Enhanced kinetic stability of a bulk metallic glass by high pressure

R. J. Xue, L. Z. Zhao, C. L. Shi, T. Ma, X. K. Xi, M. Gao, P. W. Zhu, P. Wen, X. H. Yu, C. Q. Jin, M. X. Pan, W. H. Wang, and H. Y. Bai

Articles you may be interested in

High thermal stability and sluggish crystallization kinetics of high-entropy bulk metallic glasses
J. Appl. Phys. **119**, 245112 (2016); 10.1063/1.4955060

Characterization of flow units in metallic glass through density variation
J. Appl. Phys. **114**, 123514 (2013); 10.1063/1.4823816

Crystallization of metallic glasses under the influence of high density dc currents
J. Appl. Phys. **95**, 2896 (2004); 10.1063/1.1642280

Glass transition behavior, crystallization kinetics, and microstructure change of Zr 41 Ti 14 Cu 12.5 Ni 10 Be 22.5 bulk metallic glass under high pressure
J. Appl. Phys. **88**, 3914 (2000); 10.1063/1.1290262

Ultrasonic investigation of Pd 39 Ni 10 Cu 30 P 21 bulk metallic glass upon crystallization
Appl. Phys. Lett. **77**, 1147 (2000); 10.1063/1.1289801

Enhanced kinetic stability of a bulk metallic glass by high pressure

R. J. Xue,[1,a)] L. Z. Zhao,[1,a)] C. L. Shi,[1] T. Ma,[1,2] X. K. Xi,[1] M. Gao,[1] P. W. Zhu,[2] P. Wen,[1]
X. H. Yu,[1,b)] C. Q. Jin,[1] M. X. Pan,[1,b)] W. H. Wang,[1] and H. Y. Bai[1,b)]
[1]*Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[2]*State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China*

The metastable nature of metallic glasses (MGs) limits their applications. We report the formation of a stable $Pd_{40.16}Ni_{9.64}Cu_{30.12}P_{20.08}$ MG with bulk size under high pressure at room temperature. The stable MG shows remarkably enhanced thermal and kinetic stability with substantially increased glass transition temperature T_g, crystallization temperature T_x, density and mechanical properties. The unique stability can be further reinforced by higher pressure and maintained even above T_g. This result can advance the glass design and the understanding of the fundamental issues in MGs. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4968834]

The bulk metallic glasses (MGs) have attracted extensive interest due to the outstanding properties such as high hardness, high elasticity, and corrosion resistance as functional and structural materials.[1–5] However, due to their metastable nature, the lack of stability has become one of the major obstacles that limit the applications of bulk MGs.[6–8] Therefore, the fabrication of stable or ultrastable glasses has been highly expected and the relative research has become an active and exciting area during the last decade.

Ediger *et al.* first reported the formation of ultrastable glasses which have exceptional kinetic and thermodynamic stability with substantial higher glass transition temperature T_g and lower fictive temperature T_f in organic glasses.[9] Recent experimental results have demonstrated that both ultrastable organic glasses[9–19] and ultrastable MG[20] can be fabricated by means of deposition methods with careful control of the substrate temperature and deposition rate. Simulations have revealed that such efficient packing of atoms in ultrastable glasses with abundance of regular Voronoi polyhedral could be the essential structure factor that leads to the extraordinary stability compared to normal counterparts.[21] However, the concept of ultrastable glasses is not very clear so far. Actually, there are two kinds of ultrastable glasses. One is introduced by Ediger that glass shows thermodynamic and kinetic ultrastability;[9,11–19] another is kinetic ultrastable introduced by Priestley and Samwer.[10,20] All of these ultrastable glasses are quasi two-dimensional film materials so far.[9–21] Therefore, the formation of highly stable glass with bulk size is still a major scientific and technological challenge.

In this work, high pressure (HP), as an independent dimension to temperature and time, is applied to bulk $Pd_{40.16}Ni_{9.64}Cu_{30.12}P_{20.08}$ MG at room temperature (RT) to fabricate stable bulk MG. The obtained stable MG shows extraordinary kinetic and thermal stability with enhanced glass transition temperature T_g and crystallization temperature T_x, and remarkable higher density and hardness. Furthermore, this stability can be reinforced by increasing pressure and maintained even above T_g. The local structure is probed by ^{63}Cu nuclear magnetic resonance (NMR), which can provide the structure signature and reveal the potential structural origin of bulk stable MG. We find that bulk stable MG with the exceptional kinetic and thermal stability can be prepared effectively by HP processing that can be regarded as a general processing route to produce stable glasses.

The ingot with composition of $Pd_{40.16}Ni_{9.64}Cu_{30.12}P_{20.08}$ was prepared by induction melting. The ingot was remelted in a Ti-gettered argon atmosphere and sucked into water cooled Cu mold to obtain glassy cylindrical rods (with a diameter of 2 and 3 mm). Before all experiments, the quenched MGs were initialized by heating the samples from RT to the supercooled liquid and holding for 2 min, then cooling down to RT at 60 K min^{-1} using differential scanning calorimetry (DSC). After then, the initialized samples are called as the standard MGs.

The glassy nature of all samples was ascertained using X-ray diffraction (XRD) (data shown in the supplementary material). Thermal analysis was carried out using DSC. The surface morphology was studied by a Philips XL30 scanning electron microscopy (SEM) instrument. The density was measured by using Archimedean technique. Vickers microhardness (Hv) was determined by using an EVERONE MH series unit. ^{63}Cu NMR spectra were studied by Bruker Avance Ш 400 HD spectrometer with a magnetic field of 9.39 T at 298 K (see supplementary material).

The HP experiments were performed on the multi-anvil large volume high-pressure apparatus. The standard MGs were sealed in the pyrophyllite pressure transmitting medium (PTM) and quasi-hydrostatically compressed to the target pressure through compressing the tungsten carbide anvils [Fig. 1(a)]. At the target pressure, we first stabilized the whole system for 5 min, and then held the system for 1 h at RT [Fig. 1(b)]. After unloading the pressure, the HP processed samples were released from the capsules for further characterizations. The representative HP processed MG samples with 3 mm in diameter and 3 mm in length [Fig. 1(c)], show no observable shear bands which can be demonstrated by SEM [Fig. 1(d)] characterizations.

The kinetic and thermodynamic properties of the HP processed MGs were measured by using DSC and compared with the standard MG. The DSC traces of the standard and

---

a)R. J. Xue and L. Z. Zhao contributed equally to this work.
b)Authors to whom correspondence should be addressed. Electronic addresses: yuxh@iphy.ac.cn, panmx@iphy.ac.cn, and hybai@iphy.ac.cn

109, 221904-1
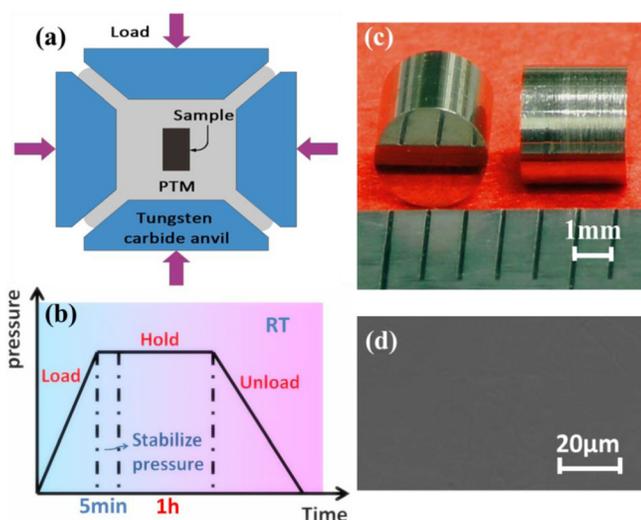
FIG. 1. Illustration of HP experiments and HP bulk-size stable MGs. (a) The schematic picture of HP sample assembly and pressure device. (b) The HP experiments process of loading-stabilizing-holding (1 h)-unloading at room temperature. (c) HP processed stable MGs with bulk size (3 mm in diameter and 3 mm in length). (d) The SEM image of surface morphology of the HP processed stable MG. No observable shear bands.

HP processed MGs show distinct glass transitions [Fig. 2(a)] and typical sharp crystallization peaks (data shown in the supplementary material). Further inspection reveals that the DSC curves of the HP processed samples integrally shift to the higher temperatures substantially. Remarkably, the glass transition temperature T_g derived from heating process at $20\,\mathrm{K\,min^{-1}}$ increases about 6 K and 11 K [Fig. 2(a)] after HP processing under 10 GPa and 17 GPa for 1 h at RT, respectively, indicating that the HP processed MGs have higher kinetic stability and need higher temperature to dislodge atoms from their glassy configurations. The similar results also have been observed in Ce-based bulk MG. In addition, we find that the onset of crystallization temperature T_x [Fig. 2(b)] also increases about 11 K after HP processing under

17 GPa, revealing that the HP treatment can also raise the energy barrier of the MG to rearrange atoms to form the crystalline structure. Furthermore, we isothermally annealed the standard samples for 90 days at RT and 1 h at 538 K, respectively [Fig. 2(c)], and note that the standard MG aged for 90 days at RT and 1 h at 538 K have a much lower kinetic stability than that of the MG treated under HP for only 1 h at RT.

For the deposited ultrastable organic glass films, an important feature is the relatively low position on the potential energy landscape (PEL).[9,11,14,16,21] For comparison, we calculated the enthalpies of the Pd-based samples by integrating the heat capacity to compare the relative locations on the PEL (see supplementary material). It is found that the enthalpy of the HP processed MG is higher than that of the standard MG and increases with increasing pressure [Fig. 2(d)]. When 17 GPa of external pressure is applied, the enthalpy of the Pd-based MG reaches a maximum value of about $0.26\,\mathrm{kJ\,mol^{-1}}$ higher than that of the standard MG. The increased enthalpy indicates that the bulk stable MG is not in the low energy state on PEL, but in a relatively higher position. This phenomenon is in agreement with the ultrastable deposited glasses (a polymer glass film[10] and a Zr-based MG film[20]), but inconsistent with other molecular ultrastable glass films.[9,11,14,16,21] Our results further suggest that the glasses with higher kinetic stability are not necessarily located in the low energy states in thermodynamics.

To further explore the enhanced stability of the HP processed MG, we study the thermodynamic behaviors by heating with DSC. We first heated the samples from RT to 593 K that was well above T_g (denoted as the first heating), and cooled the samples to RT. Then these samples were heated again to the temperature beyond the crystallization temperature T_x (the second heating). It is found that the aged MG (annealed at 538 K for 1 h) transforms back to the standard MG after the first heating. However, the HP processed MG can trace the exact same route of the first heating during the second heating and obviously deviates from the standard
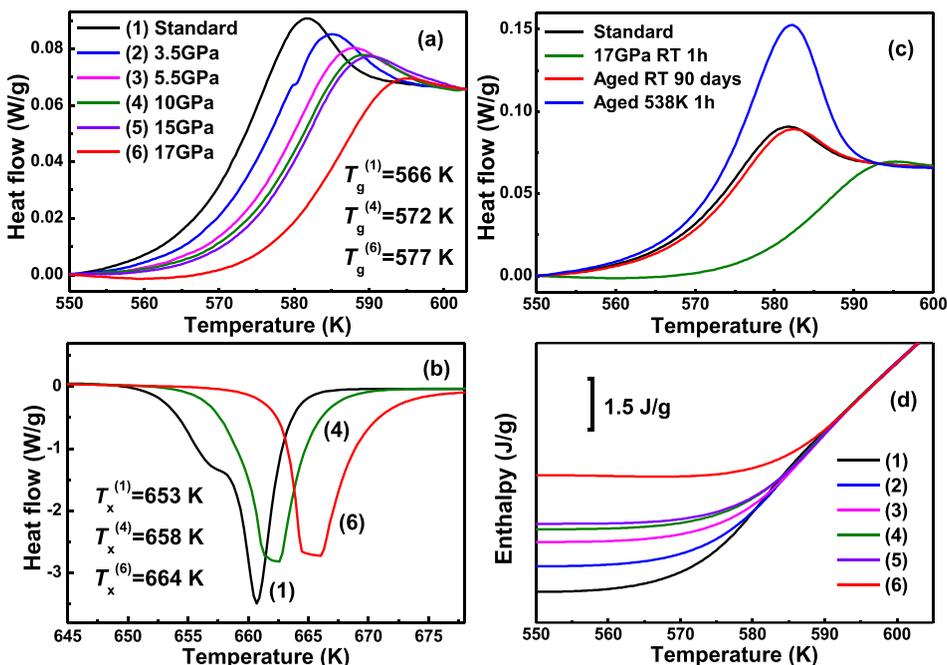
FIG. 2. Differential scanning calorimetry (DSC) of Pd-based MGs. DSC traces of standard MGs processed under HP (3.5 GPa, 5.5 GPa, 10 GPa, 15 GPa and 17 GPa) for 1 h at room temperature, (a) Evolution of glass transition; (b) Crystallization process. (c) DSC traces of the stable, standard, and two aged MGs (isothermally annealed at RT and 583 K for 90 days and 1 h, respectively). (d) Enthalpy obtained by integrating the heat capacity of standard and HP processed MG.

MG shown in Fig. 3(a). It suggests that the HP processed MGs can sustain the higher stability even at temperature above T_g, which has never been observed in other ultrastable glasses in the previous studies.[9–20] Although the HP processed MG is in the relatively higher position on the PEL [Fig. 3(b)], it performs an outstanding stability at higher temperature conditions. Our results indicate that the absolute position on the PEL may not be the necessary criteria for the higher stability.

The PEL can be used to describe the energy states of glass materials, and energy minima and barriers on the PEL control the thermodynamics and kinetic properties of glass.[5–7,22] Previous studies suggest that stress and strain can alter the energy minima and barriers.[23–25] In the present work, because we applied quasi-hydrostatic pressure to the MG, the PEL of the HP processed MG has changed and been different from that of the standard MG. Previous experimental studies indicate that the potential activation energy of glass is represented by the height of energy valley and is proportional to the elastic modulus,[26] and the elastic modulus has a positive correlation with T_g.[4] The enhanced stability with the Pd-based MG report here may be duplicated for other MGs. We propose that our processing using high hydrostatic pressure is a more likely route to drive the MG

into an energy valley with higher energy barriers (and hence a high T_g and high modulus), whereas shear deformation often rejuvenates the MG structure instead. Figure 3(b) schematically illustrates the PEL evolution under HP and depositions for various glasses. All these stable glasses formed by HP or deposition methods have a common feature of higher T_g. However, the relative positions on PEL determined from the enthalpy are quite different. The deposited organic ultrastable glass[9,11,14,16,21] locates in a relatively lower position on PEL with much lower energy barriers that are easier to be crossed and make the glass recover back to the normal states, while the HP stable MG locates in the relatively higher position on PEL with much higher energy barriers, which make it difficult for the MG to escape from this energy valley to another one. The present results indicate that the higher energy barriers on the PEL may also be an essential prerequisite for the higher stability.

To better understand the role of pressure in the stability of HP processed MG, we investigated the change of glass transition temperature, δT_g, ($\delta T_g = T_g^{HP} - T_g^{ST}$, T_g^{ST} and T_g^{HP} are T_g of the standard MG and HP processed MGs, respectively) and the change of crystallization temperature, δT_x, ($\delta T_x = T_x^{HP} - T_x^{ST}$, T_x^{ST} and T_x^{HP} are the onset of crystallization temperatures of the standard MG and HP processed MGs, respectively) with pressure. As shown in Fig. 4(a), δT_g
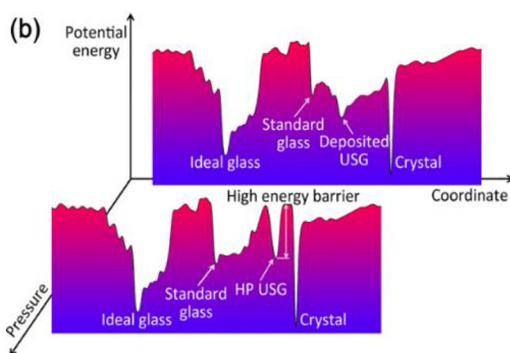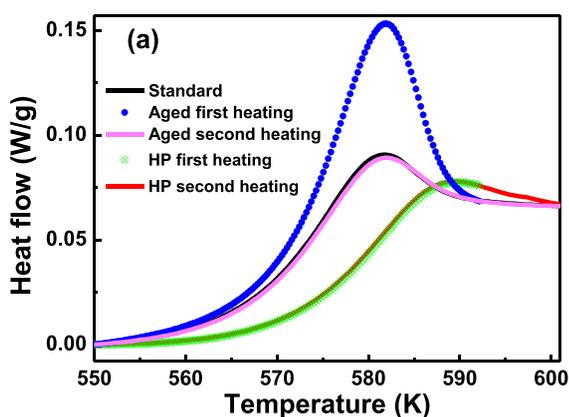
FIG. 3. (a) DSC curves of the standard MG (black), first heating (blue), and second heating (purple) of aged MG (isothermally annealed at 538 K for 1 h); and first heating (green) and second hearing (red) of HP processed MG (processed under 15 GPa). (b) Schematic illustration of the evolution of potential energy landscape (PEL) induced by pressure and two possible types of stable glasses (SG). The deposited SG is a stable organic glass[10,12,15,17,22] that has kinetic and thermodynamic stability. The HP SG is standard MG processed under high pressure that shows high kinetic and thermal stability.
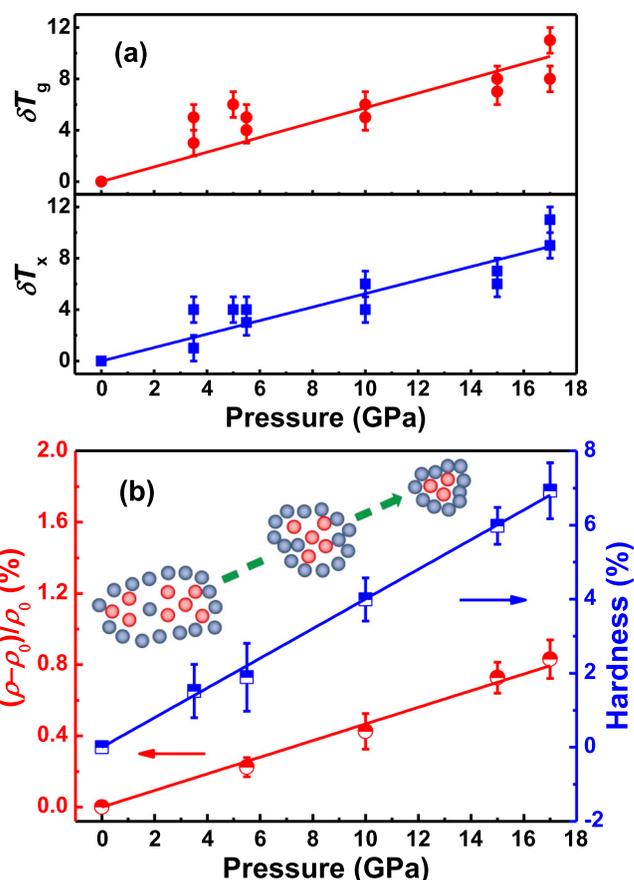
FIG. 4. Effect of pressure on stability and properties. (a) The relative variation of glass transition temperature δT_g and crystallization temperature δT_x vs. pressure (GPa). (b) The relative variation of density and hardness vs. pressure (GPa). Schematic inset depictions of the evolution of structure with pressure in HP processed MG (b). The red atoms represent flow units that loosely pack and embed in solid glassy substrate (blue atoms).

has a roughly linear relationship with pressure indicating that the higher the applied pressure, the more stable the MG is. In addition, the change of crystallization temperature δT_x also increases with increasing pressure, which is different with the previous studies,[27,28] implying that the HP processed MGs might transform directly into melting liquids without crystallization behavior if the applied pressure is sufficiently high. Thus, the HP processed MG can also be a model glass to investigate the crystallization process.

It is highly wanted to make a higher-density and higher-hardness glass in the expectation that it would also show improved stiffness and thermal stability. However, the densification process is kinetically hindered that the extremely long times are required for rearrangements of the local structure. A structure is formed that has even higher barriers to rearrangement for every step towards supercooled liquid. Thus the process of densification through physical aging slows logarithmically over time. Researchers have recently discovered that high-density glasses can be assembled in a process known as physical vapor deposition.[29] Coincident with stability, the ultrastable glasses usually possess enhanced density and mechanical properties,[9,11,20] which is also true for the present bulk HP processed MG. The density and hardness of the HP processed MG versus pressure are shown in Fig. 4(b). The relative density change $(\rho^{HP}-\rho^{ST})/\rho^{ST}$ (ρ^{ST} and ρ^{HP} are the density of the standard and HP processed bulk MGs, respectively) of the HP processed MG is substantially increased with pressure (e.g., 1% at 17 GPa), which is in agreement with the results observed in *in situ* high pressure experiments.[30] In addition, the relative hardness increases with increasing pressure monotonically (e.g., 8% increased at 17 GPa), suggesting that the HP processed MG is much stronger against deformation than the standard MG. Extensive studies have proved that MGs are actually intrinsic microstructural heterogeneous[31,32] with loosely packed liquid-like regions which are also called flow units.[33–36] When the external pressure is applied to MGs, the atoms in flow units [inset of Fig. 4(b)] can cooperatively rearrange and are packed more efficiently, leading to higher density and hardness. With this method 1% increase in density and 8% increase in hardness are easily achieved. Such transformation from lower density to higher density amorphous phases under HP in MGs has also been observed in other MG studies.[37,38]

To investigate the structural origin of the HP processed stable MG, we performed the nuclear magnetic resonance (NMR) experiments, which can be used to probe the local site symmetry and electronic properties of MGs.[39–42] As shown in Figs. 4(a) and 4(b), both T_g and H_v increase almost monotonically with increasing pressure, indicating the bonding between atoms in the local structure becomes stronger because T_g and H_v are directly proportional to Young's moduli,[4] and the Young's moduli is directly related to bonding strength. This might be the microstructural origin of the enhanced stability. To distinguish the bonding states between the standard and HP processed MGs, ^{63}Cu (spin $I = 3/2$) NMR spectroscopy was used for probing the electronic density of states within the vicinity of the Fermi level. Figure 5 shows the ^{63}Cu NMR solid state powder spectra of the standard and HP processed MGs of 15 GPa, respectively. The
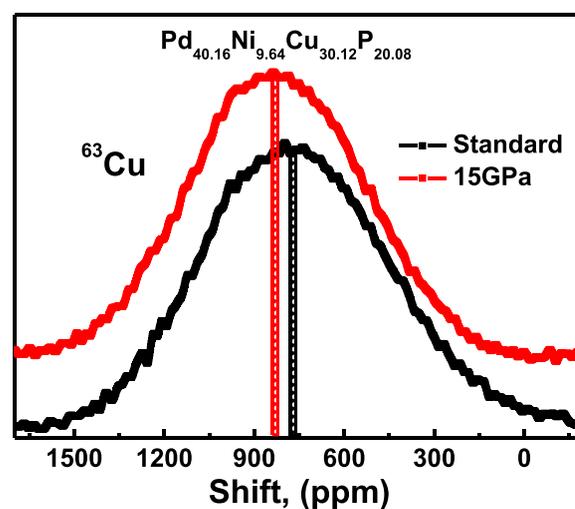
FIG. 5. NMR spectra of standard and representative HP processed (15 GPa) bulk MGs. The ^{63}Cu NMR spectra are normalized to the maximum intensity for standard MG and stable MG.

isotropic Knight shifts in MGs can be determined by the peak position of the symmetrical central lines, which can be verified by the magnetic field dependent experiments. As shown in Fig. 5, the ^{63}Cu isotropic Knight shift increases from 785 ppm for the standard MG to 840 ppm for the HP processed MG. The change in ^{63}Cu isotropic Knight shift in a metal is predominantly due to changes of local electronic density of states on the ^{63}Cu sites near the Fermi level.[39–44] Previous studies also demonstrate that the change of Knight shift is induced by the Structural change.[40,45,46] This result demonstrates that the distribution of local atoms at ^{63}Cu sites in the more stable MG is distinct from that of the standard one, indicating that the atomic configurations of the MGs have been changed by HP processing. The ^{63}Cu NMR isotropic shifts can thus be considered as a structural signature for the stability of Pd-based MG system. To be noted, this local structural information is hardly accessible by conventional diffraction methods.

In summary, the bulk-sized more stable Pd-based MG that exhibits high kinetic and thermal stability is fabricated by a high pressure method at room temperature. The high pressure processed MG has substantially enhanced glass transition temperature, crystallization temperature, and increased density and hardness. The enhanced stability of the bulk MG originates from the change of local atomic structure and the bonding states between atoms under high pressure. The results are helpful to design stable metallic glasses with bulk size. As a model glassy material, the high-pressure-fabricated stable MG with bulk size could provide insight into some fundamental issues such as glass transition, crystallization, and the nature of glass.

See supplementary material for experimental details, the way to calculate the enthalpy and data for: pressure dependence of crystallization behavior, and XRD structure.

[1] A. Inoue, Acta Mater. **48**, 279 (2000).

[2] A. L. Greer, Science **267**, 1947 (1995).

[3] A. R. Yavari, J. J. Lewandowski, and J. Eckert, MRS Bull. **32**, 635 (2007).

[4] W. H. Wang, Prog. Mater. Sci. **57**, 487 (2012).

[5] F. H. Stillinger, Science **267**, 1935 (1995).

[6] P. G. Debenedetti and F. H. Stillinger, Nature **410**, 259 (2001).

[7] C. A. Angell, Science **267**, 1924 (1995).

[8] M. D. Ediger and P. Harrowell, J. Chem. Phys. **137**, 080901 (2012).

[9] S. F. Swallen, K. L. Kearns, M. K. Mapes, Y. S. Kim, R. J. McMahon, M. D. Ediger, T. Wu, L. Yu, and S. Satija, Science **315**, 353 (2007).

[10] Y. Guo, A. Morozov, D. Schneider, J. W. Chung, C. Zhang, M. Waldmann, N. Yao, G. Fytas, C. B. Arnold, and R. D. Priestley, Nat. Mater. **11**, 337 (2012).

[11] T. Pérez-Castañeda, C. Rodríguez-Tinoco, J. Rodríguez-Viejo, and M. A. Ramos, Proc. Natl. Acad. Sci. U. S. A. **111**, 11275 (2014).

[12] A. Sepúlveda, M. Tylinski, A. Guiseppi-Elie, R. Richert, and M. D. Ediger, Phys. Rev. Lett. **113**, 045901 (2014).

[13] Z. Chen, A. Sepúlveda, M. D. Ediger, and R. Richert, J. Chem. Phys. **138**, 12A519 (2013).

[14] E. Leon-Gutierrez, A. Sepúlveda, G. Garcia, M. T. Clavaguera-Mora, and J. Rodriguez-Viejo, Phys. Chem. Chem. Phys. **12**, 14693 (2010).

[15] D. Yokoyama, Y. Setoguchi, A. Sakaguchi, M. Suzuki, and C. Adachi, Adv. Funct. Mater. **20**, 386 (2010).

[16] S. L. L. Ramos, M. M. Oguni, K. Ishii, and H. Nakayama, J. Phys. Chem. B **115**, 14327 (2011).

[17] K. J. Dawson, K. L. Kearns, L. Yu, W. Steffen, and M. D. Ediger, Proc. Natl. Acad. Sci. U. S. A. **106**, 15165 (2009).

[18] S. F. Swallen, K. Traynor, R. J. McMahon, M. D. Ediger, and T. E. Mates, Phys. Rev. Lett. **102**, 065503 (2009).

[19] H. B. Yu, M. Tylinski, A. Guiseppi-Elie, M. D. Ediger, and R. Richert, Phys. Rev. Lett. **115**, 185501 (2015).

[20] H. B. Yu, Y. Luo, and K. Samwer, Adv. Mater. **25**, 5904 (2013).

[21] S. Singh, M. D. Ediger, and J. J. de Pablo, Nat. Mater. **12**, 139 (2013).

[22] C. A. Angell, J. Res. Natl. Inst. Stand. Technol. **102**, 171 (1997).

[23] D. L. Malandro and D. J. Lacks, Phys. Rev. Lett. **81**, 5576 (1998).

[24] D. J. Lacks, Phys. Rev. Lett. **87**, 225502 (2001).

[25] D. J. Lacks and M. J. Osborne, Phys. Rev. Lett. **93**, 255501 (2004).

[26] J. Q. Wang, W. H. Wang, Y. H. Liu, and H. Y. Bai, Phys. Rev. B **83**, 012201 (2011).

[27] M. X. Pan, J. G. Wang, Y. S. Yao, D. Q. Zhao, and W. H. Wang, Appl. Phys. Lett. **78**, 601 (2001).

[28] J. Z. Jiang, W. Roseker, M. Sikorski, Q. P. Cao, and F. Xu, Appl. Phys. Lett. **84**, 1871 (2004).

[29] L. Berthier and M. D. Ediger, Phys. Today **69**(1), 40 (2016).

[30] Q. Zeng, Y. Kono, Y. Lin, Z. Zeng, J. Wang, S. V. Sinogeikin, C. Park, Y. Meng, W. Yang, H. K. Mao, and W. L. Mao, Phys. Rev. Lett. **112**, 185502 (2014).

[31] W. Dmowski, T. Iwashita, C.-P. Chuang, J. Almer, and T. Egami, Phys. Rev. Lett. **105**, 205502 (2010).

[32] Y. H. Liu, D. Wang, K. Nakajima, W. Zhang, A. Hirata, T. Nishi, A. Inoue, and M. W. Chen, Phys. Rev. Lett. **106**, 125504 (2011).

[33] Z. Wang, B. A. Sun, H. Y. Bai, and W. H. Wang, Nat. Commun. **5**, 5823 (2014).

[34] R. J. Xue, D. P. Wang, Z. G. Zhu, D. W. Ding, B. Zhang, and W. H. Wang, J. Appl. Phys. **114**, 123514 (2013).

[35] J. C. Ye, J. Lu, C. T. Liu, Q. Wang, and Y. Yang, Nat. Mater. **9**, 619 (2010).

[36] H. Wagner, D. Bedorf, S. Küchemann, M. Schwabe, B. Zhang, W. Arnold, and K. Samwer, Nat. Mater. **10**, 439 (2011).

[37] Q. S. Zeng, Y. Z. Fang, H. B. Lou, Y. Gong, X. D. Wang, K. Yang, A. G. Li, S. Yan, C. Lathe, F. M. Wu, X. H. Yu, and J. Z. Jiang, J. Phys.: Condens. Matter **22**, 375404 (2010).

[38] Q. Luo, G. Garbarino, B. Sun, D. Fan, Y. Zhang, Z. Wang, Y. Sun, J. Jiao, X. Li, P. Li, N. Mattern, J. Eckert, and J. Shen, Nat. Commun. **6**, 5703 (2015).

[39] X. P. Tang, U. Geyer, R. Busch, W. L. Johnson, and Y. Wu, Nature **402**, 160 (1999).

[40] M. T. Sandor, H. B. Ke, W. H. Wang, and Y. Wu, J. Phys.: Condens. Matter **25**, 165701 (2013).

[41] X. P. Tang, J. F. Löffler, R. B. Schwarz, W. L. Johnson, and Y. Wu, Appl. Phys. Lett. **86**, 072104 (2005).

[42] X. K. Xi, L. L. Li, B. Zhang, W. H. Wang, and Y. Wu, Phys. Rev. Lett. **99**, 095501 (2007).

[43] G. T. de Laissardière, D. N. Manh, L. Magaud, J. P. Julien, F. Cyrot-Lackmann, and D. Mayou, Phys. Rev. B **52**, 7920 (1995).

[44] J. Winter, *Magnetic Resonance in Metals* (Clarendon Press, Oxford, 1971).

[45] C. C. Yuan, J. F. Xiang, X. K. Xi, and W. H. Wang, Phys. Rev. Lett. **107**, 236403 (2011).

[46] X. K. Xi, M. T. Sandor, Y. H. Liu, W. H. Wang, and Y. Wu, Scr. Mater. **61**, 967 (2009).