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Non-Toxic, Precious-Metal-Free Titanium-Based Metallic Glasses with Exceptional Glass-Forming Ability and High Specific Strength

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Abstract

Titanium-based metallic glasses (TBMGs) are attracting broad interest due to their simultaneous light weight, superhigh strength and specific strength, exceptional wear- and corrosion-resistance and biocompatibility, desirable for electronic, biomedical, and aerospace applications. However, the glass-forming ability (GFA) of TBMGs, except some containing significant amount of toxic (Be) or precious (Pd, Ag) elements, is disappointingly low, as manifested by a critical casting diameter (d_c) no more than 6 mm, which significantly restricts their manufacturing and applications. Here we report our discovery of a series of TBMGs in the $(\text{TiZrHf})_x(\text{CuNi})_y(\text{SnSi})_z$ pseudo-ternary system. These alloys possess an exceptionally large d_c , reaching up to 12 mm, doubling the current record for Be and precious-metal free TBMGs. Moreover, these alloys exhibit a low density (7.0-7.3 g/cm³), high fracture-strength (up to ~2700 MPa), high specific fracture-strength (up to ~370 N m g⁻¹), and even good plasticity with a plastic strain of up to 9.4% upon compression. They also possess high activation energy for crystallization and high atomic packing efficiency which provide an initial physical account for their exceptional GFA and manufacturability.

Metallic glasses (MGs) are next-generation metals/alloys that possess an overall disordered atomic structure (with short-range ordering but no long-range translational or rotational symmetry). Because of the unique structure, MGs behave drastically different than crystalline metals/alloys (including high entropy alloys) when responding to external stimuli. Upon mechanical loading, they show much higher (by several hundred percent, typically) strength, hardness, elastic strain limit and wear resistance. Upon reheating, they undergo glass transition, softening and superplastic flow far below the melting temperature. Upon casting from the molten state, they acquire the pre-designed shape precisely, without suffering from crystallization shrinkage. These unique behaviors/properties make MGs promising candidates for a range of structural and functional applications (e.g., consumer electronics, sports utilities, precision thermoplastic molding, metal-insulator-metal thin film diodes, micro- and nano-electromechanical devices).¹⁻⁸ Among the many different types of MGs, Ti-based MGs (TBMGs) are particularly attractive because of their added advantages of light weight, high specific strength, exceptional corrosion resistance, and biocompatibility. TBMGs possess great potential to be used in biomedical devices (including human body implants) and aerospace components. Therefore, a great deal of effort has been devoted to discovering and developing TBMG alloys.⁹⁻²⁰

Nevertheless, current TBMGs are plagued by their poor glass-forming ability (GFA). Most TBMGs must be manufactured with at least one dimension (the shortest one) kept below 6 mm in order to obtain a fully glassy structure.^{10,11,16-20} This threshold in the shortest dimension is termed as the critical casting diameter (for a cylinder) or thickness (for a plate), d_c . Exceeding the d_c will result in partial or complete crystallization (due to insufficient cooling rate). Many other types of MG alloys (e.g., Zr-based,²¹ Fe-base,²² Cu-based,^{23,24} Hf-based²⁵) have been discovered with d_c exceeding 10 mm. For TBMGs, in contrast, only certain alloys in the Ti-Zr-Cu-Fe(Ni)-Be¹² and Ti-Zr-Cu-Pd-Sn^{13,14} systems have been found to reach above the 10 mm landmark. Unfortunately, these alloys contain substantial amounts of the toxic element Be or the precious metal Pd. Other than the Be or Pd bearing alloys, a d_c of 7 mm has been reported for an alloy in the Ti-Zr-Cu-Fe-Ag-Sn-Si system which still relies on the precious metal Ag.¹⁵

Here, we report our discovery of a series of Be and precious-metal free TBMGs in the $(\text{TiZrHf})_x(\text{CuNi})_y(\text{SnSi})_z$ pseudo-ternary system. We show that alloys with compositions around $(\text{TiZrHf})_{55}(\text{CuNi})_{40.5}(\text{SnSi})_{4.5}$, more specifically, $\text{Ti}_{55-a-b}\text{Zr}_a\text{Hf}_b\text{Cu}_{40.5-c}\text{Ni}_c\text{Sn}_{3.2}\text{Si}_{1.3}$ ($3 < a < 4.5$, $6 < b < 10$ and $4 < c < 15$), have exceptional GFA and manufacturability. In particular, the $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{28.3}\text{Ni}_{12.2}\text{Sn}_{3.2}\text{Si}_{1.3}$ alloy exhibits a d_c of 12 mm, the largest for all Be and precious-metal free TBMGs known to date. We also report the thermal and mechanical properties of these alloys and examine the physical origin of their exceptional GFA and manufacturability through crystallization activation energy and atomic packing efficiency.

Alloy ingots of different compositions were prepared through arc-melting mixtures of ultrasonically cleansed Ti (99.9+%, crystal bar), Zr (99.9+%, crystal bar), Hf (99.2+%, crystal bar), Cu (99.99%, oxygen-free shot), Ni (99.98%, slugs), Sn (99%, shot), and Si (99.9+%, lump) pieces. Prior to the melting of the raw materials, the arc melter chamber was vacuumed to $\sim 3 \times 10^{-4}$ mbar residual pressure and filled with ultrahigh purity (UHP) argon, and then a Zr-getter was used (melted) to absorb the remaining oxygen and further clean the atmosphere. The alloy ingots were flipped and re-melted at least eight times each to acquire complete chemical homogeneity. Then, the ingots were melted again and tilt cast into a copper mold placed underneath the melting stage to form cylindrical rods of various diameters. Cross-sections of the cast rods were analyzed with an X-ray diffractometer (Rigaku Smartlab) using a $\text{Cu-K}\alpha$ source to reveal the amorphous or crystalline structure. Thermal behaviors, including glass transition and crystallization, of the alloys were studied with a differential scanning calorimeter (DSC, Mettler Toledo DSC3) at a heating rate of 0.333 K/s in a flowing nitrogen atmosphere. For the best composition ($\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{28.3}\text{Ni}_{12.2}\text{Sn}_{3.2}\text{Si}_{1.3}$), DSC scans at additional heating rates (0.083, 0.167, 0.333, 0.500, 0.667, and 0.833 K/s) were conducted to obtain the crystallization activation energy based on the Kissinger method. Compression tests were performed on specimens of ~ 1.35 mm diameter and 2.7 mm length using the Deben MT5000 (maximum load: 5 kN) test module at a nominal strain rate of $\sim 6 \times 10^{-4} \text{ s}^{-1}$. Vickers hardness was measured on a LECO M400A microhardness tester using a pyramid-shaped indenter, a 500

gf load and a 15 s dwelling time. Densities were determined according to the Archimedes' Principle using the Pioneer Scale – OHAUS PA84 and Density measurement kit.

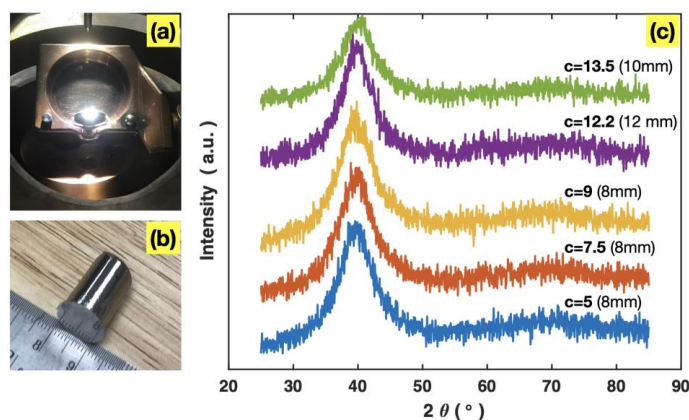


Fig. 1. (a) tilt casting setup inside the arc melter; (b) an exemplary 12 mm diameter cast rod; (c) X-ray diffraction patterns of $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{40.5-c}\text{Ni}_c\text{Sn}_{3.2}\text{Si}_{1.3}$ with varied Ni content and cast diameter.

Figure 1(a) shows the tilt casting setup inside the arc melter, with an alloy ingot sitting on the melting stage and a copper mold placed under. Figure 1(b) is the photo of a 12 mm diameter cast rod of the $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{28.3}\text{Ni}_{12.2}\text{Sn}_{3.2}\text{Si}_{1.3}$, as an example. The cast surface is very smooth and reflective, typical of metallic glass samples. Figure 1(c) presents the X-ray diffraction (XRD) patterns of the cast rods of $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{40.5-c}\text{Ni}_c\text{Sn}_{3.2}\text{Si}_{1.3}$ alloys with varied Ni content ($c=5, 7.5, 9, 12.2, 13.5$) and diameters (8, 10 and 12 mm). These patterns only exhibit diffuse maxima, without any sharp Bragg peaks. This ascertains the fully amorphous nature of the cast rods. In the previous research on TBMGs, fully amorphous structure at these diameters was obtained only for alloys containing substantial amounts of the toxic Be or the precious metal Pd.¹⁰⁻¹⁴ The $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{28.3}\text{Ni}_{12.2}\text{Sn}_{3.2}\text{Si}_{1.3}$ alloy discovered here, with a d_c of 12 mm, stands out as the non-toxic and precious-metal free TBMG with the highest GFA and manufacturability as of today. One previous study reported a d_c of 6 mm for $\text{Ti}_{41.5}\text{Zr}_{2.5}\text{Hf}_5\text{Cu}_{37.5}\text{Ni}_{7.5}\text{Si}_1\text{Sn}_5$,¹⁶ which is in the same alloy system as in the present work but different zone of the compositional space. Our alloys here employ

a higher content of Ti+Zr+Hf, and lower contents of Cu+Ni and Sn. The striking improvement in the d_c achieved here highlights the importance of finding the right compositions in the effort of developing highly processable and manufacturable MGs.

Table 1. Critical casting diameter d_c , density ρ , Vickers hardness H_v , yield strength σ_y , fracture strength σ_f , specific fracture strength $\sigma_{f,s}$, plastic strain (at fracture) ϵ_p , glass transition temperature T_g and onset crystallization temperature T_x of the TBMGs discovered in this work.

Alloy composition (in at.%)	d_c (mm)	ρ (g /cm ³)	H_v (kg/mm ²)	σ_y (GPa)	σ_f (GPa)	$\sigma_{f,s}$ (N m /g)	ϵ_p (%)	T_g (K)	T_x (K)
Ti _{42.1} Zr _{4.3} Hf _{8.6} Cu _{35.5} Ni ₅ Sn _{3.2} Si _{1.3}	8	7.3	594	1.94	2.6	356	3.9	675	726
Ti _{42.1} Zr _{4.3} Hf _{8.6} Cu ₃₃ Ni _{7.5} Sn _{3.2} Si _{1.3}	≥8	7.3	606	1.98	2.4	329	2.8	679	730
Ti _{42.1} Zr _{4.3} Hf _{8.6} Cu _{31.5} Ni ₉ Sn _{3.2} Si _{1.3}	≥8	7.3	609	1.99	2.7	370	6.1	680	729
Ti _{42.1} Zr _{4.3} Hf _{8.6} Cu _{28.3} Ni _{12.2} Sn _{3.2} Si _{1.3}	12	7.3	611	2.00	2.6	356	3.1	691	736
Ti _{42.1} Zr _{4.3} Hf _{8.6} Cu ₂₇ Ni _{13.5} Sn _{3.2} Si _{1.3}	10	7.3	615	2.01	--	--	--	692	735
Ti _{45.1} Zr _{3.3} Hf _{6.6} Cu ₃₃ Ni _{7.5} Sn _{3.2} Si _{1.3}	8	7.0	595	1.94	2.5	357	9.4	677	728

The densities (ρ , listed in Table 1) of the Ti_{42.1}Zr_{4.3}Hf_{8.6}Cu_{40.5-c}Ni_cSn_{3.2}Si_{1.3} (c=5, 7.5, 9, 12.2, 13.5) alloys are all measured to be 7.3 g/cm³, insensitive to the partition between the Cu and the Ni contents (due to the similarity of the two elements in their densities). This is close to the 7.0 g/cm³ of Ti_{41.5}Zr_{2.5}Hf₅Cu_{37.5}Ni_{7.5}Si₁Sn₅ and 6.85 g/cm³ of the Pd-bearing Ti₄₀Zr₁₀Cu₃₄Pd₁₄Sn₂ TBMGs reported in the literature.¹¹ It is noted that the Hf content has a strong impact on the alloy density here (due to the high density of Hf). At a lower Hf content, the Ti_{45.1}Zr_{3.3}Hf_{6.6}Cu₃₃Ni_{7.5}Sn_{3.2}Si_{1.3} alloy reaches a density of 7.0 g/cm³, while still retaining an excellent GFA with d_c equal to 8 mm.

Also listed in Table 1 are the Vickers hardness (H_v) values of the present TBMGs, which fall in the range from ~590 to 620 kg/mm². The hardness displays an increasing trend as more Cu is substituted with Ni (all other elemental contents fixed). This is attributable to the stronger interaction of Ni than Cu with the other five elements, as indicated by the more negative heat of mixing (ΔH_{mix}): -35, -49, -42, -4 and -40

kJ/mol for Ni with Ti, Zr, Hf, Sn, and Si, respectively, as opposed to the -9, -23, -17, 7, -19 for Cu.²⁶ For a similar reason (Zr and Hf interact more strongly than Ti with other elements), when some of the Zr and Hf percentages are shifted onto Ti while fixing all the other elements, the hardness decreases. The yield strength (σ_y) estimated from the relationship²⁷ (for isotropic materials) $\sigma_y = \frac{H_v}{3}$ is also listed in Table 1, which is in reasonable agreement with the compression tests (at 2% elastic strain).

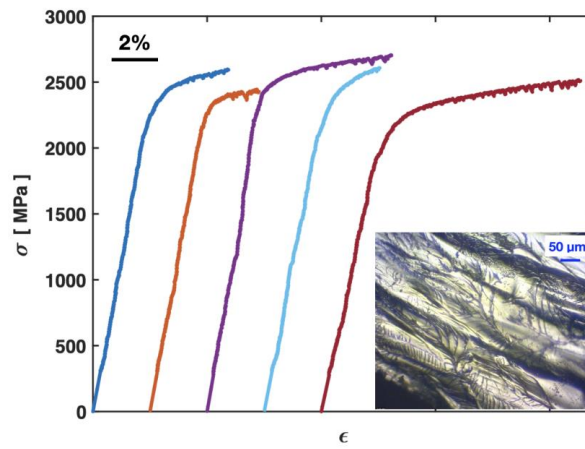


Fig. 2. Main panel: compressive stress-strain behaviors of, from left to right,

$Ti_{42.1}Zr_{4.3}Hf_{8.6}Cu_{35.5}Ni_5Sn_{3.2}Si_{1.3}$, $Ti_{42.1}Zr_{4.3}Hf_{8.6}Cu_{33}Ni_{7.5}Sn_{3.2}Si_{1.3}$, $Ti_{42.1}Zr_{4.3}Hf_{8.6}Cu_{31.5}Ni_9Sn_{3.2}Si_{1.3}$,
 $Ti_{42.1}Zr_{4.3}Hf_{8.6}Cu_{28.3}Ni_{12.2}Sn_{3.2}Si_{1.3}$, $Ti_{45.1}Zr_{3.3}Hf_{6.6}Cu_{33}Ni_{7.5}Sn_{3.2}Si_{1.3}$. Inset: optical micrograph of fracture
surface of $Ti_{45.1}Zr_{3.3}Hf_{6.6}Cu_{33}Ni_{7.5}Sn_{3.2}Si_{1.3}$.

Figure 2 (main panel) shows the engineering stress-strain curves for five of the present TBMGs obtained through compression tests. They all exhibit work hardening and serrated flow after yielding and several percent plastic strain (ϵ_p) before fracture, alluding to the intrinsic plasticity in these glassy alloys. Particularly, the $Ti_{45.1}Zr_{3.3}Hf_{6.6}Cu_{33}Ni_{7.5}Sn_{3.2}Si_{1.3}$ alloy underwent a 9.4% plastic strain before fracture, which clearly surpasses most of the previously reported TBMGs (including the Be- and Pd-bearing ones).¹¹ The fracture surface (inset in Fig. 2) exhibits significant vein-like features and a non-flat terrain with

frequent variations in height. These microscopic characteristics indicate the fair amount of resistance experienced by the final crack during its propagation, consistent with the plasticity displayed by the stress-strain curves. The fracture strength (σ_f) of the present alloys ranges from 2.4 to 2.7 GPa, which is higher than most other TBMGs.¹¹ The specific fracture strength ($\sigma_{f,s} = \sigma_f/\rho$), ~ 330 to 370 N m g^{-1} , falls in the range typical of TBMGs, and is significantly higher than that of the conventional light-weight alloys Ti-6Al-4V ($\sim 217 \text{ N m g}^{-1}$) and AZ91 ($\sim 154 \text{ N m g}^{-1}$), or other types of MGs (e.g., Zr-based: $270\text{-}310 \text{ N m g}^{-1}$, and Mg-based: $\sim 310 \text{ N m g}^{-1}$).¹¹

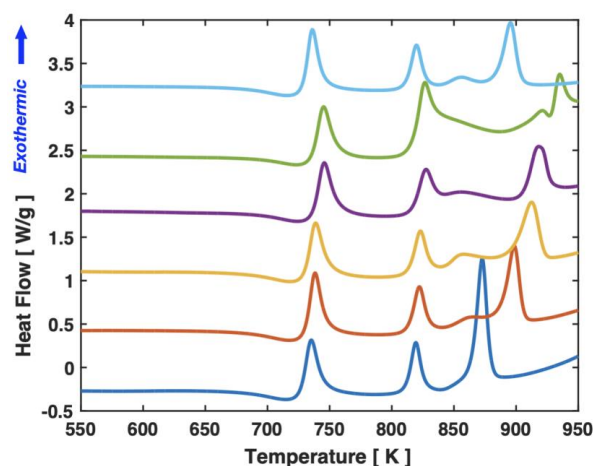


Fig. 3. Constant heating rate (0.333 K/s) DSC scans of, from bottom to top,

$\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{35.5}\text{Ni}_{5.2}\text{Sn}_{3.2}\text{Si}_{1.3}$, $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{33}\text{Ni}_{7.5}\text{Sn}_{3.2}\text{Si}_{1.3}$, $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{31.5}\text{Ni}_{9}\text{Sn}_{3.2}\text{Si}_{1.3}$,

$\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{28.3}\text{Ni}_{12.2}\text{Sn}_{3.2}\text{Si}_{1.3}$, $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{27}\text{Ni}_{13.5}\text{Sn}_{3.2}\text{Si}_{1.3}$ and $\text{Ti}_{45.1}\text{Zr}_{3.3}\text{Hf}_{6.6}\text{Cu}_{33}\text{Ni}_{7.5}\text{Sn}_{3.2}\text{Si}_{1.3}$.

The curves were shifted vertically for clarity.

The glass transition and crystallization behaviors of the TBMGs, as measured by DSC at a heating rate of 0.333 K/s, are shown in Fig.3. They all show a clear glass transition, indicated by a downslope (endothermic) of the heat flow curve between 650 and 700 K, and multiple crystallization events signified by the up-pointing (exothermic) peaks above 720 K. The values of the glass transition temperature T_g and

the onset crystallization (first event) temperature T_x , as determined by the commonly used two-tangent method, are listed in Table 1. The width of supercooled liquid region $\Delta T = T_x - T_g$ falls in the range of 43 K to 51 K. As the composition is varied, the T_g exhibits a similar trend to the hardness discussed above, reflecting its fundamental dependence on the chemical interaction (bond strength) among the constituent elements.

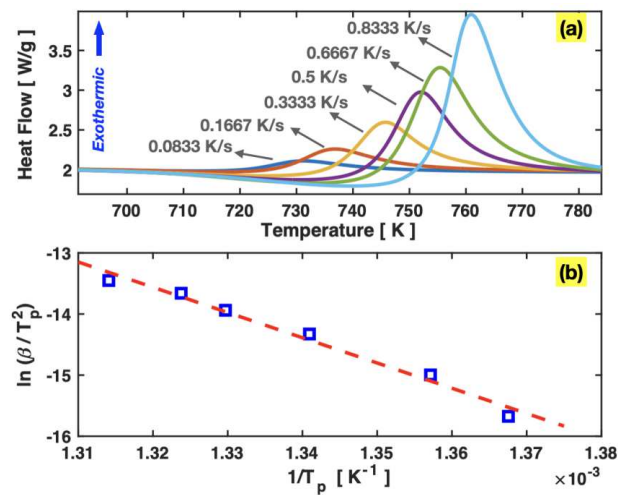


Fig. 4. (a) DSC scans of $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{28.3}\text{Ni}_{12.2}\text{Sn}_{3.2}\text{Si}_{1.3}$ with six different heating rates, showing the shift of the first crystallization peak; (b) Symbols: the Kissinger plot using the heating rate and peak temperature data from (a); dashed line: linear fit of the data.

The Kissinger method is often used to obtain the activation energy of a thermally activated process, such as a chemical reaction or phase transformation.^{28,29} It involves analyzing the correlation between the peak temperature of the process on a DSC scan and the heating rate used. Figure 4(a) shows the first (primary) crystallization event recorded by DSC at six different heating rates (from 0.0833 K/s to 0.8333 K/s) for $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{28.3}\text{Ni}_{12.2}\text{Sn}_{3.2}\text{Si}_{1.3}$ which has a d_c of 12 mm. A higher heating rate (β) leads to an increase in the peak temperature (T_p) as expected. According to the Kissinger method, the relationship

between β and T_p can be reduced to: $\ln\left(\frac{\beta}{T_p^2}\right) = -\frac{E_a}{R} \frac{1}{T_p} + \text{constant}$, that is, a linear correlation between $\ln\left(\frac{\beta}{T_p^2}\right)$ and $\frac{1}{T_p}$, with the slope equal to $-\frac{E_a}{R}$ (where E_a is the activation energy, and R is the ideal gas constant). Figure 4(b) presents the experimental data (symbols) for $\ln\left(\frac{\beta}{T_p^2}\right)$ and $\frac{1}{T_p}$ and the linear fit (dashed line). The data follow the Kissinger model quite closely, as suggested by a high fitting-goodness $R^2=0.98$. From the fitted slope, the activation energy E_a is determined to be 343 kJ/mol. This value is significantly higher than those reported in the literature for the first (primary) crystallization event in other TBMGs, for example, 287.6 kJ/mol for $\text{Ti}_{40}\text{Zr}_{10}\text{Cu}_{36}\text{Pd}_{14}$,³⁰ 179 kJ/mol for $\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Fe}_6$,³¹ and 188 kJ/mol for $(\text{Ti}_{41}\text{Zr}_{25}\text{Be}_{28}\text{Fe}_6)_{93}\text{Cu}_7$.³¹ Since glass formation requires the avoidance of crystallization, the high value of E_a for crystallization obtained here partially explains the exceptional GFA of the present TBMG.

Another perspective to understand the origin of GFA of a MG is the atomic packing efficiency. It is known that MGs with good GFA often possess high atomic packing efficiency (APE). Efficient (dense) atomic packing can increase the viscosity of a supercooled liquid and decrease the atomic mobility and thereby suppress crystallization kinetically. The APE of a MG can be calculated^{23,25} as $\text{APE} = \rho \times \left(N_A \sum_i c_i \frac{4\pi}{3} r_i^3\right) / (\sum_i c_i m_i)$, where ρ is the density of the alloy, N_A is the Avogadro's number, and c_i , r_i and m_i are the atomic percent, atomic radius and atomic (molar) mass of the i th element, respectively. The APE hence calculated (using the atomic radii in Ref. 32) is equal to 0.763, 0.765, 0.766, 0.768, 0.769 for $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{40.5-c}\text{Ni}_c\text{Sn}_{3.2}\text{Si}_{1.3}$ ($c=5, 7.5, 9, 12.2, 13.5$), respectively, and 0.757 for $\text{Ti}_{45.1}\text{Zr}_{3.3}\text{Hf}_{6.6}\text{Cu}_{33}\text{Ni}_{7.5}\text{Sn}_{3.2}\text{Si}_{1.3}$. These values are all greater than the well-known 0.74 for the close-packed fcc (face-centered-cubic) crystal structure. This reflects the efficient atomic packing in these TBMGs and aligns well with their exceptional GFA.

In summary, we have discovered a group of non-toxic and precious-metal free TBMGs that possess exceptional glass-forming ability. They belong to the pseudo-ternary (TiZrHf)-(CuNi)-(SnSi) system and possess chemical compositions around $\text{Ti}_{55-a-b}\text{Zr}_a\text{Hf}_b\text{Cu}_{40.5-c}\text{Ni}_c\text{Sn}_{3.2}\text{Si}_{1.3}$ ($3 < a < 4.5$, $6 < b < 10$ and $4 < c < 15$,

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at.%). Fully glassy rods with diameters of 8 to 12 mm can be readily manufactured through tilt casting. Particularly, the $\text{Ti}_{42.1}\text{Zr}_{4.3}\text{Hf}_{8.6}\text{Cu}_{28.3}\text{Ni}_{12.2}\text{Sn}_{3.2}\text{Si}_{1.3}$ alloy, with a critical casting diameter of 12 mm, presents the highest glass-forming ability and manufacturability for all non-toxic and precious-metal free TBMGs known to date. Moreover, the TBMGs here exhibit high fracture-strength (up to ~ 2700 MPa), high specific fracture-strength (up to ~ 370 N m g⁻¹), and good plasticity with a plastic strain of up to 9.4% upon compression. High activation energy for crystallization and high atomic packing efficiency provide an initial account for the physical origin of their exceptional glass-forming ability, while a thorough understanding requires further investigation through detailed experimental and computational studies of kinetics, thermodynamics, and structural characteristics. The alloys discovered in this work are expected to accelerate the research and development and engineering applications of TBMGs as advanced structural and functional materials.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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