Soft ytterbium-based bulk metallic glasses with strong liquid characteristic by design

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A family of Yb-based bulk metallic glasses with excellent glass-forming ability has been fabricated based on the elastic moduli correlations. The YbZnMg(Cu) glasses exhibit very strong liquid characteristic in fragility ($m=26\pm 5$), while soft mechanical characteristics, such as low bulk elastic modulus (e.g., Young's modulus is about 26.5 GPa), small Poisson's ratio (0.276), low Vickers hardness (1.52 GPa) and Debye temperature, and exceptionally low glass transition temperature ($T_g \sim 347$ K). The soft bulk metallic glasses with exceptional values of T_g, fragility, Debye temperature, and elastic moduli confirm some found correlations in metallic glasses. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3075062]

Recently, some correlations among the thermodynamic, kinetic, elastic, and physical properties of bulk metallic glasses (BMGs) have been found.[1–3] On the other hand, the elastic constants M of BMGs show a good correlation with a weighted average of the elastic constants M_i for the constituent elements as[2] $M^{-1}=\Sigma f_i M_i^{-1}$, where f_i denotes the atomic percentage of the constituent. The results imply that some features and properties of a BMG depend strongly on the elastic constants of its components. The established correlations, associated with elastic moduli, and since the moduli of glasses scale with those of their elemental components, provide useful guidelines for the development of BMGs with desirable properties by selection of components with suitable elastic moduli. Meanwhile, it is a key challenge to further verify and understand these correlations.

The BMGs are regarded as hard materials because they have high strength approaching theoretical strength, high hardness, and large toughness.[2,4–7] It is interesting if some metallic glasses with soft mechanical properties can be obtained. Ytterbium has unique physical and chemical properties such as low elastic moduli, and low melting temperature T_m. According to the elastic correlations, the Yb-based BMGs could have low elastic moduli (indicating softness in mechanical properties) and low Poisson's ratio (indicating brittleness and strong liquid behavior[1,2]). A metallic glass with exceptional values of T_g, fragility, and elastic moduli, in turn, can further verify the found correlations.

In this work, we report the formation of Yb-based BMGs by design based on elastic correlations. The formed Yb-based BMGs do exhibit extremely soft features and strong liquid fragility, which permits the BMGs a model system for verifying and understanding the various correlations found in metallic glasses. The strategy has an implication for developing glass composition with desirable properties.

We melted base element Yb with Zn and Mg (which also have low elastic moduli and their purity is better than 99.99 at. %) by using induction-melting method in a quartz tube under vacuum (better than 3.0×10^{-3} Pa). These elements also satisfy thermodynamic glass-forming criteria (such as large negative heat mixing and large atomic size difference among them).[8] Cu with strong chemical affinity with Yb and Mg was selected as minor additional element to improve the glass-forming ability. The homogeneously melted alloy was cast into a copper mold to get 20–50 mm long cylinder with diameters of 1–4 mm, or $2\times 5\times 50$ mm^3 plates. The amorphous nature of the samples was confirmed by x-ray diffraction (XRD) in a MAC M03 XHF diffractometer (Cu $K\alpha$ radiation) and differential scanning calorimeter (DSC) under a purified argon atmosphere in a Mettler Toledo DSC822e. Elastic moduli of the BMGs were obtained in a pulse echo overlap method using a MATEC 6600 model ultrasonic system with a measuring sensitivity of 0.5 ns and a carrying frequency of 10 MHz.

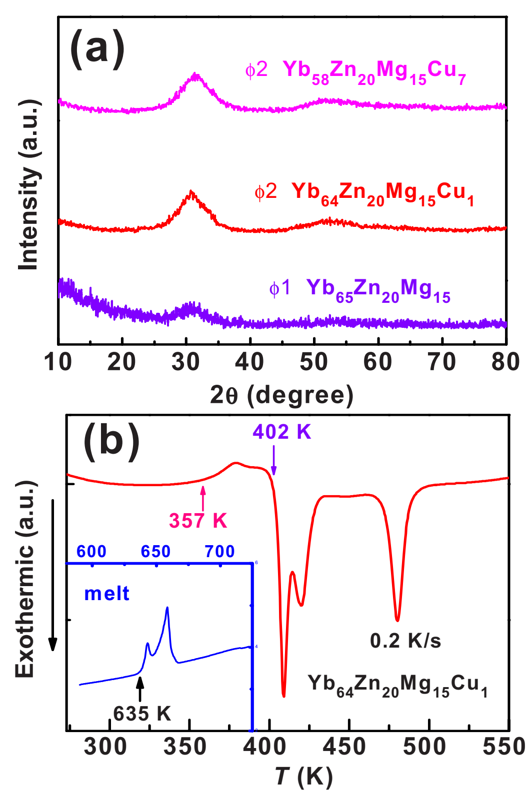

FIG. 1. (Color online) (a) XRD curves of Yb-based BMGs. (b) DSC trace of $Yb_{64}Zn_{20}Mg_{15}Cu_1$ alloy at a heating rate of 0.2 K/s. The inset shows the melting part.

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TABLE I. The values of T_g, T_x, T_m, $\Delta T = T_x - T_g$, $T_{rg} = T_g / T_l$, and critical diameter of fully amorphous rod of typical Yb-based BMGs.

Compositions (at. %)	D (mm)	T_g (K)	T_x (K)	T_m (K)	ΔT (K)	T_{rg}
$Yb_{70}Zn_{20}Mg_{10}$	1	347	386	657.5	39	0.519
$Yb_{62.5}Zn_{20}Mg_{17.5}$	2	367	398	629	31	0.560
$Yb_{64}Zn_{20}Mg_{15}Cu_1$	2	357	402	635	25	0.522
$Yb_{65}Zn_{20}Mg_{10}Cu_5$	2	384	419	641	35	0.545
$Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$	4	381	401	638	20	0.575

The XRD patterns and DSC trace of the Yb-based alloys in Fig. 1 show no obvious crystalline sharp peaks in the XRD curves and obvious glass transition and crystallization behaviors in DSC traces indicating the glassy state of the alloys. Ternary alloys (e.g., $Yb_{62.5}Zn_{20}Mg_{17.5}$) can form fully glassy rods 2 mm in diameter. Their glass-forming ability can be further enhanced by replacing 1–7 at. % Yb with Cu [Fig. 1(a)]. With composition modification, the maximum diameter for the fully glassy rod can reach 4 mm. From the DSC trace [Fig. 1(b)], the T_g, the onset temperature of crystallization T_x, T_m, and supercooled liquid temperature range $\Delta T = T_x - T_g$ of $Yb_{64}Zn_{20}Mg_{15}Cu_1$ BMG are determined to be 357, 402, 635, and 45 K, respectively. The remarkable feature of the Yb-based BMG is very low T_g. Such a low T_g and wide ΔT permit it to be processed like plastics in low temperatures such as in boiling water, which is similar to that of Ce-based metallic plastics[9] and is another family of metallic plastic. The compositions and thermal parameters of typical Yb-based BMGs are listed in Table I.

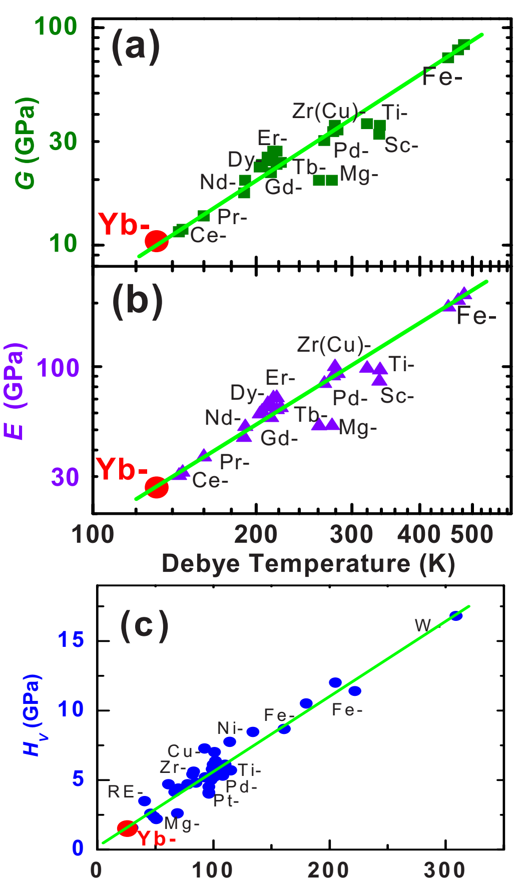

FIG. 2. (Color online) (a) Shear modulus and (b) Young's modulus of 30 kinds of BMGs vs Debye temperature. (c) Vickers hardness vs Young's modulus of 36 kinds of BMGs. The green solid lines are drawn to guide eyes.

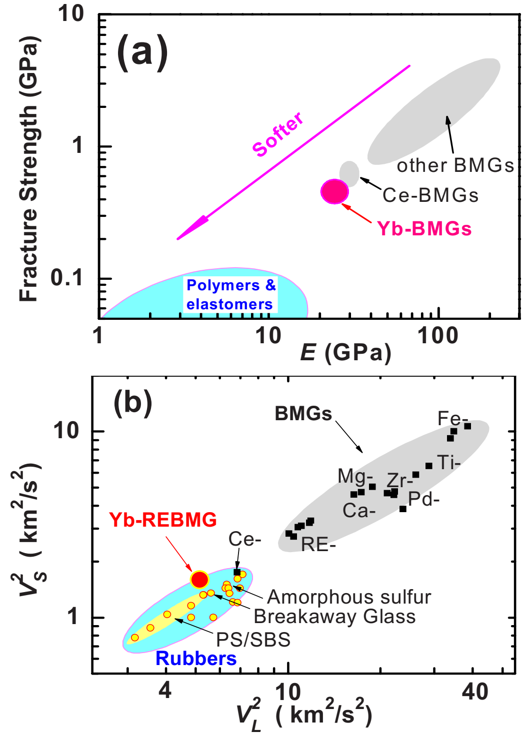

FIG. 3. (Color online) (a) Comparison of the fracture strength vs E of various BMGs and glassy polymers and elastomers. The values of Yb-based BMGs are close to the glassy polymers and elastomers (Refs. 15 and 17) (b) V_S^2 vs V_L^2 of various glassy materials. Part of the data of BMGs are from Refs. 2, 5, and 11.

The longitudinal acoustic velocity (V_L), transversal acoustic velocity (V_s), and density ρ of the $Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$ BMG are determined to be 2.272 km/s, 1.263 km/s, and 6.516 g/cm^3, respectively. The bulk modulus (K), shear modulus (G), Young's modulus (E), Poisson's ratio (ν), and Debye temperature (θ_D) are determined to be 19.8 GPa, 10.4 GPa, 26.5 GPa, 0.276, and 132.0 K, respectively. Debye temperature reveals how strong the atoms bond.[10] Then, we compare θ_D and elastic moduli among the known Zr-, CuZr-, La-, Ce-, Pr-, Nd-, Sm-, Gd-, Tb-, Dy-, Ho-, Er-, Sc-, Fe-, Mg-, Ti-, and Pd-based BMGs[2,5,11,12] (about 30 different BMGs). As shown in Figs. 2(a) and 2(b), the Yb-based BMG has the lowest θ_D and low elastic moduli among theses BMGs, which certifies its intrinsic soft nature. The soft nature is also certified by the Vickers hardness H_v measurement, and its H_v is 1.52 GPa. The comparison of the H_v and E with that of Zr-, CuZr-, Cu-, La-, Ce-, Pr-, Nd-, Sm-, Gd-, Tb-, Dy-, Ho-, Er-, Sc-, Fe-, Mg-, Ti-, Pd-, Pt-, W-, and Co-based BMGs[2,11] are shown in Fig. 2(c). We can see that the Yb-based BMG has exceptionally low values of H_v and E, and the low values of E and G, H_v, and θ_D fit the correlations very well.

The comparison between fracture strength and E of metallic glasses (>30 typical BMGs[2,13]) and glassy polymers and elastomers[4,14] is shown in Fig. 3(a). We can see that the elastic moduli of Yb-based BMGs are close to that of polymers and elastomers. The square velocity, associated with specific modulus ($G/\rho = V_S^2$, $E/\rho = V_S^2[(3V_L^2 - 4V_S^2)/(V_L^2 - V_S^2)]$), is an important parameter to evaluate the engineering properties of materials.[14] The V_L^2 versus V_S^2 of various glassy ma-

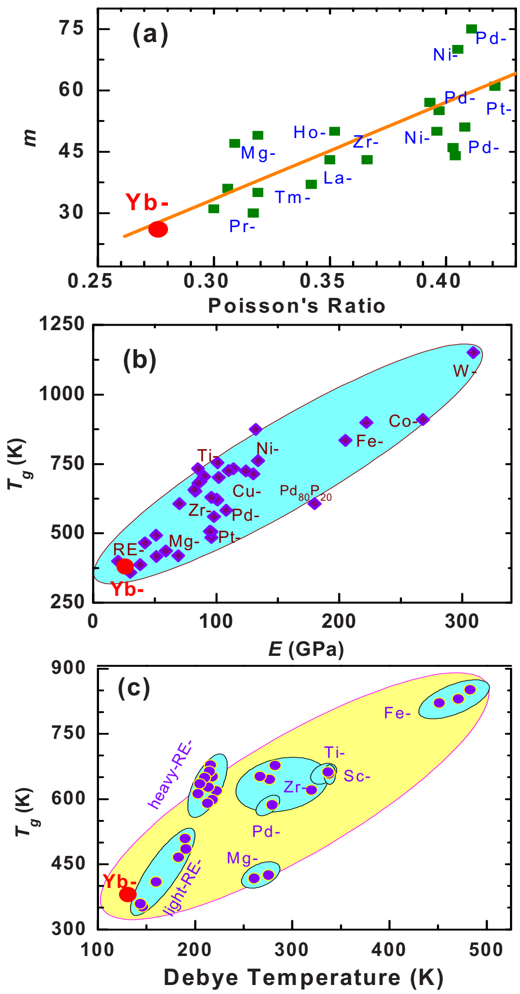

FIG. 4. (Color online) (a) The fragility m of metallic glass-forming liquids vs the Poisson's ratio of BMGs (Refs. 2, 13, and 20). The orange line is the linear fit. (b) A linear relationship between T_g and E. (c) T_g vs Debye temperature.

terials is shown in Fig. 3(b). For most transition-metal-, Mg-, and Ca-based metallic glasses, the V_L of most of the BMGs are larger than 4.0 km/s.[5] The rare earth based BMGs (except Yb- and Ce-) locate between 3.15 and 3.45 km/s.[12] While for the Yb-based BMGs (including Ce-based BMG but its acoustic velocities are 13% larger than that of Yb-based BMG), velocities are almost equal to or even smaller than that of rubber materials ($V_L < 2.65$ km/s and $V_S < 1.40$ km/s).[15–17] The comparison further confirms the rubber and polymerlike soft nature of the Yb-based BMGs.

The fragility can be quantified by the fragility parameter m as $m = d\log\langle\tau\rangle/d\langle T_g/T\rangle|_{T=T_g}$.[18] Using the method in Ref. 19, the m of the Yb-based glass is thermodynamically determined to be about 26 ± 5, indicating a "strong" characteristic of the glass-forming liquid.[18]

As proposed by Novikov *et al.*,[1] there is a plausible correlation between Poisson's ratio of glasses and the corresponding fragility of the glass-forming liquid. However, there are arguments whether they are corrected or universal for different kinds of glasses.[1,20] The Yb-based BMG with small m and ν extends the scope of the BMGs family, and can certify the correlation. The m versus ν for various metallic glasses[2,21,22] is shown in Fig. 4(a). Yb-based BMG, which gets to an extreme in all the known metallic glasses, seems to certify the relationship between m and ν. The data can be roughly fitted by a linear relationship, $m = -37.5 + 236.5\nu$, as shown in Fig. 4(a). On the basis of the linear relationship, the ν of metallic glasses should have a minimum (~ 0.230), because the minimum value of m is 17 on the definition of Angell.[18] Figure 4(b) shows the various BMGs in the form of T_g versus E. There is a clear linear relationship between T_g and E. The T_g versus θ_D as shown in Fig. 4(c) also satisfies a rough correlation. The correlation between T_g and θ_D in BMGs means that the glass transition of the BMG-forming alloys has the characteristic of melting.[3] These results indicate that even though the Yb-based BMGs have markedly different elastic, mechanical, and physical properties, and composition features, its data fit these correlations well. The obtained Yb-based BMG with combination of small elastic moduli T_g and strong glass-forming liquid properties further confirm the correlations in metallic glasses.

In summary, the metallic glasses could be soft materials like rubber or polymers. These combining unique properties of the BMGs further confirm some found correlations in metallic glasses. The polymorphism transformations of Yb crystals upon temperature or pressure[7] would allow testifying the probable polyamorphism transformations upon temperature or pressure in metallic glasses by using Yb-based BMGs.

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