In situ X-ray diffraction investigation of compression behavior in $Gd_{40}Y_{16}Al_{24}Co_{20}$ bulk metallic glass under high pressure with synchrotron radiation*

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Abstract The compression behavior of the heavy RE-based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ under high pressure has been investigated by in situ high pressure angle dispersive X-ray diffraction measurements using synchrotron radiation in the pressure range of 0∼33.42 GPa at room temperature. By fitting the static equation of state at room temperature, we find the value of bulk modulus B is 61.27 ± 4 GPa which is in good agreement with the experimental study by pulse-echo techniques of 58 GPa. The results show that the amorphous structure in the heavy RE-based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ keeps quite stable up to 33.42 GPa although its compressibility is as large as about 33%. The coexistence of normal local structure similar to that of other BMGs and covalent bond structure similar to those of oxide glasses may be the reason for the anomalous property under high pressure of the $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG.

Key words bulk metallic glass, In situ X-ray diffraction, compression behavior, high pressure, synchrotron radiation

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1 Introduction

Bulk metallic glasses (BMGs) have obtained considerable attention from both scientific and technological aspects in the past decades[1]. Among them Rare-earth based BMGs are notable for their various interesting physical properties and potential functional applications[2—8]. Recently the heavy RE based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ as a representation of RE based BMGs has been attracting great attention due to its excellently magnetic refrigeration in a wide temperature range[9]. High pressure as a thermodynamic variable as temperature can have significant effect on the chemical and physical properties of matter. The use of high pressure as a synthetic variable and as a route to RE based BMGs has a broad perspective in scientific research. Meanwhile, the measurements of compression properties (experimental compressibility) are of great importance to understand the relationship between unique mechanical properties and configurational changes under pressure[2]. However, up until now, little work on the compression behavior under high pressure at room temperature for this BMG has been reported. Compared to the conventional metallic glass, the heavy RE based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ has a different electron structure. Then, one might expect an interest if there is a fascinating change in the heavy RE based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$. Hence, it is interesting to evaluate the structural stability of the heavy RE based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ behaves under high pressure (0—33.42 GPa in our experimental conditions) at room temperature. This remains a fundamental problem in solid state physics and is strongly related to a better understanding of the structure of RE based BMGs.

In this letter, compression behavior of the heavy

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RE based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ under high pressure at room temperature has been investigated by using a synchrotron radiation source and a diamond anvil cell (DAC). Based on the equation of state (EOS), the bulk modulus B of the heavy RE based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ is determined. The volume change of the heavy RE based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ under high pressure at room temperature is so large which is quite different from that of other known BMGs. The possible reason of the compression behavior under our experimental conditions for the heavy RE based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ is discussed.

2 Experiment

The $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG was prepared by arc melting pure Al(99.99%), Co(99.99%), and Y(99.99%) with Gd(99.9%) and suction casting the molten master alloy into water-cooling copper mold in a Ti-gettered argon atmosphere. The amorphous nature was ascertained by X-ray diffraction (XRD) using a Cu $K\alpha$ radiation. The in situ angle dispersive X-ray diffraction experiment on $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG under high pressure at room temperature was performed at 4W2 High-Pressure Station of Beijing Synchrotron Radiation Facility (BSRF). The pressure was generated by using a diamond anvil cell (DAC) driven by an accurately adjustable gear-worm-level system. The culet of the diamond anvil is 500 μm in diameter. The amorphous powder sample together with the pressure-calibrator ruby was loaded into a 200 μm-diam hole of a T301 stainless steel gasket, which was preindented to a thickness of about 61 μm. Silicone oil was used as the pressure-transmitting media. The Debye rings were recorded using an image plate in transmission mode, and the XRD patterns were integrated from the images using the FIT2d software[10]. The size of X-ray spot was 130×130 μm^2. The experimental pressure was determined from the position of diffraction peak of ruby.

Room temperature ultrasonic measurements were performed by the pulse-echo method using a flaw detector (USM3-Krautkramer). X-cut transducers were employed for longitudinal modes and Y-cut for transverse modes. The pulse transiting time was measured using a Hewlett-Packard model 54502A oscilloscope. The velocity was therefore obtained by dividing the round trip distance by the elapsed time. Ultrasonic travel time was measured at a frequency of 10 MHz and at room temperature. Several effects such as multiple internal reflections within the transducer, sample thickness, and the acoustic impedance mismatch between the glass sample and the transducer influence the accuracy of ultrasonic velocity measurements. The uncertainty is estimated to be about ±1%.

The density was determined by an Archimedes technique. The accuracy of the measurement was about ±0.001 g/cm^3.

3 Result and discussion

Figure 1 shows XRD patterns of the as-cast $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG. The board diffraction peaks and no appreciable peaks corresponding to the crystalline phases can be seen within the resolution limit of the XRD for the samples, which indicates the full amorphous state of the alloys.

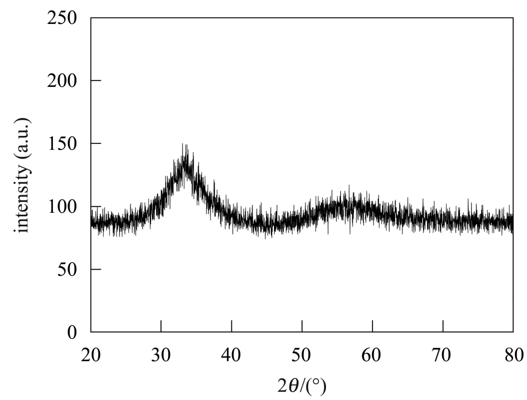

Fig. 1. X-ray diffraction pattern of the as-cast $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG.

A large number of synchrotron radiation X-ray diffraction (SRXRD) patterns of the bulk metallic-glass were recorded under pressure ranging from 0—33.42 GPa at room temperature. Fig. 2(a) displays the SRXRD patterns of $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG from 0 to 33.42 GPa at room temperature. It is apparent that the amorphous halo remains unaltered up to a pressure of approximately 33.42 GPa, indicating that no crystallization occurs. In other words, the amorphous structure of the $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG is quite stable in the pressure range investigated. The result can also be confirmed in the collected Debye rings on the image plate for $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG at pressures of 0.05 GPa, 15.21 GPa and 33.42 GPa shown in Fig. 2(b). Only a broadened diffraction ring corresponding to the amorphous nature can be detected among the whole pressure experiment which exhibits an obvious characteristic of metallic glass. As expected, the position of the main broad X-ray diffraction maximum of the sample subjected to various pressure was found to shift towards larger two-theta values, revealing a reduction of the corresponding volume of the sample with increasing pressure, which shows the compression behavior of $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG.

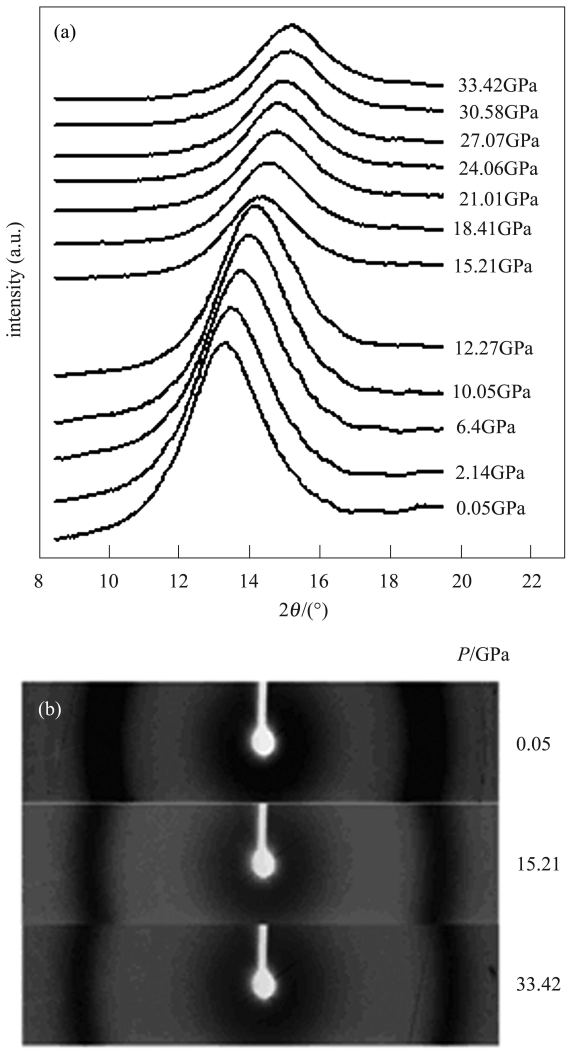

Fig. 2. (a) Angle dispersive synchrotron radiation X-ray diffraction patterns of $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG from 0 to 33.42 GPa at room temperature; (b) Debye rings on the image plate for $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG at pressures of 0.05 GPa, 15.21 GPa and 33.42 GPa.

In order to have a better understanding the compression behavior of $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG under high pressure at room temperature, it is necessary to obtain the equation of state which is presented by Bridgman as follows:[11]

$$-\Delta V/V_0 = a_0 + aP + bP^2 + cP^3 + \cdots , \qquad (1)$$

where V_0 is the volume at zero pressure, coefficients a_0, a, b, and c can be determined by using the least squares method. One can estimate the relative volume change $\Delta V/V_0$ ($\Delta V = V_P - V_0$) at a given pressure (V_P) to that at zero pressure (V_0). The experimental results between $\Delta V/V_0$ and P were shown in Fig. 3. When fitted by the Bridgman equation, EOS can be expressed as follows:

$$-\Delta V/V_0 = 5.992\times10^{-4} + 0.01632P - 2.056\times10^{-4}P^2 + 3.208\times10^{-7}P^3 . \qquad (2)$$

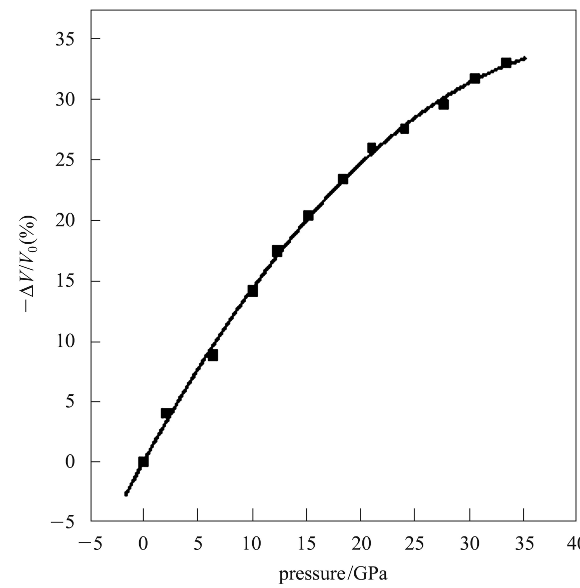

Fig. 3. The pressure dependence of the relative volume change $\Delta V/V_0$ of the $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG at room temperature.

From the equation, the zero-pressure bulk modulus B_0 can be obtained according to the relationship, $B_0 = 1/a$. The zero-pressure bulk modulus B_0 for $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG is 61.27 ± 4 GPa, which is in good agreement with the data (58 GPa) in Ref. [2], which is much less than Zr- and Pd-based BMGs'[2,12]. The relative volume change $\Delta V/V_0$ is about 33%. The smaller bulk modulus indicates that the material is relatively softer. Therefore, it is easy to understand the larger compressibility about 33%. The result indicates that the BMG has much looser atomic configuration compared with Zr- and Pd-based BMGs[2, 12], for the B- value of Zr- and Pd-based BMGs is much larger than 100 GPa and the compressibility is around 16%.

The conclusion could be confirmed by the value of B (58 GPa) in Table 1, which is in good agreement with 61.27 ± 4 GPa obtained by EOS. Therefore, for $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG, the EOS described by the relationship in Eq. (3) is reasonable. The calculated data in Table 1 is given as follows.

Table 1. The density (ρ), longitudinal (V_L) and transverse (V_T) sound velocities, the calculated second-order elastic constants (c_{11}, c_{44}, and c_{12}), bulk modulus (B) and Poisson's ratio (σ) for $Gd_{40}Y_{16}Al_{24}Co_{20}$, $Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$, $Ce_{70}Al_{10}Ni_{10}Cu_{10}$ BMGs at room temperature.

properties	$Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG	$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG	$Ce_{70}Al_{10}Ni_{10}Cu_{10}$ BMG
$\rho/(g/cm^3)$	6.656	6.125	6.67
$V_L/(km/s)$	3.646	5.174	2.518
$V_T/(km/s)$	1.879	2.472	1.313
c_{11}/GPa	88.5	164.0	42.3
c_{44}/GPa	23.5	37.4	11.5
c_{12}/GPa	41.5	89.2	19.3
B/GPa	58	114.1	27
$^a d$	1.6446	1.31	1.7037
$^a c_{44}/c_{12}$	0.5664	0.42	0.5948
reference	this work, 2	2, 20	this work, 21

a. calculated in this work.

Elastic properties of glasses show a very interesting correlation with the glass structure, the knowledge of elastic characteristics would provide considerable information about the structure of noncrystalline state solids since they are directly related to the inter-atomic forces and potentials[13]. In an amorphous solid, such as glass, the elastic strain produced by a small stress can be described by two independent elastic stiffness constants, c_{11} and c_{44}. The Cauchy relation $c_{12} = c_{11} - 2c_{44}$ allows one to determine c_{12}. For pure longitudinal waves $c_{11} = \rho V_L^2$, and for pure transverse waves $c_{44} = \rho V_T^2 = G$, where ρ is the density, V_L and V_T are the longitudinal and transverse velocity, respectively. The sound velocity also allows the determination of bulk modulus, B , by the following equations[14]:

$$B = \rho \frac{3V_L^2 - 4V_T^2}{3} . \tag{3}$$

An expression of $d = 4c_{44}/B$ which was derived by Bergman and Kantor for an inhomogeneous random mixture of fluid and a solid backbone near the percolation limit[15, 16], can give information on effective dimensionality of the materials (in this letter we use the expression as the form of $d = 4G/B$, for $c_{44} = \rho V_T^2 = G$). As is shown in Table 1: the d-value (1.6446) and c_{44}/c_{12}-value (0.5664) of $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG are similar to the d-value (1.7037) and c_{44}/c_{12}-value (0.5948) of $Ce_{70}Al_{10}Ni_{10}Cu_{10}$ BMG, therefore, it implies that a similar d-value with a possibly similar structure. As reported in Ref. [17]: the normal local structure similar to that of other BMGs and covalent bond structures similar to those of oxide glasses may coexist in the Ce-based BMG which causes anomalous property under pressure of the Ce-based BMG[18, 19]. In this case, as far as its elastic properties are concerned, the metallic glass is "well behaved" in the sense that when the material is stressed, the possibly like Ce-based BMGs structure in $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG which has much looser space favors the deformation of $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG, therefore, the compressibility of $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG is large.

Although the compressibility of $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG under high pressure(0—33.42 GPa) is large, its amorphous structure keeps stable under high pressure, which reveals that pressure only alters topological short range ordering. It is generally believed that the average interatomic distance tends to be shortened under high pressure[20]. Therefore, the inhomogeneity of the local distribution of excess free volume together with the existence of density fluctuation in amorphous materials gives rise to the inhomogeneity of local stress under pressure, which then makes the amorphous materials thermodynamically get metastable equilibrium and ultimately results in structural relaxation. The investigation of the phase change in amorphous alloy indicates that the atomic long-range diffusion is inhibited under high pressure[21]. Consequently, the structural relaxation under high pressure at room temperature caused by topological short range ordering induces the densification of the amorphous material. Therefore, Compared with other BMGs, it is not unreasonable to expect the possibly like Ce-based BMGs structure in $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG makes it have more excess free volume, this favors the $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG having a longer structural relaxation which favors the $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG continuing structural densification. Adding to a smaller zero-pressure bulk modulus $B_0 = 61.27 \pm 4$ GPa ultimately, these all make for its amorphous structure keeping quite stable in the high pressure range investigated although the relative volume change $\Delta V/V_0$ of the $Gd_{40}Y_{16}Al_{24}Co_{20}$ BMG is about 33%.

4 Conclusions

The compression behavior of the heavy RE-based BMG $Gd_{40}Y_{16}Al_{24}Co_{20}$ under high pressure has been investigated by in situ high pressure angle dispersive X-ray diffraction measurement using synchrotron radiation in the pressure range of 0—33.42 GPa at room temperature. The EOS of the BMG is obtained: $-\Delta V/V_0 = 5.992\times10^{-4}+0.01632P-2.056\times10^{-4}P^2+3.208\times10^{-7}P^3$ and the zero-pressure bulk modulus B_0 for the BMG is 61.27 ± 4 GPa, the relative volume change $\Delta V/V_0$ of the BMG is about 33%. The d-value ($d=4G/B$) is about 1.6446 which is similar to the d-value (1.7037) of $Ce_{70}Al_{10}Ni_{10}Cu_{10}$ BMG. It is found that its amorphous structure keeps quite stable in the high pressure range investigated although the relative volume change $\Delta V/V_0$ of the BMG is about 33%. Compared with other BMGs, some possible explanation for this may be (1) the larger compressibility is related to elastic properties, the most possibly like Ce-based BMGs structure unit in the glass, which the d-value ($d=4G/B$) is about 1.7037; (2) the possibly like Ce-based BMGs makes the BMG have more excess free volume, this favors the BMG having a longer structural relaxation which makes the BMG continuing structural densification in the pressure range investigated.

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