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Metal-organic frameworks (MOFs) have been extensively investigated in recent decades owing to their multi-functionalities for applications such as gas absorption, catalysis and sensing. A subset of MOFs, called zeolitic imidazolate frameworks (ZIFs), has been found to be of particular interest due to their potential to play a role like 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 family of glasses gives new angles to understand fundamental glass problems such as crystal melting, glass formation, glass transition, and glass relaxation. In the present work, we study enthalpy relaxation and thermodynamic properties in ZIF-62 ($Zn(Im)_{1.75}(bIm)_{0.25}$) glass. Its enthalpy relaxation time described by the Kohlrausch model demonstrates a broad distribution with the stretching exponent β of 0.4 to 0.8. We have found that β increases with increasing annealing temperature. These relaxation behaviors indicate a high degree of the structural heterogeneity at medium-range scale in ZIF-62 glass. Moreover, we have studied the temperature dependences of the enthalpy, entropy and Gibbs free energy of ZIF-62. The smaller Gibbs energy difference at temperatures close to T_g could be the thermodynamic origin of the ultrahigh stability of ZIF-62 glass against crystallization, e.g., compared to metallic glasses.

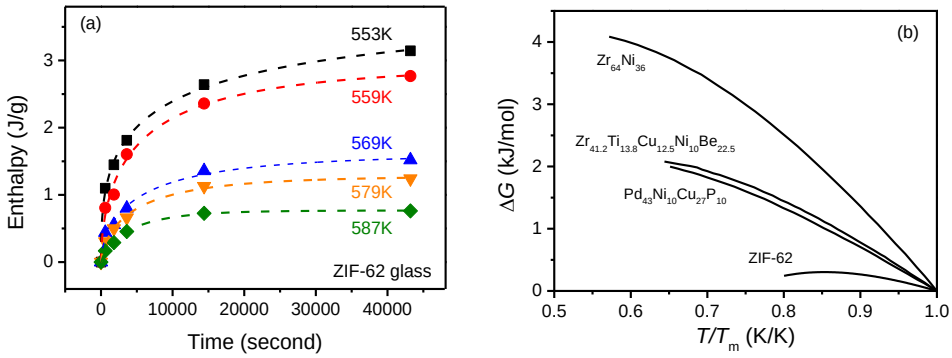

Fig. 1 (a) The recovered enthalpy of ZIF-62 annealed at different temperatures and times. (b) Temperature dependence of the difference of the Gibbs free energy difference $\Delta G(T/T_m)$ between the supercooled liquid and the crystal for ZIF-62.

References:

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