} Previous studies have reported signatures consistent with LLPS prior to crystallization in several bulk metallic glass formers. Early evidence included volumetric anomalies observed in levitated droplets of Ti–Zr–Ni–Cu–Be (Vit1), Zr–Nb–Al–Cu–Ni (Vit106), and Zr–Ti–Cu–Ni–Al–Be (LM7), interpreted as first-order liquid–liquid transitions.¹⁷ Subsequent synchrotron studies on Vit1 revealed peak splitting and viscosity changes indicative of coexisting liquid populations.¹⁸ Chemical phase separation in liquid phase has also been reported in Cu–Zr–Al–Y BMGs during heating, via in situ X-ray scattering and calorimetry, revealing distinct liquid compositions in the *supercooled liquid region* (SCLR).¹⁹ However, the temporal sequence linking LLPS to crystallization, the nanoscale pathways of chemical segregation, and rate dependence of their competition remain unresolved. More fundamentally, it is unclear whether kinetic control can reliably disentangle liquid demixing from crystallization and thereby expose metastable liquid–liquid coexistence that is otherwise masked under conventional thermal conditions.

Among metallic glass formers, the ternary Pd–Au–Si system presents a long-standing ambiguity regarding the origin of chemical heterogeneity observed prior to crystallization. Early work proposed that LLPS might precede crystallization in Pd₇₄Au₈Si₁₈,²⁰ whereas later observations attributed similar heterogeneities to direct nanocrystallization.²¹ Once crystallization is activated, distinguishing liquid demixing from solid-state transformation becomes intrinsically difficult. Resolving this ambiguity therefore requires experimental access to the supercooled liquid on timescales short enough to temporally separate competing instabilities.

Thermodynamically, the Pd–Au–Si system is predisposed to chemical partitioning due to asymmetric mixing enthalpies among its constituent elements (**Fig. 1**).^{22, 23} The larger atomic radius of Au relative to Pd and Si induces local strain that can further promote segregation into Au-rich domains.²⁴ At the same time, enhanced glass-forming ability and kinetic stabilization create a delicate balance between segregation and solidification.^{25, 26} This competition renders LLPS thermodynamically plausible yet kinetically hidden, making the system an ideal platform for probing whether rapid thermal pathways can transiently access hidden liquid states.^{27, 28}

Here we demonstrate that ultrafast heating opens a kinetic window in which liquid–liquid demixing and crystallization become temporally separable. By combining ultrafast differential scanning calorimetry (FDSC) with nanoscale real-space imaging and in situ high-energy synchrotron X-ray diffraction, we directly resolve the emergence and growth of coexisting liquid populations prior to crystallization on millisecond timescales. We identify both calorimetric and structural signatures of liquid–liquid coexistence and show how the resulting chemical partitioning preconfigures subsequent crystallization pathways. These results establish kinetic control as a general strategy for accessing metastable regions of the liquid free-energy landscape that are otherwise obscured by crystallization, providing new insight into phase selection far from equilibrium.

Main

1. Homogeneous starting structure and anomalous thermal signature

To ensure that all observed heterogeneities emerge during heating, we first established a fully amorphous and chemically homogeneous starting state (**Fig. 2a**). All FDSC measurements were recorded upon heating at $5,000 \text{ K s}^{-1}$ after cooling at rates between 100 and $40,000 \text{ K s}^{-1}$. Cooling at 100 K s^{-1} induced partial crystallization, as indicated by the attenuation of both the glass-transition signal and the crystallization exotherm upon reheating. Increasing the cooling rates to $200\text{--}5,000 \text{ K s}^{-1}$ suppressed crystallization, yielding an amorphous solid that exhibited a clear glass transition with endothermic enthalpy relaxation, immediately followed by the onset of exothermic crystallization. Cooling at $40,000 \text{ K s}^{-1}$ produced a featureless selected-area diffraction pattern (SADP) (inset of **Fig. 2a**) and uniform STEM-EDS maps, confirming the absence of pre-existing chemical segregation. This cooling rate therefore, maximizes structural homogeneity and the thermal separation between the glass transition and crystallization, and was used for all subsequent experiments. Samples prepared under these conditions are hereafter referred to as the as-quenched material.

Upon heating, the Pd–Au–Si glass exhibits two distinct crystallization exotherms, with peak temperatures that shift systematically with heating rate (**Fig. 2b**). Notably, at heating rates above $1,000 \text{ K s}^{-1}$, an additional subtle thermal feature emerges between the glass transition and the onset of crystallization. This feature, which is absent at lower rates, suggests the activation of a liquid-state process prior to solidification and forms the focus of the following analysis.

2. Sequential crystallization reflecting pre-existing liquid heterogeneity

To determine whether the two crystallization exotherms originate from distinct phases, we quenched samples immediately after each event during heating at 100 K s^{-1} , thereby capturing the structural state associated with each calorimetric peak (**Fig. 3**).

Quenching after the first exotherm, at $T_{\text{c1,endset}} = 477 \text{ }^{\circ}\text{C}$, revealed nanoscale, compositionally well-defined Au-rich domains (14.85 at.% Au) embedded within an amorphous matrix (**Fig. 3b**). These domains exhibit a mean diameter of $39.5 \pm 4.8 \text{ nm}$, a number density of $1.5 \times 10^{22} \text{ m}^{-3}$, and a volume fraction of $47.1 \pm 4.1\%$. The corresponding SADP displayed sharp rings superimposed on diffuse halos, and analysis of the ring radii identified a face-centered cubic (FCC) structure for the domains (**Supplementary Fig. 1**). STEM bright-field imaging showed uniform diffraction contrast within individual domains, either bright or dark, indicating fully single-crystalline grains with random orientations, while STEM dark-field imaging confirmed that the surrounding Au-depleted matrix (5.07 at.% Au) remained fully amorphous. These observations establish that the first crystallization event corresponds to the solidification of Au-rich liquid domains.

Quenching after the second exotherm, at $T_{c2, \text{endset}} = 495\text{ }^{\circ}\text{C}$, revealed crystallization of the matrix itself. (**Fig. 3c**) The domains increased in size to $52.8 \pm 6.4\text{ nm}$, with a number density of $6.5 \times 10^{21}\text{ m}^{-3}$, yielding a volume fraction of $50.1 \pm 7.5\%$. Compared to $477\text{ }^{\circ}\text{C}$, the Au content remained $13.74\text{ at.}\%$ in the domains and decreased to $2.86\text{ at.}\%$ in the matrix due to the increased domain volume fraction (**Supplementary Table 1**). SADPs retained the same sharp FCC rings associated with the domains but with additional diffraction spots, particularly within the first sharp ring, indicating additional crystallinity. TEM bright-field imaging showed strong contrast in the domains, while TEM dark-field imaging, using an objective aperture positioned on these additional reflections, revealed partial crystallization within the Au-depleted regions. Diffraction analysis using jEMS simulations³¹ identifies the matrix phase as structurally related to orthorhombic Pd_3Si in agreement with reported crystallographic data.³² This assignment is supported by EDS showing that Au depletion drives the matrix composition towards Pd_3Si , consistent with the Pd–Si binary phase diagram (**Fig. 1b**).

Together, these observations demonstrate a sequential crystallization pathway: the Au-rich domains—having lower glass-forming ability—crystallize first into the FCC phase near $477\text{ }^{\circ}\text{C}$, followed by crystallization of the Pd–Si-rich matrix ($2.86\text{ at.}\%$ in Au) into the orthorhombic phase near $495\text{ }^{\circ}\text{C}$. The crystallization sequence therefore, mirrors the compositional partitioning established in the supercooled liquid, providing clear evidence that the two calorimetric peaks arise from two chemically distinct liquid populations rather than from polymorphism within a homogeneous melt.

3. Ultrafast heating unveils early-stage liquid–liquid phase separation

To access the earliest stages of liquid transformation before crystallization intervenes, Pd–Au–Si was heated at an ultrafast rate of $20,000\text{ K s}^{-1}$ and quenched at selected temperatures along the calorimetric trace (**Fig. 4a,b**), enabling direct visualization of structural evolution and associated chemical fluctuations on millisecond timescales.

Immediately after the glass transition, at $T_{g, \text{endset}} = 499\text{ }^{\circ}\text{C}$, STEM-EDS mapping revealed the emergence of nanoscale, globular Au-rich regions ($11.32\text{ at.}\%$ Au) that are absent in the as-quenched glass. These droplets have a mean diameter of $33.4 \pm 2.0\text{ nm}$, a number density of $7.7 \times 10^{19}\text{ m}^{-3}$, and a volume fraction of 0.2% , representing the earliest detectable signature of incipient liquid–liquid phase separation (LLPS). Their low number density and modest size indicate nucleation at the onset of restored atomic mobility.

At the temperature of the subtle endothermic event, $T_{\text{event}} = 525\text{ }^{\circ}\text{C}$, the droplets grew dramatically to $125.1 \pm 9.0\text{ nm}$ with a number density of $5.3 \times 10^{19}\text{ m}^{-3}$, reaching a volume fraction of 5.5% . The droplets maintained a nearly constant Au content ($11.40\text{ at.}\%$), while the surrounding liquid became increasingly depleted ($7.60\text{ at.}\%$, uniform except near domains), revealing pronounced uphill diffusion of Au. The striking acceleration in domain growth, coupled with the absence of any crystallization peak, identifies this calorimetric feature as the thermodynamic signature of LLPS rather than an additional glass transition.

Further heating into the SCLR, at $T_{\text{SCL}} = 550\text{ }^{\circ}\text{C}$, intensified this partitioning. The domains further expanded to $212.2 \pm 11.0\text{ nm}$, and the volume fraction rose to 15.22% with a number density of $3.0 \times 10^{19}\text{ m}^{-3}$, indicating continued growth of domains. The domain composition remained uniform (11.04 at.%), while the matrix composition sharpened into a distinctly Au-poor liquid with a minimum of 5.30 at.% Au. Steep compositional gradients developed at the domain boundaries, hallmarks of a metastable liquid–liquid coexistence. The uniform internal composition of droplets confirms that both the droplets and the matrix remained fully liquid up to this point.

Upon reaching the crystallization endset, $T_{\text{c,endset}} = 700\text{ }^{\circ}\text{C}$, the domains transformed into the FCC phase identified earlier at slower heating, while the surrounding matrix remained amorphous. Domain size stabilized at $223.1 \pm 5.6\text{ nm}$, and number density ($5.3 \times 10^{19}\text{ m}^{-3}$) remained comparable to earlier stages, yielding a volume fraction of 21.64%. Au content in the domains increased to 14.26 at%, and decreased uniformly to 4.86 at.% in the matrix. The crystallizing domains developed a core–shell structure with Au accumulating at the solid–liquid interface due to the sharp decrease in Au diffusivity upon crystallization. This interfacial enrichment, together with the now-uniform Au-poor matrix, provides a chemical “fossil record” of the preceding LLPS.

The extreme difference between droplet sizes at $20,000\text{ K s}^{-1}$ (hundreds of nanometers) and those observed at a slower rate of 100 K s^{-1} (tens of nanometers) underscores the kinetic nature of the LLPS window: at ultrafast heating rates, the system traverses the nucleation-dominated regime within a few milliseconds, rapidly exhausting nucleation events and thereby allowing subsequent growth with fewer competing domains, producing markedly larger Au-rich liquid droplets.

4. Diffraction identification of phases and rate-dependent crystallinity

TEM diffraction enabled further identification of the phases present along the ultrafast heating pathway (**Fig. 4b**). At $T_{\text{g,endset}}$, SADP showed only diffuse rings (as in the as-quenched state) indicating an amorphous matrix; however, nanodiffraction on the few nanoscale domains revealed a certain degree of crystallinity (**Supplementary Fig. 2**). Conversely, SADPs at T_{event} and T_{SCL} displayed spots in addition to diffuse rings; TEM bright-field imaging indicated an amorphous matrix and crystalline domains (**Supplementary Fig. 3**). Post-crystallization at $T_{\text{c,endset}}$, diffraction spots persisted while the matrix remained amorphous, linking the exothermic peak to domain crystallization. SADPs along high-symmetry zone axes were obtained via tilting experiments at $T_{\text{c,endset}}$. Analysis indicated that domains possess an FCC structure consistent with earlier reports²⁰. The FCC lattice parameter—determined from SADPs using Au nanoparticles measured under identical TEM conditions as a reference (**Supplementary Fig. 4**)—was $0.3925 \pm 0.0002\text{ nm}$, matching prior work³³. At $700\text{ }^{\circ}\text{C}$, the same FCC structure was observed. Meanwhile, the diffuse rings exhibited a change relative to $550\text{ }^{\circ}\text{C}$: the second diffuse peak became broader, plausibly reflecting reduced Au content in the matrix (**Supplementary Fig. 5**).

These observations establish that nanoscale LLPS is activated immediately upon entering the supercooled liquid region, long before crystallization begins. Ultrafast heating thus exposes liquid-state instabilities that remain hidden under conventional thermal conditions, revealing a rich kinetic landscape where coexisting liquids compete with crystallization on ultrashort timescales. Curiously, however, in the ultrafast-heated samples, crystalline signatures in domains appeared even before the crystallization peak in the FDSC trace (**Fig. 2b**) was reached. This crystallinity likely developed during cooling after heat treatment. Notably, the domain composition is intrinsically non-amorphizable, as even melt-spun ribbons already exhibit crystalline order (**SupplementaryFig. 6**). Compared with the nominal $\text{Pd}_{74}\text{Au}_8\text{Si}_{18}$ (minor Pd-to-Au substitution in binary $\text{Pd}_{82}\text{Si}_{18}$ eutectic), the domains are enriched in Au and depleted in Si, shifting their composition away from eutectic points and reducing their glass-forming ability. Avoiding crystallization of such domains would require faster cooling than achieved during post-heating quench. Together, these results strongly support the occurrence of nanoscale LLPS before crystallization, but leave open important questions about how local compositional fluctuations drive broader structural transformations under very low driving force.

5. Compositional evolution and thermodynamic fingerprints of LLPS

The thermodynamic fingerprints of LLPS are encoded in the spatial distribution of elements across Au-rich domains and the surrounding matrix. STEM-EDS line profiles revealed two distinct regimes (**Fig. 4c**). Prior to the crystallization peak observed upon ultrafast heating (**Fig. 2b**), the Au-rich domains exhibited a uniform internal composition, consistent with rapid diffusion in the liquid. In contrast, the surrounding matrix displayed gradual Au depletion, indicative of uphill diffusion driven by chemical-potential gradients and followed by diffusion-limited growth of Au-rich domains as Au is continuously supplied from the adjacent liquid.

Crystallization disrupts this balance, especially at the phase boundary. Formerly uniform domains developed a core–shell structure characterized by an Au-enriched shell, while the surrounding matrix became chemically homogenized (**Fig. 4c**). This redistribution—marked by the expulsion of Au from the matrix towards domains—reflects the strong thermodynamic preference for Pd–Si enrichment in the glass-forming matrix, consistent with the mixing enthalpies of the constituent elements (**Fig. 1a–c**). In parallel, Au reduces surface (and hence interfacial) energies relative to Pd^{34} , favoring its accumulation at the domain–matrix interface. Moreover, in the crystalline state, Au diffusivity is dramatically reduced ($D \approx 10^{-19} \text{ m}^2 \text{ s}^{-1}$) compared with liquid-state diffusivities ($D \approx 10^{-9} \text{ m}^2 \text{ s}^{-1}$)^{35, 36}, kinetically constraining redistribution and limiting further growth. The emergence of core–shell structure, together with Pd–Si enrichment in the matrix and interfacial Au segregation (not observed before the crystallization peak), provides structural evidence consistent with LLPS followed by domain crystallization.

Calorimetry provides an independent thermodynamic signature. The subtle endothermic event observed in the SCLR does not arise from a secondary glass transition or enthalpy relaxation. The phase-separated domains ($\text{Pd}_{73.1}\text{Au}_{11.3}\text{Si}_{15.6}$) are enriched in Au and depleted in Si relative to the initial alloy; reducing the Si content would lower T_g , thereby ruling out a glass transition as the origin of the thermal

anomaly.²⁰ Rather, the calorimetric feature reflects the entropic and enthalpic costs associated with phase separation itself—capturing the free-energy change accompanying liquid demixing. This supports LLPS as the underlying mechanism and indicates that it proceeds via nucleation and growth rather than spinodal decomposition. The discrete droplet morphology, finite number density, and well-defined compositional plateaus within domains are inconsistent with the continuous compositional modulation expected for spinodal decomposition. Instead, the observed evolution—marked by identifiable nucleation events followed by diffusion-limited growth—supports a nucleation-and-growth mechanism for liquid demixing.

6. Structural signatures of liquid–liquid coexistence and kinetic phase selection

To bridge the nanoscale observations with mesoscale liquid structure, in situ high-energy synchrotron X-ray diffraction was performed during conventional heating at 0.1667 K s^{-1} (**Fig. 5**). Temperature-dependent scattering intensity, $I(Q)$ (**Fig. 5a**), is shown alongside DSC heat flow, highlighting characteristic transformation temperatures: the glass transition T_g , crystallization onset T_{x1} , and crystallization peaks T_{p1} and T_{p2} . The first sharp diffraction peak, Q_1 (low- q range, $\sim 2.5 \text{ \AA}^{-1}$), sharpened and intensified with temperature, while a broader second peak, Q_2 (high- q range, $\sim 4.5 \text{ \AA}^{-1}$), developed subsidiary peaks on the left (Q_{2L}) and right (Q_{2R}). Selected $I(Q)$ profiles for Q_1 and Q_2 (**Fig. 5b,c**) reveal a detailed structural evolution upon heating.

Upon entering the supercooled liquid region, Q_1 exhibited pronounced anomalies: shoulder formation on the left and splitting into two peaks that broadly overlap with the 111 and 002 diffraction peaks of an FCC structure, indicating FCC-like short-range order in one liquid population. Concurrently, the shoulder appearing at Q_1 and the broadening of Q_{2L} are consistent with changing short-range order in the surrounding matrix, supporting the coexistence of two liquid populations and LLPS. The splitting and evolution of Q_1 thus provide a reciprocal-space structural order parameter for liquid–liquid coexistence, directly linking calorimetric anomalies to distinct short-range environments. A shift of Q_1 to a lower Q corresponds to increased real-space interatomic spacing, consistent with the formation and growth of a less dense, FCC-like liquid domain.

As crystallization began, Q_1 intensity (**Fig. 5d**) rose sharply, marking the formation of FCC Au-rich crystals. At higher temperatures, simultaneous growth of Q_{2L} and Q_{2R} , coupled with the modulation of the central peak, yielded the emergence of diffraction peaks consistent with an orthorhombic Pd–Si-rich phase, mirroring the sequential crystallization observed by electron microscopy.

Taken together, the calorimetric “extra transition” and the diffraction peak splitting are not separate anomalies but coupled manifestations of a single process—heating-accessed liquid–liquid phase separation—that creates coexisting liquids and thereby preconfigures crystallization pathways. The separation between demixing and crystallization arises from the distinct activation barriers and characteristic diffusion coefficients governing chemical partitioning and crystal nucleation. Ultrafast

heating effectively shifts the system into a regime where compositional fluctuations can amplify before crystalline nuclei reach a critical size. In this sense, the kinetic window is defined not by equilibrium thermodynamics alone, but by the relative rates of atomic diffusion and structural ordering. Manipulating heating rates therefore provides a direct handle on phase selection in deeply supercooled liquids.

Conclusion

By directly correlating ultrafast thermal pathways with nanoscale and mesoscale structural evolution, we establish that liquid–liquid phase separation emerges immediately upon entering the supercooled liquid regime and precedes crystallization. Our results resolve a long-standing debate by demonstrating that the secondary endothermic feature—widely ascribed to an additional glass transition or enthalpy relaxation—constitutes a calorimetric signature of liquid–liquid phase separation. The resulting chemical partitioning strongly influences subsequent nucleation and crystallization, indicating that liquid-state instabilities actively shape solidification pathways. While demonstrated in Pd–Au–Si, the key mechanism identified here is the deliberate separation of competing transformation timescales rather than any specific thermodynamic feature of this alloy. Systems in which demixing and crystallization operate on comparable timescales may similarly exhibit kinetically hidden liquid states accessible through controlled thermal pathways. More broadly, our findings establish liquid–liquid phase separation as a hidden kinetic route to metastable liquid states far from equilibrium, providing a general framework for understanding and controlling transformation pathways across diverse classes of liquids.

Methods

Alloy synthesis

A master alloy ingot (5 g) with the nominal chemical composition Pd₇₄Au₈Si₁₈ (at.%) was synthesized by induction melting. High-purity elemental spherulites of Au (99.99% purity) and Pd (99.95% purity), together with Si single-crystal pieces (99.9999% purity), were melted in a quartz crucible and maintained in the liquid state for 60 s, during which homogenization was achieved via eddy current-induced stirring. Post-melting mass measurements indicated no significant mass loss.

The master alloy ingot was subsequently processed by melt spinning to fabricate an amorphous ribbon approximately 2 mm in width and 35 μm in thickness. Melt spinning was conducted under an Ar atmosphere. Before melt spinning, the master alloy was inductively remelted in a quartz crucible. The molten material was then ejected through a 1.5 mm diameter circular nozzle under an Ar overpressure of 300 mbar onto the surface of a rotating Cu wheel. The nozzle-to-wheel distance was maintained at 0.3 mm, and the tangential speed of the wheel was set at 23 m s^{−1}.

The chemical composition was analyzed using atom probe tomography (APT) with a LEAP 4000X HR (CAMECA Instruments, USA), indicating that the alloy composition was Pd_{73.8}Au_{7.7}Si_{18.5} (at.%) (see details in **Supplementary Table 2**).

Thermal analysis and phase transformation characterization

Conventional differential scanning calorimetry (DSC) measurements were performed using a DSC823e (Mettler-Toledo, Switzerland) device equipped with an automated sample robot. To measure the characteristic temperatures of the as-spun ribbon, samples (15 mg) were sealed in standard 40 μL Al crucibles and heated at a rate of 10 K min^{-1} under a constant Ar flow (30 mL min^{-1}).

A fast DSC (Flash DSC 2+, Mettler Toledo, Switzerland) operated with UFH 1 sensors was used to characterize the phase transformation kinetics and to prepare samples for subsequent microstructural analysis by electron microscopy. Sample names and corresponding temperature conditions are detailed in **Supplementary Table 3**. FDSC was connected to an intracooler TC100 (Huber, Germany), operating at a controlled temperature of approximately $-100\text{ }^{\circ}\text{C}$ to enable rapid cooling and precise thermal control during experiments. The sample support temperature of $16\text{ }^{\circ}\text{C}$ was selected to minimize the waiting time between sample placement and measurement. The sensor was under a continuous flow of Ar at a rate of 30 mL min^{-1} .

The melt-spun ribbons were cut with a scalpel under a binocular microscope into small pieces approximately 0.1 mm in size. Their mass was estimated from the ratio of the crystallization enthalpy ($\Delta H = 66.6\text{ J g}^{-1}$) to be between 50 ng and 200 ng , which places them in the range of negligible size dependence on nucleation and crystallization.³⁷ They were then transferred using a hairbrush onto the center of the sensor. Before each measurement, samples were heated up to $970\text{ }^{\circ}\text{C}$, above T_i (925°C). A waiting time of 2 ms at the melt was confirmed through preliminary measurements to ensure reproducibility. Samples for TEM were held at the target temperatures for 2 ms to account for thermal inertia and ensure that the target temperature was reached, before being quenched at $40,000\text{ K s}^{-1}$.

Microstructural characterization and sample preparation

Transmission electron microscopy (TEM) was performed on electron-transparent thin lamellae extracted from the FDSC-treated samples. This was accomplished using a focused Ga^+ ion beam (FIB) in a scanning electron microscope (SEM). After the FDSC heat treatment, the samples on the UFH1 sensor were transferred onto an SEM aluminum stub coated with conductive silver paint. The specimen was then sputter-coated with a 5 nm -thick layer of Pt/Pd before FIB-SEM to prevent charging during the FIB process.

TEM lamellae were prepared using a Helios 5 UX (Thermo Fisher Scientific, the Netherlands) with a standard in situ FIB lift-out procedure. To prevent sputtering of the top surface and minimize Ga implantation into the sample, the sample surface was coated in two steps: first, a thin layer of carbon was deposited onto the region of interest (ROI) using the electron beam (2 kV , 13 nA). Then, on top of the carbon layer, another stripe of carbon ($12\text{ }\mu\text{m}$ long, $2\text{ }\mu\text{m}$ wide, $1\text{ }\mu\text{m}$ thick) was deposited using the Ga^+ ion beam (30 kV , 0.75 nA). A two-step rough milling was applied (30 kV , 9.9 nA and 30 kV , 2.6 nA) to dig and shape a thin lamella about $10\text{ }\mu\text{m}$ long, $10\text{ }\mu\text{m}$ deep, and $\sim 2\text{ }\mu\text{m}$ thick, before undercutting it at 30 kV ,

2.6 nA. The lamella was then lifted out using Easy Lift (Thermo Fisher Scientific, the Netherlands) and attached to a standard copper FIB grid. The lamella was further thinned at 30 kV, 1.2 nA to about 300 nm.

Two parallel regions (windows) about 3 μm wide were thinned further with 30 kV, 90 pA, followed by 5 kV, 21 pA, and 2 kV, 17 pA polishing to reduce FIB-induced radiation damage. The remaining thicker parts surrounding and between the windows prevent potential bending due to residual stresses. A final polishing step (backpolishing) at 0.5 kV with an overtilt of 7° was applied to further minimize FIB damage and Ga implantation. The final thickness in the thinnest regions, located at the bottom of the lamella after backpolishing, was estimated to be below 10 nm.

TEM image acquisition and chemical analysis by energy-dispersive X-ray spectrometry (EDS) were performed on an FEI Talos F200X (Thermo Fisher Scientific, the Netherlands) operated at 200 kV and equipped with a field-emission gun. For EDS, a Super-X detector (Bruker, Germany) with a solid angle of 0.9 sr was used, enabling high-throughput acquisition. The uncertainty of the EDS measurements was ± 2.5 , ± 1.0 , and ± 2.0 at.% for Pd, Au, and Si, respectively (**Supplementary Note 1**). Imaging was mainly performed in high-angle annular dark-field (HAADF) scanning TEM (STEM) mode, and chemical mapping by EDS was conducted in STEM mode using VELOX software with an electron beam current of 1 nA and a typical acquisition time of 15 min per map (1024 $\times$ 1024 pixels).

In situ high-energy synchrotron X-ray diffraction

In situ high-energy synchrotron X-ray diffraction (HESXRD) experiments were performed at the P21.1 beamline of the German Electron Synchrotron (DESY, Germany). Transmission geometry was employed using monochromatic X-rays with a wavelength of 0.123 Å (corresponding to 101.4 keV). The instrument setup was calibrated against a LaB_6 standard, with a sample-to-detector distance fixed at 0.406 m, using a PerkinElmer XRD1921 detector (PerkinElmer, USA). Samples were heated at a controlled rate of 10 K min^{-1} within a Linkam TS1500 furnace (Linkam Scientific Instruments, UK) under a continuous flow of ultra-high-purity Ar (99.999 wt.%) to prevent oxidation. Diffraction patterns were acquired with an exposure time of 6 s, yielding a temperature resolution of approximately 1 K. Dark current corrections were applied automatically to all frames.

The two-dimensional diffraction images were processed using the PyFAI software to convert raw detector data into one-dimensional scattering intensity profiles, $I(Q)$. Integration parameters, including detector geometry, beam center, and sample-to-detector distance, were refined using the calibration results obtained from the LaB_6 standard. Before integration, detector dark current and geometrical distortions were corrected.

Declarations

Acknowledgments

MKK was supported by the BK21 FOUR (Fostering Outstanding Universities for Research) funded by the Ministry of Education (MOE) and the National Research Foundation (NRF) of Korea. MKK and ESP acknowledge financial support from the National Research Council of Science & Technology (NST) (No. GTL24051-300) funded by the Ministry of Science and ICT of Korea and the Mid-Career Bridging Program through Seoul National University. JFL is grateful for the support by the ETH+ initiative within the framework of SynMatLab (Laboratory for Multiscale Materials Synthesis and Hands-On Education).

The Scientific Center for Optical and Electron Microscopy (ScopeM) at ETH Zürich is acknowledged for providing access to its facilities. The authors thank Dr. P. Zeng (ScopeM) for FIB preparation for the TEM samples. The authors also thank Dr. M. Stoica and Dr. S.S.A. Gerstel of the Laboratory of Metal Physics and Technology (LMPT, ETH Zürich) for alloy preparation and APT-based composition analysis, respectively. The synchrotron X-ray diffraction experiment was carried out on P21.1 at PETRA III, DESY, Hamburg, Germany, with the assistance of Prof. C.W. Ryu (Hongik University) and Dr. F.I. Saldana (DESY).

Author contributions

Min Kyung Kwak: Writing – original draft, Methodology, Investigation, Data curation, Validation, Visualization, Formal analysis, Conceptualization, Project administration.

Robin E. Schäublin: Writing – review & editing, Methodology, Investigation, Validation, Visualization, Formal analysis, Conceptualization.

Jürgen E.K. Schawe: Writing – review & editing, Methodology, Investigation, Data curation, Validation, Formal analysis.

Eun Soo Park: Writing – review & editing, Project administration, Funding acquisition, Conceptualization, Supervision.

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Competing interest

The authors declare no competing interests.

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Figures

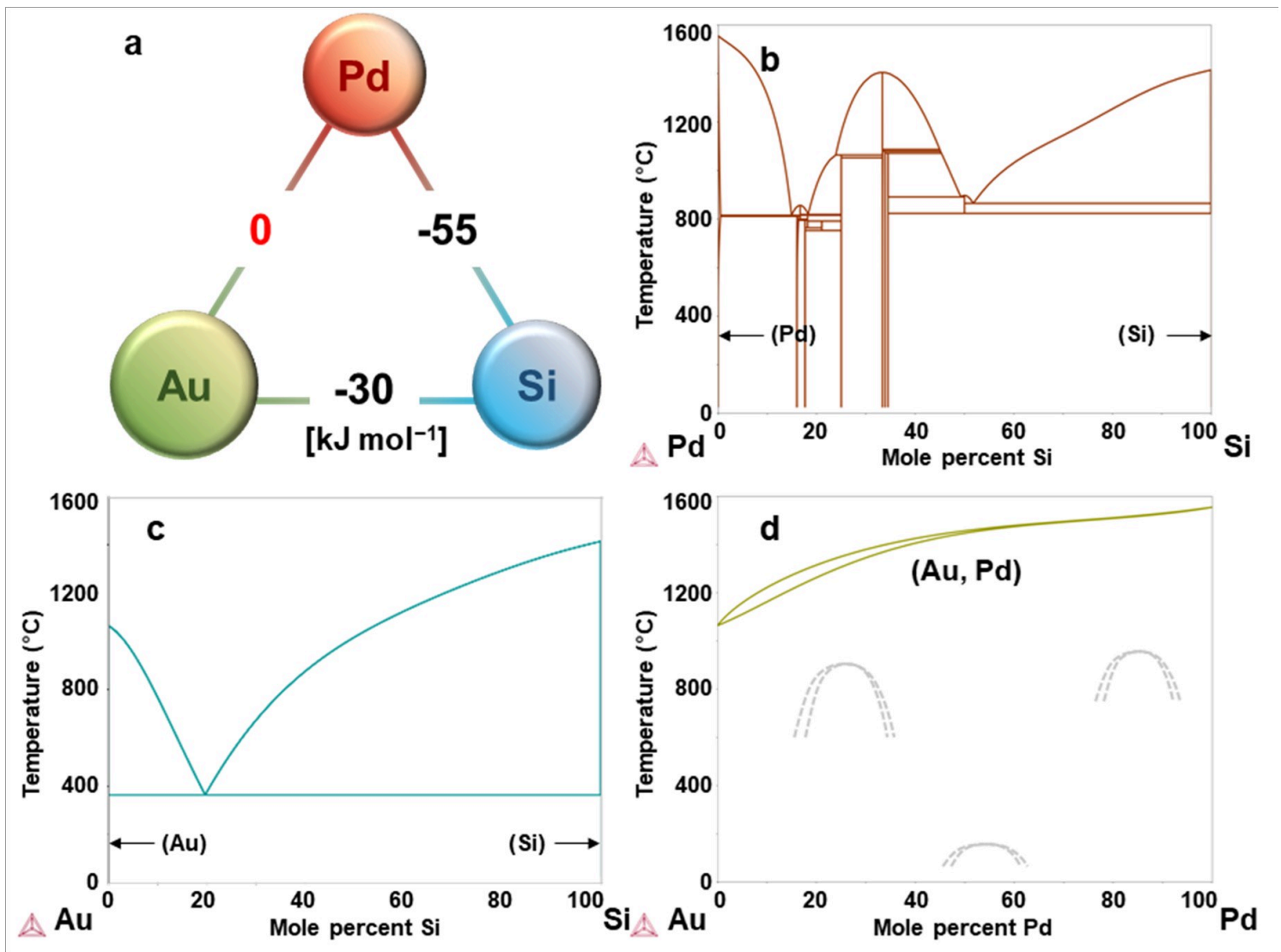


Figure 1

Pd-Au-Si thermodynamics: mixing enthalpies and calculated binary phase diagrams (Thermo-Calc software²⁹ / SSOL6 database³⁰). (a) Mixing enthalpies (ΔH_{mix}) of constituent pairs in Pd-Au-Si. (b) Pd-Si binary phase diagram showing large negative enthalpy of mixing (-55 kJ mol^{-1}), driving strong Pd-Si affinity and *intermetallic compound* (IMC) formation. (c) Au-Si binary phase diagram exhibiting a simple eutectic reaction. (d) Pd-Au binary phase diagram showing complete solid solubility at high temperatures and potentially ordered phases (Pd₃Au, PdAu, PdAu₃) at lower temperatures.

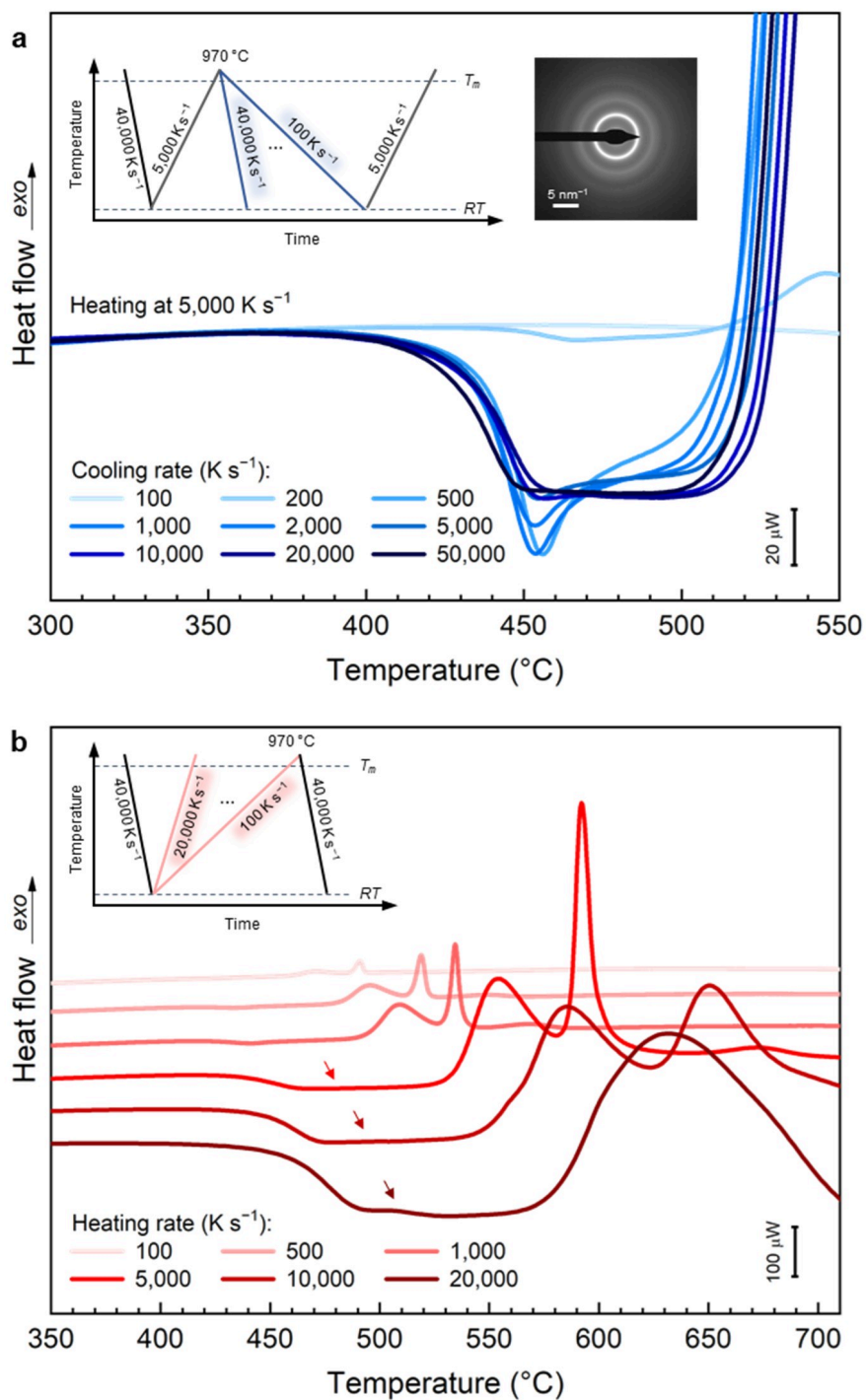


Figure 2

FDSC establishing the amorphous starting state and revealing a secondary endothermic event. (a) FDSC heating curves measured at 5,000 K s⁻¹ after different cooling rates ranging from 100 to 40,000 K s⁻¹. Inset: SADP confirming fully amorphous structure after cooling at 40,000 K s⁻¹. **(b)** Curves measured at heating rates between 100 and 20,000 K s⁻¹ after cooling at 40,000 K s⁻¹. Arrows indicate

the onset of the endothermic event between the glass transition and crystallization. Insets: schematic temperature programs.

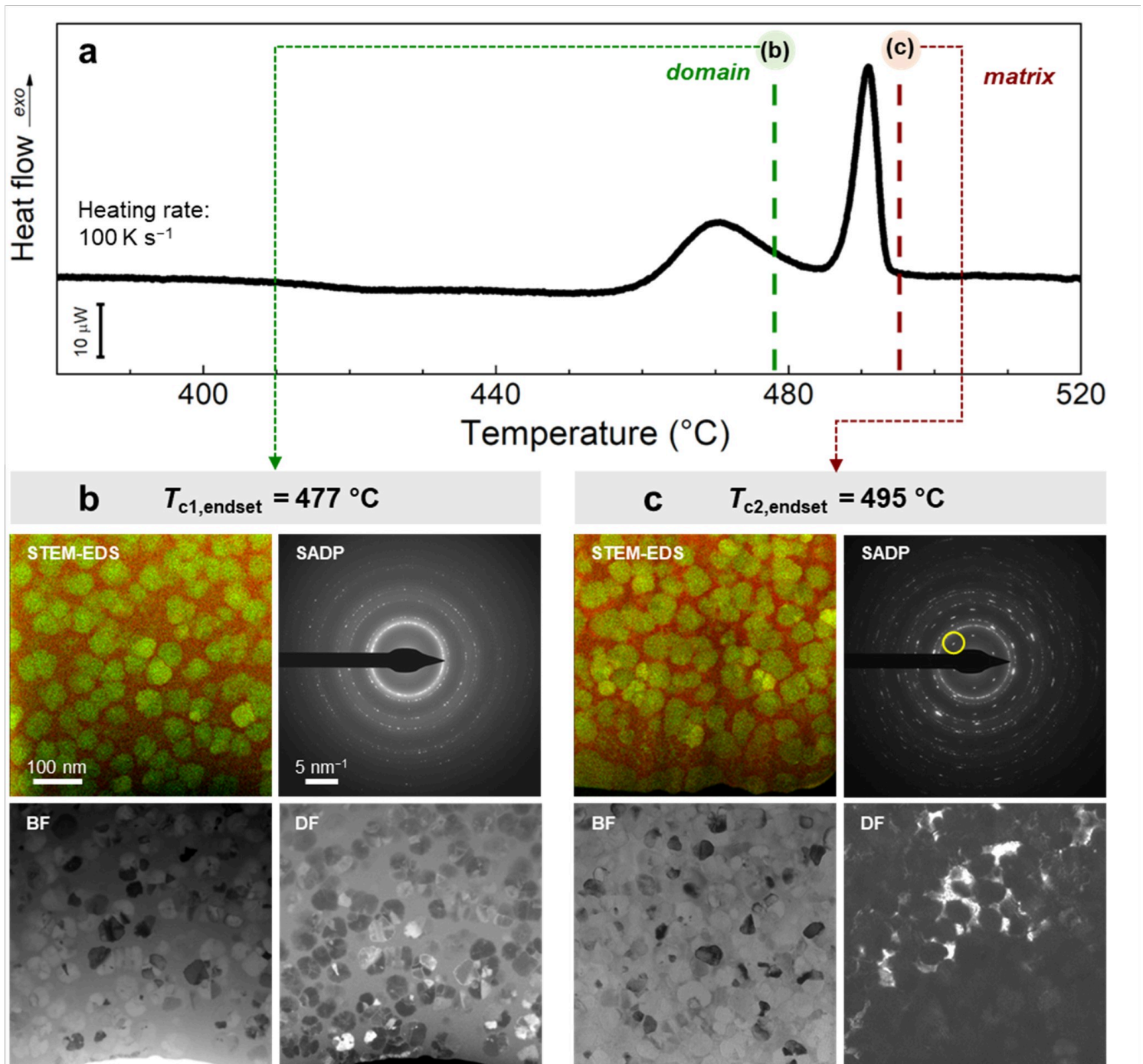


Figure 3

Quench-and-look microstructures after the two crystallization events (100 K s^{-1}). (a) DSC heating curve showing two distinct crystallization events. TEM analysis after quenching at (b) the first crystallization event ($477\text{ }^{\circ}\text{C}$) and (c) the second crystallization event ($495\text{ }^{\circ}\text{C}$). For each temperature, STEM-EDS chemical maps (Pd red, Au green, Pd + Au yellow), SADPs, bright-field (BF), and dark-field (DF) images are shown, for STEM imaging in (b) and TEM imaging in (c). Yellow circle denotes the objective aperture position for DF imaging.

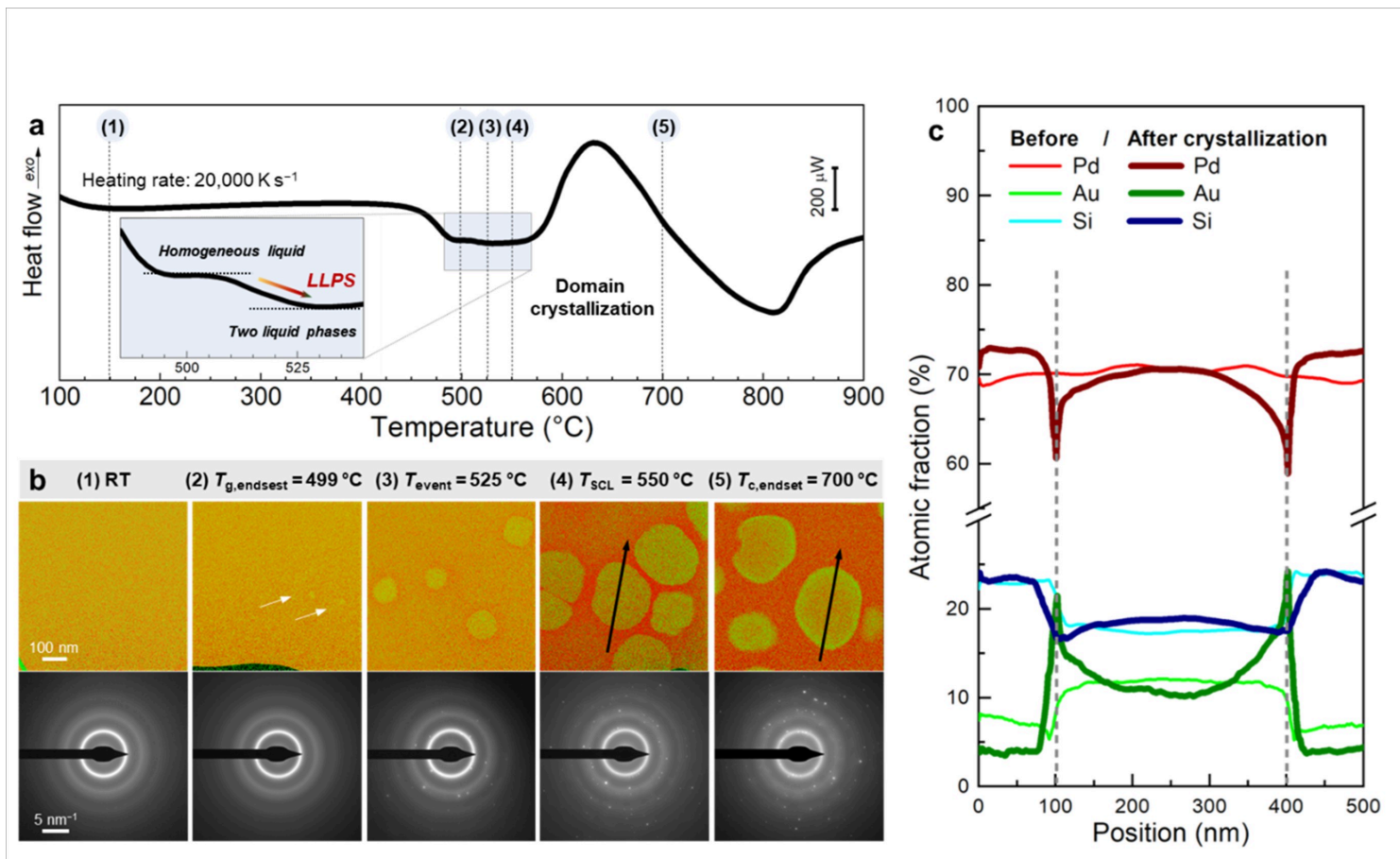


Figure 4

Ultrafast heating (20,000 K s⁻¹) reveals LLPS before crystallization **(a)** FDSC heating curve showing two endothermic events followed by crystallization and melting. **(b)** STEM-EDS maps (Pd red, Au green, Pd + Au yellow) and SADPs acquired for: as-quenched state; just after glass transition ($T_{g,endset}$, white arrows indicate Au-rich domain's nuclei), at T_{event} (showing domains' growth), at T_{SCL} (showing their further growth), and after their crystallization ($T_{c,endset}$). **(c)** EDS line profiles across domains before and after crystallization, showing transition from uniform domains with Au-depleted matrix to core-shell domains with Au-rich shells and homogenized matrix. Black arrows at T_{SCL} and $T_{c,endset}$ indicate profile locations.

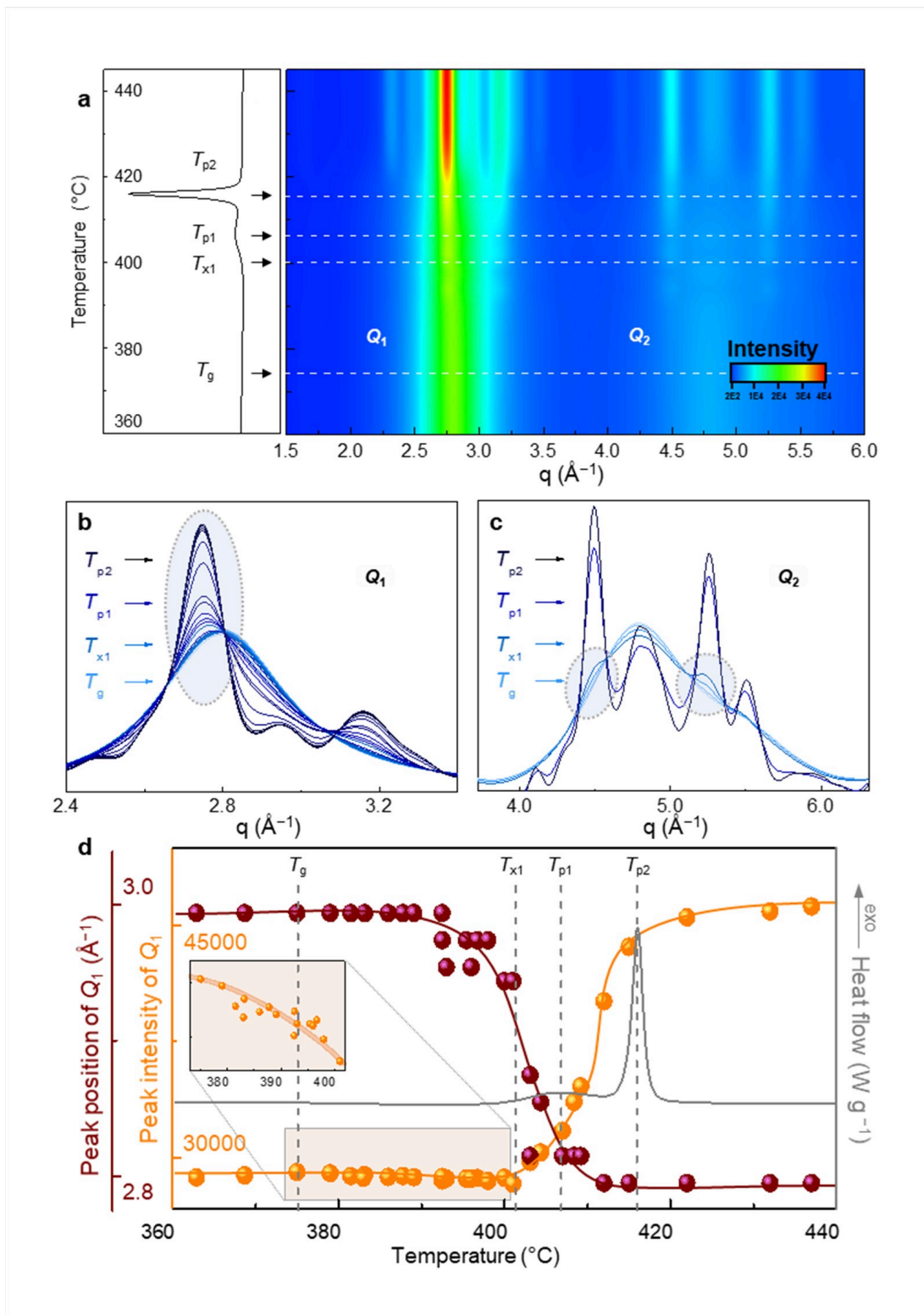


Figure 5

In situ synchrotron X-ray diffraction links LLPS to mesoscale structural evolution.

(a) Evolution of scattering intensity $I(Q)$ highlighting first nearest-neighbor peak Q_1 across the supercooled liquid region; DSC heat-flow curve on the left with T_g , T_{x1} , T_{p1} , and T_{p2} . Selected $I(Q)$ profiles focusing on the **(b)** Q_1 region (low- q range, $\sim 2.5 \text{ \AA}^{-1}$) and **(c)** the Q_2 region (high- q range, $\sim 4.5 \text{ \AA}^{-1}$, with

Q_{2L} and Q_{2R}) at representative temperatures, illustrating structural changes upon heating. **(d)** Evolution of Q_1 intensity and position showing intensity decrease, shoulder formation, peak splitting, and shift toward lower Q , consistent with LLPS preceding crystallization.

Supplementary Files

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- [LLPSSupplementaryInformation.docx](#)