

## Characteristics of the glass transition and supercooled liquid state of the $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ bulk metallic glass

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Acoustic velocities and their temperature dependence of  $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$  bulk metallic glass (BMG) have been measured up to 773 K by using an ultrasonic pulse-echo overlap method. The temperature dependence of density, Vicker's hardness, elastic constants, and thermodynamic parameters of the BMG are determined. A rapid change of the density, acoustic velocities, elastic constants, and Debye temperature near the glass transition temperature, and anomalous density, acoustic and elastic behaviors in the supercooled liquid region are observed. A striking softening of long-wavelength transverse acoustic phonons in the glassy state relative to the supercooled liquid state is found. The glass transition process is delayed to high temperature with an increase of heating rate. Our results provide evidence that the glass transition in the BMG can be regarded as a kinetically modified thermodynamic phase transformation.

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Whether a glass transition is a real phase transition or just kinetic freezing is still a matter of controversy.<sup>1,2</sup> From a theoretical point of view and experimental data obtained from different glasses, the glass transition is considered to be either a first-order,<sup>3</sup> second-order,<sup>4</sup> or third-order transition.<sup>5</sup> There are also evidences implying that the glass transition is not thermodynamic in origin, and it can only be a dynamic or kinetic phenomenon.<sup>6</sup> No theory proposed as yet can account for all experimental observations. Therefore, the characteristics and the theory of the glass transition, especially in metallic glasses have long represented an intriguing topic. For many years, however, the very high cooling rate ( $>10^5$  K/s) necessary to obtain the metallic glasses limits their geometry to be very thin ribbons or wires, and makes the studies of the intrinsic nature of the glass transition and the measurements of many physical properties difficult. The key features of the glass transition are still poorly understood. The glass transition is still a great puzzle, and remains the deepest and most important problem in condensed-matter physics and materials science.<sup>1</sup> A hotly debated issue is whether the glass transition is involved in an underlying thermodynamic (static) or kinetic (dynamic) phase transition. Reaching a final understanding would suggest how to control the nature and properties of amorphous materials better. Recently, multicomponent glass-forming systems with excellent glass-forming ability have been developed by using a conventional casting method at a low cooling rate.<sup>7-9</sup> The bulk metallic glasses (BMGs) exhibit an obvious glass transition and a wide supercooled liquid region (SLR). The BMGs provide an ideal system for studying the nature of the glass transition, and are also very suitable for accurately measuring structural and physical properties concomitant with the glass transition upon temperature ( $T$ ) and pressure. Cahn and Johnson<sup>10</sup> suggested that amorphization process of metallic alloy and melting to a liquid was manifestation of the same first-order transformation. It is interesting to know whether there is the analogy between melting and the BMG formation postulated in Ref. 10, and what kind of structural and property features accompany the glass transition. Since

acoustic property is particularly sensitive to the microstructure, the  $T$ -dependent acoustic velocities can provide critical information on the microstructural characteristics and evolution as well as the elastic and thermal properties during the glass transition of the BMG, and the method represents a very powerful tool for the study of the nature of glass transition, and metallic glassy and supercooled liquid states. We present here a systematic ultrasonic investigation on a  $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$  BMG that is an idealized model system for the study of glass transitions.<sup>7</sup> The  $T$  dependence of the density, acoustic velocities, and Vicker's hardness, which can sensitively reflect the microstructural change, was measured. The elastic constants and thermodynamic parameters are determined by ultrasonic data. Some unique temperature-dependent density, and acoustic and elastic features are found in the SLR, glass transition, and crystallization processes; these behaviors provide evidences that the glass transition is a kinetically modified thermodynamic phase transition.

The  $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$  BMG in the shape of a cylindrical rod with a 15-mm diameter was prepared by the water quenching method. The details of the experimental procedure can be seen in Ref. <sup>9</sup>. The amorphous nature as well as homogeneity of the BMG was ascertained by an x-ray diffraction (XRD), a differential scanning calorimeter (DSC), a transmission electron microscopy (TEM), and by small-angle neutron scattering (SANS).<sup>9</sup> The rod was machined down to 10 mm in diameter and cut to a length of 7 mm for ultrasonic measurements, by grinding off the outer surface; any possible oxide materials from the quartz tube container were removed. The content was carefully checked by chemical analysis. The ends of the cylinder were carefully polished flat and parallel. To ensure the same thermal history the specimens were annealed up to the desired temperature using a rate about 10 K/min, and kept at that temperature for 2 h, after which the sample was cooled down to room temperature quickly to keep the microstructure characteristics. The density, XRD, and microhardness measurements were

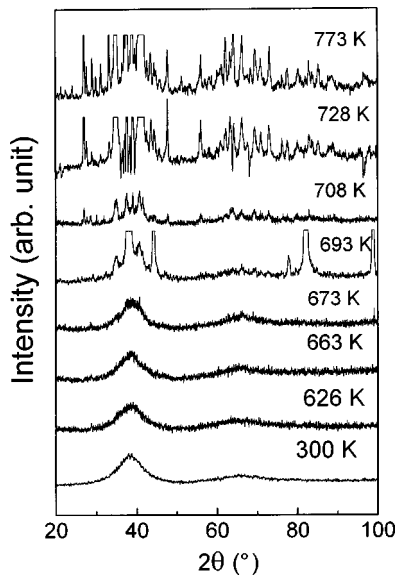


FIG. 1. XRD patterns of the  $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$  BMG at various annealing temperatures.

performed on the annealed samples. Figure 1 shows an XRD pattern of the BMG in various annealing temperatures. The structural evolution upon temperature can be clearly seen in the patterns. Below 673 K, no obvious crystallization happens with the detectable limit of XRD. When annealed near calorimetric  $T_x$ , nanocrystalline phases precipitate in the glassy matrix. Above 693 K, the BMG is completely crystallized. It is worth noting that some crystalline lines that start appearing at 693 K disappear at 708 K: the results may indicate that metastable phase forms when the BMG is annealed in the SLR; the metastable phase transforms to stable crystalline phase at higher temperature. The acoustic velocities and their temperature dependence were measured by using the pulse-echo overlap method.<sup>11</sup> The excitation and detection of the ultrasonic pulses were provided by X- or Y-cut (for longitudinal and transverse waves, respectively) 10-MHz quartz transducers. The ultrasonic waves are excited by the transducer, reflected from the opposite end of the BMG rod, and detected by the same transducer. The travel time of ultrasonic waves propagating through the sample with a 10-MHz carry frequency was measured using a MATEC 6600 ultrasonic system with a measuring sensitivity of 0.5 ns. This system is capable of resolution of the velocity changes to one part in  $10^5$  and particularly well suitable to determination of changes in velocity.<sup>12</sup> The ultrasonic velocities measurement was calibrated by the known materials of Fe and oxide glasses.<sup>13</sup> Density  $\rho$  was measured by the Archimedian principle and the accuracy was evaluated to be  $0.005 \text{ g/cm}^3$ . The elastic constants, e.g., bulk modulus  $K$ , Young's modulus  $E$ , shear modulus  $G$ , Poisson's ratio  $\sigma$ , and Debye temperature,  $\theta_D$  of the BMG, which is considered as an isotropic homogeneous solid, are derived from the acoustic velocities ( $v_l$ , longitudinal velocity,  $v_s$ , transverse velocity) and density using the well-known relation.<sup>11,14</sup> DSC measurements were carried out under a purified argon atmosphere in a Perkin Elmer DSC-7 at a heating rate ranging from 2.5 to 80 K/min. The calorimeter was calibrated for temperature and energy at

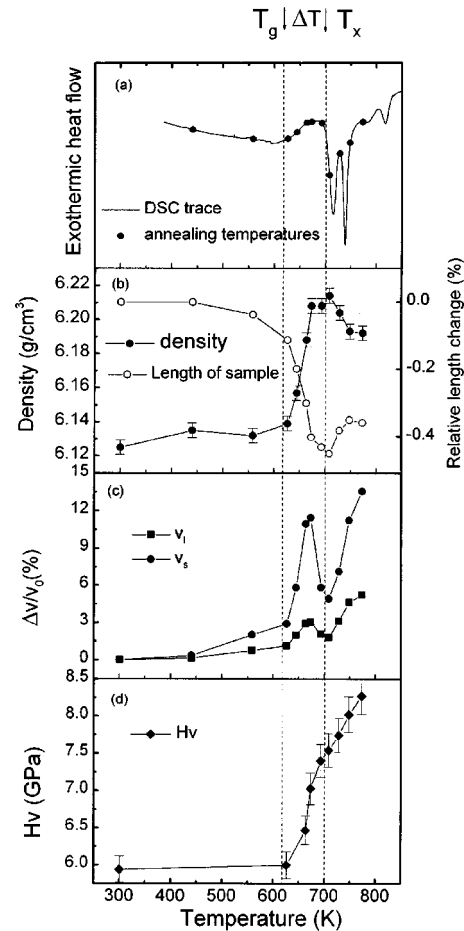


FIG. 2. (a) DSC trace of the  $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$  BMG; the significantly large SLR is indicated in the figure. The points show the annealing temperatures for density, microhardness, and acoustic velocities measurements. (b) The variation of the density and the relative change of the specimen length with temperature. (c) The relative longitudinal and transverse velocities change with temperature, ( $v = v_l, v_s$ );  $v$  is normalized by  $\Delta v/v_0 = (v - v_0)/v_0$ , where  $v_0$  is a normal velocity for the as-prepared BMG, and (d) the microhardness  $H_v$  of the BMG with temperature.

various heating rates with high-purity indium and zinc. The Vicher's hardness  $H_v$  was measured with a Newphoto-21 microhardness tester at a load of 100 g.

Figure 2(a) shows a DSC trace of the BMG with a heating rate of 10 K/min. It exhibits an endothermic characteristic of a glass transition followed by several exothermic crystallization peaks at higher temperatures. The onset glass transition temperature,  $T_g$ , the onset temperature of the first crystallization event,  $T_x$ , are 623 K and 698 K, respectively. A remarkable feature is a significantly large SLR,  $\Delta T = T_x - T_g = 75 \text{ K}$ , as indicated in Fig. 2(a). The corresponding XRD patterns in Fig. 1 indicate no obvious crystallization when annealed in the SLR, but there is small difference in the value of  $T_x$  obtained by a DSC and XRD. Some crystalline peaks start to appear near calorimetric  $T_x$  (693 K), because the DSC is a scanning heating process, while the XRD pattern is obtained from the annealed sample at 693 K for 2 h; the long-time isoannealing near  $T_x$  results in the primary

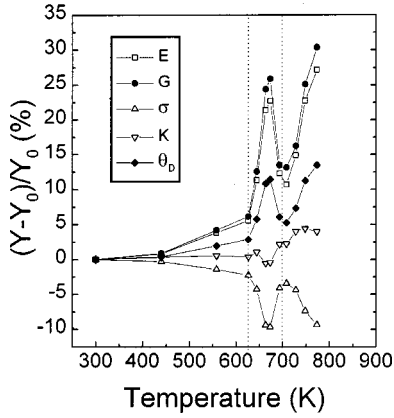


FIG. 3. The relative changes  $\Delta Y/Y_0 = (Y - Y_0)/Y_0$  of variation of  $E$ ,  $G$ ,  $K$ ,  $\sigma$ , and  $\theta_D$  ( $Y$  stands for  $E$ ,  $G$ ,  $K$ ,  $\sigma$ , and  $\theta_D$ ) of the  $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$  BMG with temperature. A large relative change of the  $G$ ,  $E$ , and  $\theta_D$  and a smaller change of  $K$  relative to the supercooled liquid state, which indicates a striking softening of long-wavelength transverse acoustic phonons in the glassy state relative to supercooled liquid state, can be clearly seen.

crystallization that has also been confirmed by other experiments.<sup>15</sup> The values of  $\rho$ ,  $v_l$ ,  $v_s$ , and  $Hv$  are 6.125 g/cm<sup>3</sup>, 5.174 km/s, 2.472 km/s, and 5.94 GPa for the as-prepared states, respectively. Figures 2(b)–2(d) show temperature dependences of  $\rho$ ,  $v_l$ ,  $v_s$ , and  $Hv$  of the BMG, respectively. As shown in Fig. 2(b), the  $\rho$  increases slightly near calorimetric  $T_g$ , and a significant increase occurs near  $T_g$ , and it reaches maximum in the SLR, followed by a slight decrease below calorimetric  $T_x$ . After full crystallization, the  $\rho$  remains almost unchanged. The relative change of the density in the supercooled state and fully crystallized state are 1.3% and 1.1%, respectively. The marked density change indicates an amount of vacancy like defects or free volume is quenched in the BMG even if it is formed at a low cooling rate. Some of the excess volume is removed during the glass transition. This result indicates that larger volume changes accompany the glass transition. The volume change in the ZrTiCuNiBe BMG has also been observed by positron annihilation studies<sup>16</sup> and volume-pressure relation measurements,<sup>17</sup> which shows that the BMG has a larger volume change upon pressure compared to crystalline metals or alloys, because the free volume can be removed through the structural relaxation induced by pressure. The similar change trend for the  $v_l$  and  $v_s$  upon temperature is presented in Fig. 2(c). The relative change of the acoustic velocities has a sudden increase near calorimetric  $T_g$ , and forms a peak in the SLR. They reach a minimum near calorimetric  $T_x$  and

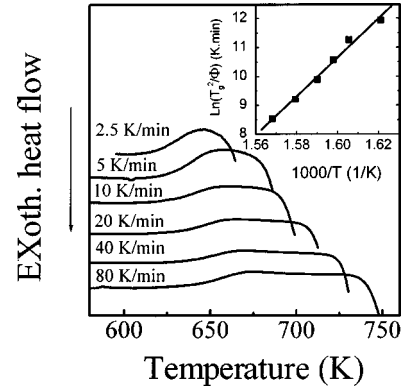


FIG. 4. The DSC traces for the  $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$  BMG showing the  $T_g$  and  $\Delta T$  dependence of the heating rate. The inset shows Kissinger's plot of the BMGs; a linear relationship between  $\ln(T_g^2/\phi)$  and  $1/T_g$  for the BMG can be seen, where  $\phi$  is the heating rate.

increase again with increasing temperature. The  $v_s$  has a much larger relative change during the glass transition and in the SLR. The nature of the chemical bond determines the microstructure of the solid; a difference in microstructure will influence the mechanical properties of a solid, resulting in the variation of the acoustic parameters. Therefore, the rapid changes of density and acoustic properties indicate a drastic microstructural change during the glass transition process. Figure 2(d) presents an  $Hv$  change with temperature;  $Hv$  shows a drastically increase near  $T_g$  and a subsequent monotonic increase. The relative variations of the elastic constant  $E$ ,  $G$ ,  $K$ ,  $\sigma$ , and  $\theta_D$  upon temperature for the BMG is shown in Fig. 3. The obtained elastic data are in good agreement with those measured using different methods.<sup>6</sup> As shown in Fig. 3, the  $E$ ,  $G$ , and  $\theta_D$  show a sudden increase near  $T_g$  and reach maximum in the SLR; the  $\sigma$  also show a drastic change near  $T_g$  but reaches a minimum in the SLR, while the  $K$  does not show similar change trends.

Table I contrasts the large changes in  $v_s$  (11.4%),  $\theta_D$  (11.4%), and  $G$  (about 26%) and small changes in  $\rho$  (1.3%),  $v_l$  (3.0%), and  $K$  (−0.4%) between the glassy and supercooled liquid states. The relative changes of  $K$  and  $G$  versus the temperature can also be seen in Fig. 3.  $G$  shows a larger relative change during the glass transition and in the SLR, while no definite trend has been observed for  $K$  due to temperature. The results indicate the softening of the shear elastic modulus (i.e., the softening of the long-wavelength transverse phonons) in the BMG relative to its supercooled liquid states. The large softening phenomenon means that an elastic instability occurs in the glass transition. The charac-

TABLE I. A comparison of properties of the amorphous state ( $Y_a$ ) and supercooled state ( $Y_L$ ) of the  $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$  BMG in the SLR (693 K).

State	$\rho$ (g/cm <sup>3</sup> )	$v_l$ (km/s)	$K$ (GPa)	$v_s$ (km/s)	$G$ (GPa)	$\theta_D$ (K)
amorphous	6.125	5.174	114.1	2.472	37.41	326.8
supercooled	6.208	5.331	113.6	2.755	47.12	364.2
$(Y_L - Y_a)/Y_a$ (%)	1.3	3.0	−0.4	11.4	26.0	11.4

teristic is also similar with the melting of a solid, in that a very high density of point defects combined with a softened phonon mode leads to melting.<sup>18,19</sup> Previous work<sup>20</sup> indicates the softening of the transverse phonon mainly attributed to the unique microstructural characteristics of the BMG. The softening phenomenon also indicates that marked differences in the electronic state, atomic interaction, and atomic mobility between the glassy and supercooled liquid states exist. The dramatic change of the acoustic velocities, density, mechanical properties, and the striking softening of transverse acoustic phonons near  $T_g$  demonstrate that the glass transition is not a continuous function of temperature, but rather a relatively abrupt microstructural change. We suggest that the glass transition in the BMG has the characteristic of the phase transition. The calculated Gibbs free-energy function of the BMG shows that the free energy of the glassy state is larger than that of the supercooled liquid state,<sup>21</sup> thermodynamically, the BMG must transform from the glass to the supercooled state. These also support the idea that there are thermodynamic origins underlying the glass transition process. In other words, if the glassy forming alloy can be cooled at a rate close to zero but without the intervention of crystallization, there should be a distinct glass transition. The ideal glass transition temperature is estimated to be 560 K.<sup>21</sup> However, the BMG is a thermodynamically metastable state; the relaxation especially in the SLR (the atomic mobility is much higher in the supercooled liquid state compared to the glassy state) is unavoidable during the annealing process. Therefore the glass transition must be affected by the relaxation. Figure 4 exhibits that the endothermic broad peak of the BMG shifts to a higher temperature gradually with increasing heating rate, indicating that the glass transition process is delayed at a higher temperature. This phenomenon indicates that the glass transition behaves with a marked ki-

netic nature. The dependence of the  $T_g$  on the heating rate follows Lasocka's relationship:<sup>22</sup>  $T_g = A + B \ln \phi$ , where  $A$  and  $B$  are constants. There are good linearities between  $T_g$  and  $\ln \phi$  with  $A = 612.5$ ,  $B = 6.63$ . The effective activation energy, for the glass transition  $E_g$ , evaluated by Kissinger's equation,<sup>23</sup> is 5.8 eV (as shown in the inset of Fig. 4). The kinetic nature is still kept when the BMG is preannealed or preannealed under high pressure.<sup>24,25</sup> Based on the experimental results obtained above, the glass transition process of the BMGs can be regarded as a kinetically modified thermodynamic phase transformation process.

In conclusion, the investigations of the acoustic velocities, elastic constants, and  $\theta_D$  upon temperature of the  $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$  bulk metallic glass indicate that the glass transition has four characteristics: (1) the discontinued changes of acoustic velocity, density, and mechanical properties demonstrate that the glass transition is not a continuous function of the temperature, but rather that a relatively abrupt phase transformation occurs, indicating the characteristic of the phase transition; (2) a larger volume change accompanies the glass transition of the BMG; (3) a striking softened transverse phonons mode happens when the supercooled liquid state transforms to glassy state; (4) the glass transition has a marked kinetic nature. Although the special case studied here does not settle the issue of the nature of glass transition, the finding provides another piece of evidence that observable glass transition in the BMG has phase transition characteristics. On the other hand, the study confirms that the glass transition behaves with a marked kinetic nature. The glass transition process could be regarded as a kinetically modified underlying thermodynamic phase transformation process.

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