

Reversible phase transition between amorphous and crystalline in $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ under high pressure at room temperature

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A reversible phase transition between amorphous and crystalline in bulk metallic glass (BMG) $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ has been investigated under high pressure at room temperature. The BMG displayed a structure memory under high pressure as detected by *in situ* synchrotron radiation of x-ray diffraction and resistance measurement in a diamond anvil cell. Direct experimental observations found that the crystallization of the BMG occurred at 24 GPa on uploading and the crystalline phase reverted back to the amorphous state during downloading. This unusual phenomenon was discussed thermodynamically. © 2000 American Institute of Physics.
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The structure and property of materials are profoundly altered under high pressure due to a large change of atom spacing, chemical bonding, and Gibbs free energy.¹⁻⁴ Materials with novel properties can be created *via* a process known as pressure-induced phase transition, such as high T_c superconductor,⁵ diamond crystal with semiconductor property,⁶ and special intermetallic compound.⁷ Recently, multicomponent bulk metallic glass (BMG) based on the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ system has been discovered,^{8,9} which exhibits excellent glass forming ability and thermal stability against crystallization at ambient condition. Considerable investigations have been concentrated on atomic diffusion,¹⁰ isothermal transition from supercooled liquid into crystalline,¹¹ and liquid separation.¹² However, there is no investigation on high-pressure behavior of this BMG to date. Here we report the observation of a reversible phase transition between amorphous and crystalline in the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ under high pressure at room temperature. This finding may provide us an insight into the phase transition kinetics of metal glass under high pressure. It also may extend the application of this new kind of BMG.

The ingots of the glass with nominal compositions $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ were prepared from a mixture of pure elements in an arc-melting furnace under Ti-gettered Ar atmosphere. The ingots were remelted in a quartz tube, and then were water quenched with a cooling rate of about 10 K/s to form a bulk glass of 10 mm in diameter. The bulk was cut and the cross section was identified by x-ray diffraction shown to be fully glass phase. In the experiments of the synchrotron radiation x-ray diffraction (SR-XRD) measurement, the monochromatic x-ray with a spot beam of $80 \times 80 \mu\text{m}$ and with wavelength $\lambda = 6.119 \text{ nm}$, 2θ value $2\theta = 22.8^\circ$, and energy $E = 40 \text{ keV}$ went through a diamond window into a sample chamber. Specimens for the measurements were the disks that were cut from the rod of the BMG

with a thickness of $200 \mu\text{m}$. The measurements were performed at high pressure and at room temperature. A mixture of ethyl alcohol and water was used as a liquid pressure medium, and pure platinum (Pt) was used as a pressure marker. For the resistance measurements, a diamond anvil cell (DAC) was employed. The details of the experiment can be found in Ref. 13.

Figure 1 shows the patterns of *in situ* (SR-XRD) for the $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ glass under various pressures. The inset is an XRD pattern of the starting BMG, showing a typical amorphous character of this type of BMG.¹⁴ Reflected on the SR-XRD pattern, the amorphous state of the BMG is represented by the dashed line (curve A in Fig. 1). The two strong peaks in the patterns were the signals originated from the pressure marker rather from the bulk glass. The broad amorphous peak centered at $E = 13.3$ corresponds to a d value of 2.358 nm (calculated using the relation of $E = hc/2d \sin \theta$), which is very close to the d value ($d = 2.361 \text{ nm}$, calculated using $\lambda = 2d \sin \theta$) obtained from conventional XRD (inset of Fig. 1).

From Fig. 1, it is seen that the SR-XRD patterns remain unchanged below 21 GPa. When the pressure reached 24 GPa, there were new diffraction lines which appeared on the pattern (curve F in Fig. 1), indicating the occurrence of crystallization at this pressure. With the further increase of pressure to $\sim 27.5 \text{ GPa}$, the intensity of the new peaks increased distinctly (curve G in Fig. 1), which implies that the crystalline fraction in the BMG increased with the pressure increase. The relative weak intensity of the diffraction lines of the crystallized phase may be due to the crystalline phases formed between these pressures (24–27.5 GPa) is in a nanosize scale¹⁵ or due to partial crystallization in the matrix of this BMG. When the pressure was released gradually from 27.5 GPa, the diffraction lines corresponding to the crystalline phase became weaker in intensity (curve H in Fig. 1) and completely vanished below 15.5 GPa (curve I in Fig. 1), suggesting that the transformation from crystalline to amorphous took place. To ensure the final product being an amor-

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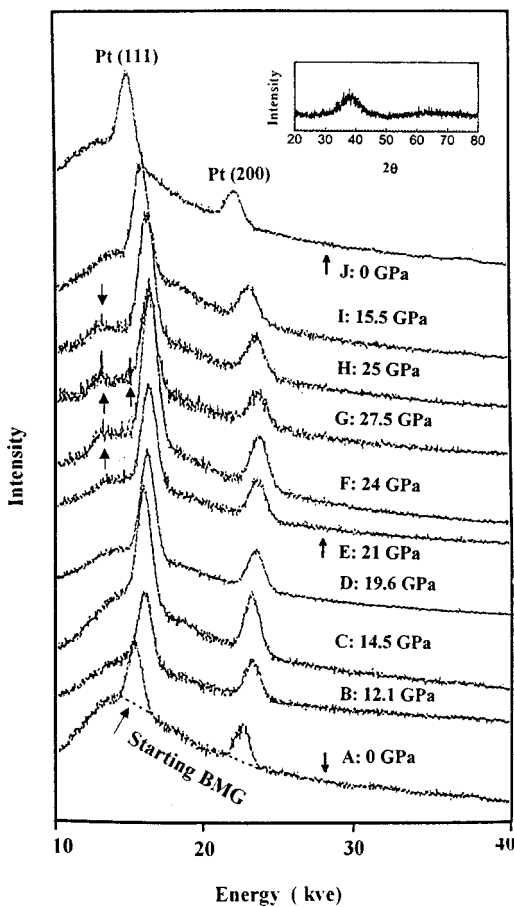


FIG. 1. *In situ* synchrotron radiation x-ray diffraction patterns of $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG under the applied pressures, showing the reversible phase transitions of amorphous–crystalline–amorphous. Inset shows x-ray diffraction pattern of the starting BMG identified by $Cu K\alpha$ radiation.

phous phase, the d value for the amorphous product was calculated to be 2.359 nm, which is close to that of the starting BMG, indicating that the amorphous has reverted back from the crystalline phase after the downloading. The above results demonstrate that $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG has a structure memory in a cycle of compressing and decompressing.

To further confirm the reversible phase transition of the BMG, an *in situ* resistance measurement was carried out in a DAC. Figure 2 shows the resistance as a function of pressure. There is a minimum in the resistance appearing at 24 GPa (peak A in Fig. 2), at which the diffraction line of the crystalline phase was detected by synchrotron radiation of x-ray diffraction (curve F in Fig. 1). With the further increase of pressure, there is another minimum of resistance appearing at 26.2 GPa (peak B in Fig. 2). This indicates that there was another crystallization which occurred following the first crystallization process. The two-stage crystallization under high pressure at room temperature is similar to that observed at ambient pressure at a relatively high temperature.¹⁴ The diffraction lines corresponding to the second crystalline phase were not detected by synchrotron radiation of x-ray diffraction, which is probably because the fraction and the size of the second crystalline phase were too small to be detected. Upon downloading, the resistance curve shows two maxima located at 16 and 10.6 GPa, which corresponds to

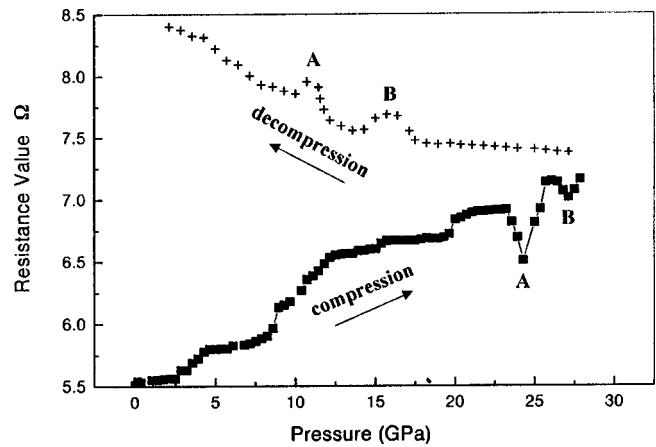


FIG. 2. Resistance changes of the BMG with pressure during compressing and decompressing, demonstrating the reversible phase transition between amorphous and crystalline (error of resistance: $\pm 5\%$).

peaks A and B of the uploading resistance curve, respectively. This result supports the occurrence of the transition from crystalline to amorphous upon downloading as detected by SR-XRD. Four runs of experiments of resistance measurements were performed under the same conditions, and we were able to reproduce the above results. It is noted that the pressure of the transition from crystalline to amorphous on downloading is lower than that of uploading. The reduced transition pressure on downloading relative to that of uploading might be attributed to a kinetic retardation of the phase transition. In addition, after downloading to ambient condition, the resistance value (8.36 Ω) was found to be higher than its initial value (5.5 Ω) for the starting BMG. The difference is probably assigned to a geometric change between the starting amorphous solid and the final amorphous product after the high pressure processing. The possibility of contaminating from external sources is precluded, because no pressure medium was used during the resistance measurements.

The reversible phase transition between amorphous and crystalline can be interpreted in terms of volume changes associated with phase changes. Normally, a phase transition from amorphous to crystalline occurs accompanied by a negative volume change, since the structure of the amorphous solid is less dense compared to its corresponding crystalline phase. It is believed that there exists a threshold value in the volume change from amorphous to crystalline, at which the atoms in the amorphous solid are forced to pack themselves leading to a structure change from a short-range order to a long-range order under high pressure. To determine the volume change of the BMG at high pressure, experiments were carried out using the starting BMG on a piston-type high-pressure apparatus that was equipped with a displacer. The dependence of volume change on pressure is plotted in Fig. 3. Fitting the data by a polynomial simulation gave a mathematics equation:

$$P = 0.011 - 335.36\Delta V + 412\,868.13\Delta V^2.$$

Extrapolation of the curve by this equation yields a volume change of 0.0072 ml/mole at 24 GPa, at which the amorphous-to-crystalline transition of the BMG was observed. This corresponds to the threshold value of volume

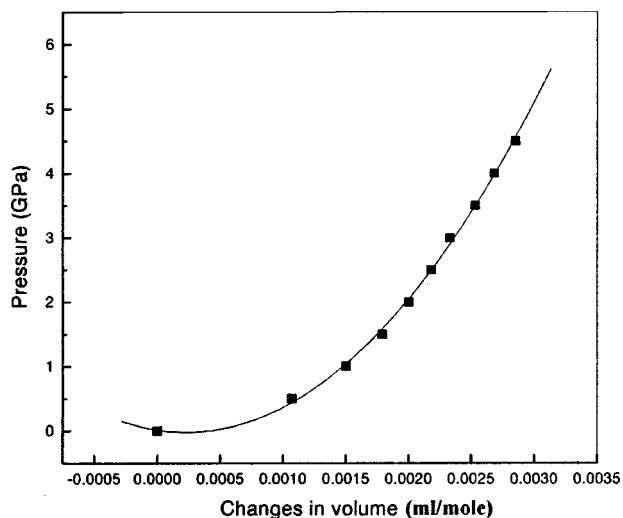


FIG. 3. Change of mole volume with pressure at room temperature for $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}\text{BMG}$.

change from the amorphous to crystalline phase in this BMG. It is thus concluded that, if the volume change in this BMG is larger than 0.0072 ml/mole under high pressure, atoms will arrange themselves from a random distributed network to a closer structure of the crystalline phases, i.e., the occurrence of amorphous–crystalline phase transition. From the fact that the crystalline phase reverts back to the amorphous state on downloading, it is known that the crystalline phase obtained at high pressure became metastable at ambient condition, having a higher free energy, which is even higher than that of the amorphous phase.¹⁶ As a result, the metastable crystalline phase transformed spontaneously to the amorphous phase after decompressing.

In conclusion, a reversible phase transition between amorphous and crystalline was observed in the $\text{Zr}_{41.2}\text{Ti}_{13.8}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}\text{BMG}$ by a compression and decompression process. *In situ* synchrotron radiation of x-ray diffraction and resistance measurement in DAC revealed that

the phase transition from amorphous to crystalline occurred at 24 GPa on uploading and the transition from crystalline back to amorphous phase occurred at 16 GPa on downloading. The resistance measurement under high pressure showed that a kinetics retardation of the transition from crystalline to amorphous existed during downloading relative to the crystallization process on uploading. The high pressure-induced phase transition affords a new property of structure memory for this BMG.

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