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Letter to the Editor

Bulk metallic superconductive $La_{60}Cu_{20}Ni_{10}Al_{10}$ glass

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Abstract

A bulk metallic superconductive $La_{60}Cu_{20}Ni_{10}Al_{10}$ glass with highly glass forming ability and large supercooled liquid temperature region is developed. The superconductive critical temperature determined by the electrical resistance and the specific heat measurements is 2.5 K. The obtained electron–phonon interaction parameter demonstrates that the bulk metallic glass is an intermediate coupling superconductor. The new nonmagnetic rare-earth based glass offers an ideal material for studying the superconductivity and other low temperature properties in the metallic glasses.

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The low temperature superconductivity is important for understanding the properties of the low-energy excitation in metallic glasses. Since the discovery of the superconductivity in metallic glasses in the early 1950s [1], more and more metallic glasses mainly in the shapes of ribbons or foils, such as Pd–Zr [2], Zr–Rh–Pd [3], Zr–Ni–Cu [4], Nb–Ge [5], La–Au [6] are found to be superconductive and attracted widely interesting. The superconductivity in the weakly localized region is affected by the quantum correlation in disordered system [7]. So the superconductivity such as the critical temperature, the upper critical field [7] of three-dimensional disordered system is different from that of two-dimensional disordered system. Bulk metallic glasses (BMGs) are recently developed metallic glassy family which exhibiting exceptional glass forming ability, unique mechanical properties and great application potentials [8]. However, the study of superconductivity in BMGs is scarcely performed so far. To our knowledge, only the superconductivity of the Zr–Ti–Cu–Ni–Be BMGs [9] has been reported. Li et al. [9] found that the disorder can suppress the superconductivity, the origin of the reduction of the superconductive critical temperature, T_c in the glass state is ascribed to a smearing of the density of states by the disordered atomic structure [9]. In the paper, a bulk metallic superconductive $La_{60}Cu_{20}Ni_{10}Al_{10}$ glass exhibiting highly glass forming ability and stable supercooled liquid state is developed. The thermal, superconductivity, density of states at Fermi level, the electron–phonon interaction parameter and Debye temperature of the BMG are studied by the measurements of the electrical resistance and the specific heat at low temperature.

Ingot of $La_{60}Cu_{20}Ni_{10}Al_{10}$ alloy was prepared by melting 99.9 at.% pure La, Cu, Ni, and Al in an arc-melting furnace under argon atmosphere. The rod sample with 2 mm in diameter was produced by suction of the melt into a copper mold. The amorphous sample was characterized by X-ray diffraction (XRD) using a MAC M03 XHF diffractometer with Cu K_α radiation. Differential scanning calorimeter (DSC) measurement was carried out in a Perkin–Elmer DSC-7 with a temperature scanning rate 20 K/min. The electrical resistivity using a standard four-probe method and the specific

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heat measurements were carried out on a Physical Properties Measurement System (PPMS, Quantum Design Co. USA).

Fig. 1 shows the DSC trace which exhibiting the glass transition, the crystallization and the melting process of the $La_{60}Cu_{20}Ni_{10}Al_{10}$ alloy. The inset is the XRD pattern of as-cast sample. The patterns of the sample mainly consist of broad diffraction maxima indicating an amorphous structure and no appreciable diffraction peaks corresponding to crystalline phases can be detected within the resolution limits of the XRD measurements. This indicates that the $La_{60}Cu_{20}Ni_{10}Al_{10}$ alloy is in full amorphous state, which has also been confirmed by transmission electron microscopy observation [8]. The DSC trace of the alloy shows an obvious endothermic characteristic before crystallization demonstrating a distinct glass transition with very low onset at $T_g = 387$ K. Following the glass transition, the alloy exhibits obvious three exothermic heat release events associated with the transformations from undercooled liquid state to the equilibrium crystalline intermetallic phases. The first crystalline temperature T_{x1} and the undercooled liquid region ΔT ($\Delta T = T_{x1} - T_g$) are 447 K and 60 K, respectively. The melting process as shown from the endothermal signal in the DSC trace indicates that the multi-component alloy is deviation from the eutectic point. The melting temperature T_m is determined to be 694 K. A rule of thumb has for many years been proposed by Turnbull: the reduced glass transition temperature, $T_{rg} = T_g/T_m$ [10]. That is: good glass formers like the bulk metallic glasses require higher T_g/T_m. It is good empirical rule for finding new metallic glass system [8]. However, the T_g and T_m itself is not correlated with glass forming ability at least in bulk glass forming systems. The reduced glass transition temperature T_{rg} of this alloy is 0.56. For comparison, thermal parameters of other typical BMGs [8,11,12] are listed in Table 1. The larger value of T_{rg} the alloy demonstrating the excellent glass forming ability of the alloy [10]. Compared with other typical BMGs, the $La_{60}Cu_{20}Ni_{10}Al_{10}$ BMG does have excellent glass forming ability and much lower T_g. The BMG which is comparable to a hard-sphere system is an ideal alloy to investigate the nature of glass transition as well as the relaxation and nucleation with a large experimentally accessible time and temperature window at very low temperature region [13–15]. On the other hand, intensive efforts have been carried out over the past decade to investigate the magnetic rare-earth based BMGs [16–18], because of the significance of the BMGs in science and application. The nonmagnetic rare-earth based BMG is important for studying, comparing and understanding the properties in rare-earth based BMGs.

Fig. 2 shows the temperature-dependent electrical resistivity of the BMG in the temperature range of 1.8–300 K. The BMG exhibits a negative temperature coefficient in the temperature range of 7 K and 300 K. The inset in Fig. 2 shows the electrical resistivity suddenly drops to zero at 2.5 K, indicating that superconductivity

Table 1
Thermodynamic parameters of $La_{60}Cu_{20}Ni_{10}Al_{10}$ and other typical BMGs [8,15–18]

BMGs	T_g (K)	T_{x1} (K)	ΔT	T_m (K)	T_{rg}
$La_{60}Cu_{20}Ni_{10}Al_{10}$	387	447	60	694	0.56
$Nd_{60}Cu_{20}Ni_{10}Al_{10}$	438	478	40	728	0.60
$Pr_{60}Cu_{20}Ni_{10}Al_{10}$	413	461	48	708	0.58
$Zr_{41}Ti_{14}Cu_{12.5}Ni_{10}Be_{22.5}$	623	680	57	941	0.66
$Pd_{40}Ni_{10}Cu_{30}P_{20}$	582	718	95	804	0.72

The DSC heating rate is 20 K/min.

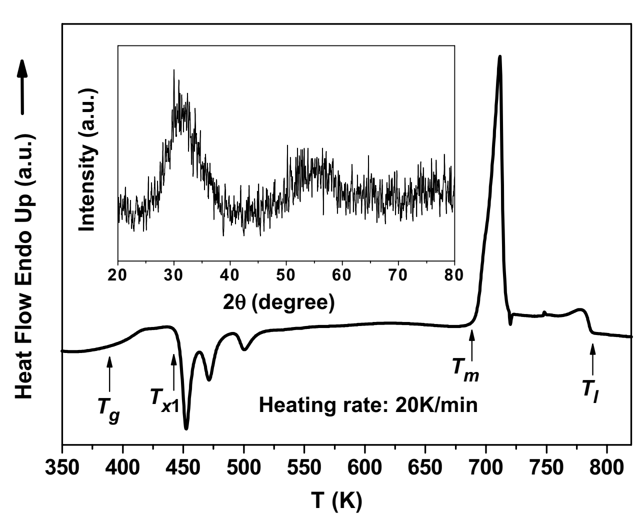

Fig. 1. The DSC trace of the $La_{60}Cu_{20}Ni_{10}Al_{10}$ sample exhibiting the glass transition, crystallization and the melting process. The inset is the XRD pattern for the $La_{60}Cu_{20}Ni_{10}Al_{10}$ alloy.

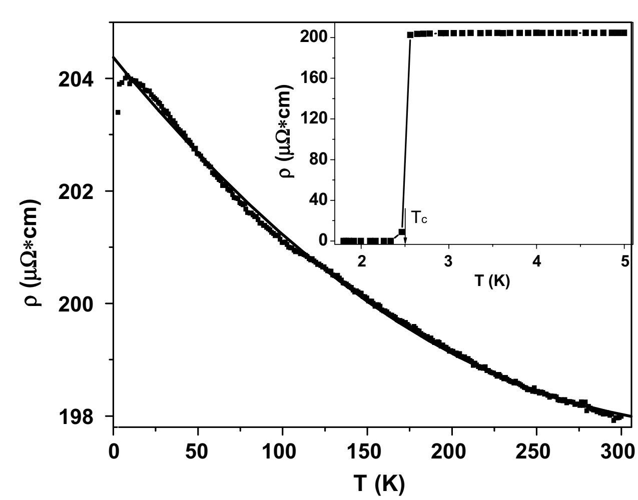

Fig. 2. The temperature dependence of the electrical resistivity. The line is the fitting result by the expression $\rho = \rho_0 + aT + bT^2$ at the temperature range of 20–300 K. The inset shows the superconductivity of the $La_{60}Cu_{20}Ni_{10}Al_{10}$ BMG at 2.5 K.

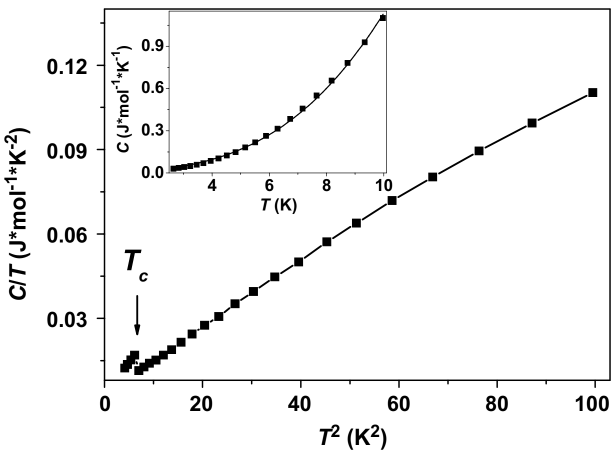

Fig. 3. The temperature dependence of the specific heat of the $La_{60}Cu_{20}Ni_{10}Al_{10}$ BMG shown as C/T versus T^2. The inset is the fitting of the specific heat of the normal state BMG between 2.5 K and 10 K by the expression: $C = \gamma T + \beta T^3$.

onset at the temperature 2.5 K as indicated in the inset of Fig. 2. Based on the generalized Faber–Ziman theory [19,20] and the Mott s–d scattering model [21], the experimental data of the resistivity in the high temperature range from 20 K to 300 K, can be least-squares fitted with the expression: $\rho = \rho_0 + aT + bT^2$, where ρ_0 is the residual resistivity, the T term depends the change of the structure factor by the generalized Faber–Ziman theory, and the T^2 term originates from the Mott s–d scattering. From the fit as shown in solid curve in Fig. 2, we get: $\rho_0 = 204.38(\pm 2)$ μΩ cm, $a = -3.67 \times 10^{-2}(\pm 2)$ μΩ cm K^{-1}, $b = 5.19 \times 10^{-5}(\pm 7)$ μΩ cm K^{-2}.

Fig. 3 shows the temperature-dependent specific heat C/T versus T^2 of the BMG between 2 K and 10 K. The superconducting transition of the BMG can also be clearly seen by the jump ΔC (=0.0117 J mol^{-1} K^{-1}) in the heat capacity curve at the critical temperature 2.5 K. To get the superconductive correlated parameters, the specific heat is fitted by the Debye model. The solid line in Fig. 3 is the result of the least-squares fitting from 2.5 K to 10 K by the expression: $C = \gamma T + \beta T^3$, where γ is the electronic specific heat coefficient associated with the electronic density of the states at the Fermi energy; $\beta = \frac{12\pi^4 R}{5}\frac{1}{\theta_D^3}$ [22], is the phonon specific heat coefficient related to the limiting Debye temperature, θ_D, R is the gas constant. The fitting results are: $\gamma = 0.0070(\pm 1)$ J mol^{-1} K^{-2}; $\beta = 0.00107(\pm 1)$ J mol^{-1} K^{-4}. The value of θ_D is derived to be 122.0 K. The Mcmillan equations [23], $\lambda = \frac{1.04+\mu^* \ln(\theta_D/1.45T_c)}{(1-0.62\mu^*)\ln(\theta_D/1.45T_c)-1.04}$ (μ^* is assumed to be 0.13 here), which is commonly accepted for T_c calculation, provides a way to estimate the electron–phonon interaction parameter λ by θ_D and T_c. The obtained amplitude of $\lambda = 0.68$ indicates that the BMG is an intermediate coupling superconductor. The corresponding decrease of the specific heat at T_c, $\Delta C/\gamma T_c = 0.67$, which is not agreement with that of other weak or intermediate coupling metallic superconductive glasses [24], is somewhat lower than the BCS value 1.43.

The value of the density of states at the Fermi level for intermediate coupling metallic glass is enhanced by the electron phonon interaction. This enhancement can be described by the factor $1 + \lambda$. So following the free-electron model: $\gamma = (1 + \lambda)\pi^2 k_B^2 N_b(E_F)/3$, where k_B is the Boltzmann's constant. The $N_b(E_F)$, which is band structure or bare density of electron states at the Fermi level can be estimated to be 1.75 eV^{-1} at.$^{-1}$ for the BMG, which is in agreement with that of other metallic glasses [2,3].

In conclusion, the nonmagnetic rare-earth based superconductive $La_{60}Cu_{20}Ni_{10}Al_{10}$ glass is obtained. The superconductive transition occurs at the critical temperature of 2.5 K. The density of states at Fermi level, the electron–phonon interaction parameter and the Debye temperature are determined to be 1.75 eV^{-1} at.$^{-1}$, 0.68, 122 K, respectively. The amplitude of λ indicates that the BMG is an intermediate coupling superconductor. The BMG with highly glass forming ability, a large supercooled liquid region and a low transition temperature offers an ideal material to study some basic issues of material science and condensed matter physics.

Acknowledgments

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