Viscoelasticity of Cu- and La-based bulk metallic glasses: Interpretation based on the quasi-point defects theory

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Submitted to *Materials Science & Engineering A*

(Version: January 29, 2018)

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Accepted for publication in Materials Science and Engineering A, February 2018

Abstract

The dynamic mechanical relaxation of metallic glasses is closely associated with the physical and mechanical properties. In the current work, the dynamic mechanical relaxation behaviors of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses are investigated by mechanical spectroscopy. In general, metallic glasses display two relaxation modes: main (α) relaxation and the slow secondary (β) relaxation. The α relaxation is linked to the dynamic glass transition phenomenon and viscous flow while the slow β relaxation is associated with many fundamental issues, such as diffusion and glass transition phenomenon. The experimental study shows $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glass displays a noticeable slow β relaxation. Contrarily, the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass relaxation process takes the form of an "excess wing". In the framework of quasi-point defects (QPD) theory, the dynamic mechanical response of the metallic glasses is discussed.

Keywords: Metallic glass; Viscoelasticity; Dynamic mechanical analysis; Mechanical relaxation; Quasi-point defect theory.

1. Introduction

Application of constant stress on a glass induces creep through three simultaneous deformation mechanisms: elastic, viscoelastic and viscoplastic. Due to its metastable state, the viscoelastic properties are one of the key concerns in glass-forming liquids. Metallic glasses, also called amorphous alloys, have been attracting tremendous research interest due to their specific combination of structural and functional properties, such as superb strength, high elastic limit, excellent thermoplastic formability, good corrosion resistance, and superior biocompatibility [1-5].

The understanding of the viscoelastic behavior of metallic glasses is very important for both the fundamental research and engineering application. Mechanical spectroscopy or dynamic mechanical analysis (DMA) is a powerful tool to investigate the viscoelastic behavior and dynamic mechanical relaxations of metallic glasses and metallic glass matrix composite [6-10]. Interestingly, metallic glasses show two relaxation kinetics processes, which are called main relaxation (α relaxation) and secondary relaxation (β relaxation) [11, 12]. On the one hand, it is widely accepted that α relaxation is connected with the dynamic glass transition and the viscous flow behavior, which corresponds to the cooperative atomic movements. On the other hand, the β relaxation is closely related to local atomic motion, which appears at lower temperature or higher frequency [13-15]. It has been regarded that the β relaxation acts as a precursor of the main α relaxation [7, 14, 16-19]. Many investigations proved that the β relaxation process is closely linked to internal physical and mechanical properties of metallic glasses [6-8, 14, 20]. However, the physical mechanism and nature of mechanical relaxation in metallic glasses is still unclear and requires further study.

Here we analyze the dynamic mechanical response of two archetypal metallic glasses. $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses were investigated by mechanical spectroscopy. We found that compared with the $Cu_{46}Zr_{45}Al_7Y_2$ metallic glass, $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ metallic glass displays an evident β relaxation below glass transition temperature T_g. The observed dynamic mechanical relaxation behaviors are analyzed within the framework of the quasi-point defect theory. It is found that the experimental results are in good agreement with the predictions of the quasi-point defect theory.

2. Experimental procedure

$Cu_{46}Zr_{45}Al_7Y_2$ (at.%) and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10})$ (at.%) bulk metallic glasses were chosen as model alloys due to their high glass forming ability (GFA) and excellent thermal stability [21, 22]. The metallic glasses were prepared by copper mold suction casting technique in a melting equipment under purified argon atmosphere. All the ingots of model alloys were re-melted at least 5 times to keep chemical homogeneity.

The amorphous nature at ambient temperature of the Cu- and La-based bulk metallic glasses was tested by X-ray diffraction (XRD), using Cu Kα radiation produced in a commercial device (XRD, Philips PW3830). The thermal stability of the metallic glasses was examined by differential scanning calorimetry (DSC, Netzsch DSC 200F3) at a constant heating rate of 3 K/min. The thermal parameters, such as glass transition temperature T_g, crystallization onset temperature T_x and super-cooled liquid temperature range (ΔT, $\Delta T=T_x-T_g$) were obtained based on the experimental results.

Mechanical spectroscopy or dynamic mechanical analysis was used to study the bulk properties (i.e., modulus, compliance, internal friction) of materials. In the current research, dynamic mechanical behavior of the metallic glasses was studied by commercial dynamic mechanical analysis (DMA, TA Q800) and an inverted torsion pendulum for internal friction measurements (homemade apparatus in INSA de Lyon, France). The dynamic mechanical relaxation behavior of the metallic glasses have been described in the previous literature [23]. When the sinusoidal stress $\sigma=\sigma_0\sin(\omega t)$ (σ_0 is the initial stress, ω is the angular frequency and $\omega=2\pi f$, where f is the driving frequency) is applied to the sample, the strain in the materials can be measured. The mechanical response of the sample is $E=\sigma/\varepsilon$, which consists in two parts: the storage modulus E' and the loss modulus E''.Similarly it is also define shear storage and loss moduli during the deformation as G' and G''. The phase lag δ between the applied stress and the recorded strain depends on the material, frequency and temperature. While elastic materials show no phase lag ($\delta = 0$), positive phase lags are due to the viscoelastic behavior during the deformation.

According to deformation modes of the instrument, in complex notation, on the one hand, for the DMA Q800 (measured at single cantilever bending model), one can write the complex modulus $E^* = E' + iE''$, where E^* is the complex modulus. On the other hand, for the inverted torsion pendulum apparatus (tested at torsion model), the complex shear modulus $G^* = G' + iG''$, where G^* is the complex shear modulus. As a consequence, the loss factor (also called internal friction) or mechanical damping $\tan\delta = \frac{E''}{E'} = \frac{G''}{G'} = \frac{1}{2\pi}\frac{\Delta W}{W}$ is also determined. It needs to be mentioned that the energy loss (ΔW) induced during one loading cycle, which reveals the atomic or molecular mobility, is then directly connected to the phase lag δ.

The dimension of experimental samples for the DMA TA Q800 and the inverted torsion pendulum testing is around 30 mm (length) ×3mm (width) ×1mm (thickness). Experiments were carried out in two modes: (I) Isochronal measurements were performed in DMA TA Q800 at a constant heating rate of 3 K/min with a different driving frequencies (i.e., 1, 2, 4, 8 and16 Hz). (II) Isothermal tests were carried out at the inverted torsion pendulum under frequency ranges from 10^{-2} to 2 Hz.

3. Experimental results

3.1 XRD analysis and thermal properties of the metallic glasses

Fig. 1 shows XRD patterns of the $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses. The XRD patterns display the typical profile of glassy materials, with no detectable sharp Bragg peaks, which indicates that the whole volume of the metallic glass samples is in amorphous state. The thermal properties of the studied bulk metallic glasses were investigated by the DSC technique at a constant heating rate of 3 K/min. The corresponding DSC curves are shown in **Fig.2** and the glass transition temperatures (T_g) and the onset temperature of crystallization (T_x) are defined. The characteristic temperatures T_g and T_x of the two studied alloys are listed in **Table1**. The current DSC results are in excellent agreement with previously reports [21, 22].

3.2 Dynamic mechanical properties of the bulk metallic glasses

3.2.1 Isochronal testing

The dynamic mechanical analyzer plays an important role in studying the viscoelastic response of materials. **Fig. 3** shows the storage modulus E' and the loss modulus E'' of the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass (as-cast state) with increasing testing temperature at a fixed driving frequency of 1Hz and heating rate of 3K/min. For temperatures up to about 660K, the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass exhibits mainly elastic deformation with a low loss modulus. As the temperature continues to increase, the storage modulus E' decreases dramatically. In parallel, the loss modulus E'' reaches a maximum. In this temperature range, the deformation mainly corresponds to the large viscoelastic component. This phenomenon corresponds to the occurrence of α relaxation of the metallic glass. Similar phenomenon has been widely observed for other glassy materials, such as polymers, oxide glasses and metallic glass matrix composites [9, 24]. At even higher temperatures, the storage modulus rises again while the loss modulus starts to decrease, which corresponds to a complex procedure of crystallization.

Fig. 4 shows the temperature dependence of the normalized loss modulus at different frequencies at a heating rate of 3 K/min for the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass. (E_u is the unrelaxed modulus which can be represented by E' at room temperature). It can be noted that the peak of the loss modulus decreases and the corresponding peak temperature increases as the driving frequency increases.

The temperature of loss modulus peak increases along with the increase of the driving frequency. This dependence is well described by Arrhenius equation

$$\omega_{max}=\omega_0\exp(-E_\alpha/kT) \qquad (1)$$

which describes the temperature dependence of thermally activated reaction rates as a function of the energy of activation. ω_{max} is the characteristic frequency, which is linked to the maximum of the relaxation. ω_0 is the pre-exponential factor, E_α is the activation energy of the α relaxation in glassy materials. The logarithm of the equation (1) yields to

$$\ln(\omega_{max}) = -E_\alpha/kT + \ln\omega_0 \qquad (2)$$

On the basis of the equation (2), we obtained that the apparent activation energy E_α of the main α relaxation of the $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$) metallic glass is 5.56 eV and 3.27 eV, respectively. It should be noted that the current results are in good agreement with the previously work [25-27]. In the case of the metallic glasses, it is well-known that the activation energy of the slow β relaxation is around 1-1.5 eV [8, 28, 29].

It has been proven that the slow β relaxation in metallic glass depends on the chemical composition [28]. **Fig. 5** illustrates the difference in the slow β relaxation between the $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses. Compared to Cu-based metallic glass, it is worth noting that La-based metallic glass displays a pronounced slow β relaxation (shoulder) at lower temperature. However, the Cu-based metallic glass does not exhibit an obvious slow β relaxation. As a result, these two different kinds of the slow β relaxation will affect the mechanical properties. The reason of the appearance of the slow β relaxation is that the metallic glass under room temperature is metastable and the atoms of the glassy alloy are in “frozen” state. When the temperature rises but it is still well below the glass transition temperature T_g, the “frozen” atoms will absorb some amount of energy, displaying the slow β relaxation on the temperature dependence profile of the normalized loss modulus.

The atomic origin of the distinct behavior of the β relaxation in the two studied alloys is yet not understood. While it is generally accepted that β relaxation is due to string-like atomic rearrangements [30, 31]. It is not clear why these rearrangements are more probable in some alloys. According to Ref. [28] “*Pronounced β-relaxations are associated with systems where all the atomic pairs have large similar negative values of enthalpy of mixing, while positive values, or large fluctuations in the values, of enthalpy of mixing suppress β-relaxations*”. It must be noted that neither $Cu_{46}Zr_{45}Al_7Y_2$ nor $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ show a pronounced β-relaxation. Table 2 shows the mixing enthalpies according to the Miedema’s model [32, 33] . Using this model, the average mixing enthalpy and standard deviation of $Cu_{46}Zr_{45}Al_7Y_2$ are -26.3 KJ/mol and 8.3 KJ/mol, while those of $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ is -27.2 KJ/mol and 8.9 KJ/mol. That is, there is no significant difference in the mixing enthalpies of both alloys. Thus, the more intense β-relaxation of $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ can be attributed to the enhanced mobility of the Ni/Co pairs in rare-earth based metallic glasses [34].

3.2.2 Isothermal testing

In order to properly understand the dynamic mechanical relaxations of the metallic glass, isothermal spectra was obtained at various temperatures. **Fig.6** shows the frequency evolution of the normalized storage modulus G'/G_u and loss modulus G''/G_u as a function of frequency for the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass at various temperatures. G_u is the non-relaxed modulus which is assumed by the storage modulus G' at ambient temperature. One can found that: (i) At constant temperature, the storage modulus decreases by decreasing the frequency while the loss modulus increases by decreasing the frequency; (2) At constant frequency (i.e. the isothermal testing temperature less than 700 K in the current work), the storage modulus decreases by increasing temperature while the loss modulus increases by increasing the temperature. These results are in good accordance with the previous investigations [35, 36]. It must be noted that the α relaxation peak can be only observed at high isothermal testing temperature or at the higher temperature (i.e. when the temperature above 700 K) in isochronal measurements.

With the help of the time-temperature superposition (TTS) principle, master curves of glassy materials can be determined by a simple horizontal shift (one temperature could be fixed as a reference temperature T_f). **Fig.7** shows the master curve of the normalized storage modulus G'/G_u and loss modulus G''/G_u of the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass.

4. Discussion

4.1 Description of master curves by a stretched exponential function

It is well established in the literature that the main α relaxation process of the glassy materials can be well described with a Kohlrausch-Williams-Watts (KWW) relaxation function [37]:

$$G''(\omega) = \Delta G_\alpha \, L_{i\omega}\left[-\frac{d\varphi_\alpha(t,\tau_\alpha)}{dt}\right]$$
$$with \quad \varphi_\alpha(t,\tau_\alpha) = \exp\left[-(t/\tau_\alpha)^{\beta_{KWW}}\right] \tag{3}$$

where $L_{i\omega}$ indicates the Laplace transform, τ_α is the characteristic time of the α relaxation in glassy materials, φ_α is the so-called stretched exponential and the Kohlrausch exponent β_{KWW} ranges from 0 and 1 in glassy materials [38]. The relaxation strength is $\Delta G = G_u - G_r$, G_u the unrelaxed modulus and G_r the relaxed modulus. The value these exponents obtained from the fit of the isothermal spectra to the KWW function is β_{KWW}=0.546 in $Cu_{46}Zr_{45}Al_7Y_2$ metallic glass and β_{KWW}=0.456 in $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ metallic glass. Significantly, it is usually observed that the stretched exponent $\beta_{KWW}{\sim}0.5$ could be well described the master curve of bulk metallic glasses at the glass transition region, which is independent of the chemical composition and fragility [6, 39-41]. Interestingly, it should be noted that the Kohlrausch exponent β_{KWW} of La-based metallic glass is smaller that of Cu-based metallic glass; it may be concluded that the La-based metallic glass presents a wider distribution of relaxation times. This wider relaxation time maybe associated with the microstructural heterogeneity in metallic glasses.

4.2 Physical aging on the metallic glass below T_g

Physical aging (or structural relaxation below the glass transition temperature T_g) in metallic glasses is always linked to modifications of physical, mechanical properties and densities [42-45]. In order to study the influence of physical aging on the evolution on mechanical properties in the $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ and $Cu_{46}Zr_{45}Al_7Y_2$ metallic glasses, an *in-situ* DMA testing was carried out at 385 K for the La-based and 660 K for the Cu-based metallic glasses. **Fig.9** shows the evolution of storage modulus, loss modulus and loss factor of the aging time for $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$

and $Cu_{46}Zr_{45}Al_7Y_2$ metallic glasses . It can be observed that physical aging induces an increase of the storage modulus and a decrease of the loss factor and loss modulus. The glassy material shifts to a more stable state during the physical aging process.

4.3 Quasi-point defects (QPD) theory

In order to establish the link between the dynamic mechanical properties of metallic glass and its microstructure, Perez *et al.* developed quasi-point defect theory based on the quasi-point defect (QPD) model, giving a framework to describe mechanical response of glassy materials [46-48]. Quasi-point defect theory proposes that glassy materials contain quasi-point or flow detects in nanoscale. It has been reported that amorphous materials show density fluctuations in the nanoscale, which corresponds to fluctuations of enthalpy and entropy. The existence of quasi-point defects can be verified by small angle Synchrotron X-ray scattering [49]. Thanks to these quasi-point defects, the atoms of the metallic glass can perform a cooperative motion, which leads to the relaxation behavior in the macroscopic scale. On the basis of the QPD theory, the characteristic relaxation time of relaxation of a glassy material can be denoted as

$$\tau_{relax} = t_0 \left(\frac{\tau_\beta}{t_0}\right)^{1/\chi} \tag{4}$$

where τ_{relax} is the mean time of a structural unit jumping over the distance equivalent to its dimension, t_0 is the time scale parameter, τ_β is the mean time of the thermally activated jump of a structural unit in glassy materials, which corresponds to the characteristic time of β relaxation, and χ is the correlation factor which is related to the quasi-point defect concentration (C_d) ranging from 0 (full order—perfect crystal) to 1 (full disorder—perfect gas) .

The loss factor tan δ of glassy materials at a high temperature and low frequency (low enough to avoid the resonating frequency) can be denoted as

$$\tan\delta = K_0(\omega\tau_{relax})^{-\chi} \tag{5}$$

In the framework of QPD theory, the evolution of the loss factor tanδ can be given as

$$\ln(\tan\delta) = -\frac{U_\beta}{kT} - \chi\ln\omega - \chi\ln(\tau^*) + \ln K_0 \tag{6}$$

here, $\tau^*$is the characteristic time associated with the β relaxation in glass, $\tau^* =$

$t_0\left(\frac{\tau_{0\beta}}{t_0}\right)^{1/\chi}$. U_β is the apparent activation energy of the β relaxation.

According to eq. (6), for a fixed temperature ln(tanδ) varies linearly with ln ω, and the slope of this linear relation is χ. **Fig. 10 (a)** shows the variation of ln (tan δ) versus frequency of the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass at various temperatures (the data obtained in the inverse torsion pendulum). Note that the proposed linear relationship between ln(tanδ) and ln ω holds over 5 decades, showing that the experimental data can be well described by the QPD theory. **Fig. 10 (b)** shows the evolution of the correlation factor χ with temperature in the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass. The behavior of the correlation factor χ is clearly correlated to the state of the glass. While χ remains almost constant below the glass transition temperature, it increases above T_g. According to the QPD model, below the glass transition temperature T_g the glassy system stays in an iso-configurational state. Thus, the correlation factor χ is independent of the temperature. On the contrary, above the glass transition temperature T_g the main α relaxation process, associated with the cooperative atomic motion, is activated. Thus, the correlation factor χ increases by increasing the temperature.

Fig. 11 shows the loss tan δ and the correlation factor χ as a function of temperature in $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glass. It should be noted that the change in the behavior of the correlation factor χ shows clearly the intensity of the slow β relaxation. It should be stressed that the quasi-point defect model is able to describe the main relaxation for glass-forming liquids. However, it fails when the slow β relaxation is noticeable. According to the **Fig.11**, tendency of the correlation factor with the temperature in $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ metallic glass shows a very similar result than that of the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass. It is found that the theoretical prediction of QPD is fulfilled in the $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass.

5. Conclusion

In the current research, the dynamic mechanical properties of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses were investigated by mechanical spectroscopy. The main results are listed as follows:

● $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glass shows an obvious slow β relaxation while $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass presents an "excess wing" relaxation process.

● Physical aging leads to an increase of the storage modulus and a decrease of the loss modulus and loss factor in metallic glasses.

● The dynamic mechanical response of the metallic glasses is discussed on the basis on the quasi-point defects theory. In good agreement with the QPD theory, the state of metallic glasses is well described by the correlation factor χ. χ describes properly the "defect" concentration, which remains constant below the glass transition temperature and increases above it.

Acknowledgement

This work is supported by the NSFC (Grant Nos. 51611130120, 11772257 and 11572249), the Fundamental Research Funds for the Central Universities (No. 3102017HQZZ012), the Natural Science Foundation of Shaanxi Province (No. 2016JM5009), the Aeronautical Science Foundation of China (2015ZF53072), the Astronautics Supporting Technology Foundation of China, the fund of the State Key Laboratory of Solidification Processing in NWPU (Grant No. SKLSP201608), Shaanxi Province Postdoctoral Scientific Research Projects and the Ministry of Education and Science of the Russian Federation under the project 3.1310.2017/4.6. D.C. acknowledges the support from MINECO projects FIS2014-54734-P and PCIN-2016-027.

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Table 1 Characteristic temperatures of the $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ metallic glasses

Chemical composition	T_g(K)	T_g^{onset}(K)	T_g^{end}(K)	T_x(K)
$Cu_{46}Zr_{45}Al_7Y_2$	698	685	710	761
$La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$	414	403	424	458

Table 2 Enthalpies of mixing (kJ/mol) of the constituting elements according to Miedemas' model (Ref.[32, 33]).

Element	Co	Ni	Cu	Y	Zr	Ag	La
Al	-19	-22	-8	-38	-44	-4	-38
Co		0	6	-21	-41	19	-17
Ni			4	-31	-49	15	-27
Cu				-22	-23	2	-21
Y					9	-29	0
Zr						-21	13
Ag							-29

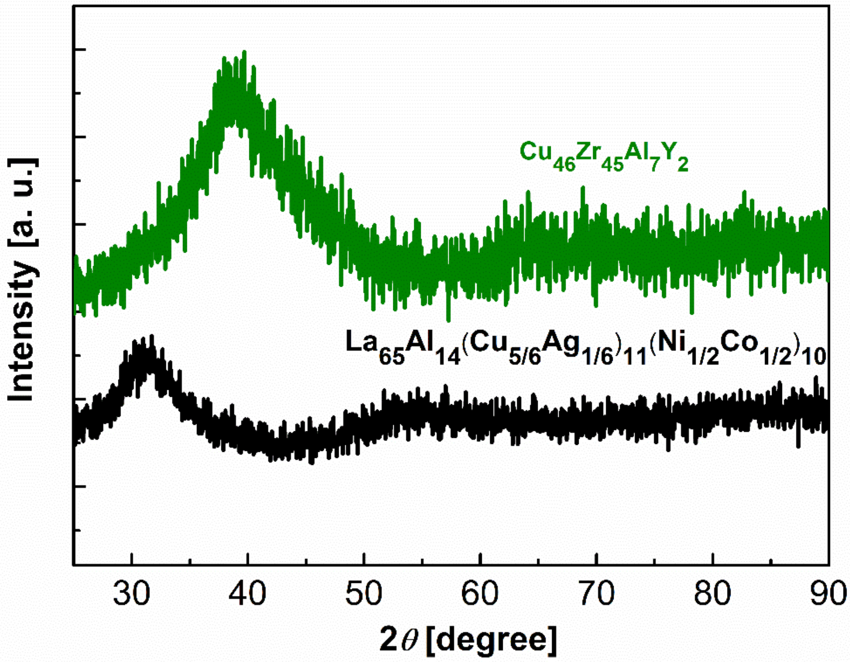

Fig. 1. XRD patterns of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses.

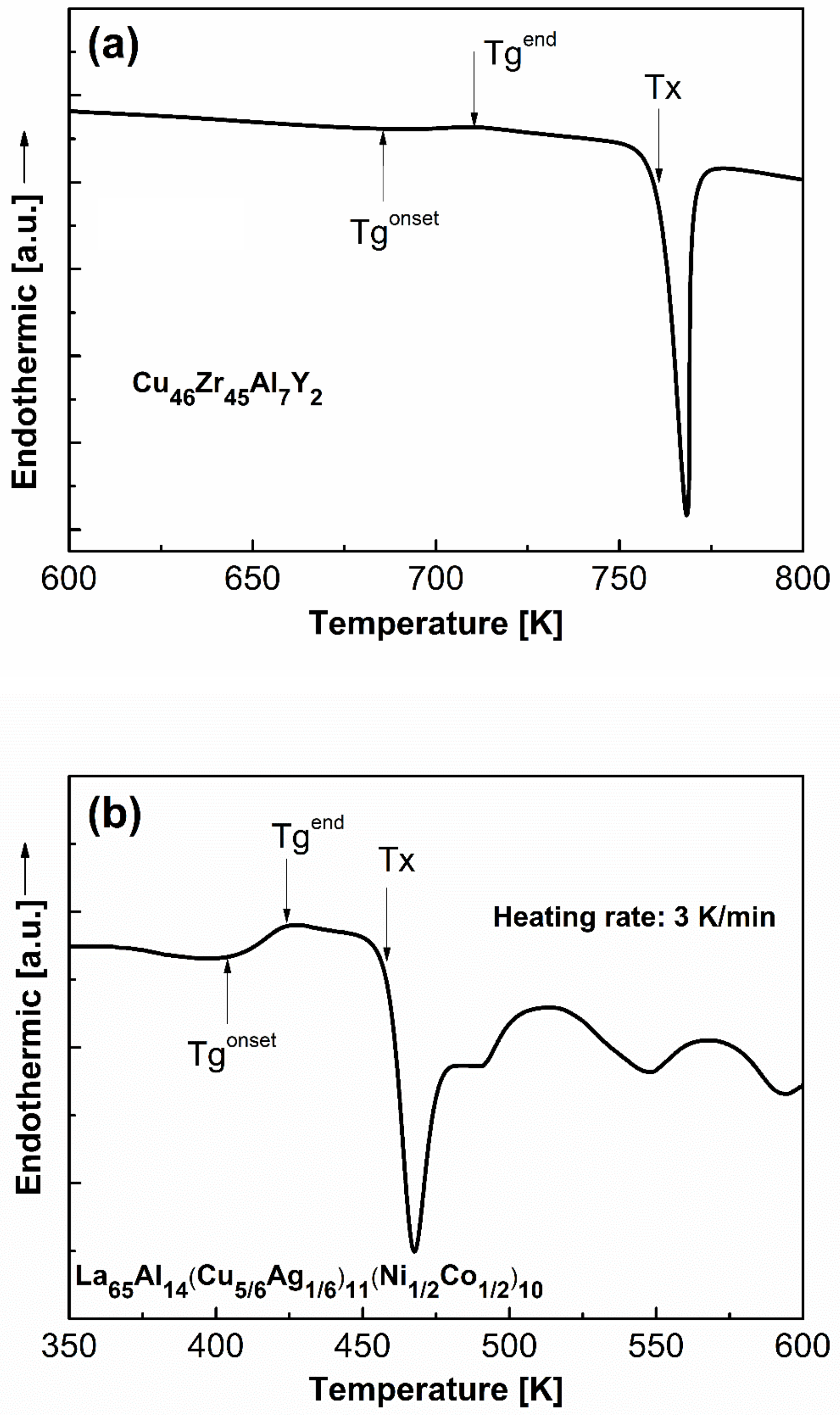

Fig. 2. DSC curves of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses (heating rate is 3 K/min).

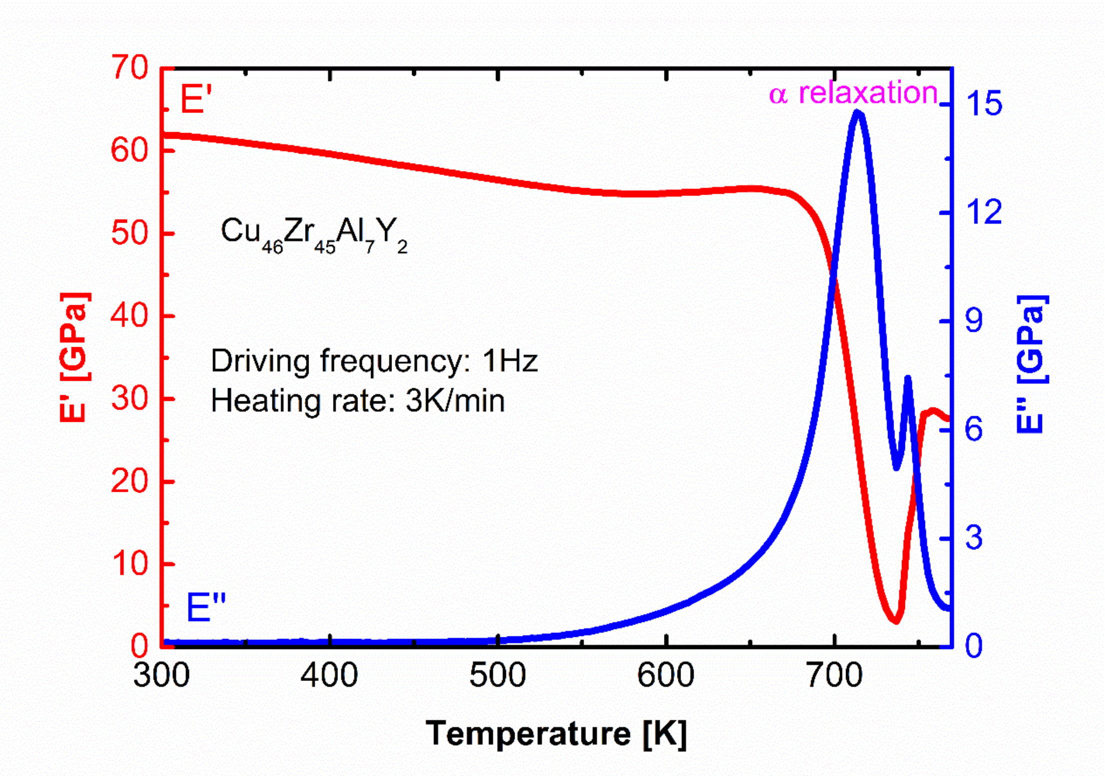

Fig. 3. Evolution of storage (*E'*) and loss (*E''*) moduli of $Cu_{46}Zr_{45}Al_7Y_2$ metallic glass (heating rate: 3 K/min, driving frequency: 1 Hz).

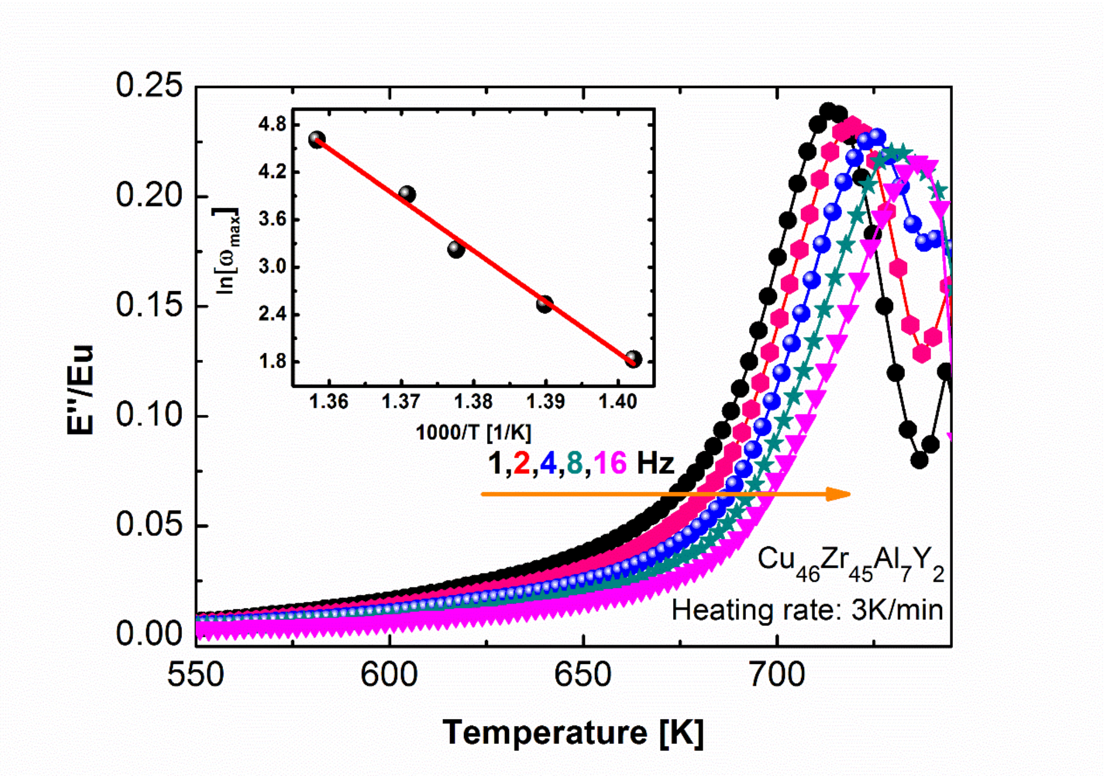

Fig. 4. Normalized loss modulus *E''*of $Cu_{46}Zr_{45}Al_7Y_2$ metallic glass as a function of temperature with different driving frequencies. Inset is the Arrhenius plot of ln(*f*) *vs* 1000/*T*. The activation energy E_α of the α relaxation is around 5.56 eV.

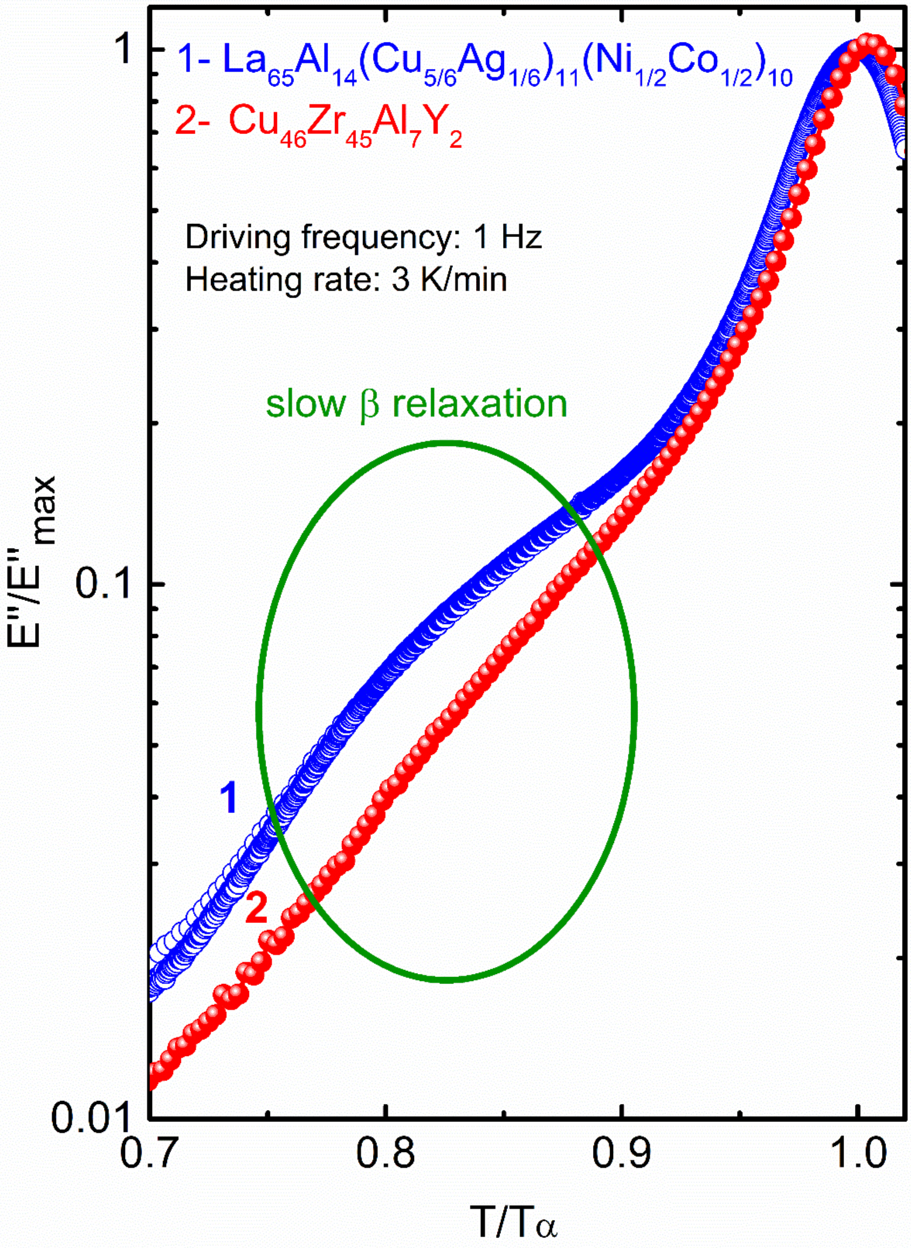

Fig.5. Temperature dependence of normalized loss modulus of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses (Driving frequency of 1Hz and heating rate of 3K/min).

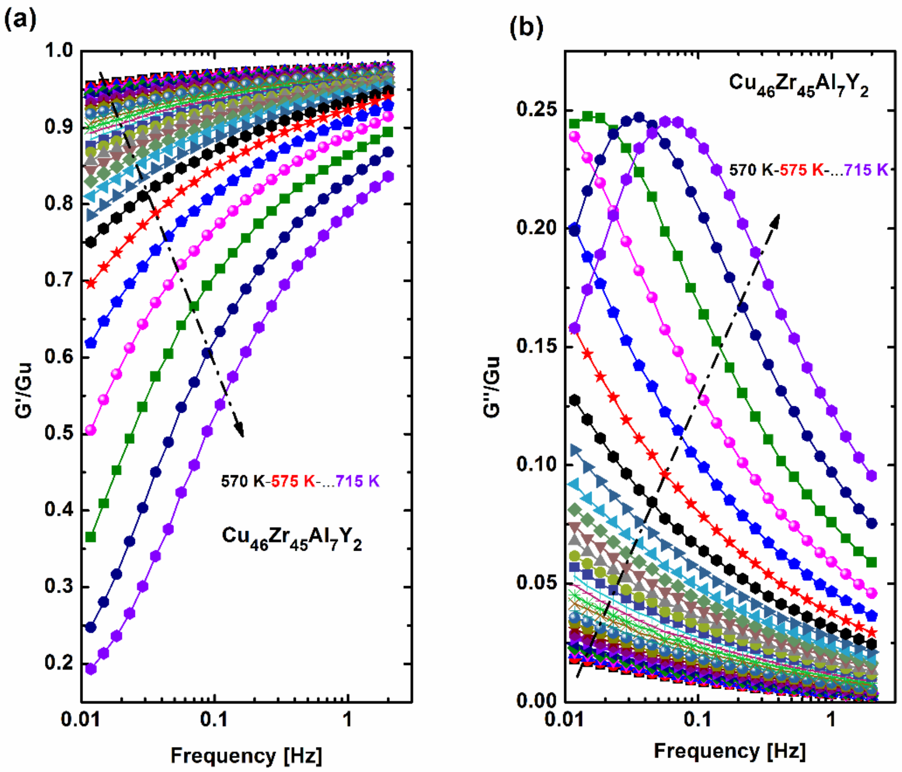

Fig. 6. Dependence of the normalized storage *G'/Gu* (a) and loss *G''/Gu* (b) moduli on frequency at various temperatures for $Cu_{46}Zr_{45}Al_7Y_2$ bulk metallic glass. Temperature ranges from 570 to 715 K on intervals of 5 K.

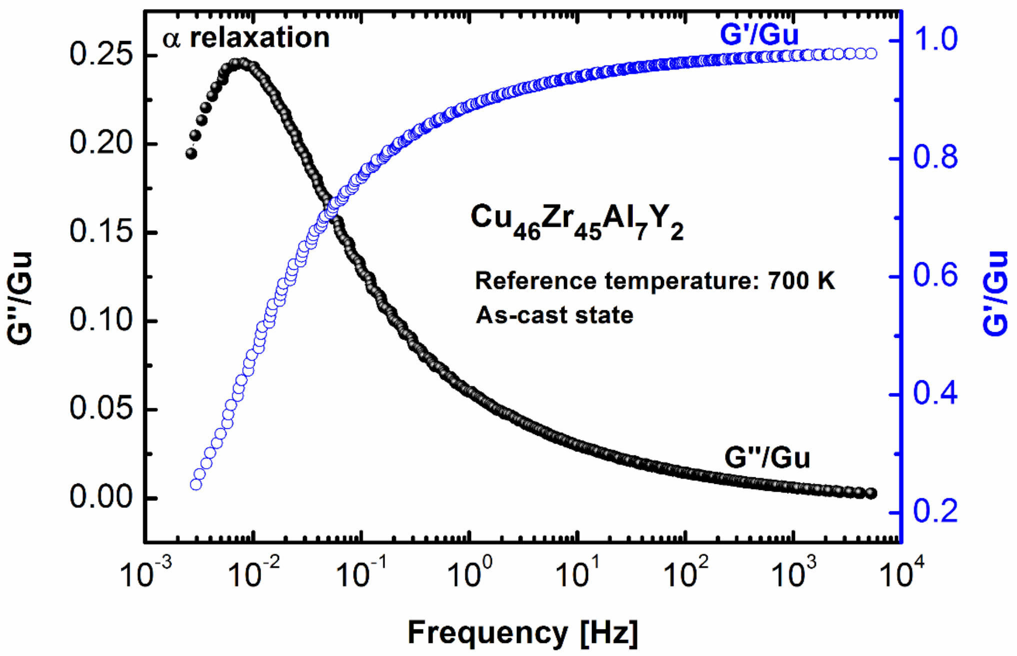

Fig.7. Master curve of the normalized storage modulus G'/G_u and the normalized loss modulus G''/G_u for $Cu_{46}Zr_{45}Al_7Y_2$ metallic glass. The reference temperature is 700 K.

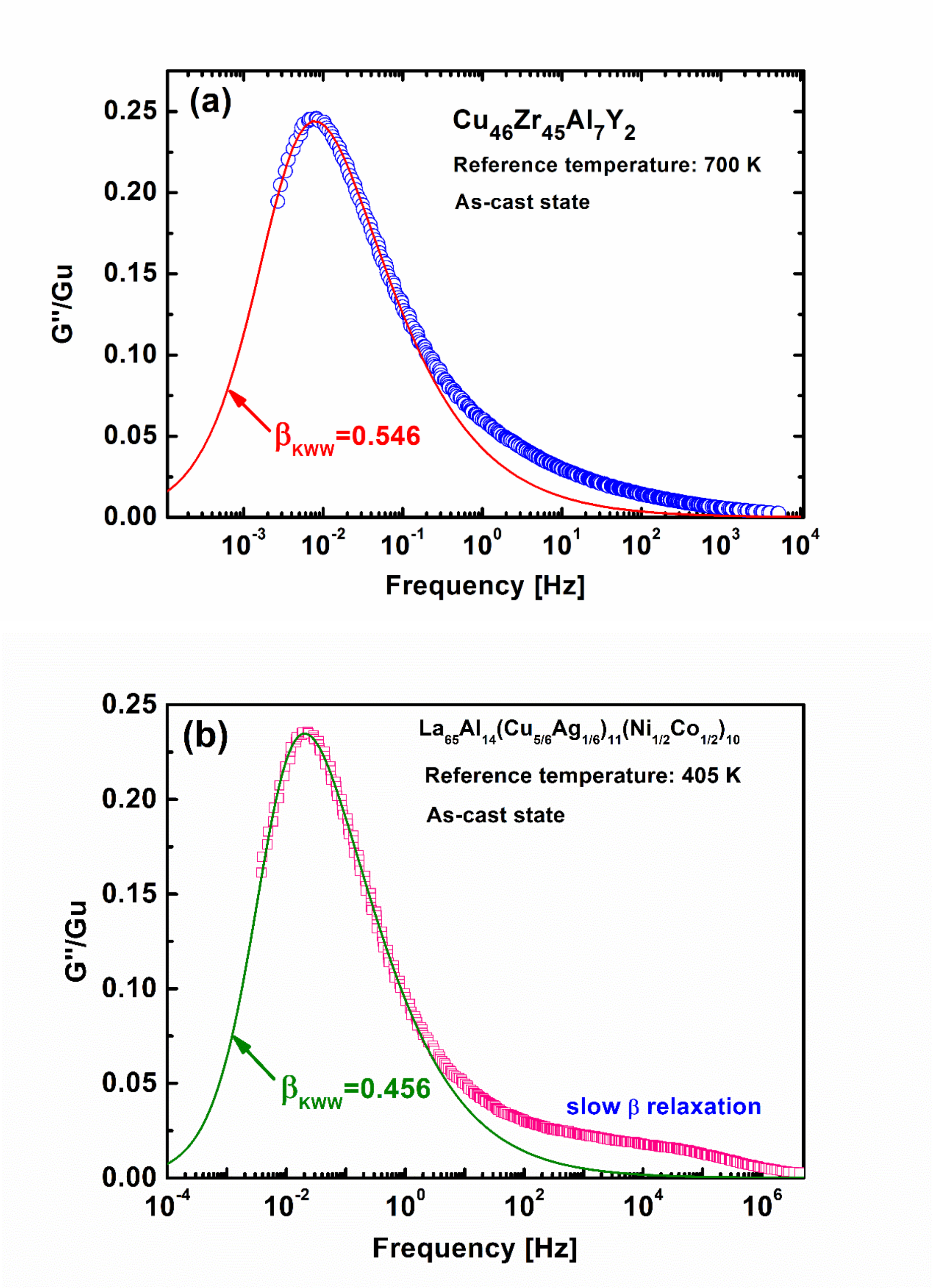

Fig. 8 Master curve of the normalized loss modulus G''/G_u of $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glasses, respectively. The solid lines are fitted by KWW equation (equation 3).

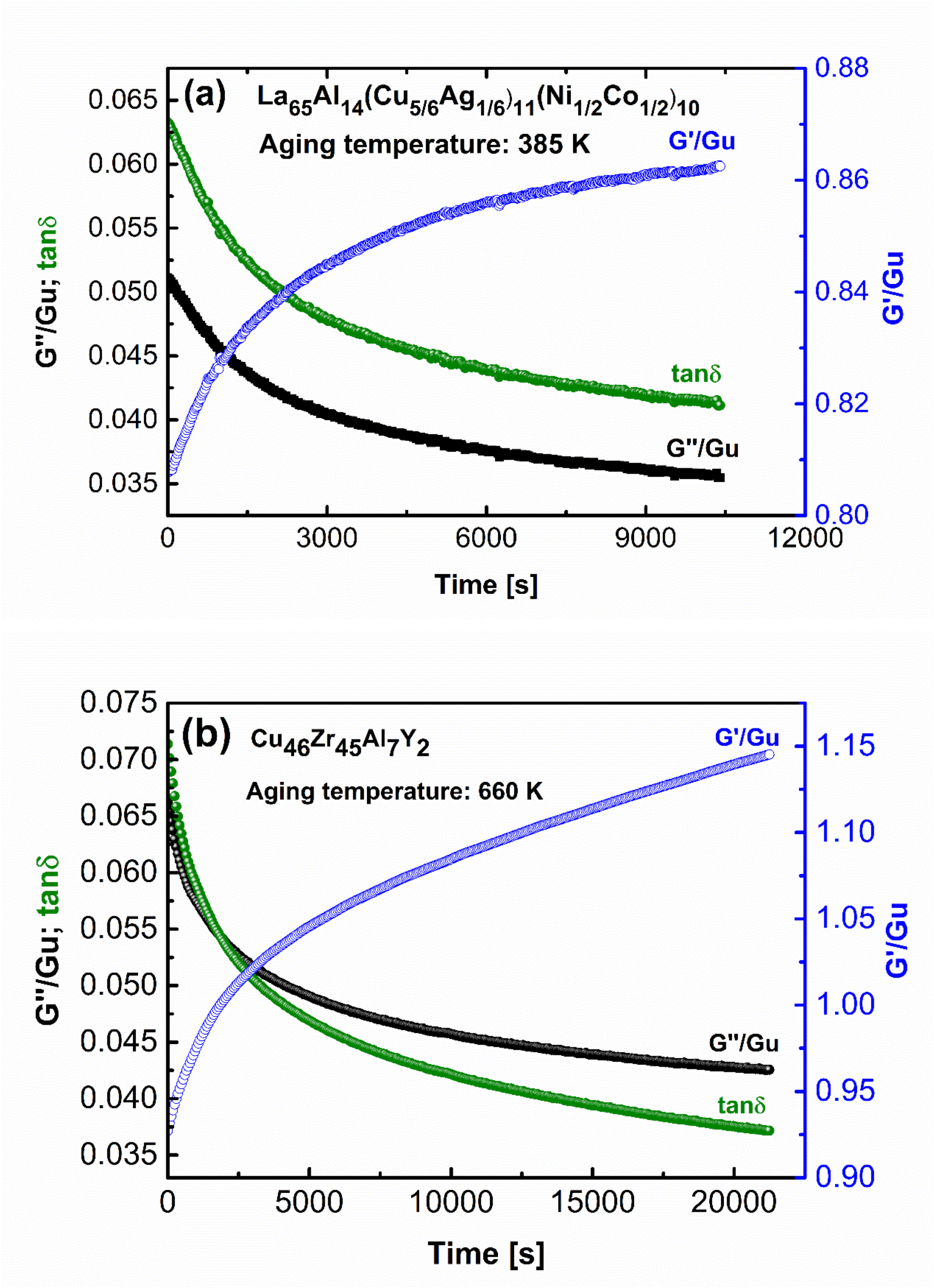

Fig. 9 The normalized storage modulus G'/Gu, loss modulus G″/Gu and loss factor tan δ in $Cu_{46}Zr_{45}Al_7Y_2$ and $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ metallic glasses as a function of annealing time at given aging temperatures (Driving frequency is 0.3 Hz).

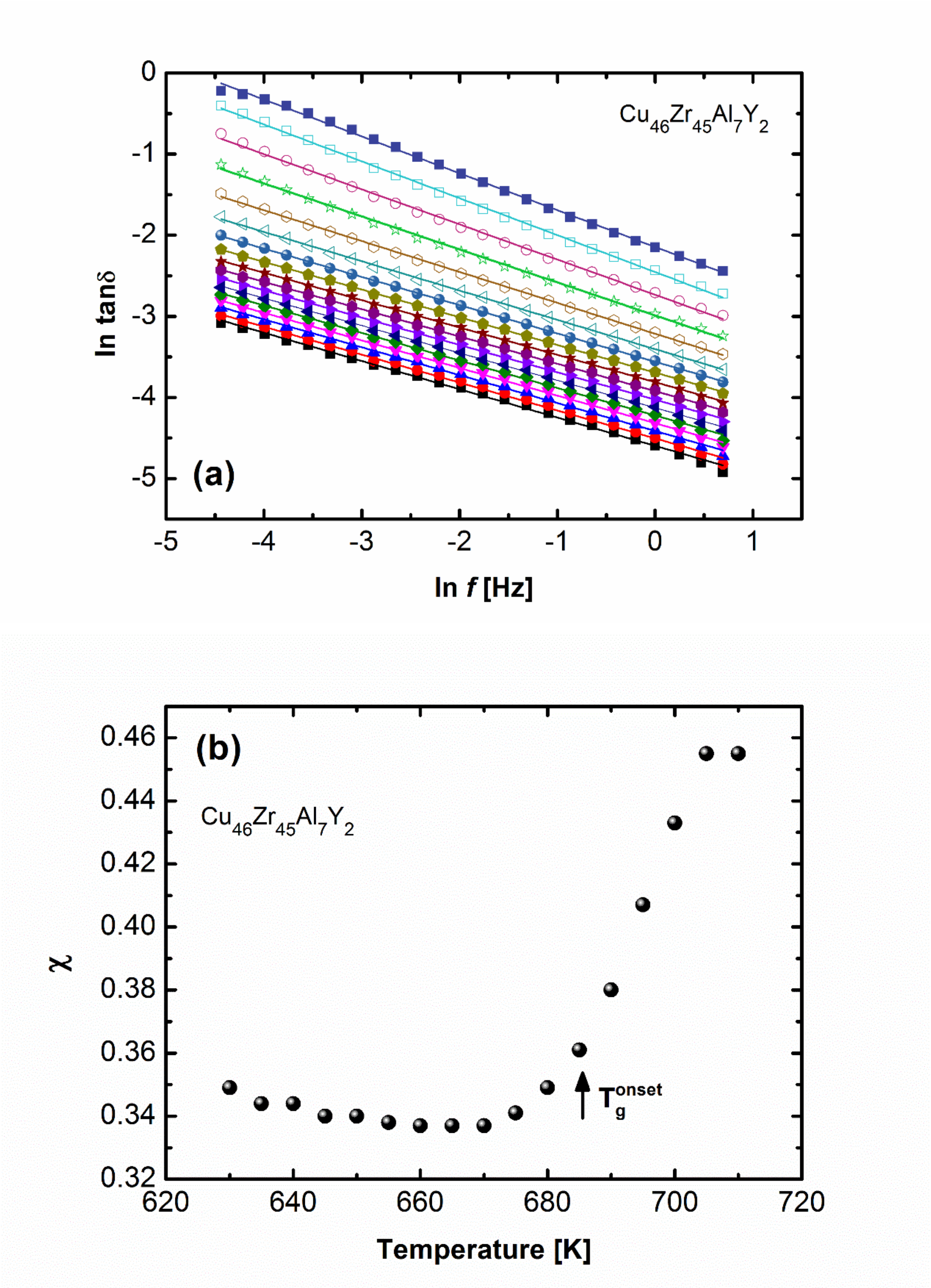

Fig. 10 (a) Influence of the driving frequency on the loss factor tanδ at different temperatures in Cu$_{46}$Zr$_{45}$Al$_7$Y$_2$ bulk metallic glass (the isothermal temperature ranges from 630 to 710 K, on an interval of 5 K). Solid lines are fitted by equation (6). **(b)** Evolution of the correlation factor χ with temperature.

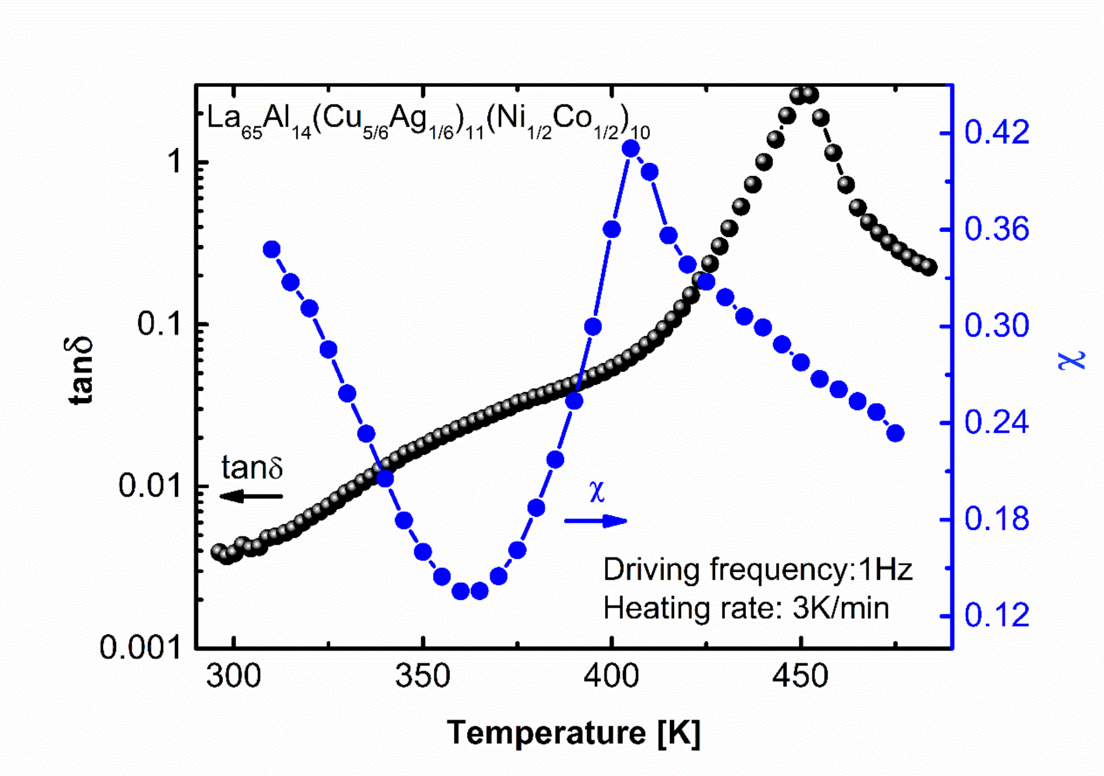

Fig. 11 Evolution of loss tan δ and correlation factor χ with temperature for $La_{65}Al_{14}(Cu_{5/6}Ag_{1/6})_{11}(Ni_{1/2}Co_{1/2})_{10}$ bulk metallic glass.