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Melt-quenched metal-organic framework glass: Insights from annealing and calorimetric experiments

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Recently a new family of melt-quenched glass has been discovered, i.e., the metal-organic framework (MOF) glass, which is a hybrid of both organic and inorganic component.¹⁾ MOFs are a family of porous 3D frameworks of exceptional interest for gas storage and separation, catalysis and drug delivery. Yet, non-crystalline examples are extremely rare and this is the first example of a glass. Compared to conventional glasses the MOF glass has unique properties, e.g., mechanical properties in between those of organic and inorganic glasses, adjustable pore structure, special optical properties, and hence has various potential applications. Besides technical importance, MOF glass is of scientific significance. Especially, the correlation of glass formation with structure and topology of MOF is far from being understood. Here we are interested in the zeolitic imidazolate framework (ZIF) family, a subset of MOFs with zeolitic structures. There are many types of ZIFs, but here we focus only on one of these, i.e., ZIF-4 ($\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$). The thermal response of ZIF-4 is complex but fascinating since upon heating it undergoes structural collapse, polyamorphic transition, glass transition and recrystallization, melting and decomposition. It has been found in Fig. 1 that the glass transition temperature (T_g) of the melt-quenched ZIF-4 glass is equal to that of the final high density amorphous phase (HDAP) from the collapsed ZIF-4. This can be seen in Fig. 1, where the glass has a smaller heat capacity (C_p) overshoot during glass transition than the HDAP. The question is whether the structure and thermodynamic state are the same for both. To answer this question, we have performed annealing and calorimetric measurements on both the glass and the HDAP and analyzed their thermal responses to annealing time.

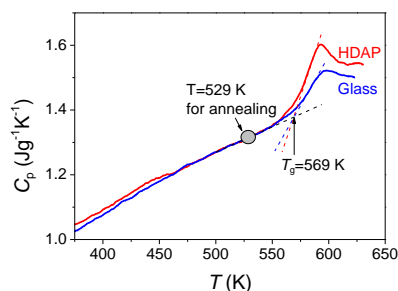


Figure 1. Comparison between the glass transition of the high-density amorphous phase (HDAP) and the melt-quenched glass, both of which were derived from ZIF-4. The upscan DSC curves of isobaric heat capacity (C_p) vs. temperature (T) were obtained at 20 K/min in argon. Filled circle: Annealing temperature for the samples measured in Fig. 2.

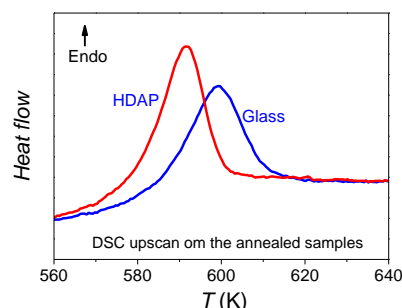


Figure 2. Comparison of annealing effects on the glass transition between HDAP and glass. Both were annealed at 529 K (well below T_g as shown in Fig. 1) for 12 hours. The DSC upscan were performed at 20 K/min in argon.

In Fig. 2 we demonstrate the annealing time effect on glass transition for both the melt-quenched glass and the HDAP. But after same degree of annealing, the glass and the HDAP show a pronounced contrast in terms of calorimetric glass transition. Through 12 hours annealing at 529 K (well below T_g), the enthalpy overshoot of both the glass and the HDAP have been greatly enhanced. Another striking phenomenon in Fig. 2 is that the glass transition peak of the melt-quenched glass shifts to a higher temperature, whereas that of the HDAP does not shift. The reason could be related to three aspects. First, the bulk glass has a much smaller surface area, and hence thermodynamically more stable compared to the powdered HDAP. Second, the glass sample has been subjected to a higher degree of structural ordering during quenching, and thus shows a smaller overshoot. To confirm this, we have varied the melt quenching rate to see the evolution of the C_p overshoot of the glass. Third, the relaxation of the glass sample is of higher non-exponentiality²⁾ than the HDAP, implying that the glass has higher structural heterogeneity in the medium-range order compared to the HDAP. The question is which of these three aspects is the dominant factor determining the difference in glass transition between them. Here we attempt to answer this question, and also discuss both the primary and secondary relaxation in the samples.

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