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Citation: Applied Physics Letters **107**, 241902 (2015); doi: 10.1063/1.4937458
View online: http://dx.doi.org/10.1063/1.4937458
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/107/24?ver=pdfcov
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Role of low melting point element Ga in pronounced β-relaxation behaviors in LaGa-based metallic glasses

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(Received 6 November 2015; accepted 26 November 2015; published online 14 December 2015)

In contrast to most metallic glasses (MGs) which exhibit weak β-relaxation peak in their dynamic mechanical spectra, the LaGa-based MGs we report here show a distinct β-relaxation peak with the ratio of β/α-relaxation peaks up to ~0.32 in the mechanical relaxation measurements. Moreover, the β-relaxation behavior can be tuned by modification of the chemical composition and the concentration of flow units. The effects of gallium and structural origin of the β-relaxation in the MGs have been discussed. The LaGa-based MGs with pronounced slow β-relaxation could provide a model system to investigate some underlying issues of the relaxation and plastic mechanism of MGs. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4937458]

The nature of relaxation in glass-forming liquid and glass is an important issue in condensed matter physics.[1,2] The relaxation behaviors of liquid and glass show two different motion modes: α-relaxation, which is a large scale atoms movement process; and β-relaxation (also called Johari-Goldstein relaxation[2]), which is local atoms motion and flow behavior.[1–7] The β-relaxation can be activated below glass transition temperature T_g while α-relaxation is frozen below T_g, which has practical significance to many features and properties of glassy solids.[8–11] The study on β-relaxation is an effective route to understand the nature of glass-forming liquid and glass and has strong correlation with some key issues in glass; further understanding of the structural and physical origins of the β-relaxation are critical for clarifying the nature of glass transition, the mechanical properties, plastic deformation mechanisms, and stability of metallic glasses (MGs).[6–13]

Previous studies on β-relaxation have been conducted in non-metallic glasses.[14–17] However, due to the complex intra-molecular effects in molecular and polymer glasses, it is still a debate in understanding the underling mechanism of β-relaxation.[16–19] In contrast, metallic glasses are considered as relatively simple glasses because their structures are close to the dense random packing of hard spheres.[20–22] Recently, the β-relaxation is found to be the intrinsic and universal feature in some metallic glasses.[6–9,18,19,23–25] The β-relaxation in different MGs exhibits various forms: peaks,[25–28] broad humps,[24] or excess wings[9] that will merge with the α-relaxation in dynamic mechanical spectra. Intensive investigations suggest that the β-relaxation has correlation with chemical bonding, atomic size disparity, atoms diffusion and flow behaviors of MGs.[18,19,23–27] However, the nature of β-relaxation is still a mystery. Besides, there are few MG systems show pronounced β-relaxations,[25–28] and this limits the experimental study and the understanding of the nature and origin of the β-relaxation.[29–31]

In this letter, we report the formation of a series of LaGa-based MG systems containing the element Ga with melting point near room temperature and negative volume change on fusion. Our study shows that the system has a pronounced β-relaxation peak in its dynamic spectrum. The effects of the composition on the evolution of the β-relaxation are investigated. We determine the activation energy of the β-relaxation in the MGs which further confirms the relationship between β-relaxation and the structural heterogeneity or the distribution of flow units in MGs. Through the variation of the Ga content, we get the implications for the structural information on the origin of the β-relaxation and the effect of Ga on the β-relaxation.

LaGa-based amorphous ribbons were obtained by the melt spinning technique. The glassy nature was identified by X-ray diffraction (XRD) with a Cu $K\alpha$ radiation source, and differential scanning calorimetry (DSC) at a heating rate of 20 K/min under a purified argon atmosphere in a Perkin-Elmer DSC8000. Dynamic mechanical measurements were performed using a dynamic mechanical analyzer (DMA) TAQ800 by tensile method for ribbons in a nitrogen-flushed atmosphere. The storage modulus E' and loss modulus E'' were measured by a temperature ramp mode at a heating rate of 3 K min^{-1}, a strain amplitude about 0.02%, and varied testing frequency f. The stress relaxation experiments were performed on DMA TAQ800 instrument in a nitrogen-flushed atmosphere at temperature of β-relaxation peak T_β with 0.4% strain. Before the experiment, 3 min delay was applied to allow the samples to equilibrate at test temperature.

Figure 1(a) shows the XRD patterns of four typical LaGa-based MGs. The broad diffraction peak without distinct sharp crystalline peaks in the XRD pattern indicates the amorphous nature of these alloys. The continuous DSC traces of these LaGa-based MGs focusing on the glass transition and crystallization behavior are shown in Fig. 1(b). The distinct glass transition and sharp crystallization peak in the DSC curves of LaGa-based MGs further confirm the glassy structure of alloys. The detail information of compositions and thermodynamic parameters like glass transition temperature T_g and the crystallization temperature T_x of LaGa-based MGs are shown in Table I. The metal gallium has very low

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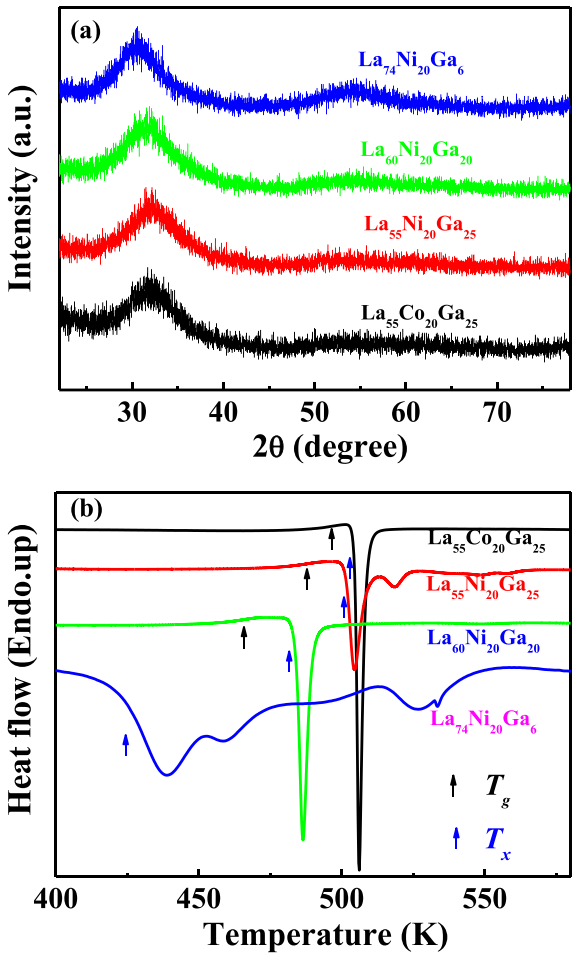

FIG. 1. (a) XRD patterns of $La_{55}Ni_{20}Ga_{25}$, $La_{55}Co_{20}Ga_{25}$, $La_{60}Ni_{20}Ga_{20}$, and $La_{74}Ni_{20}Ga_{6}$ four typical LaGa based MGs; (b) DSC traces focusing on glass transition and crystalline process of these four typical LaGa based MGs.

melting point very close to room temperature (302.8 K) which is one with lowest melting point among all solid elements in room temperature. The addition of over 25 at. % Ga does not significantly reduce the glass transition and crystallization temperatures of the LaGa-based MGs. Compared with $La_{60}Ni_{15}Al_{25}$, the glass transition temperature and the crystallization temperature of $La_{60}Ni_{15}Ga_{25}$ MG are just 18 K higher and 17 K lower than that of $La_{60}Ni_{15}Al_{25}$ MG, while the melting temperature of gallium is 630 K lower than aluminum.

TABLE I. Thermal properties, the peak temperatures of β-relaxation, strength of β-relaxation parameter E''/E''_α, and the enthalpy of mixing of LaGa-based MGs.

Composition	T_g (K)	T_x (K)	T_β (K)	E''/E''_α	ΔH^{mix} (kJ/mol)
$La_{55}Ni_{25}Ga_{20}$	463	498	353	0.141	−35.89
$La_{55}Ni_{20}Ga_{25}$	465	503	363	0.177	−37.43
$La_{55}Ni_{15}Ga_{30}$	…	510	383	0.319	−38.67
$La_{55}Co_{25}Ga_{20}$	471	492	383	0.138	−29.59
$La_{55}Co_{20}Ga_{25}$	490	505	394	0.189	−32.23
$La_{55}Co_{15}Ga_{30}$	…	520	394	0.246	−34.65
$La_{60}Ni_{20}Ga_{20}$	455	484	343	0.105	−35.04
$La_{60}Ni_{15}Ga_{25}$	473	490	350	0.183	−36.57
$La_{60}Ni_{10}Ga_{30}$	…	498	366	0.258	−37.8
$La_{74}Ni_{20}Ga_{6}$	…	422	313	0.189	−23.99
$La_{74}Ni_{18}Ga_{8}$	…	427	314	0.180	−24.96
$La_{74}Ni_{16}Ga_{10}$	…	432	314	0.211	−25.88

The behavior of β-relaxation in different MGs varies significantly. We define E''/E''_α (normalized E'', where E''_α is the maximum loss modulus of the α-relaxation peak) as a parameter to evaluate the strength of β-relaxation: the bigger value of the E''/E''_α, the stronger β-relaxation and vice versa. Figures 2(a)–2(c) present the temperature dependences of E''/E''_α at 1 Hz of $La_{55}Ni_{(15+x)}Ga_{(30-x)}$, $La_{55}Co_{(15+x)}Ga_{(30-x)}$, and $La_{(55+x)}Ni_{15}Ga_{(30-x)}$ MGs. We note that most MGs show excess wing or shoulder[6,24] instead of a well-defined peak in the E''/E''_α curves. Remarkably, the E''/E''_α curves of these

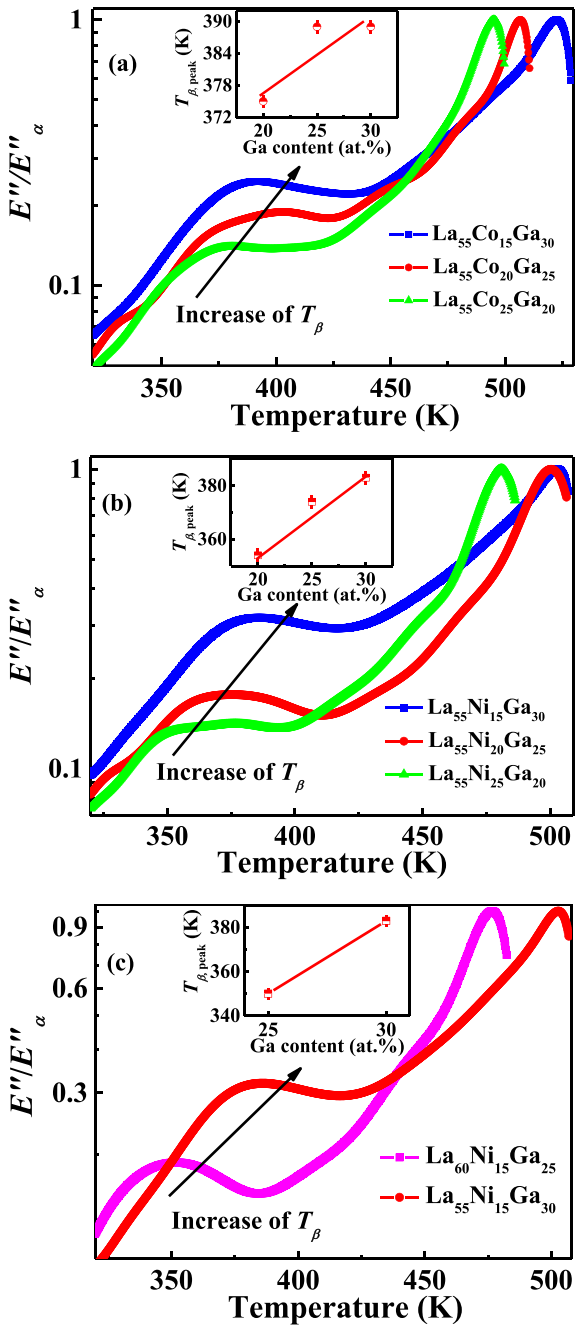

FIG. 2. Temperature dependences of normalized loss modulus E''/E''_α and β-relaxation behaviors at 1 Hz of the series of LaGa-based MGs: (a) $La_{55}Ni_{(15+x)}Ga_{(30-x)}$ MGs; (b) $La_{55}Co_{(15+x)}Ga_{(30-x)}$ MGs; (c) $La_{(55+x)}Ni_{15}Ga_{(30-x)}$ MGs. The inset figures show the temperature of β-relaxation peak $T_{\beta,peak}$ vs. content of Ga.

LaGa-based MGs show two distinct peaks: a α-relaxation peak and a pronounced β-relaxation peak. The insets of Figs. 2(a)–2(c) show the β-relaxation peak temperature dependence of $La_{55}Ni_{(15+x)}Ga_{(30-x)}$, $La_{55}Co_{(15+x)}Ga_{(30-x)}$, and $La_{(55+x)}Ni_{15}Ga_{(30-x)}$ MGs with variation of Ga content, respectively. It can be seen that when Co, Ni, and La are partially replaced by Ga, the β-relaxation peak position shifts to higher temperature, and the β-relaxation peak becomes more pronounced indicating significant influence of the Ga content. We also find that the β-relaxation behavior of LaGa based MGs is more pronounced with the increase of content of gallium. Above results and other researches[31,32] demonstrate that the composition and constituent elements play an important role in the modification of β-relaxation behavior, and minor addition or substitution of elements can result in a significant variation in β-relaxation behavior. To understand the mechanism of the pronounced β-relaxation, we adjust the composition ratio or replace the element in the LaGa-based MGs, and try to find the link between the microstructural characteristics and the relaxation mechanism in this simple MG system. We adjust the composition ratio of La and Ga, and replace the Ni/Co by Ga as shown in Fig. 2 and Table I. When the La/Ni/Co was replaced by Ga, one can find that the β-relaxation peak becomes stronger. The β-relaxation becomes stronger with the increase of Ga in La-Ni-Ga and La-Co-Ga systems. From this, we can see that the different constituent elements markedly influence the β-relaxation behavior for the LaGa-based MGs.

Figure 3(a) plots the mean chemical affinity ΔH of LaGa-based MGs, where the ΔH is estimated with a weighted average approach, $\Delta H = 4\sum \Delta H_{AB}^{mix} c_A c_B$ (c_A, c_B refer to the molar percentage of elements A and B, respectively),[33,34] and the enthalpy of mixing of each two elements are illustrated in the inset of Fig. 3(a). We can see that the system with similar negative enthalpy of mixing among all the constituent elements favors the pronounced β-relaxation peak, whereas the large fluctuations in the values of enthalpy of mixing between constituent elements suppress the β-relaxation in the La-Ni(Co)-Ga MG system by comparing the value of E''/E''_α shown in Table I. The value of mean chemical affinity of MG decreases with the content of Ga increase both in La-Ni-Ga and La-Co-Ga MGs systems. As shown in Fig. 2, the β-relaxation behavior of LaGa based MG with more content of Ga is more pronounced, the value of E''/E''_α is larger and the ratio of β/α-relaxation peaks is up to ~0.32 for a $La_{55}Ni_{15}Ga_{30}$ glassy alloy (Table I), this is due to the enthalpy of mixing of MG becomes more negative with the content of Ga increase.

The enthalpy (−41 kJ/mol) of mixing between La and Ga is more negative than the enthalpy (−38 kJ/mol) of mixing between La and Al. This means generally that the binding force of La-Ga bonds is stronger than that of La-Al. On the other hand, the enthalpy (−15 kJ/mol) of mixing between Ni and Ga is less negative than the enthalpy (−22 kJ/mol) of mixing between Ni and Al, but the content of Ni is much less than La and Ga or Al. Therefore, the higher temperature is needed to break the La-Ga bonds than that of the La-Al. The mean chemical affinity (−36.57 kJ/mol) of $La_{60}Ni_{15}Ga_{25}$ is more negative than that (−35.82 kJ/mol) of $La_{60}Ni_{15}Al_{25}$, and $La_{60}Ni_{15}Ga_{25}$ thus needs higher temperature (indicated by higher T_g) to dislodge the atoms from its glassy configurations.

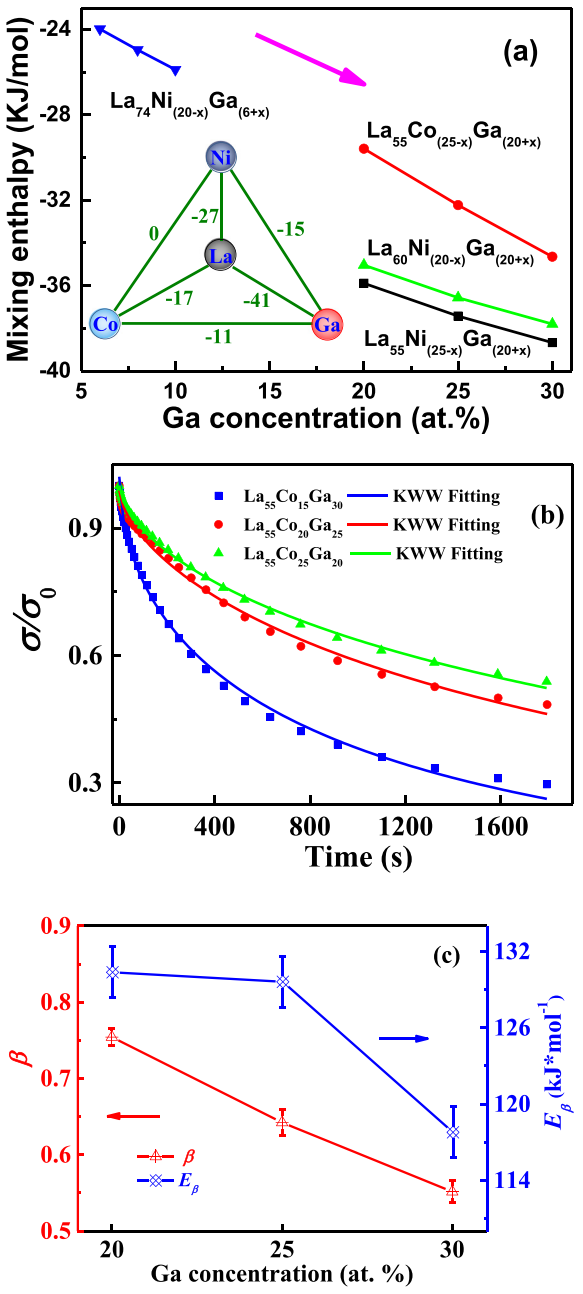

FIG. 3. (a) Mean chemical affinity ΔH of LaGa-based MGs vs. content of Ga; (b) The stress relaxation curves of La-Co-Ga MGs measured at the temperature of β-relaxation peak T_β; (c) The coefficient β and activation energy of β-relaxation E_β of La-Co-Ga MGs vs. content of Ga.

Intensive studies suggested that the microstructural origin of β-relaxation is related to the inhomogeneous microstructure and can be regarded as the motion of the loose packing atoms in the soft regions or potential flow units of MGs.[26–29] Both the β-relaxation and the activation of the flow units relate to the dynamics of the nano-scale structural inhomogeneous or liquid-like regions in the MGs where the atoms packing is relatively loose,[6,18] and the intensity of the β-relaxation are closely correlated with the average activation energy and distribution of the flow units in the MGs.[29,35] Stress relaxation method[36,37] can experimentally show the distribution and evolution of flow units in the MGs and also can reflect the β-relaxation behavior in the MGs.

Figure 3(b) show the stress relaxation curves in the La-Co-Ga MGs system at the temperature of β-relaxation peak T_β. The curves can be fitted by the Kohlrausch-Williams-Watts (KWW) function of $\sigma(t) = \sigma_0 \exp(-t/\tau)^\beta$, where τ_c is the average relaxation time, and β is a non-exponential parameter related with dynamic heterogeneity and the smaller β indicates larger dynamic heterogeneity of a system.[38,39] Figure 3(c) shows the evolution of the coefficient β obtained from the KWW fitting of stress relaxation curves and evolution of activation energy of β-relaxation E_β derived from the ln$f$ vs. $1000/T_\beta$ plot.[29] The activation energy E_β of β-relaxation and coefficient β decreases with the increasing concentration of gallium in LaGa-based MGs. The β-relaxation behavior of MG with higher content Ga is much easier to be activated because of lower activation energy E_β. Generally, the reduced value of coefficient β means that the structure of MG becomes more inhomogeneous.[38,39] The change tendency of the β value of the LaGa MGs confirms the β-relaxation of MG is closely related to the microstructure of MG. The MG which relaxes faster means its microstructure and distribution of flow units are more heterogeneous.[40–45] The results demonstrate that the MG with higher concentrations of gallium shows more pronounced β-relaxation behavior and more inhomogeneous microstructure and distribution of flow units. Our observations confirm that the β-relaxation behavior is closely correlated with the activation of flow units which control the mechanical behaviors of MGs.

To understand the role of Ga content in the β-relaxation behavior of LaGa based MGs, Fig. 4 schematically illustrates the structure of LaGa based MGs showing local packing of solvent atoms La (black) and solute atoms Ga (red) and Co/Ni (blue). Figures 4(a) and 4(b) show the local atoms packing structure of MG with lower content of Ga and higher content of Ga. The atoms Ga will occupy the position of solvent La or solute Ni/Co with the content of Ga increasing in the MGs that make it has more possibility to form Ga-Ga bonding as shown in Fig. 4(b). The melting point of gallium element is 302.8 K, which is close to room temperature. With increasing Ga content, the possibility of the formation of Ga-Ga weak solvent-solvent bonds becomes large,[46] and some Ga-Ga junction bonding among the solute-centered clusters can form. The Ga-Ga bonds are relatively easier to be broken, and the regions with more Ga-Ga bonds prefer to be acted as flow units or liquid-like regions in LaGa-based MGs. Due to the high density of flow units in the LaGa-based system with the increase in the content of Ga, the microstructure of the high Ga content MG is more inhomogeneous and its β-relaxation of MG is then more pronounced. While when replacing the Ga atoms with smaller Ni or Co atoms as shown in Fig. 4(a), the MG becomes more densely packed, and the density of the flow units decreases and flow units also become hard to be activated, and the related MGs then show much weak β-relaxation peak [see Fig. 2].

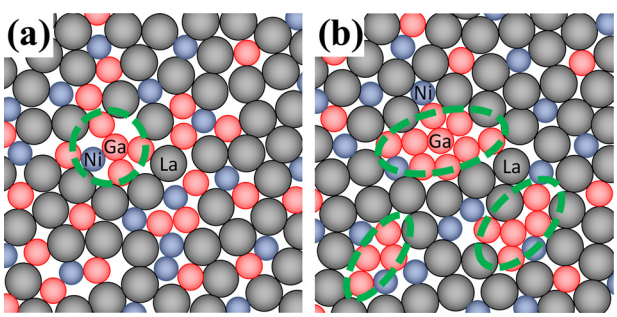

FIG. 4. Schematic illustration of a hypothetical disorder structure of LaGa based MGs showing local packing of solvent atoms La (black) and solute atoms Ga (red), and Co/Ni (blue), (a) MG with lower content of Ga shows low concentration of flow units and (b) MG with higher content of Ga presents high concentration of flow units.

In summary, we synthesized the LaGa-based MGs with a pronounced β-relaxation peak in their dynamic spectra. The β-relaxation is found to be sensitive to the composition and components, and the gallium element plays a very important role in β-relaxation behavior of the LaGa-based MGs. The pronounced β-relaxation in the MGs is found to be closely correlated with the easier activation of flow units in MGs. The LaGa-based MGs might provide a model system for studying controversial issues such as the structural origin of the β-relaxation, the decoupling between β- and α-relaxations in supercooled liquids, and the correlation between β-relaxation and mechanical properties in glasses.

The financial supports of the NSF of China (Grant Nos: 51271195 and 51322103) and MOST 973 Program (No. 2015CB856800) are appreciated. We thank K. L. Ngai, Y. Z. Li, Z. G. Zhu, Z. Wang, P. Wen, and D. Q. Zhao for the experimental assistance and insightful discussions.

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