

Amorphous-amorphous transition in a porous coordination polymer

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The amorphous state plays a key role in porous coordination polymer and metal-organic framework phase transitions. We investigate a crystalline-to-amorphous-to-amorphous-to-crystalline (CAAC) phase transition in a Zn based coordination polymer, by X-ray absorption fine structure (XAFS) and X-ray pair distribution function (PDF) analysis. We show that the system shows two distinct amorphous phases upon heating. The first involves a reversible transition to a desolvated form of the original network, followed by an irreversible transition to an intermediate phase which has elongated Zn-I bonds.

1 Introduction

Polyamorphism i.e. the existence of several amorphous phases of the same material, is of interest in inorganic materials and glasses as functional properties may vary drastically between several amorphous states. Such polyamorphism is rare in the field of coordination polymer/metal-organic frameworks and no structural characterization exists. Here we report the first observation and structural characterization of multiple amorphous phases for the same PCP. Amorphization from a crystalline state in this case is followed by recrystallization to a more stable coordination network. The amorphous phases are a crucial intermediate in final crystalline network formation.

2 Experiment

We examined the phase transition of the coordination polymer, $[(\text{ZnI}_2)_3(\text{TPT})_2]$ (TPT = 2,4,6-tris(4-pyridyl)-1,3,5-triazine).¹ Upon heating phase **1**, it became amorphous phase (phase **2**) at 550 K, and then, by further heating at 600 K, it became a 1D crystalline phase (phase **4**) which has permanent porosity. In this study, we closely investigated this phase transition. Zn *K*-edge XAFS (X-ray absorption fine structure) were measured in BL-12C/BL-9A beamline in KEK.

3 Results and Discussion

Thermal analysis revealed that one more amorphous phase (phase **3**) existing before reaching to phase **4**. We isolated two amorphous phases, phase **3** and phase **4**, and investigate its structure by XAFS and X-ray PDF (pair distribution function) analysis. From XAFS analysis (Fig.1), The first amorphous phases has the same geometry around Zn with crystalline phase **1** and **4**, indicating phase **2** formation is coming from desolvation of the solvent inside the pore. However, phase **3** has totally different PDF (Fig.2) from the other phases, indicating significant change in the Zn coordination

environment accompanied with Zn-I elongation from the normal geometry. This is the first example of the characterization of subsequent solvent collapsed and amorphous states in MOF/PCPs.

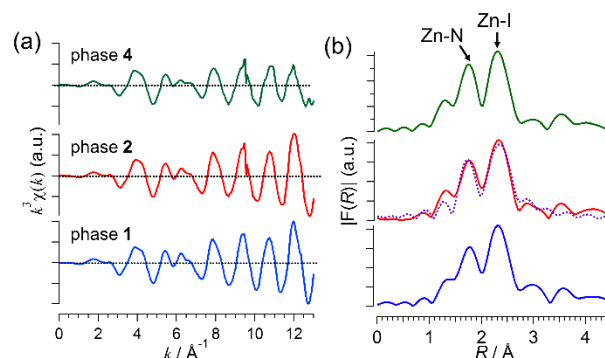


Fig. 1: (a) k^3 -weighted XAFS spectra of each phase (b) Fourier transformed k^3 -weighted XAFS spectra

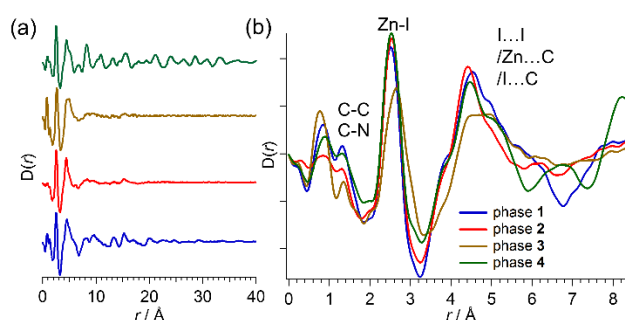


Fig. 2: PDF function of each phase

References

[1] H. Ohtsu, T. D. Bennett, T. Kojima, D. A. Keen, Y. Niwa, M. Kawano, *Chem. Commun.* **53**, 7060 (2017).

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