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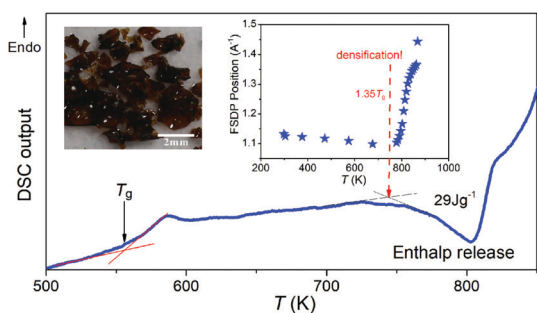
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Structural evolution in a melt-quenched zeolitic imidazolate framework glass during heat-treatment

Jiayan Zhang, Louis Longley, Hao Liu, Christopher W. Ashling, Philip A. Chater, Kevin A. Beyer, Karena W. Chapman, Haizheng Tao, David A. Keen, Thomas D. Bennett* and Yuanzheng Yue*

A pronounced enthalpy release occurs around $1.38T_g$ in the prototypical metal–organic framework glass formed from ZIF-4 [$\text{Zn}(\text{C}_3\text{H}_3\text{N}_2)_2$], but there is no sign for any crystallization (*i.e.*, long-range ordering) taking place.

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Structural evolution in a melt-quenched zeolitic imidazolate framework glass during heat-treatment†

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A pronounced enthalpy release occurs around 1.38T_g in the prototypical metal–organic framework glass formed from ZIF-4 [Zn(C₃H₃N₂)₂], but there is no sign for any crystallization (*i.e.*, long-range ordering) taking place. The enthalpy release peak is attributed to pore collapse and structural densification.

Metal–organic frameworks (MOFs) consist of metal clusters or ions linked by organic ligands into large open-networks with various pore architectures.^{1,2} Amongst these, the zeolitic imidazolate frameworks (ZIFs) are of interest due to their excellent chemical stabilities.³ The M–Im–M (M – transition metal, Im – imidazolate, C₃H₃N₂[−]) angle in ZIFs is analogous to the Si–O–Si bond angle in zeolites, and so many ZIFs adopt zeolitic tetrahedral network topologies.^{4,5} Thermal⁶ and pressure-induced⁷ amorphization of the crystalline state is observed, with one structure, ZIF-4, melting to form a ‘liquid-MOF’ at *ca.* 860 K.⁸ Quenching this liquid yields a glass with a continuous random network of corner-sharing Zn(Im)₄ tetrahedra.⁹ Given the structural similarities to conventional SiO₂ glass, this presents opportunities to study MOF-glasses in the context of existing inorganic glass materials.^{10–12}

In particular, the dynamic properties of the glasses upon heating should be investigated, given the rich behavior of the structural evolution upon heating of other supercooled liquid families.^{13–15} Motivated by an initial study on the glass formed

by melt-quenching ZIF-62 [Zn(Im)_{1.75}(bIm)_{0.25}] (bIm – benzimidazole C₇H₅N₂[−]), which demonstrates ultrahigh stability against crystallization,¹⁶ here we investigate the effect of heat-treatment upon a melt-quenched zeolitic imidazolate framework glass, formed from ZIF-4 [Zn(Im)₂]. Consistent with prior literature, the ZIF-liquid quenched back to room temperature at a rate of 10 K min^{−1} is referred to as a_gZIF-4.¹⁷

Differential scanning calorimetry (DSC) experiments were performed on a crystalline sample of ZIF-4, and show desolvation, amorphization, recrystallization (to the dense ZIF-zni phase, also of composition Zn(Im)₂), and subsequent melting events. These are labelled features A–D respectively, in the black dashed curve in Fig. 1, and are consistent with previous results.⁹ In a second experiment, a sample of ZIF-4 was heated to 853 K, *i.e.*, above the melting temperature, *T*_m, and quenched back to room temperature at a rate of 20 K min^{−1}, which is twice as fast as the quench rate used for previous ZIF-4 glass samples. The resultant material is termed fq-a_gZIF-4 (fq – fast

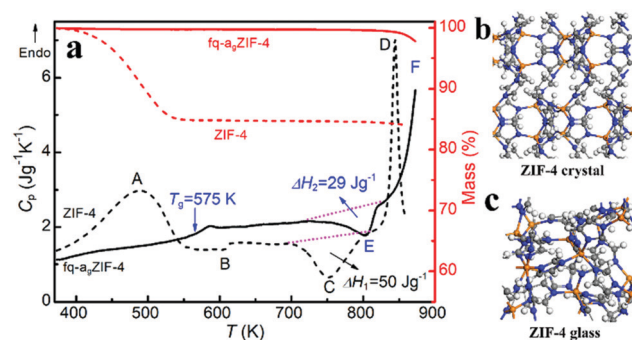


Fig. 1 (a) *C_p* measurements (black) and thermogravimetric analysis (red) of as-synthesized crystalline ZIF-4 (dashed line) and a_gZIF-4 (solid line), at a heating rate of 10 K min^{−1}. A: desolvation; B: amorphization; C: recrystallisation to ZIF-zni; D: melting; F: decomposition. *T_g*: glass transition temperature; Δ*H*₁: enthalpy released during crystallization of ZIF-zni; Δ*H*₂: enthalpy released during the exothermal peak E. (b) Unit cell of ZIF-4 crystal and (c) atomic configuration of the melt-quenched a_gZIF-4 from ref. 10. Zn – orange, N – blue, C – grey, H – white.

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1 quenched) for clarity. Reheating fq- a_g ZIF-4 (under argon) in the
 DSC, revealed a glass transition in the region of 565–595 K with
 the glass transition temperature (T_g) of 575 K (black solid curve
 in Fig. 1). Curiously, after the glass transition, a broad exothermic
 5 peak (marked as E) occurs at *ca.* 725–820 K. The enthalpy
 released during this process is 29 J g⁻¹, lower than that of the
 formation of the crystal ZIF-zni (50 J g⁻¹). Decomposition of the
 liquid of ZIF-4 glass is then evident at *ca.* 840 K (point F), which
 10 is 30 K lower than the decomposition temperature of the liquid
 of ZIF-zni, without quenching back to room temperature.⁹

In poor inorganic glass formers, crystallization above the
 glass transition is common, which causes a narrow and sharp
 exothermic peak, due to energy release during fast nucleation
 and crystal growth.^{18,19} To determine whether this occurs here,
 15 isothermal heat-treatments were performed on fq- a_g ZIF-4, at
 varying treatment temperatures (T_h), for times (t_h) of 5 and 30
 minutes, in the region of the exothermic peak E. PXRD measure-
 ments of the resultant material show no sharp Bragg peaks,
 implying that long-range ordering (LRO) does not occur, *i.e.*,
 20 the samples did not recrystallize (Fig. 2a). This behavior is in
 contrast with many other glass systems where an exothermic
 response occurred during heat-treatment is representing LRO.

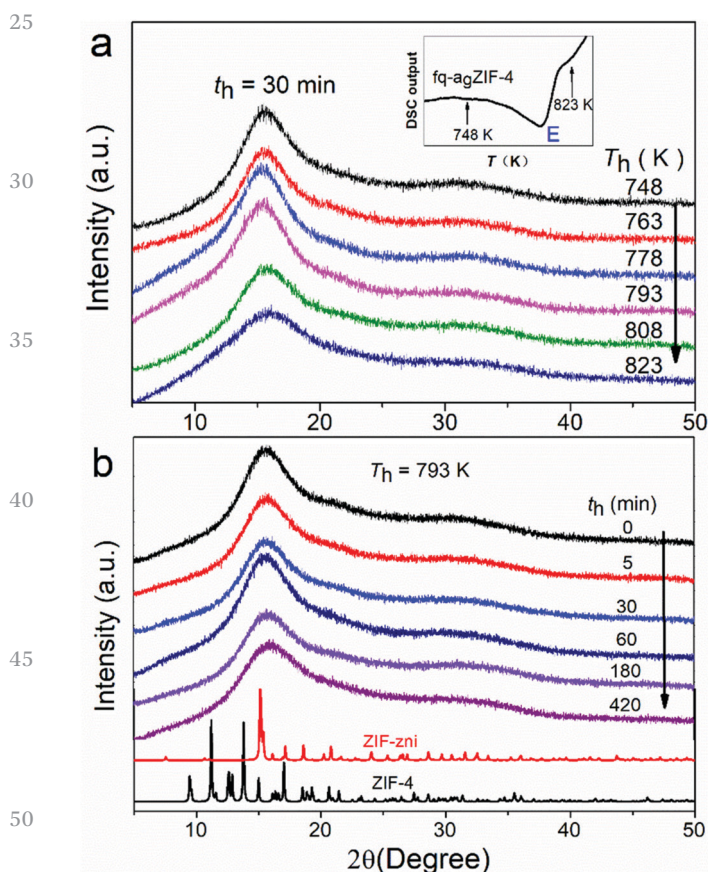


Fig. 2 (a) Powder X-ray diffraction (PXRD) patterns of fq- a_g ZIF-4, heat-
 treated at different temperatures for 30 min. Inset: DSC curve of fq- a_g ZIF-4,
 showing the range of T_h , (b) PXRD patterns of ZIF-4, ZIF-zni, and fq- a_g ZIF-4
 heat-treated at $T_h = 793$ K for various durations from 0 to 420 min. t_h : heat-
 treatment duration; T_h : heat-treatment temperature.

Even prolonged heating of fq- a_g ZIF-4 at $T_h = 793$ K for 420 min,
 did not result in sharp Bragg diffraction (Fig. 2b). This tem-
 perature was chosen due to its location at the top of exothermic
 peak E (Fig. 2a inset). The absence of Bragg diffraction confirms
 that peak E is not associated with a crystallization process, *i.e.*,
 5 LRO, but instead must be attributed to a lowering of enthalpy of
 the system, and hence, causes the exothermic response, *i.e.*, the
 release of 29 J g⁻¹ energy.

Samples of fq- a_g ZIF-4 were also heat-treated for 5 minutes at
 temperatures ranging from 748 K to 823 K, before cooling to
 room temperature (Fig. S1, ESI[†]). DSC experiments show T_g to be
 largely unaffected, *i.e.*, both long-range disorder and the glass
 network connectivity remain unchanged. Heat-treatment at
 823 K however resulted in disappearance of the glass transition
 peak (Fig. S2, ESI[†]). A sample of fq- a_g ZIF-4 was heat-treated at
 793 K for 420 min, and the product is hereby referred to as ht-fq-
 a_g ZIF-4 (ht – heat-treated), for clarity. DSC experiments con-
 15 firmed that the exothermic peak E is present in both fq- a_g ZIF-4
 and ht-fq- a_g ZIF-4 (Fig. S3, ESI[†]). SEM images show little differ-
 ence between the two samples, though optical photographs
 show a distinct darkening in colour after heat-treatment
 (Fig. S4, ESI[†]). ¹³C liquid NMR spectroscopy measurements were
 carried out (Fig. S5 and S6, ESI[†]) and, as expected, the two ¹³C
 signals for the glass remain unchanged with increasing T_h ,
 indicating that the local chemical environments of C-1 and C-2
 25 on the imidazolate ring are unaltered during heat-treatment.
 Pycnometric density measurements demonstrated an increase in
 density during melt-quenching and heat-treatment. Densities of
 ZIF-4 crystal, fq- a_g ZIF-4 and ht-fq- a_g ZIF-4 were recorded as 1.25,
 1.67 and 1.76 g cm⁻³, respectively.

Fourier transform infrared (FTIR) spectra using the KBr disc
 technique were obtained. The full spectra of mid-IR region for
 the samples of ZIF-4, fq- a_g ZIF-4 and ht-fq- a_g ZIF-4 are shown in
 Fig. S7, ESI[†]. The peaks located at 1681–1475 cm⁻¹ are charac-
 35 teristic of C=C, C=N and imidazolate ring stretching.^{20,21}
 Both the decreased absorption of the peak near 1680 cm⁻¹ and
 the increased absorption of the associated weak peak near
 1600 cm⁻¹ indicate possible distortion of the imidazolate rings
 in the ZIF-4 glass upon melt-quenching and heat-treatment.
 This is further confirmed by the noticeable change of the C-H
 40 bending peak near 1387 cm⁻¹. The peak at around 530 cm⁻¹ is
 assigned to imidazolate ring out-of-plane bending.^{21,22}

To probe any structural differences induced by heat-treatment,
 room temperature X-ray total scattering measurements were
 performed on fq- a_g ZIF-4 and ht-fq- a_g ZIF-4, and compared to
 previous data on a sample of ZIF-4 glass formed by natural cooling
 from 853 K, referred to as a_g ZIF-4 (Fig. 3).⁸ The absence of
 Bragg diffraction in the structure factor $S(Q)$ of all samples con-
 45 firms their amorphous nature and long-range disorder (Fig. 3a),
 while those for a_g ZIF-4 and fq- a_g ZIF-4 are near identical. The
 first sharp diffraction peak (FSDP) for ht-fq- a_g ZIF-4 appears to
 shift slightly to higher Q , which is in accordance with the higher
 density of this heat-treated sample. Pair distribution functions
 (PDFs) data were produced by a Fourier transform of these data.
 The short-range order (SRO) of the samples, *i.e.* correlations below
 55 6 Å indicating local intra-imidazolate bonds and four local Zn-Im
 coordinating

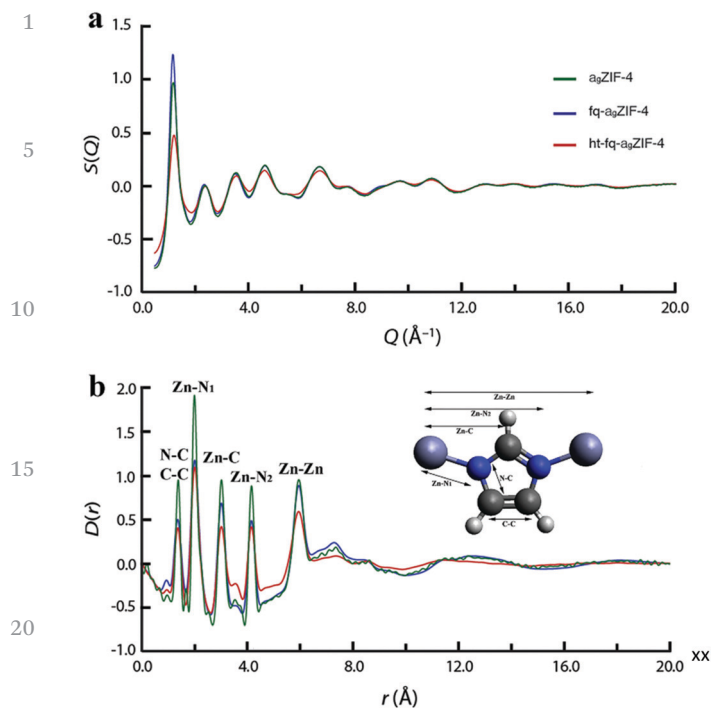


Fig. 3 (a) X-ray total scattering data $S(Q)$ and (b) corresponding X-ray pair distribution functions $D(r)$.

bonds forming a tetrahedron are consistent with those witnessed for glass ZIFs previously.²³ Positions of the peaks belonging to the C-C/C-N, Zn-N, Zn-C, Zn-N and Zn-Zn distances at *ca.* 1.33, 2, 3, 4 and 6 Å are largely unchanged between samples. Specifically, correlations between 6 Å and 8 Å for ht-fq-a₉ZIF-4 are less distinct upon heat-treatment above T_g . The feature at 7.5 Å, which has previously been ascribed to a M-L-M-L interaction (*i.e.* between Zn and a nitrogen atom of the 2nd nearest imidazolate in this sample),²⁴ is less pronounced. The weaker degree of atomic pair correlations in this region is perhaps associated with structural relaxation (and the associated densification) upon heat-treatment.

To provide a firm structural origin for the exothermic peak E in the DSC scans, high temperature X-ray total scattering measurements, collected on a sample of a₉ZIF-4 at the APS synchrotron and published previously, were reanalysed.⁸ These data were collected on heating a₉ZIF-4 at the Advanced Photon Source, US. Temperature intervals were roughly 100 K, from 298 to 778 K (Fig. S8 left, ESI[†]), and showed little change in the FSDP. However, those obtained in 6 K steps from 778 K to 862 K (Fig. S8 right, ESI[†]) demonstrated marked changes. A Pseudo-Voigt peak fit was applied to model the position, intensity and width of the FSDP as a function of temperature (Fig. 4). A sharp change at approximately 770 K (*i.e.* close to the onset of the exothermic peak E in Fig. 1a) was seen in all parameters reflecting structural changes in the glass at this temperature (Fig. 4 and Fig S9, ESI[†]). The increase in position and decrease in intensity qualitatively indicate a densification of the structure.

Hence, holding the as-quenched ZIF-4 glass at 793 K (1.38 T_g) for 420 min can lead to structural densification, towards a lower energy state (*i.e.*, 29 J g⁻¹ lower). The energy released by

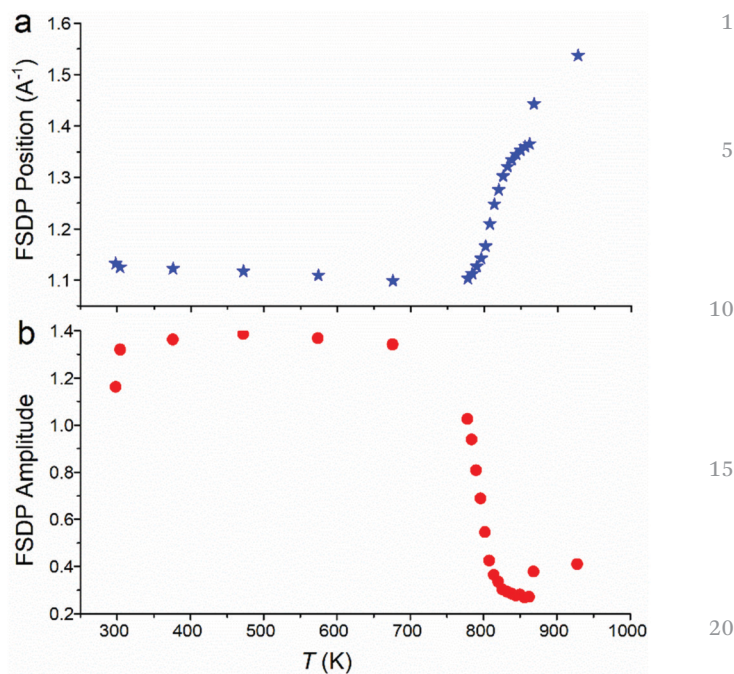


Fig. 4 Variable temperature synchrotron X-ray total scattering data $S(Q)$ showing changes in the (a) position and (b) amplitude of the first sharp diffraction peak (FSDP) with temperature. The two highest temperature points were collected during sample decomposition and above 900 K the pattern mostly consisted of that of the silica capillary.

this process is 3/5 of the energy released by LRO, *i.e.*, crystallization (Peak C in Fig. 1a). This type of relaxation has not been observed in inorganic network glasses. The degree of relaxation is driven by two structural factors of the ZIF-4 glass. First, the size of Zn[Im]₄ tetrahedron is much larger than that of SiO₄ tetrahedron since the Zn-Zn distance (5.9 Å) is much longer than the Si-Si distance (3.1 Å). Second, the coordinating bond between Zn and Im is significantly weaker than the Si-O bonds in oxide glasses. These two factors make the Zn(Im)₄ tetrahedron more ‘floppy’, and hence more distorted after melt-quenching, and therefore pose a higher thermodynamic driving force for relaxation.

Piecing the results together yields a complex picture of structural evolution in a₉ZIF-4. The absence of crystallization in the glass, even after heat-treatment at high T_h for a long duration, is encouraging for the development of future applications.

YY designed the project. JZ, TDB and YY wrote the manuscript with inputs from other co-authors. All samples were prepared by JZ. DSC, XRD, SEM, L-NMR and FT-IR experiments were performed by JZ and HL, analysed by JZ, YY, HT and HL. Ambient temperature PDF data was collected by LL, CWA, TDB, DAK and PAC. Analysis was performed by LL and DAK. Variable temperature PDF data was collected by TDB, DAK, KAB and KWC, and analysed by LL and DAK.

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10 Conflicts of interest

There are no conflicts to declare.

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