

## Equation of state of bulk metallic glasses studied by an ultrasonic method

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The acoustic velocities and their pressure dependence of various Zr- and Pd-based bulk metallic glasses (BMGs) have been measured by using a pulse echo overlap method. The elastic constants as well as their pressure dependence of the BMGs have been determined, and the equation of state of these BMGs was obtained and compared to that of other glasses and crystalline solids. The structural characteristic of the BMGs is discussed. © 2001 American Institute of Physics. [DOI: 10.1063/1.1426272]

The equation of state (EOS) of a solid plays an important role in condensed matter physics, geophysics and application.<sup>1,2</sup> However, little information about EOS is obtained for metallic glasses, because the measurements of EOS have been impeded mainly by the inability to prepare bulk metallic glassy specimens. A fundamental understanding of microstructural configuration and properties in amorphous solids is not as developed as that in crystalline solids. Recently, glass forming systems with a larger three-dimension size have been developed.<sup>3–9</sup> Due to the large size and high thermal stability of the bulk metallic glasses (BMGs), detailed and accurate studies of various properties in large temperature and pressure ( $p$ ) range become possible. The ultrasonic method is a powerful tool for studying the elastic wave propagation of a solid, and providing important information about the structural and vibrational characteristics. The BMGs are in a very suitable form for acoustic investigation, the measurements of pressure dependent acoustic properties provide an opportunity for studying the EOS of the metallic glasses, and they open a way for the understanding of the metallic glassy state. In this work, we present *in situ* acoustic studies upon pressure on the various BMGs.<sup>10–13</sup> The elastic constants as well as their change upon pressure up to 2 GPa have been determined, and the EOS of these BMGs is then obtained. The EOS and elastic property of the BMGs are compared with those of other solids.

The  $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$  (BMG1),  $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_9\text{Be}_{22.5}\text{C}_1$  (BMG2),  $\text{Zr}_{48}\text{Nb}_8\text{Cu}_{12}\text{Fe}_8\text{Be}_{24}$  (BMG3),  $\text{Zr}_{50.6}\text{Ti}_{5.2}\text{Cu}_{18.8}\text{Ni}_{14.1}\text{Al}_{14.3}$  (BMG4), and  $\text{Pd}_{39}\text{Ni}_{10}\text{Cu}_{30}\text{P}_{21}$  (BMG5) were prepared by the water quenching method, and the details of the preparation can be seen in Refs. 10–13. The amorphous nature of the BMGs was ascertained by x-ray diffraction, differential scanning calorimeter, and transmission electron microscopy.<sup>10–13</sup> The amorphous rod was cut to a length of about 10 mm, and its ends were carefully polished flat and parallel. The acoustic velocities and their pressure dependence of the BMGs were measured at room temperature by using a pulse echo overlap

method.<sup>14</sup> The excitation and detection of the ultrasonic pulses were provided by quartz transducers. The frequency of the ultrasonic is 10 MHz. The transducers were bonded to the specimen using honey for high pressure experiments. The effects of honey on the acoustic velocities under pressure have been already determined. Its bond quality can be kept unchanged up to 2 GPa.<sup>15</sup> The traveling time of ultrasonic waves propagating through the sample was measured using a MATEC 6600 ultrasonic system with a measuring sensitive of 0.5 ns. This system is particularly well suited for the determination of  $p$ -induced changes in velocity.<sup>16</sup> The sample with a bonded transducer was immersed in electric insulation oil (as the pressure transmitting media, for which hydrostaticity has already been determined.) in the pressure experiment. The high pressure was performed in a piston-cylinder pressure apparatus. The high pressure measurements were performed for several pressure load–unload cycles to examine the reproducibility and minimize error.  $P$ -induced changes in the sample dimensions were accounted for by using the Cook's methods.<sup>17</sup>  $\rho$  was measured by the Archimedian principle with an accuracy of about 0.005 g/cm<sup>3</sup>. The elastic constants (e.g., bulk modulus  $K$ ) are derived from the acoustic data and density.<sup>16,18</sup>

The values for the longitudinal velocity,  $v_l$ , transverse velocities  $v_s$ , and  $\rho$  of the BMGs and other glasses at ambient condition, and the elastic moduli calculated from the acoustic data are listed in Table I. The obtained elastic data are in good agreement with the available data of the BMGs measured using different methods confirming that the acoustic method is an effective way to study the BMGs.<sup>4,5</sup> The pressure variations  $\Delta v(p)/v(p_0) = [v(p) - v(p_0)]/v(p_0)$  of  $v_l$  and  $v_s$ , for these BMGs at room temperature are shown in Fig. 1(a) and 1(b) respectively, where  $p_0$  is the ambient pressure. The data are reproducible under  $p$  cycling and show no measurable hysteresis effects up to 2 GPa. The changes in both  $v_l$  and  $v_s$  are reproducible for repeated compression at least up to 0.5 GPa. The change of  $v_l$  with  $p$  of these BMGs is much larger than  $v_s$ . No density increase in the sample after testing was found here within experimental error. These results indicate the elastic behavior in the BMG under hydrostatic compression up to 0.5 GPa. Both  $v_l$  and  $v_s$  increase smoothly with increasing of  $p$  in loading and unloading pro-

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TABLE I. The acoustic data and elastic constants ( $E$  is Young's modulus and  $G$  is shear modulus) and the values of  $K_0$ ,  $K'_0$ , and  $\gamma$  for typical oxide glasses and BMGs at ambient pressure.

Sample	$\rho$ (g/cm <sup>3</sup> )	$V_l$ (km/s)	$V_s$ (km/s)	$E$ (GPa)	$G$ (GPa)	$K_0$ (GPa)	$K'_0$	$\gamma$
Zr <sub>41</sub> Ti <sub>14</sub> Cu <sub>12.5</sub> Ni <sub>10</sub> Be <sub>22.5</sub>	6.125	5.17	2.47	101	37.4	114.1	4.058	1.85
Zr <sub>41</sub> Ti <sub>14</sub> Cu <sub>12.5</sub> Ni <sub>9</sub> Be <sub>22.5</sub> C <sub>1</sub>	6.161	5.10	2.53	106.0	39.5	107.3	3.942	1.80
Zr <sub>48</sub> Nb <sub>8</sub> Cu <sub>12</sub> Fe <sub>8</sub> Be <sub>24</sub>	6.436	4.994	2.338	95.7	35.2	113.6	4.099	1.84
(Zr <sub>0.59</sub> Ti <sub>0.06</sub> Cu <sub>0.22</sub> Ni <sub>0.13</sub> ) <sub>85.7</sub> Al <sub>14.3</sub>	6.608	4.890	2.269	92.7	34.0	112.6	4.344	1.95
Pd <sub>39</sub> Ni <sub>10</sub> Cu <sub>30</sub> P <sub>21</sub>	9.152	4.74	1.96	98.2	35.1	159.1	6.277	2.97
Window glass	2.421	5.593	3.385	67.2	27.7	38.7	2.880	1.27
Water-white glass	2.479	5.836	3.423	71.924	29.055	45.707	1.777	0.71
Fused quartz	2.201	5.96	3.75	72.7	31.0	36.9	-4.666	-2.50
Float glass	2.518	5.85	3.47	74.5	30.3	45.7	2.096	0.88
SiO <sub>2</sub> ·TiO <sub>2</sub> glass	2.196	5.745	3.615	67.3	28.7	34.2	-7.713	-4.02
Microcrystal glass	2.556	6.49	3.666	87.0	34.4	61.9	-6.854	-3.59
Amorphous carbon	1.56	3.88	2.407	21.4	9.01	11.4	4.404	2.03

cesses and shows an approximately linear pressure dependence over a range of pressure up to 0.5 GPa, whereas,  $v_s$  of the silicate glasses and amorphous carbon decrease with increasing of pressure. The BMGs have similar  $p$ -dependence of sound velocities to crystalline alloys.<sup>15</sup> The application of pressure up to 2 GPa does not induce acoustic mode softening of the BMGs,<sup>19</sup> while it results in a larger change of  $v_l$  (for the Zr<sub>41</sub>Ti<sub>14</sub>Cu<sub>12.5</sub>Ni<sub>10</sub>Be<sub>22.5</sub> BMG, the relative change of  $v_l$  is 2.2%) compared with that of  $v_s$  (1.2% for Zr<sub>41</sub>Ti<sub>14</sub>Cu<sub>12.5</sub>Ni<sub>10</sub>Be<sub>22.5</sub> BMG). This result means the longitudinal acoustic phonons are softer than the transverse phonons in the BMGs under pressure.

Cook's method,<sup>17</sup> by which the elastic constants and sample dimensions can be calculated simultaneously and self-consistently, was used for the dimensional or density correction with compression. The pressure variations  $(K - K_0)/K_0$  of  $K$  calculated from the ultrasonic velocities for the BMGs are shown in Fig. 2. The  $K$  monotonically increases roughly linearly with increasing pressure, the in-

crease can be attributed to the denser packing of the BMG.<sup>20</sup> As shown in Fig. 2,  $dK/dp$ , of these BMGs is positive, the elastic constants exhibit a positive deviation with pressure from linearity, showing that the modulus stiffness under hydrostatic pressure. The application of pressure does not induce acoustic mode softening for the BMGs, while for some silicate glasses and amorphous carbon,  $dK/dp < 0$ , indicates that pressure can induce acoustic mode softening.<sup>15</sup> In the nonphase transitional case, the volume compression  $V_0/V(p)$  and its hydrostatic-pressure dependence using an EOS is credited to Murnaghan,<sup>21</sup> which is based on the empirical observation that the isothermal bulk modulus is a linear function of pressure. The logarithmic form of EOS of Murnaghan is:<sup>21</sup>

$$\ln\left(\frac{V_0}{V(p)}\right) = \frac{1}{K'_0} \ln\left(\frac{K'_0}{K_0} p + 1\right), \quad (1)$$

where  $K_0$  and  $K'_0$  are the bulk modulus and its pressure derivation at zero pressure, respectively. Inspection of the data for  $K$  in Table I and Fig. 2, we obtain  $K = K'_0 p + K_0$  for the BMGs by assuming the linear relationship between sound velocities and pressure. The obtained values of  $K'_0$  and  $K_0$  for these materials are listed in Table I. By substituting the data of  $K_0$  and  $K'_0$  into Eq. (1), the EOS for the BMGs in the nonphase transitional case is obtained and plotted in Fig. 3. In Fig. 3(a), the Zr-based BMGs have similar compression curves and are much larger than that of the Pd<sub>39</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>21</sub> BMG. Comparing with oxide glasses and amorphous carbon, the Pd- and Zr-based BMGs exhibit small volume changes upon  $p$  shown in Fig. 3(b). For comparison, the compression

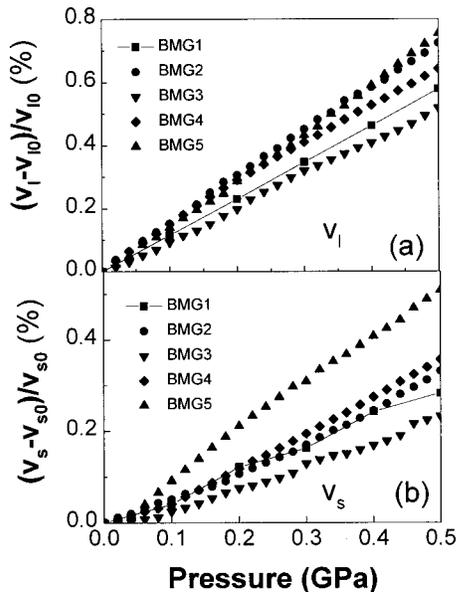


FIG. 1. Variation of longitudinal (a) and transverse (b) velocities of the Zr<sub>41</sub>Ti<sub>14</sub>Cu<sub>12.5</sub>Ni<sub>10</sub>Be<sub>22.5</sub> (BMG1), Zr<sub>41</sub>Ti<sub>14</sub>Cu<sub>12.5</sub>Ni<sub>9</sub>Be<sub>22.5</sub>C<sub>1</sub> (BMG2), Zr<sub>48</sub>Nb<sub>8</sub>Cu<sub>12</sub>Fe<sub>8</sub>Be<sub>24</sub> (BMG3), (Zr<sub>0.59</sub>Ti<sub>0.06</sub>Cu<sub>0.22</sub>Ni<sub>0.13</sub>)<sub>85.7</sub>Al<sub>14.3</sub> (BMG4), and Pd<sub>39</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>21</sub> (BMG5) BMGs with pressure.

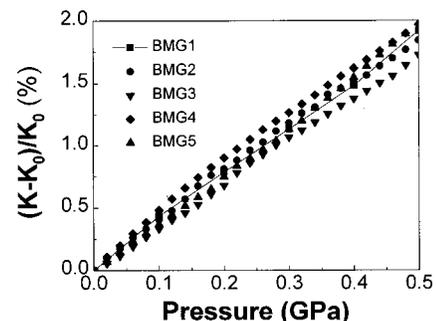


FIG. 2. Variation of  $K$  of these BMGs with pressure.

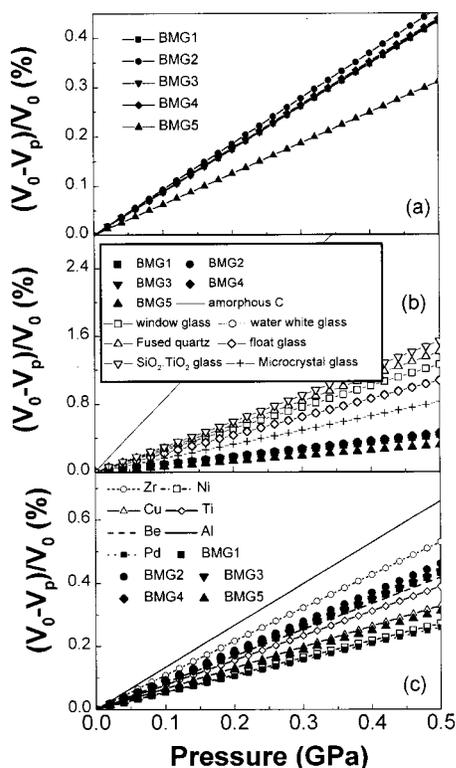


FIG. 3. Pressure and volume relation of the BMGs. (a) EOS of the BMGs, (b) a comparison of the EOS of silicate glasses, and BMGs (c), a comparison of EOS of crystalline components and BMGs.

curves of Zr, Ti, Cu, Ni, Be, Pd, and Al (Ref. 22) are also plotted in Fig. 3(c). The compression curves of all the BMGs are interposed among their metallic components, e.g., the compression curve of the Pd<sub>39</sub>Ni<sub>10</sub>Cu<sub>30</sub>P<sub>21</sub> BMG is interposed among Pd, Cu, and Ni, and those of the Zr-based BMGs are interposed among their components Zr, Ti, Be, Ni, Al, and Cu. This indicates that the compression curves of the BMGs have a correlation with that of their metallic components and exhibit a roughly average result of these elements. The compressibility of a solid is determined by the nature of the interatomic potential and the atomic configurations, and thus the aforementioned results imply that the short-range order structure of the BMGs has a close correlation with the atomic configurations in their metallic components. The existence of metalloid phosphorus and carbon in the BMGs does not significantly change the nature of the metallic bond. Since those metallic components are of cubic close-packed structures, it is very likely that the similar atomic close-packed configurations dominate the short-range structure of the BMGs. These highly packed structures have also been confirmed by density measurements. The relative density change of the BMGs between the amorphous and fully crystallized states is about 1.0%.<sup>23</sup>

In the absence of phase changes, an increase in  $K$  with increasing  $p$  is generally expected as a consequence of the vibrational anharmonicity.<sup>24</sup> The Grueneisen constant  $\gamma$ , which is related to the derivative of  $K$ , can be estimated by using of Slater's equation:<sup>25</sup>  $\gamma = -1/6 + 1/2(\partial K/\partial p)_T$ . The estimated values of  $\gamma$  of these BMGs are listed in Table I. They are close to the reported values for oxide glasses<sup>26</sup> and metal elements.<sup>27</sup> This classifies the BMG among the larger anharmonic solids.<sup>8</sup>

In conclusion, the EOS of the BMGs has been determined by ultrasonic measurements. The compression curves of the BMGs are interposed among their components, and the BMGs exhibit small volume changes upon pressure compared with oxide glasses, indicating that the BMGs have similar atomic close-packed configurations with elements and markedly different microstructure and properties from oxide glasses. The large value of  $\gamma$  classifies the BMG among the larger anharmonic solids.

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