Metal-Organic Framework Glass Formation and "Reordering"

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Abstract

Metal-organic frameworks (MOFs) are microporous inorganic-organic hybrid materials. Recently, some types of MOFs can be vitrified by melt-quenching technique [1-4]. However, we still do not exactly know why some MOFs can be vitrified, but some not. We also do not know why the MOF glass cannot crystallize, i.e., the long-range order cannot be recovered, under accessible laboratory conditions. Therefore, scientists including our group have made considerable effort to answer those questions. In this presentation, we report our recent understanding of MOF glass formation and 'reordering' by characterizing two MOF glass formers: ZIF-4 (Zn(Im)2) and ZIF-62 (Zn(Im)1.75(bIm)0.25). The former shows polyamorphic transitions, ZIF-zni crystal formation and narrow melting transition, whereas the latter exhibits ultrahigh glass forming ability and wider melting range. Upon isothermal treatment in the supercooled region, a drop in potential energy is detected in ZIF-4, but surprisingly the degree of medium-range order is lowered. This might imply that upon heating the link between tetrahedral ZnIm4 units is more disordered, driven by structural densification of, whereas the ligand rings become less distorted. ZIF-62 glass is extremely stable against crystallization. The ratio between the glass transition temperature (Tg) and the melting point (Tm) of ZIF-62 is higher than that of any other glass forming systems measured so far. By combining the dynamic data with structure analysis, we present our understanding of the above-mentioned anomalous features of ZIF-4 and -62 glasses.

References:

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