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High-pressure behaviors of Yb-based bulk metallic glass

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The acoustic velocities of $Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$ bulk metallic glass (BMG) was measured in situ under hydrostatic pressure using a pulse echo overlap method. The elastic constants under high pressure, the equation of state and the Grüneisen parameters of the BMG were determined. It was found that the Yb-based BMG with a soft nature show weaker anharmonic characteristics, and the change in its physical parameters induced by pressure was much bigger than that of other BMGs. The anharmonic effect in BMGs correlates with the molar volume V_m, the bulk modulus K and Poisson's ratio.

Keywords: Elastic properties; Metallic glass

The equation of state (EOS) and anharmonic effects of glassy materials, including metallic glasses, are important for the applications of the glass [1–6]. The EOS of metallic glass and the vibrational anharmonicity that derives from the nonlinearity of the atomic forces with respect to atomic displacement can be determined by measuring the pressure (p)-dependent elastic constants. However, measurements were limited by the small geometric size of metallic glasses before the advent of bulk metallic glasses (BMGs). The EOS of only a few metallic glasses has been determined so far [1–3]. Recently, the discovery of Yb-based BMGs [7] with a critical diameter of up to 5 mm has allowed the ultrasonic properties of the BMGs to be measured under high pressure. What is more, the very low elastic moduli, especially the lower bulk modulus, would induce much bigger changes in parameters and some new phenomenon may be observed. In this letter, we measure the in situ acoustic properties under hydrostatic high pressure up to 0.5 GPa. The pressure-dependent elastic constants changes, the EOS and the anharmonic characteristic are determined and compared with those of other BMGs [2,3]. It is shown that the Yb-based BMG undergoes the biggest changes in volume and elastic moduli when under a pressure of 0.5 GPa, confirming its soft nature [7,8].

The $Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$ BMG was prepared using the induction-melting method in a quartz tube under vacuum (better than 3.0×10^{-3} Pa). The preparation details can be seen in Ref. [7]. The sample was cut into a plate $2 \times 5 \times 5$ mm^3 in size and its ends were carefully polished flat and parallel. The acoustic velocities and their p-dependent behavior were measured at room temperatures by using a pulse echo overlap method [9]. Crystalline quartz was used for the transducers to excite and detect ultrasonic pulses, with honey as the bonding material [10]. The traveling time of ultrasonic waves propagating through the sample was measured using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. The high hydrostatic pressure up to 0.5 GPa was performed in a piston–cylinder pressure apparatus, using electric insulation oil as the pressure-transmitting medium. Two pressure load–unload cycles were performed, and the reproducibility and measuring error were determined. The density of the sample was measured according to the Archimedean principle with an accuracy of about 0.005 g cm^{-3}. The p-induced changes in the sample dimensions were accounted for by using Cook's methods [11]. The elastic constants, such as Young's modulus E, bulk modulus K, shear modulus G and Poisson's ratio ν, were derived from the acoustic data and density [12,13].

The longitudinal (v_l), transversal (v_s) acoustic velocities and density (ρ) of the $Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$ BMG at ambient conditions were measured to be 2.272 km s^{-1}, 1.263 km s^{-1} and 6.516 g cm^{-3}, respectively. The K, G, E, ν and Debye temperature (θ_D) calculated from the acoustic data were 19.8 GPa, 10.4 GPa, 26.5 GPa, 0.276 and 132.0 K, respectively. Before calculating the moduli under high pressures, the p-induced changes in the sample dimensions were corrected using Cook's methods [11],

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which can calculate the elastic constants and sample dimensions simultaneously and self-consistently. Figure 1(a) shows the reduced ρ, v_l and v_s for Yb-based BMGs, all of which show a nearly linear relation with the pressure within the errors. The velocities show less change than the volume at high pressures, and show that the v_l is more sensitive to the change of density than the v_s. Figure 1(b) shows a comparison of the volume changes under 0.5 GPa for various BMGs [2,3,14]. Among these, the Yb-based BMG shows the biggest volume change, 2.75%, which is more than five times larger than of that of typical $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG (vit1), denoting the softest nature of the Yb-based BMG. Figure 1(c) lists the data of relative volume change vs. bulk modulus K. These data can be well fitted by an exponent correlation $\Delta V/V \sim K^{-1}$ which is consistent with the definition of bulk modulus $K = \frac{P}{\Delta V/V}$. We can see that the Ce-based

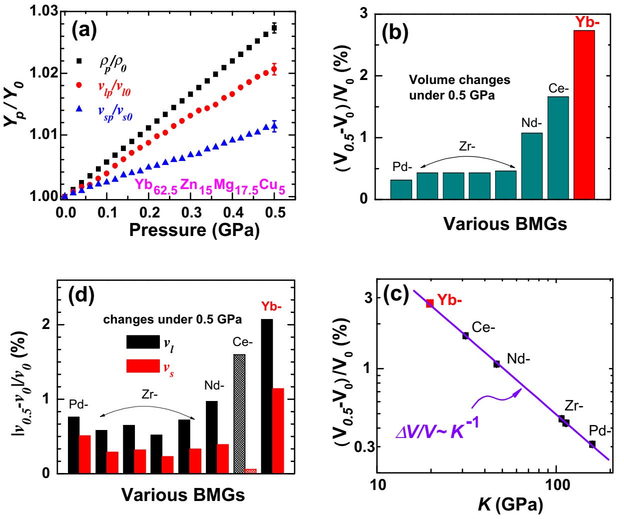

Figure 1. (a) The p-dependent reduced parameters ρ, v_l and v_s for $Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$ BMG (Y_p and Y_0 stand for the ρ, v_l and v_s at high pressure and under ambient conditions, respectively). (b) Comparison of relative volume changes under 0.5 GPa for various BMGs [2,3,14]. (c) The relation between volume change and K for various BMGs fitted by the relation $\Delta V/V \sim K^{-1}$. (d) Comparison of the velocities changes under 0.5 GPa for various BMGs.

BMGs, which have abnormal properties under high pressure [2], also fit this correlation well within the errors. The absolute value of velocity changes for various BMGs at 0.5 GPa, $|v_{0.5} - v_0|/v_0$, are listed in Figure 1(d). The changes in v_l and v_s for the Yb-based BMG are determined to be 2.1% and 1.2%, respectively, which are the biggest of all the BMGs studied. The p-dependent coefficient of the velocities for various glassy samples, dv_l/dp and dv_s/dp, are also listed in Table 1. Among these data, both v_l and v_s increase for most glasses, except the Ce-based BMG [2].

Figure 2(a) shows the p-driven moduli of Yb-based BMG. The moduli increase with a nearly linear relationship with pressure. Under 0.5 GPa, the increases in K, E, G and ν are determined to be 8.6%, 5.7%, 5.1% and 2.8%, respectively. The comparison of E and G of various BMGs are shown in Figure 2(b). We can see that the Yb-based BMG shows a much bigger increase, which denotes that the bonding between the atoms has also increased much more. As shown in Figure 3(c), except for the Ce-based BMG [2], the K of all the other BMG systems increases under high pressure, while the Yb-based BMG shows the biggest increase, 8.6%, indicating its easily compressible nature.

According to Murnaghan's theory [15], the isothermal bulk modulus is a linear function of p when no phase transition occurs. The EOS can be written in the following form:

$$\ln\left(\frac{V_0}{V_p}\right) = \frac{1}{K_0'}\ln\left(\frac{K_0'}{K_0}p + 1\right) \qquad (1)$$

where K_0 and K_0' are the bulk modulus and its p-deviation at ambient pressure, and V_0 and V_p are volumes at ambient and high pressure, respectively. From linear fitting, the values of K_0 and K_0' are determined to be 19.8 and 3.157 GPa, respectively. The EOS of $Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$ BMG is then determined, and is shown in Figure 3. Vit1 and metalloid window glass are also shown for comparison. The Yb-based BMG shows bigger volume changes under high pressure.

Based on the above acoustic results, the vibrational anharmonicity characterized by the Grüneisen parameters can be determined by the following equations [1,2,9]:

Table 1. The p-derivative of velocities, dv_l/dp and dv_s/dp, average molar volume V_m, bulk modulus K, Poisson's ratio ν and Grüneisen parameters γ_l, γ_s and γ_{av} of various glassy materials.

Samples	dv_l/dp (km s^{-1} GPa^{-1})	dv_s/dp (km s^{-1} GPa^{-1})	V_m (cm^3 mol^{-1})	K (GPa)	ν	γ_l	γ_s	γ_{av}
$Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$	0.095	0.029	19.24	19.8	0.276	1.17	0.70	0.86
$Nd_{60}Al_{10}Fe_{20}Co_{10}$	0.97	0.389	15.07	46.5	0.306	1.37	0.64	0.89
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	0.055	0.014	9.79	114.1	0.352	1.60	1.01	1.20
$Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$	0.057	0.009	9.65	107.3	0.336	1.49	0.71	0.97
$Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$	0.055	0.011	10.17	113.6	0.360	1.54	0.88	1.10
$(Zr_{59}Ti_6Cu_{22}Ni_{13})_{85.7}Al_{14.3}$	0.062	0.017	10.74	112.6	0.363	1.76	0.67	1.03
$Pd_{39}Ni_{10}Cu_{30}P_{21}$	0.072	0.021	7.97	159.1	0.397	2.75	2.02	2.26
$Pd_{40}Ni_{40}P_{20}$	0.064	0.019	7.98	185	0.402	3.30	2.23	2.59
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	0.063	0.016	9.50	128.2	0.369	2.10	1.34	1.59
$Ce_{69.8}Al_{10}Cu_{20}Co_{0.2}$	−0.081	−0.0017	–	–	–	−0.74	0.31	−0.04
Amorphous carbon	0.150	−0.153	–	–	–	0.76	−0.45	−0.04
Windows glass	−0.009	−0.097	–	–	–	0.27	−0.78	−0.43
Water white glass	−0.015	−0.053	–	–	–	0.22	−0.38	−0.18
Microcrystal glass	−0.390	−0.180	–	–	–	−3.17	−2.60	−2.79

For reference data, see Refs. [1–8].

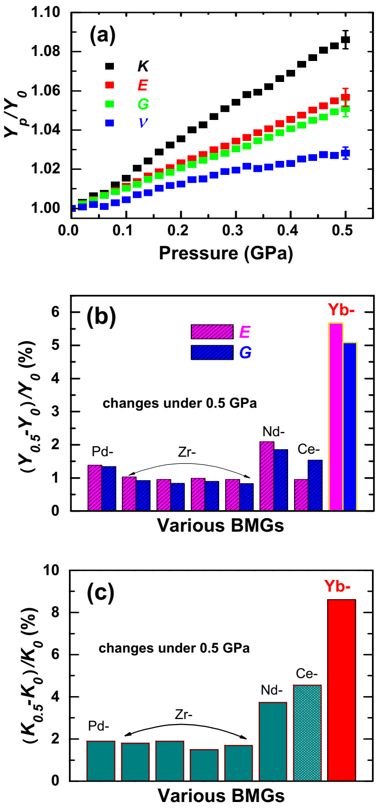

Figure 2. (a) The *p*-dependent reduced parameters *K*, *E*, *G* and *v* for $Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$ BMG (Y_p and Y_0 stand for the *K*, *E*, *G* and *v* at high pressure and under ambient conditions, respectively). Comparison of the changes of *E* and *G* (b) and *K* (c) for various BMGs.

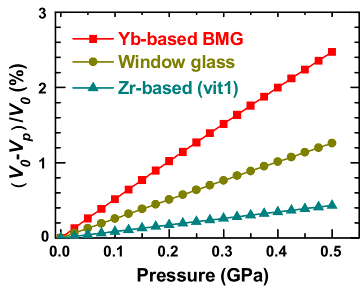

Figure 3. The EOS of $Yb_{62.5}Zn_{15}Mg_{17.5}Cu_5$ (red square symbols) BMG. The EOSs of typical $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG (vit1, filled cycles symbols) and metalloid window glass (filled triangle symbols) are shown for comparison.

$$\gamma_l = -\frac{K}{6\rho V_l^2}\left(3 - 2\frac{\rho V_l^2 - 2\rho V_s^2}{K} - 3\frac{dK}{dp} - 4\frac{dG}{dp}\right) \quad (2)$$

$$\gamma_s = -\frac{1}{6G}\left[2G - 3K\frac{dG}{dp} - \frac{3}{2}K + \frac{3}{2}\left(\rho V_l^2 - 2\rho V_s^2\right)\right] \quad (3)$$

$$\gamma_{av} = \frac{1}{3}(\gamma_l + 2\gamma_s) \quad (4)$$

where γ_l, γ_s and γ_{av} are the longitudinal, shear and average Grüneisen parameters, respectively. From the linear fit of the *p*-dependent moduli of the Yb-based BMG, the values for γ_l, γ_s and γ_{av} are determined to be 1.17, 0.70 and 0.86, respectively. The available Grüneisen parameters of various BMGs, oxide glasses and amorphous carbon [1–6] are collected in Table 1. We can see that the Yb-based BMG shows small positive Grüneisen parameters. The Grüneisen parameters represent the anharmonic vibrational behaviors of atoms [1,3], $\gamma_i = -d\ln\omega_i/d\ln V$, in which ω_i is the normal mode frequency and V is the volume. The positive signs of the Grüneisen parameters are due to the increase in long-wavelength acoustic mode frequencies under pressure, which would induce higher acoustic velocities, namely an anharmonic effect. This is a common character for BMGs, such as the Zr-based [5], Pd-based [1,4], Nd- and Cu-based BMGs [2] and some other metalloid glasses [1,16]. The negative values of the Grüneisen parameters of the Ce-based BMGs [2] and some metalloid glasses [1–3] show that the acoustic modes in these materials soften under pressure. The estimated Yb-based BMG shows smaller positive values. This shows that, when under pressure, the long-wavelength vibrational mode in Yb-based BMG shows a smaller increase, which can be ascribed to its high coordination number [1]. The small value of the Grüneisen parameters of Yb-based BMG is also related to its big *K*/*G*, d*G*/d*p* and d*K*/d*p*, according to Eqs. (2) and (3).

It is noted that there exist correlations between the average Grüneisen parameter γ_{av} and the molar volume V_m for various BMGs, as shown in Figure 4(a). We can see that there is a clear trend that BMGs with a smaller V_m possess a bigger γ_{av}. This means that the anharmonic effects are much stronger in systems with a smaller V_m. Figure 4(b) shows the smooth correlation between γ_{av}

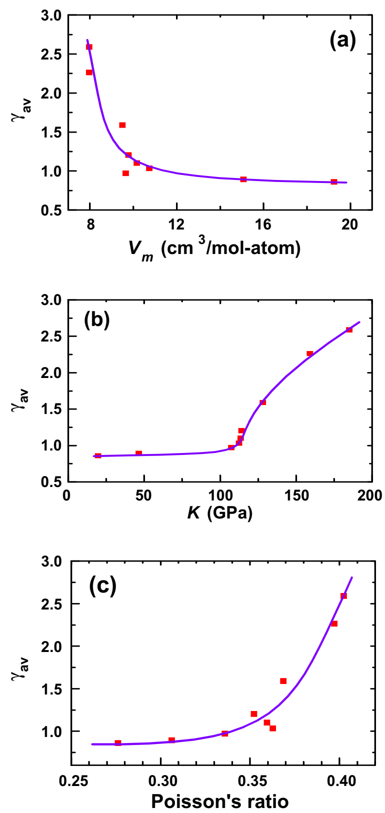

Figure 4. The average Grüneisen parameter shows clear correlation with (a) V_m, (b) *K* and (c) Poisson's ratio. The scattered symbols are experiment data, and the violet lines are drawn to guide the eyes.

and K. There seems to be an abrupt increase in γ_{av} at $K \sim 110$ GPa, and the systems with $K < 110$ GPa tend to have similar γ_{av} values around 0.9, while the systems with $K > 110$ GPa increase sharply. Figure 4(c) shows that a clear correlation exists between γ_{av} and Poisson's ratio. Systems with a bigger Poisson's ratio also tend to have a bigger γ_{av}. The anharmonic effects in BMGs under pressures correlate with V_m, K and Poisson's ratio, and the BMGs with a bigger V_m, a smaller K and a smaller Poisson's ratio display weaker anharmonic effects.

In conclusions, the big changes in density or volume, acoustic velocities and elastic moduli under high pressure confirm the soft nature of Yb-based BMGs. This also extends the scale of the BMGs and could help to find new correlations between properties. The small Grüneisen parameters classify the Yb-based BMGs as among the smaller anharmonic solids under the pressures measured. It is found that the anharmonic effect for BMGs under pressure depends on the V_m, K and Poisson's ratio.

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[1] E.F. Lambson, W.A. Lambson, J.E. Macdonald, M.R.J. Gibbs, G.A. Saunders, D. Turnbull, Phys. Rev. B 33 (1986) 2380.
[2] B. Zhang, R.J. Wang, W.H. Wang, Phys. Rev. B 72 (2005) 104205;
B. Zhang, R.J. Wang, M.X. Pan, D.Q. Zhao, W.H. Wang, Phys. Rev. B 70 (2004) 224208.
[3] W.H. Wang, P. Wen, L.M. Wang, Y. Zhang, M.X. Pan, D.Q. Zhao, R.J. Wang, Appl. Phys. Lett. 79 (2001) 3947.
[4] L.M. Wang, L.L. Sun, W.H. Wang, R.J. Wang, W.H. Wang, Appl. Phys. Lett. 77 (2000) 3734;
L.M. Wang, W.H. Wang, R.J. Wang, Z.J. Zhan, D.Y. Dai, L.L. Sun, W.K. Wang, Appl. Phys. Lett. 77 (2000) 1147.
[5] W.H. Wang, R.J. Wang, F.Y. Li, D.Q. Zhao, M.X. Pan, Appl. Phys. Lett. 74 (1999) 1803;
W.H. Wang, J. Appl. Phys. 99 (2006) 093506.
[6] R.J. Wang, F.Y. Li, J.F. Wang, W.H. Wang, Appl. Phys. Lett. 83 (2003) 2814;
R.J. Wang, W.H. Wang, F.Y. Li, Li Min Wang, Y. Zhang, P. Wen, J. Phys. C 15 (2003) 603.
[7] J.Q. Wang, W.H. Wang, H.Y. Bai, Appl. Phys. Lett. 94 (2009) 041910.
[8] J.Q. Wang, W.H. Wang, H.B. Yu, H.Y. Bai, Appl. Phys. Lett. 94 (2009) 121904.
[9] D. Schreiber, Elastic Constants and Their Measurement, McGraw-Hill, New York, 1973.
[10] W.H. Wang, F.Y. Li, M.X. Pan, D.Q. Zhao, R.J. Wang, Acta Mater. 52 (2004) 715.
[11] R.K. Cook, J. Acoust. Soc. Am. 29 (1957) 445.
[12] L.A. Girifalco, Statistical Physical of Materials, Wiley, New York, 1973.
[13] E.P. Papadakis, J. Acoust. Soc. Am. 42 (1967) 1045.
[14] W.H. Wang, Prog. Mater. Sci. 52 (2007) 540.
[15] F.D. Murnaghan, Proc. Natl. Acad. Sci. USA 30 (1944) 244.
[16] E.F. Lambson, G.A. Saunders, B. Bridge, R.A. El-Mallawany, J. Non-crys. Solids 69 (1984) 117.