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Enthalpy relaxation in melt-quenched metal-organic framework glasses

The metal-organic framework (MOF) glass is a new member of the family of melt-quenched glasses (MQG) besides organic glass, inorganic non-metallic glass and metallic glass. It is hybridized between metal atoms and organic molecules. Original MOFs are microporous materials of special interest for gas storage and separation, catalysis and drug delivery. It has been found that upon heating some of MOFs can be melted and then quenched to bulk glass. As the MOF glass is of recent origin, numerous fundamental problems need to be explored. In the present work we explore the enthalpy relaxation in MOF glasses. The focus is placed on ZIF-4 ($\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$) - a kind of zeolitic imidazolate frameworks (ZIFs). We investigate both α - and β -relaxation behaviors of ZIF-4 MQG by varying quenching rate and performing long time sub- T_g annealing. The stability of the medium-range order structure of ZIF-4 MQG upon annealing is studied using both DSC and small angle XRD methods. The structural heterogeneity in ZIF-4 MQG is revealed in terms of the non-exponentiality of enthalpy relaxation, and then is compared with that of HDAP. Our enthalpy relaxation study provides also insights into the polyamorphic transition in collapsed ZIF-4.