

# Responses of glassy structure and properties to pressure and devitrification

R. J. Wang, F. Y. Li, J. F. Wang, and W. H. Wang<sup>a)</sup>

*Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

(Received 23 June 2003; accepted 8 August 2003)

The pressure (up to 2 GPa) and devitrification-induced properties and structural changes in glasses studied by an ultrasonic method are summarized. The pressure has a larger effect on the longitudinal mode for a crystallized state and on the shear mode for a glassy state in oxide glasses. The crystallization significantly affects the longitudinal mode for oxide glasses and the shear mode for metallic glasses. The different effects are contributed to their different microstructures in short-range order for different glasses. © 2003 American Institute of Physics. [DOI: 10.1063/1.1616200]

The common structural feature of glasses is long-range disorder. However, different types of glasses have different microstructural features or different short-range orders.<sup>1</sup> For example, bulk metallic glasses (BMGs) have a random close-packing (rcp) atomic configuration,<sup>2–5</sup> oxide glasses are in continuous-random networks (crns),<sup>6,7</sup> and the polymer is connected with chainlike forming substances.<sup>8</sup> The microstructural difference leads to various special properties of different glasses.<sup>1</sup> However, a fundamental understanding of the relation between the microstructural configuration and properties of glasses is still lacking so far. Since the acoustic property is particularly sensitive to the microstructure, the pressure and temperature dependence of the structural and physical properties of the glasses could be investigated by the ultrasonic method which can provide critical information on the microstructural and properties characteristics.<sup>9,10</sup> In this letter, we summarize the high pressure and devitrification effects on structure and properties in various oxide glasses and BMGs.

The microcrystallization oxide glass (Micro-G) was a crystallized oxide glass which was heated and crystallized into microcrystalline grains with the size 0.05–20  $\mu\text{m}$ . The main composition of the Micro-G was 72%  $\text{SiO}_2$  with some Al, and Ti. The Micro-G mainly consisted of crystalline  $\text{SiO}_2$ . The sample was machined down to 15 mm in diameter and 10 mm in length for ultrasonic measurements. The longitudinal velocity ( $V_\ell$ ) and shear velocity ( $V_s$ ) were measured by using a pulse–echo overlap method.<sup>11</sup> The travel time of the propagation of the ultrasonic wave through the sample with a 10 MHz frequency was measured using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. Density,  $\rho$ , was measured by the Archimedian principle. The experiments performed *in situ* under high pressure up to 2 GPa were completed using a piston-cylinder high pressure apparatus. Electric insulation oil was used as the pressure-transmitting medium to ensure hydrostaticity. Upon pressure loading, the density,  $\rho$ , was modified by Richard Cook method.<sup>11</sup> The elastic constants of bulk modulus  $B$ , Young's modulus  $E$ , shear modulus  $G$  and Poisson's ratio  $\sigma$ , and their pressure dependence were derived from the acoustic velocities and density.<sup>10</sup>

The measured velocities,  $\rho$ , and determined elastic constants for Micro-G and other oxide glass, such as window glass (WG), water-white glass (WWG), and float glass (Na-G) are listed in Table I. Table I shows that the three oxide glasses have very a close value of  $V_\ell$ ,  $V_s$ ,  $\rho$ , and elastic constants because of their similar amorphous state and chemical components (about 70%  $\text{SiO}_2$ ).<sup>10</sup> Because the Micro-G has a similar chemical composition to oxide glasses, it can be considered as a crystallized state of the oxide glasses. From Table I, one can see that the  $V_\ell$ ,  $V_s$ ,  $\rho$ , and elastic constants show large relative change between Micro-G and the three glasses. The differences are mainly induced by crystallization of the glass.

The relative change of various parameters ( $\Delta v/v_0 = (v_c - v_g)/v_g$ ,  $v = \rho, V_\ell, V_s, B, E, G$ , and  $\sigma$ ) between the glassy state ( $v_g$ ) and fully crystallization state ( $v_c$ ) for typical Zr-, Pd-, and Nd-based BMGs are listed in Table II. The relative change of all parameter increase after BMGs are fully crystallized except for  $\sigma$ . Here, we note that the  $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$  BMG actually exhibits a large number of nanocrystals in its glassy matrix.<sup>12</sup> So the relative changes of various parameters for the Nd-based BMGs are smaller than those of other BMGs in Table II. The elastic constants of the BMGs obtained by the acoustic method, small relative density, and  $B$  change, and the striking relative change of  $G$  and  $E$  agree with the result of others.<sup>13–16</sup>

The pressure-dependent  $V_\ell$ ,  $V_s$ ,  $B$ ,  $G$ ,  $E$ , and  $\sigma$  for Micro-G under hydrostatic pressure are shown in Figs. 1 and 2, respectively.  $V_\ell$  and  $V_s$  decrease with increasing pressure and show an approximately linear pressure dependence. The

TABLE I. The measured density, velocities, and elastic constants for the Micro-G and oxide glasses. The relative change  $R = (Y_M - \bar{Y}_g)/\bar{Y}_g$  is also listed.  $Y = \rho, V_\ell, V_s, B, G, E$ , and  $\sigma$ .  $\bar{Y}_g (= \rho, V_\ell, V_s, B, G, E, \text{ and } \sigma)$  is the corresponding average value for WWG, WG, and Na-G.  $Y_M (= \rho, V_\ell, V_s, B, G, E, \text{ and } \sigma)$  is for Micro-G.

Sample	$\rho$ ( $\text{g/cm}^3$ )	$V_\ell$ (km/s)	$V_s$ (km/s)	$V_\ell/V_s$ (s)	$B$ (GPa)	$G$ (GPa)	$E$ (GPa)	$\sigma$
Micro-G	2.556	6.492	3.666	1.77	61.90	34.36	86.98	0.266
WWG	2.479	5.836	3.423	1.70	45.70	29.05	71.91	0.238
WG	2.421	5.593	3.385	1.65	38.75	27.74	67.19	0.211
Na-G	2.518	5.850	3.470	1.69	45.75	30.32	74.46	0.228
$\bar{Y}_g$	2.472	5.760	3.426	1.68	43.40	29.04	71.19	0.226
$R$	3.4%	12.7%	7.8%	5.3%	42.6%	18.3%	22.2%	17.9%

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: whw@aphy.iphy.ac.cn

TABLE II. Relative change (%) of various parameters ( $\Delta v/v_0 = (v_c - v_g)/v_g$ ,  $v = \rho, V_\ell, V_s, B, E, G$ , and  $\sigma$ ) between the glassy state and fully crystallized state for Zr-, Pd-, and Nd-based BMGs.

Sample	$\Delta\rho/\rho_0$	$\Delta V_\ell/V_{\ell_0}$	$\Delta V_s/V_{s_0}$	$\Delta B/B_0$	$\Delta E/E_0$	$\Delta G/G_0$	$\Delta\sigma/\sigma_0$
Zr <sub>41</sub> Ti <sub>14</sub> Cu <sub>12.5</sub> Ni <sub>5</sub> Be <sub>22.5</sub>	1.1	5.2	13.5	3.9	27.2	30.3	-9.4
Pd <sub>39.1</sub> Ni <sub>10.1</sub> Cu <sub>29.9</sub> P <sub>20.9</sub>	0.6	3.2	12.5	1.2	25.1	27.2	-6.0
Nd <sub>60</sub> Al <sub>10</sub> Fe <sub>20</sub> Co <sub>10</sub>	0.4	2.2	3.9	2.6	7.8	8.3	-2.8

relative changes of the elastic constants also show an approximately linear pressure dependence. The linear fit of the pressure-dependent velocities and  $B$  for the Micro-G and oxide glasses are listed in Table III. For Table III, one can see that  $V_\ell$  is more sensitive to pressure for Micro-G, e.g.,  $|dV_\ell/dP| > |dV_s/dP|$ , while, for the glassy state,  $V_s$  is more sensitive to pressure, e.g.,  $|dV_s/dP| > |dV_\ell/dP|$ . The glassy and crystallized states of oxide glasses have different pressure responses confirming that crystallization has greatly changed the microstructure of the oxide glass.

All parameters for Micro-G obviously increase relative to other three oxide glasses in Table I. Positive  $R$  indicates that the crystallization process induces longitudinal and shear mode stiffness. For BMGs shown in Table II, the relative change of  $V_s$  is much larger than that of  $V_\ell$  after the BMGs are fully crystallized, i.e.,  $\Delta V_s/V_{s_0} \gg \Delta V_\ell/V_{\ell_0}$  (or  $V_\ell/V_s$  decreases), so the relative change of  $G$  and  $E$  between the glass and crystallized states of BMGs are much larger than that of  $B$ . This indicates that a striking softened transverse phonons mode happens in glassy state BMGs. Compared with BMGs, however, the relative change 12.7% of  $V_\ell$  is much larger than 7.8% of  $V_s$  between crystallized oxide glass of Micro-G and the oxide glasses, i.e.,  $\Delta V_\ell/V_{\ell_0} \gg \Delta V_s/V_{s_0}$ ,  $V_\ell/V_s$  increases after crystallization. Thus, a large relative change of 42.6% for  $B$  can be found between the oxide glasses and its crystallized state.  $B$  and  $G$  characterize the deformation property of a material on volume and shape, respectively. The results indicate that crystallization strongly affects deformation property on volume for oxide glasses than that for BMGs. The density of a crystal is closely related with chemical component and crystal structure. The density of quartz crystal is 20% higher than that of quartz glass.<sup>17</sup> The relative change of density for Micro-G compared with other oxide glasses is about 3.4% (see Table I), while the change is only about 1% between the glass and crystallized state for BMGs.<sup>18,19</sup> The difference is due to the completely different structural characteristic of rcp for BMGs and crn for oxide glasses. The structural order in glass

is constrained at short distances by the physical and chemical interactions of the atom-atom bonds. The breaking and reforming of bonds are required for the crystallization. So, it leads to an obvious change of the physical properties. The above results show that the effects of crystallization on acoustic and elastic properties are different for oxide glass and BMGs. Oxide glass is a covalent bonded glass<sup>20</sup> with crn structure. The dominant SiO<sub>2</sub> composition makes the glasses have a structural characteristic of significant spread in Si—O—Si bond angles, which is not permitted in its crystal state. Si and O have complete chemical ordering, and SiO<sub>2</sub> has no dangling bonds in the bulk glasses. A larger volume concentration occurs in their crystallization process. So it exhibits the larger change of  $\rho$  and  $B$ ,  $\Delta V_\ell/V_{\ell_0} \gg \Delta V_s/V_{s_0}$ , and increasing  $V_\ell/V_s$  and  $\sigma$  in the crystallized oxide glass. Under high pressure, the change of the bond angles between atoms in oxide glass leads to negative pressure-dependent velocities. For BMGs with an rcp structure, however, the nature of metallic bond is retained, although atomic long-range order is lacking.<sup>14</sup> In the transition process from the glass to crystal state, there is no large change of the number of nearest-neighbor atoms and the distance between atoms. However, the small change of the volume can sensitively induce the electron configuration, atomic interaction force, and the relative flow between atoms. So, BMGs have a large shear modulus change,  $\Delta V_s/V_{s_0} \gg \Delta V_\ell/V_{\ell_0}$  and decreasing  $V_\ell/V_s$  in crystallization.

In conclusion, the devitrification mainly affects the shear mode for metallic glasses and the longitudinal mode for oxide glasses because of their different microstructures in short-range order. The pressure has a larger effect on the longitudinal mode for the crystallized state and on the shear mode for the glassy state in oxide glasses. The different responses of the properties of the glasses contribute to their different microstructures in short-range order.

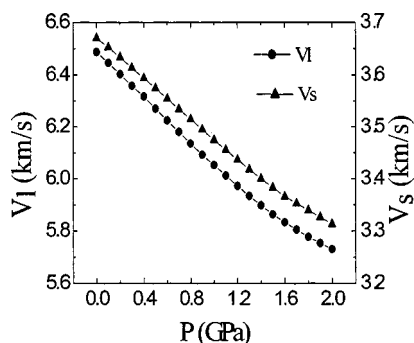


FIG. 1. The pressure dependence of the longitudinal and shear velocities for the Micro-G.

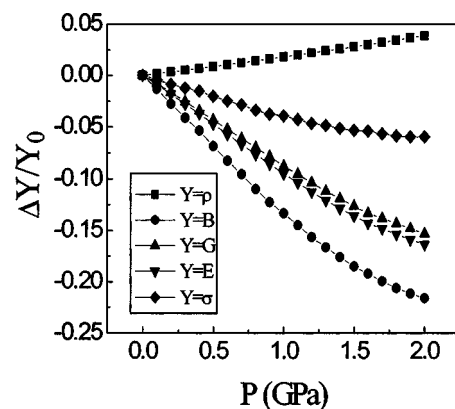


FIG. 2. The relative change of various parameters ( $\Delta Y/Y_0 = (Y - Y_0)/Y_0$ ,  $Y = \rho, V_\ell, V_s, B, E, G$ , and  $\sigma$ ) for the Micro-G.  $Y$  and  $Y_0$  stand for the properties of under high pressure and in ambient conditions, respectively.

TABLE III. The pressure dependence of  $V_\ell$ ,  $V_s$ , and  $B$  for Micro-G and three oxide glasses.

Sample	$dV_\ell/dP$ (km/s GPa <sup>-1</sup> )	$dV_s/dP$ (km/s GPa <sup>-1</sup> )	$dB/dP$ ( $P=0$ )	Comparison
Micro-G	-0.39	-0.18	-6.85	$ dV_s/dP  <  dV_\ell/dP $
WWG	-0.01	-0.05	-1.78	$ dV_s/dP  >  dV_\ell/dP $
WG	-0.01	-0.10	-2.88	$ dV_s/dP  >  dV_\ell/dP $
Na-G	-0.01	-0.05	-2.10	$ dV_s/dP  >  dV_\ell/dP $

The authors are grateful for the financial support of the National Natural Science Foundation of China (Grant Nos. 59925101 and 50031010)

<sup>1</sup>R. W. Cahn, *Glasses and Amorphous Materials* (VCH Press, Weinheim, 1991).

<sup>2</sup>A. L. Greer, *Science* **267**, 1947 (1995).

<sup>3</sup>W. L. Johnson, *MRS Bull.* **24**, 42 (1999).

<sup>4</sup>W. L. Johnson, *Prog. Mater. Sci.* **30**, 81 (1986).

<sup>5</sup>W. H. Wang, Q. Wei, and S. Friedrich, *Phys. Rev. B* **57**, 8211 (1998).

<sup>6</sup>R. J. Bell and P. Dean, *Nature (London)* **212**, 1354 (1966).

<sup>7</sup>F. Y. Li, R. J. Wang, and M. H. Murli, *Acta Phys. Sin.* **49**, 2129 (2000).

<sup>8</sup>C. A. Angell, *Science* **267**, 1924 (1995).

<sup>9</sup>R. J. Wang, F. Y. Li, and M. H. Murli, *Chin. J. High Pressure Phys.* **8**, 177 (1994).

<sup>10</sup>D. Schreiber, *Elastic Constants and Their Measurement* (McGraw-Hill, New York, 1973), Chaps. 1 and 3.

<sup>11</sup>R. Cook, *J. Acoust. Soc. Am.* **29**, 445 (1957).

<sup>12</sup>Z. Zhang, R. J. Wang, and W. H. Wang, *Appl. Phys. Lett.* **81**, 4371 (2002).

<sup>13</sup>R. D. Conner, R. B. Dandliker, and W. L. Johnson, *Acta Mater.* **46**, 6089 (1998).

<sup>14</sup>N. Q. Lam and P. R. Okamoto, *MRS Bull.* **17**, 41 (1994).

<sup>15</sup>N. Nishiyama, A. Inoue, and J. Z. Jiang, *Appl. Phys. Lett.* **78**, 1985 (2001).

<sup>16</sup>L. Q. Xing, J. Eckert, W. Loser, S. Roth, and L. Schultz, *J. Appl. Phys.* **88**, 3565 (2000).

<sup>17</sup>R. E. Newnham, *Structure-Property Relations* (Springer, Berlin, 1975), Chap. 1.

<sup>18</sup>W. H. Wang, R. J. Wang, F. Y. Li, and D. Zhao, *Appl. Phys. Lett.* **74**, 1803 (1999).

<sup>19</sup>W. H. Wang, R. J. Wang, and Y. S. Yao, *Phys. Rev. B* **62**, 11292 (2000).

<sup>20</sup>R. Zallen, *The Physics of Amorphous Solids* (Wiley-Interscience, New York, 1983), Chap. 2.