Temperature dependence of elastic moduli in bulk metallic glasses down to liquid nitrogen temperature

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Temperature dependences of elastic moduli for representative bulk metallic glasses (BMGs) are *in situ* studied by the ultrasonic method down to liquid nitrogen temperature. The elastic moduli display a monotonous increase with the decreasing temperature, and the temperature dependences of the elastic moduli can be well described by the Varshni expression for various BMGs. The elastic Grüneisen parameters, the molar specific heat, and the Debye temperature in low temperature limit are obtained for the BMGs and compared to those of nonmetallic glasses. The results might provide useful information for understanding the unique properties of the BMGs © *2007 American Institute of Physics*. [DOI: 10.1063/1.2749838]

Recently, there has been increasing interest in bulk metallic glasses (BMGs) due to their promising physical and mechanical properties.[1–4] The elastic moduli are the second derivatives of the internal energy with respect to strain and thus depend sensitively on the interatomic potentials.[5] The investigation of elastic moduli provides a stringent connection to the properties, especially the mechanical properties of a BMG. It is found that the toughness of BMGs correlates with Poisson's ratio σ, alternatively the ratio of shear and bulk moduli.[4] The correlation is now regarded as an indicator of plasticity and has been used as a guideline to explore plastic BMGs. Except for the structural factor, the mechanical properties of metallic glasses are also strongly dependent on temperature.[6] The glassy alloys in the undercooled liquid region and high temperatures, in which they display superplasticity and good molding ability, have been extensively studied.[7,8] In contrast, the mechanical properties of BMGs at cryogenic temperatures have not been investigated in detail.

In this letter, cryogenic and acoustic experiments are performed on representative Zr-based, CuZr-based, La-based, and Mg-based BMGs. The velocities of ultrasonic waves have been measured *in situ* for the BMGs as a function of temperature down to liquid nitrogen temperature. The elastic moduli and their temperature dependences are then determined. Based on the results, we attempt to reveal the characteristics of their elastic behavior and to obtain the structural and thermodynamic information for the metallic glass materials at low temperatures.

The $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ (Vit1 or BMG1), $((Cu_{50}Zr_{50})_{95}Al_5$ (BMG2), $La_{68}Al_{10}Cu_{20}Co_2$ (BMG3), and $Mg_{65}Cu_{25}Gd_{10}$ (BMG4) with a 5 mm diameter were prepared by a Cu-mold casting method.[1] The BMG rods were cut into a length of about 7 mm, and its ends were polished flat and parallel. The acoustic velocities of the BMG from liquid nitrogen temperature to room temperature were measured by using the pulse-echo overlap method. The travel time of ultrasonic waves propagating through the rods with a 10 MHz carry frequency was measured using a MATEC 6600 ultrasonic system with *x*- and *y*-cut quartz transducers. The measuring sensitivity was about 0.5 ns. The density ρ was measured by the Archimedean technique and within an accuracy of 0.1%. Elastic moduli (e.g., Young's modulus E, shear modulus G, bulk modulus B, and σ) and Debye temperatures Θ_D were derived from the longitudinal (V_L) and transverse (V_T) velocities and the densities.[5]

The acoustic data and the moduli of these BMGs at room temperature are listed in Table I, which are consistent with the measured values reported earlier for these BMGs.[9] The temperature variations of V_L and V_T for these BMGs are shown in Figs. 1(a) and 1(b), respectively. Both V_L and V_T increase roughly linearly with the decreasing T in the cooling process. The data are reproducible under temperature cycling and show no measurable hysteresis effects down to the liquid nitrogen temperature. The results show that the BMGs have a similar temperature dependence of sound velocities to that of crystalline alloys.[10] The V_T has a larger change compared with V_L upon the decreasing temperature. This result means that the temperature has a larger effect on the transverse acoustic phonons than the longitudinal phonons in the BMGs.

The variations of E, G, and B are shown in Figs. 2(a)–2(c) as a function of temperature, respectively. All the elastic moduli monotonously increase with decreasing temperature, indicating the continuous stiffness of BMGs with decreasing temperature. G and E exhibit a marked increment with the drop of temperature, while B only shows a small reduction. Moreover, the change of each modulus with temperature is different for different BMGs. The ratio of changes in the shear and bulk moduli (dG/dK) from the liquid nitrogen temperature to ambient temperature (Vit1 2.61, $((Cu_{50}Zr_{50})_{95}Al_5$ 2.63, $La_{68}Al_{10}Cu_{20}Co_2$ 3.14, and $Mg_{65}Cu_{25}Gd_{10}$ 2.69) is larger than that of conventional crystalline alloys of about 2.[11]

The variations of σ as a function of temperature and the temperature normalized to the glass transition temperature T_g for the BMGs are shown in Figs. 3(a) and 3(b), respectively. The σ of all BMGs decreases with both the decreasing temperature and the T_g scaled temperature. The dependence of σ on the T_g scaled temperature shows that the temperature variation does not markedly depend on the type of the BMGs. The change trend of Poisson's ratio upon temperature is also consistent with the behavior of conventional alloys.[10] Because large σ is relative to a better ductility,[4] the decrease

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TABLE I. Density ρ, ultrasonic velocities (V_L, V_T), elastic moduli (E, G, K), and Poisson's ratio σ at ambient temperature. $E(0)$, $G(0)$, $B(0)$, and $V_L(0)$, $V_T(0)$, which are the elastic moduli and ultrasonic velocities at low temperature limit, respectively, are calculated from the Varshni expression. $V_0(0)$ and C_{ac}/T^3 are the average sound velocity and molar specific heat at 0 K.

Sample	Vit1	$(Cu_{50}Zr_{50})_{95}Al_5$	$La_{68}Al_{10}Cu_{20}Co_2$	$Mg_{65}Cu_{25}Gd_{10}$
ρ (g/cm^3)	6.085	7.195	6.152	3.807
T_g (K)	625	695	374	406
V_L (km/s)	5.116	4.699	2.911	4.272
V_T (km/s)	2.415	2.120	1.379	2.232
E (GPa)	96.3	88.7	31.7	49.8
G (GPa)	35.5	32.3	11.7	19.0
B (GPa)	112.0	115.8	36.6	44.2
σ	0.357	0.372	0.355	0.312
$E(0)$ (GPa)	100.5	93.1	34.2	53.8
$G(0)$ (GPa)	37.1	34.0	12.6	20.7
$B(0)$ (GPa)	113.8	117.9	39.6	45.5
$V_L(0)$ (km/s)	5.180	4.763	3.028	4.382
$V_T(0)$ (km/s)	2.469	2.174	1.431	2.332
$V_0(0)$ (km/s)	2.777	2.450	1.610	2.606
γ	1.6	1.8	1.3	1.5
C_{ac}/T^3 (J/mol K^4)	5.619×10^{-5}	8.643×10^{-5}	4.552×10^{-4}	8.595×10^{-5}
$\Theta_D(0)$ (K)	325.9	282.1	162.3	282.8

of σ in low temperature could suggest a more disappointed deformation ability.

The temperature dependence of the elastic constants of the metallic glass can be universally modeled by the Varshni expression[12,13]

$$C(T) = C(0) - \frac{s}{\exp(T_E/T) - 1}, \quad (1)$$

where $C(0)$ is the value of the elastic constant at 0 K, T_E the effective Einstein temperature, and s an adjustable parameter related to the strength of the anharmonic interactions. This expression is based on the assumption that the thermal phonons which are responsible for the anharmonic effects can be represented approximately by T_E. The elastic moduli of these BMGs are well fitted with the Varshni expression, as shown in Fig. 2. Through the Varshni fitting, the elastic moduli at 0 K were obtained and listed in Table I.

The adjustable parameter s, which is determined from the temperature dependence of bulk modulus, can be expressed as[14] $s=(3k_BT_E/\Omega_0)\gamma(\gamma+1)$, where Ω_0 represents the mean atomic volume. γ is the elastic (thermodynamic) Grüneisen parameter, which measures the interatomic anhar-

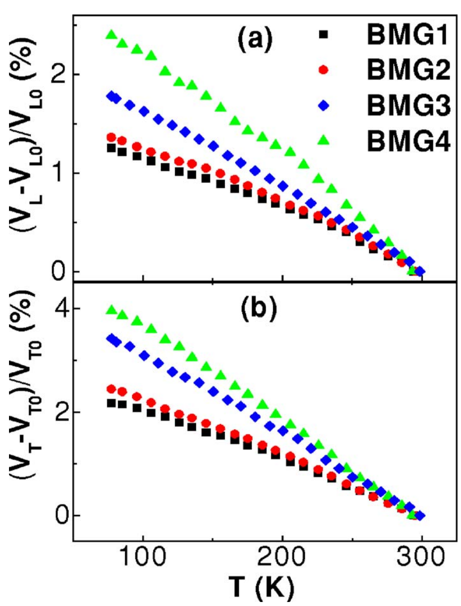

FIG. 1. (Color online) Temperature dependences of the (a) V_L and (b) V_T of the four BMGs; V_{L0} and V_{T0} are the velocities at ambient temperature.

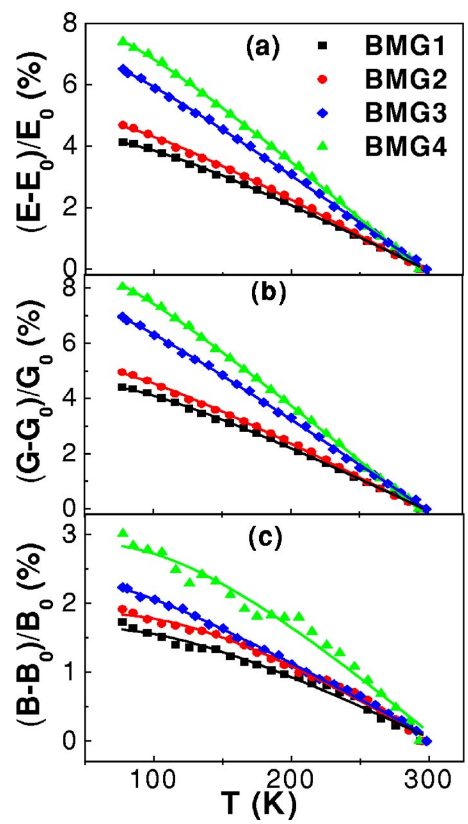

FIG. 2. (Color online) Variations of the (a) Young modulus E, (b) shear modulus G, and (c) bulk modulus B of the BMGs with temperature. The E_0, G_0, and B_0 are the moduli at ambient temperature. The Varshni fitting curves are shown with a solid line.

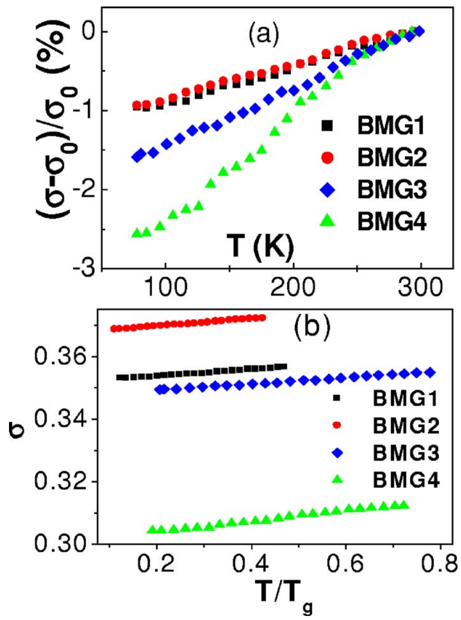

FIG. 3. (Color online) (a) Variations of σ on temperature for Vit1, CuZr-based, La-based, and Mg-based BMGs; (b) the dependence of σ on the temperature normalized to the glass transition temperature T_g.

monicity. Using the fitting parameters T_E and s from the Varshni expression for the bulk modulus, we get γ of the BMGs (listed in Table I). The values of γ for the BMGs are in the range of 1.3–1.8, which are much larger than those of the nonmetallic glasses (less than 1.0).[15] The positive Grüneisen parameters indicate a stiffness mode under low temperatures.

The long wavelength phonon contribution to the heat capacity can be calculated from the elastic moduli by

$$C_{\mathrm{ac}}=\frac{2\pi^2k_B^4}{5\hbar^3V_0^3}T^3, \qquad (2)$$

where k_B and $\hbar$ is Boltzmann's constant and Planck's constant, respectively, and V_0 is an average sound velocity given by $1/V_0^3=(1/3)(1/V_L^3+2/V_T^3)$. The V_L and V_T at the low temperature limit can be calculated from $V_L(0)=\sqrt{(4G(0)/3+B(0))/\rho}$ and $V_T(0)=\sqrt{G(0)/\rho}$. The acoustic velocities at 0 K can be calculated through the moduli $G(0)$ and $B(0)$ yielding from the Varshni fitting. Using these values, the acoustic contribution to the low temperature molar specific heat for the BMGs is obtained (listed in Table I). When the BMG is treated as a monatomic lattice with an average cellular volume, the Θ_D for the BMGs extended to 0 K can be obtained by[16] $\Theta_D=(hV_0/k_B)(3/4\pi\Omega_0)^{1/3}$. The results are listed in Table I.

The temperature dependence of elasticity is related to interatomic interactions and provides insight into the nature of the bonding. For comparison, the acoustic data of the nonmetallic water-white glass with covalent bond (main constituent is SiO_2) were measured at low temperatures. The water-white glass has a rather small temperature effect on its elastic behavior in contrast to metallic glasses (see Fig. 4). The change of temperature has a slight effect on the oxide glass because of the strong directionality and large energy of the covalent bonding, while in BMGs, the metallic bond without directionality can be easily and continuously affected by temperature.[17]

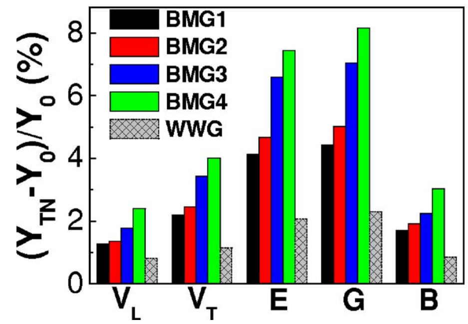

FIG. 4. (Color online) Comparison for the relative changes $\Delta Y=(Y_{\mathrm{LN}}-Y_0)/Y_0$ ($Y=V_L$, V_T, E, G, and K) between the state (Y_{LN}) of liquid nitrogen temperature and the ambient state (Y_0) for the Vit1, CuZr based, La-based, and Mg-based glasses, and oxide glass and water-white glass (WWG).

The metallic glasses, which are in the metastable glassy state, exhibit several relaxation processes.[18] The elastic moduli are directly dominated by the second derivative of potential energy in the metastable structural state between atoms. Although the process of relaxation is very slow under low temperatures, it still has an influence on their mechanical behavior. Recent results show that the mechanical behavior of BMGs has been markedly changed at low temperatures,[19] and the small change of mechanical properties can be reflected by Poisson's ratio.[20] So, the dependences of elastic moduli on temperature might provide useful information for understanding the mechanical and physical properties of BMGs at low temperatures.

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