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Effect of Zn/Co node ratio on the glass transition in the high-density amorphous ZIF-4

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Abstract: Zeolitic imidazolate frameworks (ZIFs) are an important subset of Metal-organic framework (MOF) glasses, which have been utilized for various applications. Upon heating, ZIF-4 crystals experience a polyamorphic transition, i.e., the transformation of a super-strong (i.e., very low liquid fragility in Angell's sense) low-density liquid into a relatively "fragile" high-density liquid.[1] Upon cooling, the latter transforms into the high-density amorphous phase (HDA). Understanding the connection between the glass transition temperature (T_g) and structural factors is crucial for processing the ZIF liquid phase with desired properties. By reheating the quenched HDA, the glass-to-liquid transition occurs. Despite notable progress in studying ZIF glasses, the nature of the HDA of ZIFs remains to be revealed. Particularly, the influence of metal node substitution on T_g of the ZIF-4 HDA has not yet been investigated. Here, we report the preparation of bimetallic Zn/Co-ZIF-4 HDAs and their T_g values [2]. The temperature dependence of the isobaric heat capacity (C_p) of ZIF-4 HDAs was measured to determine the T_g. The T_g non-linearly decreases with the molar ratio R, where R is Co/(Co+Zn), indicating the presence of a mixed-metal node effect [3]. The mixed-metal node effect on T_g is attributed to the difference in the degree of configurational freedom owing to the difference in tetrahedral symmetry. The degree of configurational freedom is influenced by the electronic structure and metal-nitrogen bonding nature [2]. Our study provides insight into the mixed-metal node effect on the glass transition in the HDA of ZIFs. The insight also helps design meltable ZIFs.

Key words: Zeolitic imidazolate frameworks; Mixed-metal node effect; High-density amorphous phases; Glass transition

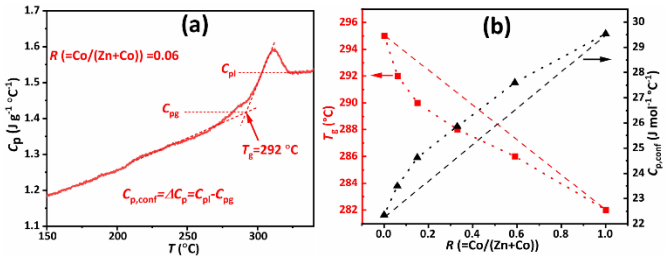

Fig. 1 (a) Isobaric heat capacity (C_p) curve for $Zn_{0.94}Co_{0.06}$-HDA at the heating rate of 10 °C min^{-1} in argon. (b) The molar ratio R dependence of T_g and $C_{p,conf}$. Dotted lines: guide for the eyes. Dashed lines: Linear lines connecting the two end-member compositions.

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