

Formation and properties of Pr-based bulk metallic glasses

Z.F. Zhao, P. Wen, R.J. Wang, D.Q. Zhao, M.X. Pan, and W.H. Wang^{a)}

Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

(Received 17 May 2005; accepted 8 August 2005)

The data on the compositional dependence of glass-forming ability, glass transition, and properties of bulk metallic glasses (BMGs) are important for understanding the nature and glass-forming ability of metallic glasses and for their application. In this paper, we report the formation of rare-earth-based Pr-(Cu,Ni)-Al pseudo-ternary BMGs with a large bulk glass-forming composition range and distinct glass transition. The compositional dependence of glass-forming ability, glass transition, and properties were systematically studied. The contrasting effects of Al and Pr on glass formation and glass transition, unique elastic properties, and phonon softening of the BMGs are discussed from the structural point of view.

I. INTRODUCTION

During the past decade, intensive efforts have been made to investigate the magnetic rare-earth-transition metal-based (RE-TM) bulk metallic glasses (BMGs).^{1–3} However, unlike others, some RE-TM-based BMGs have neither a distinct glass transition nor a large supercooled liquid region in their differential scanning calorimetry (DSC) traces,⁴ although glassy samples with large diameter can be prepared. It was first believed that a glass transition temperature too close to the crystallization onset temperature might be the primary reason for this. Later, careful microstructural investigations showed that these RE-TM-based BMGs, such as NdFeAl(Co), are actually a mixture of nanocrystalline clusters and glassy matrix.⁵ Recently, a series of different RE-TM-based BMGs, which have a distinct glass transition and a fully glassy structure, have been developed.^{6–9} Independently, Zhao et al.^{6–8} and Zhang et al.⁹ have reported that full bulk amorphous Pr-based alloys can be formed. The excellent glass-forming ability (GFA), stable supercooled liquid region, distinct glass transition, and, especially, the large glass-forming composition range make these BMGs ideal candidates to investigate the composition-dependent GFA, physical properties, and glass transition. The BMGs are also promising for future applications.^{3,6–9}

To guide the development of BMGs, various criteria have been proposed.^{10–13} Turnbull¹⁰ predicted that as the ratio of the glass transition temperature T_g to the liquidus temperature T_l of an alloy (referred to as the reduced glass transition temperature $T_{rg} = T_g/T_l$) increased to

values near 2/3, the homogeneous nucleation of the undercooled melt should become very sluggish on the experimental time scale, and formation of BMGs should be possible. Inoue et al.¹² developed three empirical rules to guide the formation of BMGs. Liu et al.¹³ recently proposed a new criterion of γ [$\gamma = T_x/(T_g + T_l)$], where T_x is the crystallization temperature. However, with the development of BMGs, there is increasing evidence that these criteria are not consistent with all experimental results. Study of the criteria for GFA of an alloy attracts great interest both in application and theory. A glass is formed by cooling the liquid to solid without crystallization. Therefore, the crystallization of undercooled liquid during cooling process needs to be considered.

The metallic glass, which is different from the crystalline materials, is characterized by the existence of short-range structural order without long-range structural order. This intrinsic structural difference is the origin of the anomalies, e.g., localization effects, diverse acoustic, magnetic properties, and abnormal behaviors under low temperature observed in amorphous materials.^{4,13–17} BMGs are among the simplest glasses, whose structural units are simple atoms interacting with metallic bonding, and close to dense random packing of spheres. The simple structure and large glass-forming composition range offer a model for investigating the compositional and structural dependence of the glassy properties.

In this work, glass formation and the compositional dependence of the glass transition and properties (in particular the elastic properties) were studied in the BMG-forming Pr-Cu-Ni-Al alloys. The experimental results show that the optimum composition for the glass formation in the Pr-(CuNi)-Al pseudo ternary system is at a eutectic composition. The contrasting effects of Al and Pr on the glass transition and properties, the unique elastic properties, and the phonon softening of the BMGs are discussed.

^{a)}Address all correspondence to this author.

e-mail: whw@aphy.iphy.ac.cn

DOI: 10.1557/JMR.2006.0067

II. EXPERIMENTAL

Multicomponent Pr-based master alloys were prepared by arc-melting in titanium-gettered argon atmosphere starting from Pr, Al, Ni, and Cu elements with a purity of 99.9% or higher. To ensure homogeneity of the samples, the ingots were remelted several times. From the pre-alloyed ingots, bulk cylindrical specimens 1–5 mm in diameter and 50 mm in length were prepared by suction-casting into a water-cooled copper mold. The fully crystallized sample was prepared by annealing the BMG at 663 K in vacuum for 1 h and the annealing temperature is far above T_x . The thermal properties were studied using a Perkin-Elmer DSC-7 (Perkin Elmer Inc., Wellesley, MA) differential scanning calorimeter (DSC) under a continuous argon flow. The melting was measured by a Perkin Elmer DTA-7 (Perkin Elmer) under a continuous argon flow. The calorimeter was calibrated for temperature and energy at various heating rates with high purity indium and zinc. Firstly, an empty Al pan was performed to establish a baseline, and then the same Al pan including the sample was measured again in identical thermal conditions. The values of T_g and the crystallization temperature T_x , were determined from the DSC traces with the accuracy of ± 2 K.

The acoustic velocities of the BMGs were measured at room temperature at a frequency of 10 MHz by using a MATEC 6600 ultrasonic system (MATEC Inc., Northborough, MA) with a measuring sensitivity of 0.5 ns. The samples for ultrasonic measurements were cut from the rod and the ends of cylinder were carefully polished flat

and parallel. The effect due to the bonding material used between the transducer and the sample was neglected as the typical thickness of the band was less than 4 μm . The density ρ was measured by the Archimedean principle. The elastic constants (e.g., the bulk modulus B , Young's modulus E , and shear modulus G) and the Debye temperature Θ_D were derived from the ultrasonic velocities and density.^{18,19}

III. RESULTS

A. Formation of Pr-(Cu-Ni)-Al pseudo-ternary BMGs

Basic verification of amorphicity throughout the thickness of the samples was examined by x-ray diffraction (XRD). In samples below the critical diameters given in Table I, the XRD patterns show only two broad maxima associated with an amorphous phase and no detectable Bragg peaks corresponding to crystalline phases (examples of XRD patterns from similar glasses can be found in Ref. 6). High-resolution transmission electron microscopy is more sensitive than XRD to minor volume fractions of dispersed crystals but still shows only the uniform contrast expected for a single glassy phase. Figure 1 shows the compositional dependence of the formation of the cylindrical Pr-(Cu-Ni)-Al pseudo-ternary BMGs 1 mm in diameter produced by copper mold casting. As shown in Fig. 1, within a wide composition range—Al content from 5 to 35 at.% and Pr content from 50 to 65 at.%—the alloys can be cast into BMG. Among

TABLE I. Compositions, critical diameter (R_{max}), and thermal properties of the Pr-(Cu_{0.67}Ni_{0.33})-Al BMGs.

Compositions (at.%)	$T_g \pm 2$ (K)	$T_x \pm 2$ (K)	$T_m \pm 2$ (K)	$T_i \pm 2$ (K)	$\Delta T \pm 2$ (K)	γ	T_{rg}	$R_{\text{max}} \pm 0.5$ (mm)
Pr ₆₀ Cu ₂₃ Ni ₁₂ Al ₅ ^a	389	431	703	720	42	0.389	0.540	0
Pr ₆₅ Cu ₂₀ Ni ₁₀ Al ₅ ^a	390	421	704	720	31	0.379	0.542	1
Pr ₅₅ Cu ₂₃ Ni ₁₂ Al ₁₀ ^a	428	485	707	725	57	0.421	0.590	1
Pr ₆₀ Cu ₂₀ Ni ₁₀ Al ₁₀ ^{a,c}	417	469	710	725	52	0.411	0.575	5
Pr ₆₅ Cu ₁₇ Ni ₈ Al ₁₀ ^a	402	438	692	727	36	0.388	0.553	1
Pr ₅₅ Cu ₂₀ Ni ₁₀ Al ₁₅ ^a	445	510	705	736	65	0.432	0.605	2
Pr ₆₀ Cu ₁₇ Ni ₈ Al ₁₅ ^a	424	510	708	754	86	0.433	0.562	3
Pr ₆₅ Cu ₁₃ Ni ₇ Al ₁₅	421	464	715	752	43	0.396	0.560	1
Pr ₇₀ Cu ₁₀ Ni ₅ Al ₁₅	412	451	699	720	39	0.398	0.572	0
Pr ₅₅ Cu ₁₇ Ni ₈ Al ₂₀ ^b	458	530	710	787	72	0.426	0.582	3
Pr ₆₀ Cu _{13.3} Ni _{6.7} Al ₂₀ ^b	446	494	704	786	48	0.401	0.567	2
Pr ₄₅ Cu ₂₀ Ni ₁₀ Al ₂₅	510	562	712	788	52	0.433	0.647	0
Pr ₅₀ Cu _{16.7} Ni _{8.3} Al ₂₅ ^b	485	553	762	785	68	0.435	0.618	1
Pr ₅₅ Cu _{13.3} Ni _{6.7} Al ₂₅ ^{b,c}	473	532	758	788	59	0.422	0.600	3
Pr ₆₀ Cu ₁₀ Ni ₅ Al ₂₅ ^b	451	510	758	838	59	0.396	0.538	0
Pr ₅₀ Cu _{13.3} Ni _{6.7} Al ₃ ^b	509	574	762	820	65	0.432	0.621	1
Pr ₅₅ Cu ₁₀ Ni ₅ Al ₃₀ ^b	498	545	763	822	47	0.413	0.606	2
Pr ₆₀ Cu _{6.7} Ni _{3.3} Al ₃₀	491	561	762	845	70	0.420	0.581	0
Pr ₆₅ Cu _{3.3} Ni _{1.7} Al ₃₀	443	504	764	799	61	0.406	0.554	0

^aBMGs taken into account in group 1 (dot circle in Fig. 1).

^bBMGs taken into account in group 2 (solid circle in Fig. 1).

^cBMGs with best GFA within their group.

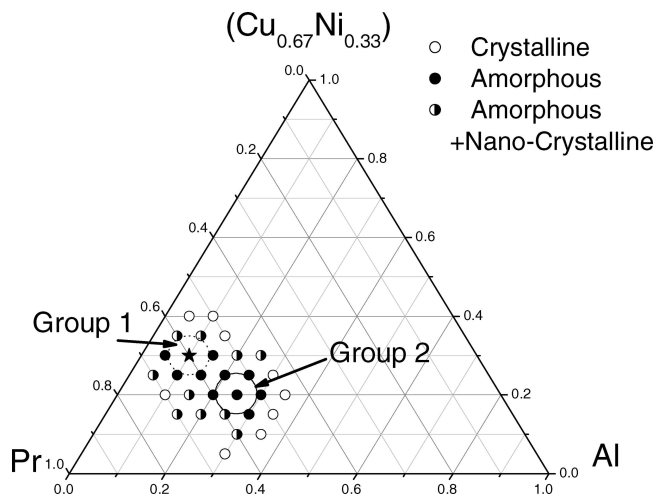


FIG. 1. Glass-forming composition range of Pr-(Cu_{0.67}Ni_{0.33})-Al alloy system. Open circles represent the occurrence of completely crystalline phases in these compositions; the solid circles represent completely glassy phase; and the half open circles means the existence of nano-crystallization in these alloys. The star-shaped point represents the composition with the best GFA in this BMG.

them, the Pr₆₀Cu₂₀Ni₁₀Al₁₀ alloy (indicated by the star in Fig. 1) is found to have the best GFA, with critical diameter of at least 5 mm. Apart from this composition, the critical diameter will decrease. The results imply that the Pr-(Cu-Ni)-Al alloy has large glass-forming composition range and the GFA is composition dependent.

Table I lists the compositions, critical diameter R_{\max} , and the various parameters to evaluate the GFA (T_{rg} , ΔT , and γ^{13}) of Pr-(Cu_{0.67}Ni_{0.33})-Al alloys. As listed in Table I, the calculated values of T_{rg} and ΔT within the limits of experimental errors do not fully agree with the experimental results. For example, R_{\max} of Pr₅₅Cu₂₃Ni₁₂Al₁₀ and Pr₅₀Cu_{16.7}Ni_{8.3}Al₂₅ alloys with larger ΔT (57 and 65 K, respectively) is only 1 mm, while R_{\max} of Pr₆₀Cu₂₀Ni₁₀Al₁₀ with smaller ΔT (52 K) is 5 mm. The Pr₆₀Cu₂₀Ni₁₀Al₁₀ alloy with $T_{\text{rg}} = 0.575$ can form a BMG with diameter of 5 mm, while Pr₅₀Cu_{13.3}Ni_{6.7}Al₃₀ with $T_{\text{rg}} = 0.62$ can form a BMG only 1 mm in diameter. The phenomenon has also been found in some other BMG-forming systems.^{12,15}

The T_{rg} criterion is based on some suppositions, particularly that T_1 has a strong dependence on composition, but T_g does not. Eutectic liquids have the lowest T_1 , their interval between T_g and T_1 is the smallest, and they have the largest value of T_{rg} . Thus, the probability of cooling this supercooled liquid to avoid crystallization is enhanced, i.e., a better GFA. In this sense, T_{rg} is a guide to GFA (the larger the value of T_{rg} , the better GFA of the glass former). The inconsistency of the T_{rg} criterion with the experimental results indicates that the above supposition of the compositional dependence of T_1 and T_g does not work as assumed in this alloy system. This can be attributed to two factors: first, the experiments show that

the T_g depends on the composition strongly in some BMG systems,^{9,16} and second, the T_1 of an eutectic alloy is the lowest compared with that of its corresponding off-eutectic alloys. Therefore, more attention should be paid to the compositional dependence of T_g and T_1 .

Turnbull¹¹ supposed that eutectic alloys have better GFA, and the GFA worsens for off-eutectic alloys. For the formation of BMGs it is necessary to determine the eutectic composition. However, this is not easy for complex multicomponent BMG-forming alloys. To check the relation between the GFA and the eutectic composition, the alloys were divided into two groups as shown in Fig. 1: group 1 is represented by dotted circles and group 2 by solid circles. The values of T_g , T_m , and T_1 for different alloys are listed in Table I. Within experimental error, T_m is almost independent of the composition variation of the alloys. In contrast, T_1 is more sensitive to the composition. For the Pr₆₀Cu₂₀Ni₁₀Al₁₀ alloy, the temperature interval of the melting ($T_1 - T_m$) is about 15 K, which is the smallest in group 1. This indicates that the Pr₆₀Cu₂₀Ni₁₀Al₁₀ alloy is very close to the eutectic composition, and the compositions around it correspond to off-eutectic compositions. The Pr₆₀Cu₂₀Ni₁₀Al₁₀ alloy has the best GFA in group 1. This indicates that the eutectic composition has a better GFA than the corresponding off-eutectic compositions. Similar results are exhibited for group 2, marked in Fig. 1. Pr₅₅Cu_{13.3}Ni_{6.7}Al₂₅ is another composition close to eutectic composition with better GFA. In agreement with above-mentioned T_{rg} criteria, the Pr₅₅Cu_{13.3}Ni_{6.7}Al₂₅ alloy should have a better GFA than Pr₆₀Cu₂₀Ni₁₀Al₁₀. However, on the contrary, Pr₆₀Cu₂₀Ni₁₀Al₁₀ has the better GFA. With the limited experimental results for the given system, we assume that the eutectic alloy with lower liquidus temperature has a better GFA. The lower T_1 indicates the liquid is relatively stable against the crystalline phases. Correspondingly, the GFA should be better.

B. Composition dependence of T_g

In Table I, T_g is found to be composition-dependent. Usually, T_g depends also on the experimental time scale. However, within the available experimental time scale range, T_g does not change much. T_g is usually considered to be an important intrinsic characteristic of a glass. Figure 2(a) shows the change of T_g , T_x , T_m , and T_1 for the Pr_x(Cu_{0.67}Ni_{0.33})_{85-x}Al₁₅ ($55 \leq x \leq 70$) BMGs relative to Pr₅₅(Cu_{0.67}Ni_{0.33})₃₀Al₁₅ BMG. In Fig. 2, Y ($Y = T_g, T_x, T_m$, or T_1) is normalized by $\Delta Y/Y_0 = (Y - Y_0)/Y_0$, where Y_0 was set as the value for the Pr₅₅(Cu_{0.67}Ni_{0.33})₃₀Al₁₅ BMG listed in Table I. T_g , T_x , T_m , and T_1 are determined by DSC at a heating rate of 40 K/min. For Pr₅₅(Cu_{0.67}Ni_{0.33})₃₀Al₁₅ BMG, T_g , T_x , T_m , and T_1 are 445, 510, 705, and 736 K, respectively. With the increase of Pr concentration from 55 to 70 at.%, T_g

decreases up to 7.4% gradually, while the changes of T_m and T_l with Pr content are irregular. T_g of the $\text{Pr}_{55}(\text{Cu}_{0.67}\text{Ni}_{0.33})_{45-x}\text{Al}_x$ alloys increases almost linearly from 428 to 498 K (16.4%) with Al increasing from 10 to 30 at.%. Compared with the effect of Pr, the effect of Al content on the change of T_g is more obvious.

It is understood that the glass transition means a failure of the material to support shear stress on the typical laboratory timescale. Similar to the melting of a crystal, the structural units in glasses will be translated freely from their original positions when the temperature is above T_g . That is, at or above T_g , thermal activation can overcome the energy gaps restricting the structural units in glasses and make the glassy structure fail to shear stress. In fact, more and more evidence is accumulating that the glass transition can be considered as a disorder-driven melting process. A universal approach is proposed for melting and amorphization.^{20,21} So the glass transition is associated with a certain density of packing of the atoms and the energy state associated with the packing. The increasing Al content in Pr-based BMGs may stabilize the short-range structure as well as increase the energy needed to change the energy state of the system, i.e.,

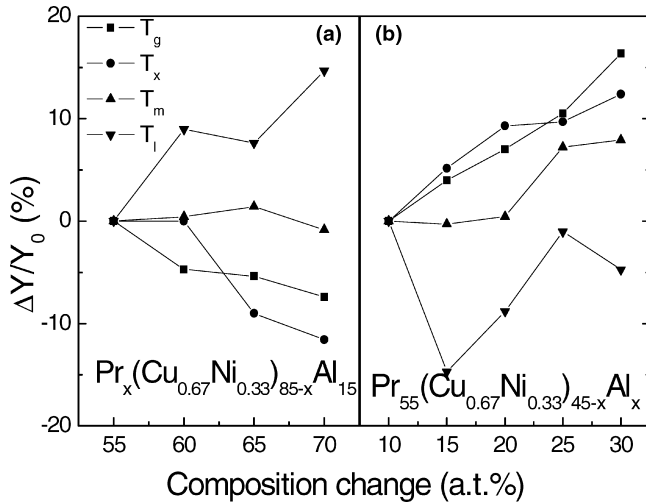


FIG. 2. Compositional dependence of the glass transition temperature T_g , crystallization temperature T_x , the melting temperature T_m , and the liquidus temperature T_l in (a) $\text{Pr}_x(\text{Cu}_{0.67}\text{Ni}_{0.33})_{85-x}\text{Al}_{15}$ ($55 \leq x \leq 70$) and (b) $\text{Pr}_{55}(\text{Cu}_{0.67}\text{Ni}_{0.33})_{45-x}\text{Al}_x$ ($10 \leq x \leq 30$) BMGs. $Y = T_g, T_x, T_m$, or T_l , Y is normalized by $\Delta Y/Y_0 = (Y - Y_0)/Y_0$, where Y_0 was set as the value for the $\text{Pr}_{55}(\text{Cu}_{0.67}\text{Ni}_{0.33})_{30}\text{Al}_{15}$ (see Table I).

make atomic diffusion more difficult, leading to a higher T_g . Recently, Gao et al. proposed that the effect of stabilization of Al content may partially be attributed to the covalent bonding trend between Al atoms and other atoms.²²

To study the effect of Al on the microstructure of Pr-based BMGs, the ultrasonic technique, which is very sensitive to the change of microstructure, was applied. Figure 3 shows the T_g dependence of the Debye temperature Θ_D , shear modulus G , and the number of the atoms in unit volume n (defined as $n = \rho/A$, where A is the average atomic weight) of the Pr-based BMGs. For $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pr}_{60}\text{Cu}_{17}\text{Ni}_8\text{Al}_{15}$, $\text{Pr}_{55}\text{Cu}_{17}\text{Ni}_8\text{Al}_{20}$, and $\text{Pr}_{55}\text{Cu}_{13.3}\text{Ni}_{6.7}\text{Al}_{25}$ BMGs, T_g increases from 417 to 473 K as the Al content varies from 10 to 25 at.% (see Table I). The relative change Y ($Y = \Theta_D, n$, or G) was calculated as follows: $\Delta Y/Y_0 = (Y - Y_0)/Y_0$, where Y_0 was set as the value for the $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ BMG (see Table II). The change of Θ_D and G with Al content is consistent with that of T_g . That is, Θ_D and G increase with increasing T_g . The change of Θ_D and G with T_g

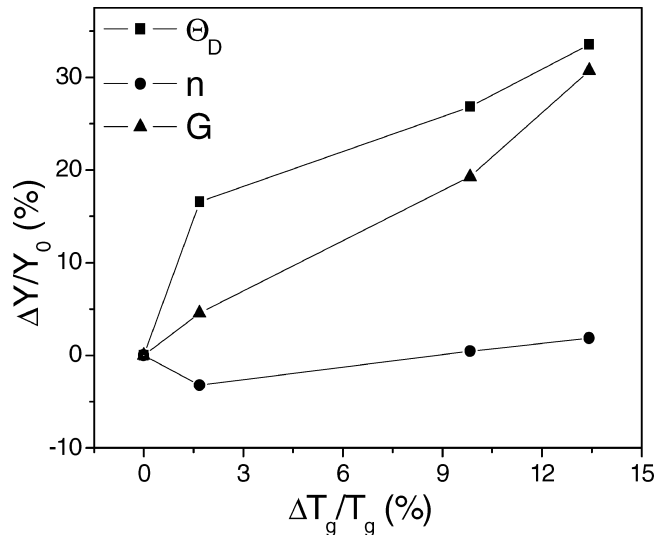


FIG. 3. Relative change in Debye temperature Θ_D , number of atoms in unit volume n , and shear modulus G as a function of glass transition temperature for $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$, $\text{Pr}_{60}\text{Cu}_{17}\text{Ni}_8\text{Al}_{15}$, $\text{Pr}_{55}\text{Cu}_{17}\text{Ni}_8\text{Al}_{20}$, and $\text{Pr}_{55}\text{Cu}_{13.3}\text{Ni}_{6.7}\text{Al}_{25}$ BMGs. ΔT_g is the change of T_g relative to that of $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ BMG. Y ($Y = \Theta_D, n$, or G) is normalized by $\Delta Y/Y_0 = (Y - Y_0)/Y_0$, where Y_0 was set as the value for the $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ BMG (see Table II).

TABLE II. Comparison of the acoustic velocities, elastic constants, and the Debye temperature of the $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ samples in glassy (Y_a) and crystallized states (Y_c) and the elastic moduli calculated by $M^{-1} = \sum f_i M_i^{-1}$.

	$\rho \pm 0.005$ (g/cm ³)	$v_l \pm 0.005$ (km/s)	$v_s \pm 0.005$ (km/s)	$E \pm 1$ (GPa)	$K \pm 1$ (GPa)	$G \pm 1$ (GPa)	$\Theta_D \pm 1$ (K)
Glassy state	6.875	3.032	1.403	36.9	45.2	13.5	160
Crystallized state	6.899	3.294	1.643	49.7	50.0	18.6	166
$(Y_c - Y_a)/Y_a$ (%)	3.5	8.6	17	34.7	10.6	37.8	17
Calculated	50.8	41.7	20.3	...

confirms that the short-range microstructure is dependent on the Al content in the BMGs. As shown in Fig. 3, with increasing the Al content, n first decreases (3.2%) and then increases (up to 1.8%); nevertheless the increase of Θ_D and G are monotonic. Therefore, the Θ_D and G are not related to n in the studied BMGs. For ZrTiCuNiAl BMG, the high-pressure experiments showed similar results; i.e., the increase of G and Θ_D induced by the incorporation of Al could not mainly be attributed to the change of the atomic packing density.¹⁶ Wang et al.²¹ proposed that the relationship between T_g and Θ_D should obey a rule similar to that of melting temperature. For various BMGs, the value of $1000T_g/A\Theta_D^2$ converge into a constant (where A is the average atomic weight), which is within the 0.136–0.153 range.²¹ For Pr-based BMGs studied in this paper, the values of $1000T_g/A\Theta_D^2$ are between 0.136 and 0.153 further confirming the correlation between T_g and Θ_D .

The correlation between T_g and Θ_D^2 in BMGs may mean that the glass transition of the bulk glass-forming alloys has certain characteristics of melting. In fact, a unified approach has ever been proposed for melting and amorphization.²⁰ The glass transition, approaching from the solid and inducing the transition of the glass state to supercooled liquid state, may be regarded as a melting process of a metallic glass. In fact, the typical $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ BMG can be directly transformed to melt state by glass transition, and the crystallization process can be prevented when the heating rate is above 200 K/s²³ or heating under high pressure.²⁴ On the other hand, the correlation more or less indicates that the glass transition is in connection with anharmonicity coupling of the vibration, and configurational energy manifolds as suggested by Angell.²⁵

It worth noting that a rule of thumb was proposed by Turnbull: T_g/T_l larger than 2/3. That is, good glass formers like the bulk metallic glasses require T_g/T_l to be higher than 0.67.¹¹ It is a good empirical rule for finding new metallic glass. However, the T_g and T_l are not correlated well with glass forming ability, at least in bulk glass-forming alloys. The values of the ratio T_g/T_l vary for the Zr-based alloys between 0.59 and 0.69 and even more for the other glasses.³ The La- and Mg-based alloys have a value of $T_g/T_l = 0.70$, but their glass-forming ability is not as good as that of Zr-based alloys with $T_g/T_l = 0.65$. Therefore, even though the T_g/T_l is a good criterion for developing new bulk metallic glass, T_g and T_l cannot be considered to have good correlation. This indicates that the correlation of T_g and Θ_D^2 found in this work is different from the T_g/T_l criterion.

C. Lower elastic moduli of Pr-based BMGs

Besides a low T_g , the Pr-based BMGs have low elastic moduli. Table III lists the acoustic data and elastic

TABLE III. Acoustic data and elastic modulus and Poisson ratio σ for $Pr_{60}Al_{10}Ni_{10}Cu_{20}$ BMG, non-metallic glasses, and some typical metallic glasses. The data for other BMGs are from Ref. 3.

Glasses	$E \pm 1$ (GPa)	$G \pm 1$ (GPa)	$K \pm 1$ (GPa)	$\sigma \pm 0.01$
$Pr_{60}Cu_{20}Al_{10}Ni_{10}$	37.2	13.6	45.2	0.360
Window glass	67.2	27.7	38.8	0.211
Fused quartz	72.9	31.3	36.4	0.166
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	97.8	36.1	113.0	0.356
$Pd_{39.1}Ni_{10.1}Cu_{29.9}P_{20.9}$	98.6	35.3	159.4	0.397
$Mg_{60}Cu_{25}Gd_{15}$	52.2	19.9	46.6	0.313
$Cu_{60}Zr_{20}Hf_{10}Ti_{10}$	101.1	36.9	128.2	0.369
$Cu_{50}Zr_{45}Al_5$	91.2	33.3	117.3	0.370

moduli for $Pr_{60}Al_{10}Ni_{10}Cu_{20}$ BMG as well as non-metallic glasses and other typical BMGs. It can be seen that the $Pr_{60}Al_{10}Ni_{10}Cu_{20}$ BMG possesses the lowest E , G , and K among all glasses. They are comparable to those of amorphous carbon and oxide fused quartz³ and close to those of polymers,²⁶ indicating that these BMGs exhibit elastic properties similar to those of non-metallic glasses, and have much “softer” elastic constants than other BMGs.³ The extremely small value of Θ_D also reveals that these BMGs are much less rigid than other BMGs. However, the value of Poisson’s ratio, σ (see Table III) of the Pr-based BMG is much larger than that of non-metallic glasses and similar to that of other BMGs. The σ value directly reflects the bonding forces of a material. The result reveals that the BMG’s short-range structure is still based on metallic bonds as other BMGs.⁸ The Pr-based BMG with structural characteristics of a metallic glass exhibits elastic constants similar to those of non-metallic glasses. The above results are partially caused by the major Pr component, which possesses much lower elastic moduli compared with that of other components indicating a weaker bonding between Pr and other atoms. After fully crystallization of the BMG, E , K , and G increase from 36.9, 45.2, and 13.5 GPa (glassy state) to 49.7, 50.0, and 18.6 GPa (crystallized state), respectively (the E , K , G , and Θ_D of the BMG are respectively 34.7%, 10.6%, 37.8%, and 17.0% smaller relative to the crystallized state). This indicates that the long wavelength phonons in the BMG are markedly softened.^{27,28} The softening effect was believed closely related to the change from a periodic distribution of atoms to the heterogeneous regrouping of atoms during the amorphization process. Due to the absence of long-range order in metallic glasses, the interactions between the atoms are restricted to short-range region. Thus when metallic glasses are shear deformed, the changes in the local atomic density may be non-uniform. This may finally result in the large reduction of elastic moduli. For a glass-forming alloy, its elastic constants agree well with the calculated value from its constituent elements as follows²⁹

$$M^{-1} = \sum f_i M_i^{-1}, \quad (1)$$

where M is an elastic constant and f_i is the atomic percentage of the component elements. The calculated elastic constants of the $\text{Pr}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ alloy according to Eq. (1) are also listed in Table II. It is obvious that the calculated elastic constants of the Pr-based alloy are very close to those of its crystalline state, but much higher than those observed in glassy state. This could further support the assumption that the large softening of the Pr-based BMG should be attributed to its intrinsic glassy structure.

IV. CONCLUSIONS

We analyzed the GFA of Pr-based Pr–Cu–Ni–Al BMG system. The experimental results show that for the Pr-based pseudo-ternary system, there is more than one eutectic composition, and among them, the eutectic composition with the best GFA has the lowest melting point. The glass transition temperature and physical properties of Pr-based BMGs are composition dependent. Compared with the major element Pr, the Al content has more obvious effect on the properties of the BMGs. Moreover, the relationship between T_g and Θ_D upon the composition and the softening of phonons in the Pr-based BMGs further supports the idea that the glass transition observed by DSC is the melting of glass. The finding of the Pr-based BMG with a large bulk glass-forming composition range is of significance for study of the metallic glass-formation and for their applications.

ACKNOWLEDGMENT

The authors are grateful for the financial support of the National Science Foundation of China (Grant Nos. 50321101 and 50371097).

REFERENCES

1. A. Inoue, T. Zhang, A. Takeuchi, and W. Zhang: Hard magnetic bulk amorphous Nd–Fe–Al alloys of 12 mm in diameter made by suction casting. *Mater. Trans. JIM* **37**, 636 (1996).
2. A. Inoue, T. Zhang, W. Zhang, and A. Takeuchi: Bulk Nd–Fe–Al amorphous alloys with hard magnetic properties. *Mater. Trans. JIM* **37**, 99 (1996).
3. W.H. Wang, C. Dong, and C.H. Shek: Bulk metallic glasses. *Mater. Sci. Eng. R* **44**, 45 (2004).
4. B.C. Wei, W.H. Wang, M.X. Pan, and B.S. Han: Domain structure of a $\text{Nd}_{65}\text{Al}_{10}\text{Fe}_{25-x}\text{Co}_x$ bulk metallic glasses. *Phys. Rev. B* **64**, 12406 (2001).
5. Z. Zhang, R.J. Wang, B.C. Wei, and W.H. Wang: Structural evolution and property changes in $\text{Nd}_{60}\text{Al}_{10}\text{Fe}_{20}\text{Co}_{10}$ bulk metallic glass during crystallization. *Appl. Phys. Lett.* **81**, 4371 (2002).
6. Z.F. Zhao, Z. Zhang, P. Wen, and W.H. Wang: A highly glass-forming alloy with low glass transition temperature. *Appl. Phys. Lett.* **82**, 4699 (2003).
7. B. Zhang, M.X. Pan, D.Q. Zhao, and W.H. Wang: “Soft” bulk metallic glasses based on cerium. *Appl. Phys. Lett.* **85**, 61 (2004).
8. M.B. Tang, D.Q. Zhao, M.X. Pan, B.C. Wei, W.H. Wang: A paramagnetic $\text{Nd}_{60}\text{Cu}_{20}\text{Ni}_{10}\text{Al}_{10}$ alloy with high glass-forming ability. *J. Phys. D: Appl. Phys.* **37**, 973 (2004).
9. Y. Zhang, H. Tan, H.Z. Kong, B. Yao, and Y. Li: Glass-forming ability of Pr–(Cu,Ni)–Al alloys in eutectic system. *J. Mater. Res.* **18**, 664 (2003).
10. A.L. Greer: Through a glass, lightly. *Nature* **366**, 303 (1993).
11. D. Turnbull and J.C. Fisher: Rate of nucleation in condensed systems. *J. Chem. Phys.* **17**, 71 (1949).
12. A. Inoue, T. Zhang, and T. Masumoto: Zr–Al–Ni amorphous alloys with high glass transition temperature and significant supercooled liquid region. *Mater. Trans. JIM* **31**, 177 (1990).
13. Z.P. Lu and C.T. Liu: Glass formation criterion for various glass-forming systems. *Phys. Rev. Lett.* **91**, 115505 (2003).
14. J. Schroers, A. Masuhr, W.L. Johnson, and R. Busch: Pronounced asymmetry in the crystallization behaviour during constant heating and cooling of a bulk metallic glass-forming liquid. *Phys. Rev. B* **60**, 11855 (1999).
15. K.F. Kelton: A new model for nucleation in bulk metallic glasses. *Philos. Mag. Lett.* **77**, 337 (1998).
16. P. Wen, R.J. Wang, M.X. Pan, D.Q. Zhao, and W.H. Wang: Characteristics of microstructure and glass transition of $(\text{Zr}_{0.59}\text{Ti}_{0.06}\text{Cu}_{0.22}\text{Ni}_{0.13})_{100-x}\text{Al}_x$ bulk metallic glasses. *J. Appl. Phys.* **93**, 759 (2003).
17. H. Tan, Y. Zhang, D. Ma, Y.P. Feng, and Y. Li: Optimum glass formation at off-eutectic composition and its relation to skewed eutectic coupled zone in the La based La–Al–(Cu,Ni) pseudo ternary system. *Acta Mater.* **51**, 4551 (2003).
18. W.H. Wang, R.J. Wang, F.Y. Li, D.Q. Zhao, and M.X. Pan: Elastic constants and their pressure dependence of $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_9\text{Be}_{22.5}\text{C}_1$ bulk metallic glass. *Appl. Phys. Lett.* **74**, 1803 (1999).
19. D. Schreiber: *Elastic Constants and Their Measurement* (McGraw-Hill, New York, 1973).
20. P.R. Okamoto, N.Q. Lam, and L.E. Rehn: *Solid State Physics*, Vol. 52, edited by H. Ehrenreich and F. Spaepen (Academic Press, San Diego, CA, 1999), pp. 1–135.
21. W.H. Wang, P. Wen, D.Q. Zhao, M.X. Pan, and R.J. Wang: Relationship between glass transition temperature and Debye temperature in bulk metallic glasses. *J. Mater. Res.* **18**, 2747 (2003).
22. F.Q. Guo, S.J. Poon, and J.G. Shiflet: CaAl-based bulk metallic glasses with high thermal stability. *Appl. Phys. Lett.* **84**, 37 (2004).
23. J. Schroers, A. Masuhr, W.L. Johnson, and R. Busch: Pronounced asymmetry in the crystallization behavior during constant heating and cooling of a bulk metallic glass-forming liquid. *Phys. Rev. B* **60**, 11855 (1999).
24. W.H. Wang, Z.X. Wang, D.Q. Zhao, M.B. Tang, W. Utsumi, and X.L. Wang: High-pressure suppression of crystallization in the metallic supercooled liquid $\text{Zr}_{41}\text{Ti}_{14}\text{Cu}_{12.5}\text{Ni}_{10}\text{Be}_{22.5}$: Influence of viscosity. *Phys. Rev. B* **70**, 092203 (2004).
25. C.A. Angell, K.L. Ngai, G.B. McKenna, P.F. McMillan, and S.W. Martin: Relaxation in glass forming liquids and amorphous solids. *J. Appl. Phys.* **88**, 3113 (2000).
26. C.L.J.A. Verbraak, J. Van Dam, and A.K. Van Der Vegt: High modulus of isotactic polypropylene attained by coextrusion with atactic polystyrene. *Polym. Eng. Sci.* **25**, 431 (2004).
27. B. Golding, B.G. Bagley, and F.S.L. Hsu: Soft transverse phonons in a metallic glass. *Phys. Rev. Lett.* **29**, 68 (1972).
28. M. Li and W.L. Johnson: Instability of metastable solid solutions and the crystal to glass transition. *Phys. Rev. Lett.* **70**, 1120 (1993).
29. A. Voronel and S.J. Rabinovich: On glassification temperatures of simple metallic alloys. *J. Phys. F: Met. Phys.* **17**, L193 (1987).