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Metal-Organic Framework Glasses: Several Fundamental Problems

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Metal-organic frameworks (MOFs) are being extensively studied and developed owing to their potential applications such as gas absorption, catalysis, sensing, and so on. A subset of MOFs, called zeolitic imidazolate frameworks (ZIFs), has been found to be of particular interest due to their similar structure to that of zeolites. However, the melt-quenched ZIF glasses are of recent origin. It has been discovered that certain types of ZIFs can melt prior to decomposition, and hence, can be vitrified upon quenching.¹⁻³⁾ Study of this new category of glasses will provide new insights into general glass problems such as crystal-melting, glass formation, glass transition and relaxation. Compared to other categories of glasses (e.g., metallic, organic, and oxide glasses), ZIF glasses have been investigated to very limited extent. In this work, we present some initial advances in understanding the melting and glass formation of ZIFs, and enthalpy relaxation of ZIF glass. ZIF-4 ($\text{Zn}(\text{Im})_2$) and ZIF-62 ($\text{Zn}(\text{Im})_{1.75}(\text{bIm})_{0.25}$), where Im and bIm refer to imidazole and benzimidazole, respectively, are chosen as the objects of this study. Both ZIFs are different in many ways. ZIF-4 exhibits a striking polyamorphic transition, whereas ZIF-62 does not. Compared to ZIF-4 glass, ZIF-62 glass is far more stable against crystallization. The T_g/T_m ratio (0.84) of ZIF-62 has been found to be higher than that of any other glass-forming systems including ZIF-4, indicating that ZIF-62 is an extremely good glass former. The viscosity (10^5 Pa s) of ZIF-62 at T_m is significantly higher than that of most of glass-forming systems, but its fragility ($m=23$) is much lower. By analyzing the dynamic and structural data, we infer that the high steric hindrance and rigidity of the structure network are the origin of the ultrahigh glass forming ability of ZIF-62. We propose that the melting mechanism of glass-forming ZIF systems manifests as a combination of the Zn-N coordinating bond breaking-forming mode (described by Lindemann criterion) and the highly cooperative motion of structural units (metal-linker tetrahedra). From sub- T_g enthalpy relaxation study, we have found that a high degree of the structural heterogeneity is present in ZIF-62 glass.

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