Revealing insights into the amorphization mechanism of ZIF-4 and ZIF-62 by ball milling using in-situ PXRD, and ex-situ XAS, PDF and DSC

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Ball milling facilitates the synthesis of metastable materials characterized by nanometric crystallite sizes and significant microstrain, which often deviate from bulk stability. Building upon our earlier data collection and data analysis strategies,[1,2] we have developed a new set-up at the Diamond Light Source (beamline I11) for time resolved in situ (TRIS) monitoring of mechanochemical transformations using PXRD with optimal peak to background ratio, ideal for microstructural studies.[3] Investigating the amorphization of ZIF-4 and ZIF-62 upon milling, we found that crystallite size plateaus early in the process, while microstrain continues to rise. This identifies defect accumulation as the primary driver for the loss of crystallinity. While X-ray absorption spectroscopy and total scattering pair distribution function analysis confirm that local structure remains intact, differential scanning calorimetry reveals that mechanically amorphized ZIF-4 possesses a unique thermal profile with a significantly depressed melting point, thus suggesting the formation of a distinct mechanically induced amorphous phase.

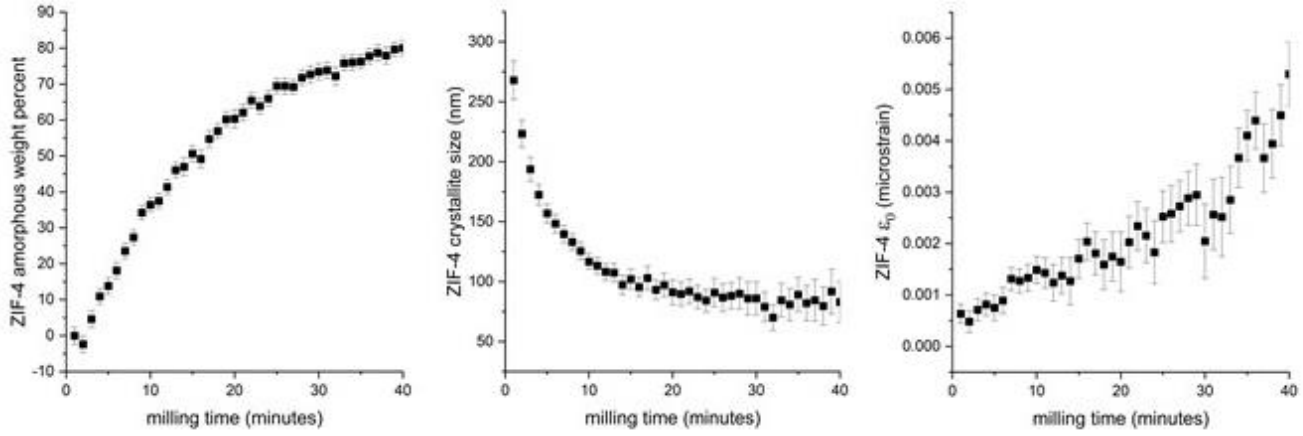


Figure 1. *TRIS-PXRD data analysis output of the amorphization of ZIF-4under milling conditions. Estimated standard deviations are shown as error bars.*

[1] G.I. Lampronti et al., Nature Communications 12.1 (2021): 6134.. (References style, Arial 9)
[2] P.P. Mazzeo et al., Faraday Discussions 241 (2023): 289-305.
[3] M.E. Charlesworth et al., Crystal Growth & Design, (2026) just published.