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Superstrong supercooled zeolitic hybrid frameworks and topological melting.

Neville Greaves^{1,2}, Jin-Chong Tan³, Yuanzheng Yue^{2,4}, Thomas Bennett¹, Anthony Cheetham¹, Zhou Zhongfu⁵

¹Department of Materials Science & Metallurgy, University of Cambridge, Cambridge CB3 0FS, United Kingdom

²State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China

³Department of Engineering Science, University of Oxford, Parks Road, Oxford OX1 3PJ, UK

⁴Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark

⁵School of Materials Science and Engineering, Shanghai University, No.149, Yanchang Road, Shanghai City, China, 200072

Polyamorphism is a supercooled phenomenon, resulting in glassy phases having the same composition, but differing in entropy and density. These also occur during amorphisation, not least for zeolites which readily collapse to form novel glasses under modest pressures or when temperatures approach the glass transition T_g . A sequence of phase transitions is involved: the first, topologically invariant, converting the microporous crystal into a low density low entropy phase; the second, topologically disordering, transforming this into a polymorph, similar what is recovered by melt-quenching (Greaves et al, *Science*308, 1219 (2005)). Moreover, the melting temperature T_m can be projected from T_g from the well-known empirical relation $T_m \sim 3/2T_g$. It coincides for inorganic zeolites with feldspar melting points. More recently amorphisation of zeolitic imidazole frameworks (ZIFs) has been demonstrated leading to hybrid glasses (Bennett et al, *PRL*104, 115503 (2010)). These are microporous (Chapman et al, *JACS*131,17546 (2009)) and also mechanically stronger than their ZIF precursors (Tan & Cheetham, *Chem. Soc. Rev.*40, 1059 (2011)). We report *in situ* X-ray scattering and DSC experiments of ZIF 4 amorphised at different heating rates from which we observe the glass polyamorphic transition temperatures T_g and the associated rheological properties. As with inorganic zeolites, we find that the supercooled ZIF liquid is extremely strong and reminiscent of low entropy low density polymorphs. Furthermore evidence for an order-disorder transition resides in dramatic peaks in X-ray scattering with rising temperature. These reflect deep minima in the bulk modulus at the liquid-liquid transition, typical of first order transitions (Greaves et al, *Nat. Mat.*10, 823 (2011)). Finally for zeolitic hybrids we define a topological melting point $\sim 3/2T_g$, sometimes unreachable because of the dissociation of the organic imidazole linkages at intermediate temperatures, but affording a measure of the mechanical stability of the hybrid structure.