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Abstract
The longitudinal and shear velocities, and their pressure dependences, for various bulk amorphous materials, including bulk metallic glasses and non-metallic glasses, have been measured by the ultrasonic pulse echo overlap method under hydrostatic pressure (maximum: 2 GPa) or uniaxial compression in ambient conditions. The second- or third-order elastic constants and the long-wavelength acoustic mode Grüneisen parameter are calculated. The results reveal that all metallic glasses have positive pressure dependences of both the longitudinal and shear velocities, while for most non-metallic glasses both the longitudinal and shear velocities decrease with increasing pressure. Thus, the Grüneisen parameters evaluated for the mean mode and shear mode for metallic glasses and non-metallic glasses have opposite signs. This indicates that the influences of the short-range-order structure and bonding, correlating closely with the atomic configurations in the various amorphous materials, play an important role in the properties determined by vibrational anharmonicity. The negative and positive Grüneisen parameters exhibit mode softening and stiffness under high pressure, respectively. The results also clearly demonstrate that the Grüneisen parameter is affected by the pressure derivative of the shear modulus, especially for non-metallic glasses.

The equation of state (EOS) of a solid plays an important role when studying thermodynamic properties in condensed matter physics, nucleonics and geophysics. The mode Grüneisen parameter (or ratio) γ_i is a significant thermodynamic parameter, showing the relationship

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between the thermodynamic and statistical physics. It characterizes the change of lattice vibrational frequency with volume, and can be written [1] as

$$\gamma_i = -\mathrm{d}\ln\omega_i/\mathrm{d}\ln V = \left(\frac{B_T}{\omega_i}\right)\left(\frac{\mathrm{d}\omega_i}{\mathrm{d}P}\right) \tag{1}$$

where ω_i is the frequency of the ith vibrational mode in a solid, V is the volume and B_T is the isothermal bulk modulus. To describe a theoretical thermodynamic property of solid reasonably well, one has to relate extremely complex interactions between grains. So γ is both an important parameter for describing anharmonic properties and an elusive parameter in the EOS.

Commonly, the Grüneisen parameter γ can be obtained directly from some thermodynamic parameters as well as the volume expansivity α, the isothermal (or adiabatic) bulk modulus B_T (or B_s) and the specific heat C_v at constant volume (or C_p, at constant pressure). This is a thermal Grüneisen parameter, γ_{th}. γ can also be approximated by means of continuum models from elastic data. It is an acoustic mode Grüneisen parameter, γ^{el}. Anderson has reviewed the progress in research on γ for the last 30 years [2] and detailed some problems and shortcomings that are yet to be overcome or bypassed. One of the problems is the effect of $\mathrm{d}G/\mathrm{d}P$ on γ. Here G is the shear modulus.

In a Debye solid, the model frequency, ω_i, is found in terms of the acoustic velocity v_i related to acoustic modes at low wavenumber k; i.e. $\omega_i = v_i k$. The slope of the ω versus k curve is v. So ultrasonic measurement is a powerful tool for studying elastic wave propagation through a solid, and providing important information on the microstructural and vibrational characteristics. The fundamental understanding of microstructural configurations and properties for amorphous solids is not as developed as that for crystalline solids. In the past decade, bulk metallic glasses (BMGs) with a larger three-dimensional size, with complex multicomponent chemistry and excellent glass-forming ability (GFA), have been developed [3, 4]. The BMGs can be made in a suitable form for measurement of elastic wave propagation. So systematic study of anharmonic properties and microstructural characteristics of various amorphous solids, including BMGs and non-metallic glasses such as oxide glasses and amorphous carbon, is of importance.

Usually, a scalar parameter γ and tensor $\gamma_{jk's}$ are expressed in terms of second- and third-order elastic coefficients for arbitrary crystal symmetry [1]. Amorphous materials possess only short-range order; they can be considered as isotropic solids. There are two components of the Grüneisen parameter for acoustic modes at the long-wavelength limit. They are written as follows [5]:

$$\gamma_l = -\frac{B}{6C_{11}}\left[3 - \frac{2C_{12}}{B} - 3\frac{\mathrm{d}B}{\mathrm{d}P} - 4\frac{\mathrm{d}\mu}{\mathrm{d}P}\right] \tag{2}$$

$$\gamma_s = -\frac{1}{6\mu}\left[2\mu - 3B\frac{\mathrm{d}\mu}{\mathrm{d}P} - \frac{3}{2}B + \frac{3}{2}C_{12}\right] \tag{3}$$

where γ_l and γ_s are the longitudinal and shear mode Grüneisen parameter, respectively. B is the bulk modulus and $\mu = C_{44} = \rho V_s^2$, $C_{11} = \rho V_l^2$, $C_{12} = C_{11} - 2C_{44}$. The mean mode Grüneisen parameter is

$$\gamma_{av}^{el} = \tfrac{1}{3}(\gamma_l + 2\gamma_s). \tag{4}$$

They are also written in terms of second- and third-order elastic coefficients as follows [6] for an isotropic and cubic system:

$$\gamma_l = -\frac{1}{13}\left[\frac{3C_{11} + 2C_{12} + C_1}{2C_{11}} + \frac{2(5C_{11} + 10C_{12} + 8C_{44} + 3C_1 + 4C_2 - 4C_3)}{3(C_{11} + 2C_{12} + 4C_{44})}\right.$$

$$\left. + \frac{2(2C_{11} + 3C_{12} + 2C_{44} + C_1 + C_2 - C_3)}{C_{11} + C_{12} + 2C_{44}}\right] \tag{5}$$

$$\gamma_s = -\frac{1}{26}\left[\frac{2(C_{11} + 2C_{12} + 2C_{44} + C_2)}{C_{44}} + \frac{4(5C_{11} + 4C_{12} + 2C_{44} + C_2 + 2C_3)}{3(C_{11} - C_{12} + C_{44})}\right.$$

$$\left. + \frac{2(2C_{11} + C_{12} + C_3)}{C_{11} - C_{12}}\right] \tag{6}$$

$$C_1 = C_{111} + 2C_{112} \qquad C_2 = C_{144} + 2C_{166} \qquad C_3 = \tfrac{1}{2}(C_{111} - C_{123}). \tag{7}$$

However, the Slater equation [7] which assumes that the Poisson's ratio σ is independent of pressure is

$$\gamma_{Slater} = -\frac{1}{6} + \frac{1}{2}\left(\frac{\partial B_T}{\partial P}\right)_T \tag{8}$$

where the adiabatic bulk modulus B_s is used as an approximation instead of the isothermal bulk modulus B_T.

In this work, we present *in situ* acoustic studies under hydrostatic pressure on various bulk glasses including ZrTi-, ZrNb- and Pd-based BMGs and non-metallic glasses such as oxide glasses and single-composition carbon glass. Using the pulse echo overlap method [8, 9], the longitudinal velocity (V_l) and shear velocity (V_s) of the ultrasonic wave propagating through the sample, and their pressure dependences, were measured under ambient conditions and under pressure (P) up to 0.5 GPa (maximum: 2 GPa for ZrTiCuNiBe$_{22.5}$), respectively, in a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns and the carrier frequency of 10 MHz. The experiments under high pressure were completed using a piston–cylinder high-pressure apparatus; electric insulation oil was used as the pressure-transmitting medium to ensure hydrostaticity. So the shear stress caused by non-hydrostaticity can be eliminated. Upon pressure loading, the density and the length of the sample were modified by the Cook method [10].

The experimental results (see figures 1 and 2) found that the change of V_l with P for these BMGs is much larger than that of V_s, i.e. $dV_l/d_P \gg dV_s/dP$. This result means that the longitudinal acoustic phonons are softer than the transverse phonons under high pressure in the BMGs. Both V_l and V_s increase smoothly with increasing pressure P and show an approximately linear pressure dependence for $dV_l/dP > 0$, $dV_s/dP > 0$ over a range of pressure up to 0.5 GPa; whereas V_l and V_s for most oxide glasses decrease with increasing pressure for $dV_l < 0$, $dV_s/dP < 0$ and $dV_s/dP \gg dV_l/dP$. In particular, amorphous carbon has $dV_l/dP > 0$ and $dV_s/dP < 0$; the change of V_l for float glass is very small and $dV_l/dP > 0$ up to 0.6 GPa and $dV_l/dP < 0$ beyond that pressure up to 2 GPa.

Making a linear fit for the velocity versus pressure and using the above formulae (2)–(4) and (8), the long-wavelength acoustic mode Grüneisen parameter γ_l, γ_s, γ_{av} and γ_{Slater} for the various glasses are calculated and the results are listed in the table 1.

Table 1 shows clearly that both γ_l and γ_s are positive for BMGs because $dV_l/dP > 0$, $dV_s/dP > 0$ and $dV_l/dP \gg dV_s/dP$, so $\gamma_l > \gamma_s$ and the mean mode Grüneisen parameter $\gamma_{av} > 0$; whereas for oxide glasses, $dV_l/dP < 0$, $dV_s/dP < 0$ and $dV_s/dP \gg dV_l/dP$ lead to $\gamma_s < 0$ and $\gamma_{av} < 0$. For fused quartz, microcrystal glass and (SiO$_2$ + TiO$_2$) glass, a larger negative change of V_l than of V_s under pressure below 0.5 GPa leads to a negative γ_l and to a larger negative γ_{av}. BMGs and oxide glasses have opposite signs of γ_s and γ_{av}. This indicates different characteristics of the vibration frequency corresponding to the shear wave under high pressure: γ_s increases gradually for BMGs, which means that the vibration
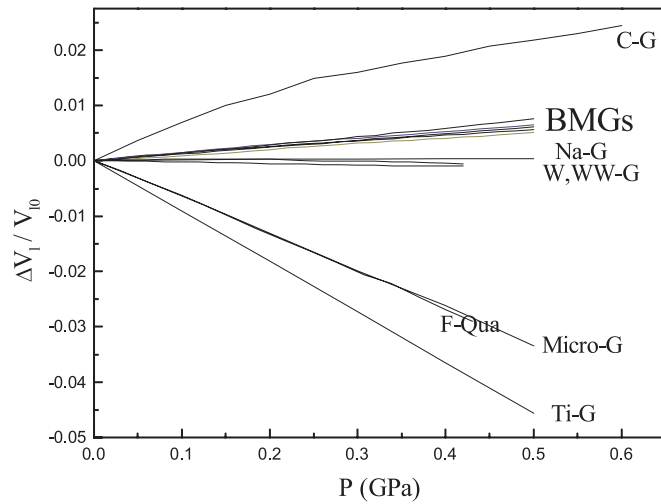
Figure 1. The pressure dependences of the longitudinal velocity for various bulk glasses including Zr-, Pd-based BMGs, oxide glasses (window glass: W-G; water-white glass: WW-G; float glass: Na-G; SiO_2 + TiO_2 glass: Ti-G; fused quartz: F-Qua; microcrystal glass: Micro-G); single-composition carbon glass (C-G).
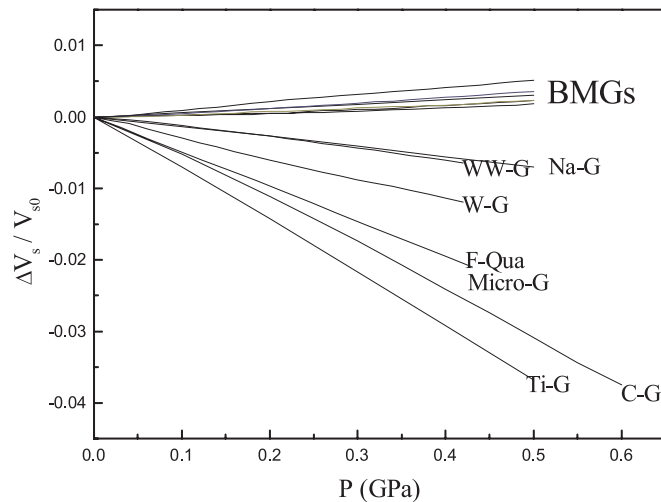
Figure 2. The pressure dependences of the shear velocity for the various bulk glasses including Zr-, Pd-based BMGs, oxide glasses and single-composition carbon glass.

frequency increases and the mode stiffness; while, in contrast, γ_s decreases gradually for oxide glasses and carbon glasses—this is a soft-mode behaviour. There is a clear effect of dV_s/dP (or dG/dP) on γ_s and γ_{av}. It is noteworthy that this effect is not caused by the shear stress, because the hydrostaticity of the applied pressure is guaranteed.

In the short range, correlated closely with atomic configurations, all BMGs have dense randomly packed microstructure with a metallic bond. The degree of densification between the atoms increases with applied pressure, so BMGs exhibit positive pressure derivatives of V_l and V_s. Non-metallic glasses such as oxide glasses form chain-like objects or networks. The

Table 1. The long-wavelength acoustic mode Grüneisen parameter for the various bulk glasses.

Sample	dV_l/dP (km s^{-1} GPa^{-1})	dV_s/dP (km s^{-1} GPa^{-1})	γ_l	γ_s	γ_{av}	γ_{Slater}
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}B_{22.5}$	0.055	0.014	1.60	1.01	1.20	1.85
			1.45b	0.66[b]	0.93[b]	
			1.65[a]	0.86[a]	1.12[a]	
$Zr_{41}Ti_{14}Cu_{12.5}Ni_9Be_{22.5}C_1$	0.057	0.009	1.49	0.71	0.97	1.80
$Zr_{48}Nb_8Cu_{12}Fe_8Be_{24}$	0.055	0.011	1.54	0.88	1.10	1.84
$(Zr_{59}Ti_6Cu_{22}Ni_{13})_{85.7}Al_{14.3}$	0.062	0.017	1.76	0.67	1.03	1.95
$Pd_{39.1}Ni_{10.1}Cu_{29.9}P_{20.9}$	0.072	0.021	2.75	2.02	2.26	2.97
Amorphous carbon			0.76	−0.45	−0.04	
	0.150	−0.153	1.25[a]	−0.27[a]	0.24[a]	2.03
Window glass	−0.009	−0.097	0.27	−0.78	−0.43	1.27
Water-white glass	−0.015	−0.053	0.22	−0.38	−0.18	0.71
Float glass	0.008	−0.046	0.27	−0.42	−0.19	0.88
$SiO_2 + TiO_2$ glass	−0.462	−0.273	−2.25	−2.10	−2.15	−2.42
Fused quartz	−0.403	−0.218	−2.10	−1.75	−1.86	−2.50
Microcrystal glass	−0.390	−0.180	−3.17	−2.60	−2.79	−3.59

[a] Data obtained using (5)–(7) from third-order elastic constants.
[b] Uncorrected data—that is, the length and density of the sample are considered constant under high pressure.

bond angles between atoms turn under pressure and lead to negative pressure dependence of the shear modulus. Carbon glass has a special structure—the C–C linkage is a superposition of a covalent and a metallic bond, while the linkage between layers is a van der Waals bond—so it not only exhibits a negative pressure derivative of V_s similar to that of oxide glasses, but also exhibits a positive pressure derivative of V_l similar to that of the BMGs. This difference in microstructure causes different pressure dependences of V_l and V_s, so it leads to different anharmonic behaviour related mainly to the shear vibration γ_s under high pressure.

Table 1 also shows a large difference between γ_{av} and γ_{Slater}. This arises from Slater equation (5), which assumes that Poisson's ratio σ is independent of pressure. But our experiment found that σ depends more strongly on pressure for carbon glass and oxide glasses than for BMGs. If σ_0 is defined as σ under ambient conditions, then when the pressure increases to 0.5 GPa, $\Delta\sigma/\sigma_0 = (\sigma - \sigma_0)/\sigma_0$ for the former and the latter can be about 2%–5% and 2‰–5‰, respectively. The pressure dependence of σ should be considered, especially for non-metallic glasses. So the values of γ_{av} listed in table 1 are more reasonable than those of γ_{Slater}. By contrast, the Grüneisen parameters γ_l, γ_s and γ_{av} of the BMG $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ were calculated carefully in a different way. The results show that the standard errors of γ_{av}, γ_{av}^{**} and γ_{av}^{*} are about ±0.065, while those of γ_{av} and γ_{av}^{**} are about ±0.028. This means that the changes of length and density of the sample under high pressure cannot be neglected.

For a number of glasses, there is a correlation between the mean long-wavelength acoustic mode Grüneisen parameter γ_{av} and the linear coefficient α of thermal expansion [11] (see figure 2 in [11]). We can estimate from the values of γ_{av} listed in table 1 that the values of α for BMGs are much large than those for other non-metallic glasses. This is in conformity with the thermal properties of BMGs [12].

In conclusion, the short-range microstructure correlated closely with atomic configurations of amorphous materials causes different pressure dependences of the velocities V_l and V_s, so it leads to different anharmonic behaviours under high pressure. The mode stiffness for the BMGs and soft modes for non-metallic glasses relate mainly to the shear vibration. The effect

of $\mathrm{d}G/\mathrm{d}P$ on γ_{av} is evident, especially for non-metallic glasses. The pressure dependence of σ should be considered in calculating Grüneisen parameters.

Acknowledgment

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