

Extreme Flexibility in a Zeolitic Imidazolate Framework: Porous to Dense Phase Transition in Desolvated ZIF-4**

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Abstract: Desolvated zeolitic imidazolate framework ZIF-4(Zn) undergoes a discontinuous porous to dense phase transition on cooling through 140 K, with a 23 % contraction in unit cell volume. The structure of the non-porous, low temperature phase was determined from synchrotron X-ray powder diffraction data and its density was found to be slightly less than that of the densest ZIF phase, ZIF-zni. The mechanism of the phase transition involves a cooperative rotation of imidazolate linkers resulting in isotropic framework contraction and pore space minimization. DFT calculations established the energy of the new structure relative to those of the room temperature phase and ZIF-zni, while DSC measurements indicate the entropic stabilization of the porous room temperature phase at temperatures above 140 K.

It has become apparent in the last few years that a number of metal–organic framework (MOF) compounds exhibit remarkable structural flexibility.^[1,2] Soft porous crystals (SPCs), a subclass of MOFs, possess impressive structural compliance and even shape memory effects under the influence of external stimuli.^[2–4] MIL-53 is a classic example, undergoing a dramatic breathing transition on the adsorption or desorption of small gas molecules, by cooling or on application of pressure.^[5–7] As such, the mechanical properties of MIL-53 have been extensively studied.^[8–10] Structural flexibility is also known for specific examples of zeolitic imidazolate frameworks (ZIFs): ZIF-7^[11–13] deforms on exchange of guest molecules, whilst the prototypical compound, ZIF-8, undergoes a gate-opening type transition on either application of mechanical pressure or upon gas adsorption.^[14,15] Whilst flexibility in MIL-53 and SPCs is

mediated through bending about the carboxylate coordinative bond,^[5] in ZIFs it is achieved through rotations of the imidazolate linker, thought to be related to low energy phonons of the framework.^[16] Understanding the nature of this flexibility is of the utmost importance for applications in gas storage, drug delivery and sensing.^[17,18] It is therefore of great significance that another MOF, the well-known ZIF-4(Zn) adopting the **cag** topology,^[19,20] exhibits exceptional flexibility. On cooling to approximately 140 K, desolvated ZIF-4(Zn) shows a phase transition involving an isotropic decrease in unit cell volume by 23 %. Herein, we study this remarkable behavior by synchrotron powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC), and density functional theory (DFT) calculations.

Rietveld refinement was performed on a synchrotron PXRD pattern of the desolvated compound ZIF-4(Zn)-DS (details of the synthesis are given in the Supporting Information). The pattern was collected at 298 K under dynamic vacuum on beamline I11 at Diamond Light Source (Oxon., UK; $\lambda = 0.826952$ Å). The data were indexed and analyzed in space group *Pbca* with a final unit cell volume of 4344.27(7) Å³, which is consistent with the reported single crystal structure of DMF-containing ZIF-4(Zn) (lattice parameters and agreement factors are given Table 1; full details in the Supporting Information). This confirms that the structure of ZIF-4(Zn)-DS is not strongly sensitive to the presence of guest molecules in the pores at room temperature. For convenience, this structure is referred to as the high-temperature phase (ZIF-4(Zn)-DS_HT).

The thermal response of ZIF-4(Zn)-DS was investigated by variable temperature synchrotron PXRD, also at beamli-

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Table 1: Lattice parameters and agreement factors from the Rietveld refinements of the high-temperature (HT) and low-temperature (LT) ZIF-4(Zn) phases.

	ZIF-4(Zn)-DS_HT, 298 K	ZIF-4(Zn)-DS_LT, 80 K
Space Group	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> [Å]	15.50051(15)	14.26686(9)
<i>b</i> [Å]	15.52013(14)	14.28427(8)
<i>c</i> [Å]	18.05823(17)	16.41270(11)
<i>V</i> [Å ³]	4344.27(7)	3344.77(4)
<i>R</i> _{wp} / <i>R</i> _{Bragg} /χ ²	2.42%/2.23%/26.485	1.47%/0.91%/9.613

ne I11. Eight diffraction patterns were measured at approximately 30 K intervals from 298 K to 80 K under dynamic vacuum with only minor changes observed in the measured diffraction patterns on cooling to 180 K. However, at 150 K new reflections were observed, which were indexed and fitted to a smaller orthorhombic unit cell (space group *Pbca*, cell volume 3344.77(4) Å³). Both sets of reflections co-exist from 150 K to 120 K; the increasing intensities of the new reflections upon cooling come at the expense of the ZIF-4(Zn)-DS_HT reflections. As-prepared ZIF-4(Zn), with DMF guest molecules in the pores, has been reported to show flexibility on application of mechanical pressure (converting to a monoclinic structure before amorphizing^[21]) and on heating (where it amorphizes before recrystallizing as ZIF-zni^[22]). Furthermore, its desolvated form has one of the lowest bulk moduli of any known MOF (2.56 GPa), recently confirmed by DFT calculations.^[21,23] However, this new orthorhombic phase, referred to as low-temperature ZIF-4(Zn)-DS_LT, has not previously been observed. Moreover, although cooling-induced phase transitions are known for other MOFs and also zeolites,^[6,7,24–26] they have hitherto been unreported for ZIFs.

To ascertain the structural changes occurring during this transition, a Rietveld refinement was performed on the diffraction pattern collected at 80 K. The similarity of the ratios of the lattice parameters of the HT and LT phases indicates some correspondence between the two structures (Table 1). Thus, a starting model for the refinement was developed by an empirical geometry optimization of the undecorated **cag** network in the new cell, followed by a further geometry optimization of the complete structure. Rietveld refinement against this model gave an excellent fit (Table 1 and Figure 1; see the Supporting Information for full details of the development of the model).

The structures of the HT and LT phases are shown in Figure 2. Importantly, the space group symmetry and network connectivity are preserved during the displacive phase transition, while the structure undergoes an isotropic volume contraction of 23 %, thereby eliminating the accessible pore volume present in the HT structure. This conclusion accounts for an observation from previous N₂ adsorption studies at 77 K, where the adsorption isotherm features a large step at 35 kPa indicative of a gate opening process.^[28] It seems very likely, therefore, that the transition from a porous to a dense structure on cooling ZIF-4(Zn)-DS can be reversed by nitrogen adsorption at low temperatures.

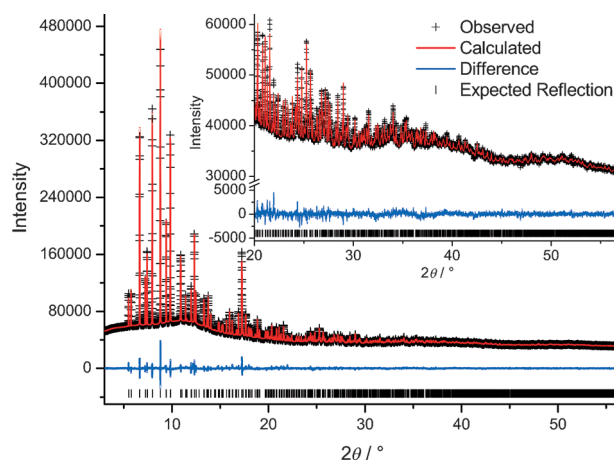


Figure 1. Rietveld plot for the refinement of ZIF-4(Zn)-DS_LT at 80 K. The inset shows the region from 20–56° 2θ.

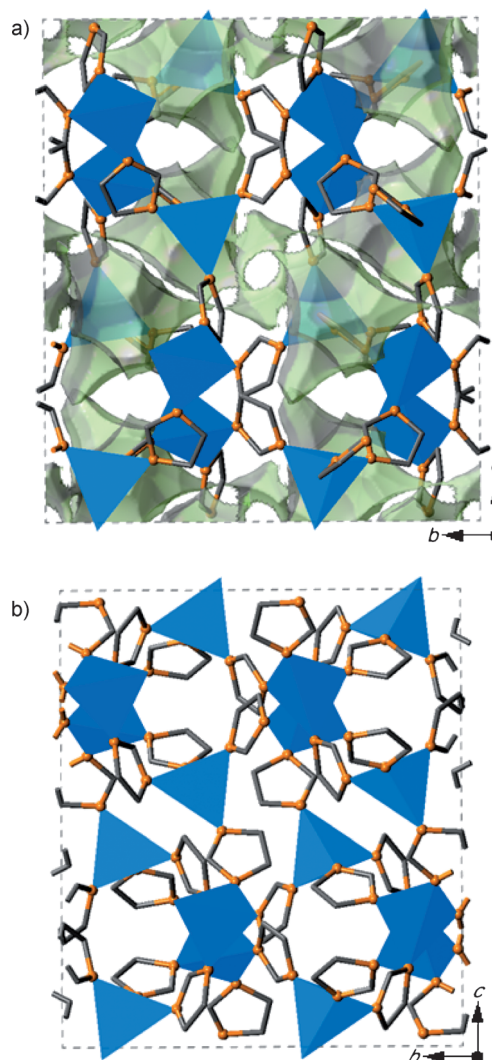


Figure 2. The structures of the HT (a) and LT (b) forms of ZIF-4(Zn)-DS.^[41] Accessible volumes in the HT phase were calculated using a nitrogen probe molecule and are indicated in transparent green.^[27] No accessible volume was found in the LT phase. Zn coordination polyhedra are shown in blue, nitrogen orange, carbon gray.

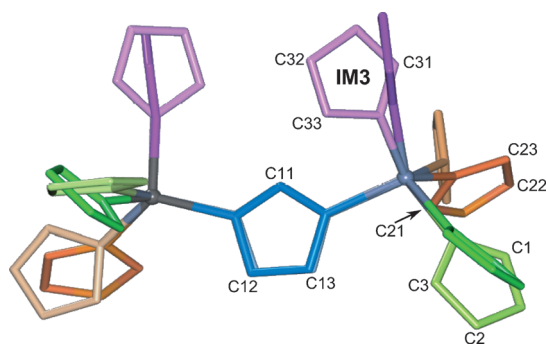


Figure 3. Rotations of the imidazolate ligands between the ZIF-4(Zn)-DS_HT and LT structures (shown in dark and pale colors, respectively). Note that a similar illustration could be made by selecting any of the other three imidazolates as the fixed reference point for the figure.

The dramatic reduction in pore space on going from the HT to the LT structure is achieved by relatively small changes in the Zn–Zn distances (from +0.030 Å to –0.222 Å) but with substantial rotations of the imidazolate linkers (up to 69.3°). The latter are illustrated in Figure 3, where we approximately superimpose the two inequivalent zinc sites and one of the imidazolate ligands that lies between them. Large rotations of the other imidazolate ligands are clearly apparent, notably IM3 (Figure 3), which in the structure reported by Park et al. is disordered over two sites.^[19] We have observed similar disorder in single-crystal data; however, attempts to model IM3 as disordered in the Rietveld refinement of ZIF-4(Zn)-DS_HT resulted in poorer fits to the data. Low-energy phonons of the framework may explain the dynamic behavior of IM3,^[16] which is only possible with the open pores of the HT structure. Studies are on-going to understand the dynamic motion within both the HT and LT structures. The concerted rotation of all imidazolates results in a three-dimensional inward folding of the framework scaffold and a nearly isotropic contraction of the framework. This mechanism is entirely different to the hinge-like motion observed for wine-rack-like structures such as MIL-53 or pillared-layered MOFs, which contract in a highly anisotropic fashion.^[6,7,24,25]

To investigate the phase fractions of the HT and LT phases over the whole temperature range, a parametric Rietveld refinement was performed on the VT-PXRD data^[29] (Supporting Information, Section S3 and Table S6.1). Good fits to the data were obtained across all temperatures ($R_{wp}(\text{min}) = 3.49\%$; $R_{wp}(\text{max}) = 5.91\%$). Figure 4 shows the results of the parametric Rietveld refinement as well as the fractions of both phases as a function of temperature.

As a consequence of the decrease in cell volume, the density of ZIF-4(Zn) increases dramatically on going from the HT form ($\rho = 1.220 \text{ g cm}^{-3}$) to the LT form ($\rho = 1.585 \text{ g cm}^{-3}$). In fact, the crystallographic density calculated for the LT phase is slightly greater than that determined for the dense amorphized ZIF-4(Zn) ($\rho = 1.576 \text{ g cm}^{-3}$) and only just less than the densest crystalline ZIF compound, ZIF-zni ($\rho = 1.603 \text{ g cm}^{-3}$).^[30]

DFT studies on Zn-based ZIF energy landscapes^[31–33] have highlighted the enthalpic stabilization of dense structures over porous ones in a linear fashion with respect to framework density, in agreement with calorimetric thermochemical analysis.^[33,34] These results point towards dispersive interactions as the key stabilizing factor for denser polymorphs. Indeed, inclusion of dispersion interactions has been

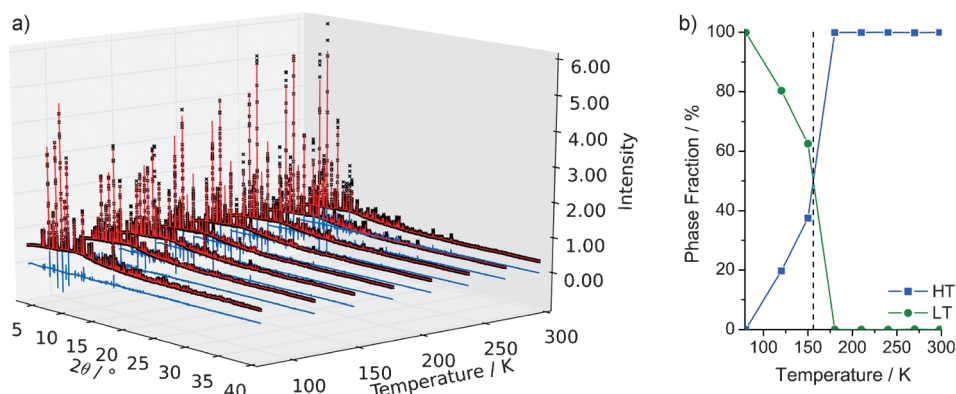


Figure 4. Results of parametric Rietveld refinement of the VT-PXRD data. a) Final Rietveld plots for each temperature (black crosses: observed data; red: calculated profile; blue: difference profile). b) Variation of the HT (purple) and LT (green) phase fractions with temperature.

critical for modeling flexibility in several flexible MOFs and in particular ZIFs.^[25,35,36] DFT-D2 calculations were performed to estimate the electronic energies of both ZIF-4(Zn) phases (HT and LT) to enable comparison of their relative stabilities. Atomic positions were relaxed without symmetry constraints using the generalized gradient approximation (GGA) based on the Perdew–Burke–Ernzerhof (PBE)^[37] exchange–correlation functional with a semi-empirical long-range dispersion correction (using the PBE-D2 method of Grimme^[38]). Similar calculations were also performed on ZIF-zni as the most-dense reference structure. The DFT-D2 calculations predict that the LT structure is more stable in total electronic energy than the HT structure by 7.4 kJ mol^{–1} when considering crystal structures relaxed with their cell parameters maintained at their experimentally determined values. Furthermore, the calculations predict the dense ZIF-zni phase to be more stable than ZIF-4(Zn)-DS_LT by a further 7.2 kJ mol^{–1}. This result is significant in light of previous attempts to quantitatively understand the impact of density on the enthalpy of framework solids (see Supporting Information).^[34]

For experimental verification of the relative energies of the porous and dense ZIF-4(Zn) structures, we carried out

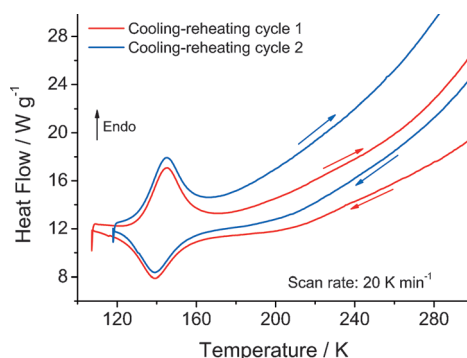


Figure 5. Plot of DSC scans for ZIF-4(Zn)-DS. Data were measured under He gas. A sequence of two experiments, performed on the same sample, is shown (red and blue). Peaks occur in each experiment at approximately the same temperature and in both the heating and cooling limbs, indicating that the phase transition is reversible.

a thermodynamic study. DSC measurements reveal a broad exothermic signal (HT–LT phase transition) with a peak temperature of 139 K upon cooling of ZIF-4(Zn)-DS from room temperature to 110 K (Figure 5). On heating, the reverse endothermic LT–HT transition was observed ($T_{\text{peak}} = 145$ K), showing that the transition is indeed reversible. A second DSC run on the same sample yielded identical results. From these data, the enthalpy change for the exothermic (HT to LT) transition was determined as 8.28 kJ mol^{-1} and 8.84 kJ mol^{-1} for the endothermic (LT to HT) one, in very good agreement with the computational results (note that DFT calculations refer to total electronic energies at 0 K, while calorimetric measurements refer to enthalpies in the range of the transition, so that the comparison is not expected to be perfect). Although the DSC measurements indicate the reversibility of the phase transition, with only a slight hysteresis of approximately 5 K between both transitions, it should be noted that ex situ powder diffraction experiments with larger sample quantities point toward a strongly hysteretic behavior (Supporting Information, Figure S7.1).

Given that the dense ZIF-4(Zn)-DS_LT has a more favorable enthalpy, it is reasonable to ask why it transforms to an open structure at higher temperatures. The driving force for the transition is the much higher entropy of the porous structure. It has been reported for zeolitic silica polymorphs that the entropy is higher for siliceous faujasite, for example, than it is for α quartz.^[39] It is also observed in the thermodynamics of the closed and open-pore forms of MIL-53.^[5,25] In both situations, the origin lies in the greater flexibility of the open-pore structures. In the present case we can estimate the entropy change since we know that $\Delta H = T\Delta S$ at the transition temperature of 140 K. Taking the average value of ΔH from the DSC measurements (8.5 kJ mol^{-1}), we obtain $\Delta S \approx 60 \text{ J K}^{-1} \text{ mol}^{-1}$. This is much larger than the values found in zeolites owing to the greater flexibility and the larger number of atoms in the formula unit of ZIF-4.

The structural flexibility can also be blocked by guest molecules in the pore space. A second VT-PXRD study of DMF-containing ZIF-4 showed no phase transition on cooling from 295 K to 80 K in 5 K steps (full details of the

refinement in the Supporting Information). To investigate whether particle size can also hinder the phase transition, we performed a single-crystal diffraction study. Cooling a large crystal of ZIF-4(Zn)-DS to below 100 K in a N_2 cryostream does not cause a transition to the contracted LT phase (see the Supporting Information for full details). This may be an effect of the larger crystal size compared to the powder samples, but may also be a consequence of the sample environment (N_2 atmosphere instead of vacuum), which leads to adsorption of N_2 within the porous HT structure, thus preventing the transition on cooling.

In summary, we have demonstrated the first example of a thermally induced displacive phase transition in a ZIF material. On cooling, desolvated ZIF-4(Zn) shows a 23 % decrease in unit cell volume through an isomorphic phase transition at about 140 K. Guest molecules present in the pores inhibit the phase transition, confirming that it is the closure of the pore space and consequent enthalpic gain which drives the transition from HT to LT phase. The mechanism of the phase transition is new and differs from those in other breathing MOFs, such as MIL-53,^[5] where the structure adopts a wine-rack topology, demonstrating highly anisotropic flexibility. In ZIF-4(Zn)-DS, the flexibility is achieved by a concerted sequence of rotations of the imidazolate groups resulting in a massive isotropic contraction of the framework. The density of the resulting low-temperature phase is comparable to amorphous ZIF-4(Zn) and close to that of the dense ZIF-zni. Furthermore, the relative stabilities of the HT and LT phases were determined by computational and calorimetric methods, with both results pointing towards the greater enthalpic stability of the LT phase as well as an entropic stabilization of the HT phase at higher temperature. Phase transitions in several ZIFs are mediated by concerted rotations of the imidazolate linker.^[13,14,21] This work is the first example of thermal activation of these rotations and we expect that such behavior may be of major importance in this class of compounds. The magnitude of the rotations is determined by the topology and thus the space group symmetry of the structure.^[40] Therefore, other **cag** network ZIFs may also be expected to demonstrate such dramatic phase transitions. In further studies we shall explore whether such open-pore to closed-pore transitions occur more widely in desolvated ZIF materials and other MOF systems in general.

Keywords: imidazoles · metal–organic frameworks · phase transitions · porosity · zeolitic imidazolate frameworks

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- [1] L. Sarkisov, R. L. Martin, M. Haranczyk, B. Smit, *J. Am. Chem. Soc.* **2014**, *136*, 2228–2231.
- [2] A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel, R. A. Fischer, *Chem. Soc. Rev.* **2014**, *43*, 6062–6096.
- [3] S. Horike, S. Shimomura, S. Kitagawa, *Nat. Chem.* **2009**, *1*, 695–704.
- [4] Y. Sakata, S. Furukawa, M. Kondo, K. Hirai, N. Horike, Y. Takashima, H. Uehara, N. Louvain, M. Meilikhov, T. Tsuruoka, et al., *Science* **2013**, *339*, 193–196.

- [5] C. Serre, S. Bourrelly, A. Vimont, N. A. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, et al., *Adv. Mater.* **2007**, *19*, 2246–2251.
- [6] Y. Liu, J.-H. Her, A. Dailly, A. J. Ramirez-Cuesta, D. A. Neumann, C. M. Brown, *J. Am. Chem. Soc.* **2008**, *130*, 11813–11818.
- [7] A. Ghoufi, A. Subercaze, Q. Ma, P. G. Yot, Y. Ke, I. Puente-Orench, T. Devic, V. Guillerm, C. Zhong, C. Serre, et al., *J. Phys. Chem. C* **2012**, *116*, 13289–13295.
- [8] P. Serra-Crespo, E. Stavitski, F. Kapteijn, J. Gascon, *RSC Adv.* **2012**, *2*, 5051–5053.
- [9] P. Serra-Crespo, A. Dikhtiarenko, E. Stavitski, J. Juan-Alcaniz, F. Kapteijn, F.-X. Coudert, J. Gascon, *CrystEngComm* **2015**, *17*, 276–280.
- [10] A. U. Ortiz, A. Boutin, A. H. Fuchs, F.-X. Coudert, *Phys. Rev. Lett.* **2012**, *109*, 195502.
- [11] C. Gücüyener, J. van den Bergh, J. Gascon, F. Kapteijn, *J. Am. Chem. Soc.* **2010**, *132*, 17704–17706.
- [12] S. Aguado, G. Bergeret, M. P. Titus, V. Moizan, C. Nieto-Draghi, N. Bats, D. Farrusseng, *New J. Chem.* **2011**, *35*, 546–550.
- [13] P. Zhao, G. I. Lampronti, G. O. Lloyd, M. T. Wharmby, S. Facq, A. K. Cheetham, S. A. T. Redfern, *Chem. Mater.* **2014**, *26*, 1767–1769.
- [14] S. A. Moggach, T. D. Bennett, A. K. Cheetham, *Angew. Chem. Int. Ed.* **2009**, *48*, 7087–7089; *Angew. Chem.* **2009**, *121*, 7221–7223.
- [15] D. Fairen-Jimenez, S. A. Moggach, M. T. Wharmby, P. A. Wright, S. Parsons, T. Düren, *J. Am. Chem. Soc.* **2011**, *133*, 8900–8902.
- [16] M. R. Ryder, B. Civalieri, T. D. Bennett, S. Henke, S. Rudić, G. Cinque, F. Fernandez-Alonso, J.-C. Tan, *Phys. Rev. Lett.* **2014**, *113*, 215502.
- [17] G. Férey, C. Serre, *Chem. Soc. Rev.* **2009**, *38*, 1380–1399.
- [18] H. Furukawa, K. E. Cordova, M. O’Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.
- [19] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe, O. M. Yaghi, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 10186–10191.
- [20] Y.-Q. Tian, Z.-X. Chen, L.-H. Weng, H.-B. Guo, S. Gao, D. Y. Zhao, *Inorg. Chem.* **2004**, *43*, 4631–4635.
- [21] T. D. Bennett, P. Simoncic, S. A. Moggach, F. Gozzo, P. Macchi, D. A. Keen, J.-C. Tan, A. K. Cheetham, *Chem. Commun.* **2011**, *47*, 7983–7985.
- [22] E. O. R. Beake, M. T. Dove, A. E. Phillips, D. A. Keen, M. G. Tucker, A. L. Goodwin, T. D. Bennett, A. K. Cheetham, *J. Phys. Condens. Matter* **2013**, *25*, 395403.
- [23] J.-C. Tan, B. Civalieri, A. Erba, E. Albanese, *CrystEngComm* **2015**, *17*, 375–382.
- [24] S. Henke, A. Schneemann, R. A. Fischer, *Adv. Funct. Mater.* **2013**, *23*, 5990–5996.
- [25] A. M. Walker, B. Civalieri, B. Slater, C. Mellot-Draznieks, F. Corà, C. M. Zicovich-Wilson, G. Román-Pérez, J. M. Soler, J. D. Gale, *Angew. Chem. Int. Ed.* **2010**, *49*, 7501–7503; *Angew. Chem.* **2010**, *122*, 7663–7665.
- [26] S. R. G. Balestra, J. J. Gutiérrez-Sevillano, P. J. Merklings, D. Dubbeldam, S. Calero, *J. Phys. Chem. C* **2013**, *117*, 11592–11599.
- [27] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* **2008**, *41*, 466–470.
- [28] T. D. Bennett, S. Cao, J. C. Tan, D. A. Keen, E. G. Bithell, P. J. Beldon, T. Friscic, A. K. Cheetham, *J. Am. Chem. Soc.* **2011**, *133*, 14546–14549.
- [29] G. W. Stinton, J. S. O. Evans, *J. Appl. Crystallogr.* **2007**, *40*, 87–95.
- [30] R. Lehnert, F. Seel, *Z. Anorg. Allg. Chem.* **1980**, *464*, 187–194.
- [31] D. W. Lewis, A. R. Ruiz-Salvador, A. Gomez, L. M. Rodriguez-Albelo, F.-X. Coudert, B. Slater, A. K. Cheetham, C. Mellot-Draznieks, *CrystEngComm* **2009**, *11*, 2272–2276.
- [32] R. Galvelis, B. Slater, A. K. Cheetham, C. Mellot-Draznieks, *CrystEngComm* **2012**, *14*, 374–378.
- [33] I. A. Baburin, S. Leoni, G. Seifert, *J. Phys. Chem. B* **2008**, *112*, 9437–9443.
- [34] J. T. Hughes, T. D. Bennett, A. K. Cheetham, A. Navrotsky, *J. Am. Chem. Soc.* **2013**, *135*, 598–601.
- [35] J. van den Bergh, C. Gücüyener, E. A. Pidko, E. J. M. Hensen, J. Gascon, F. Kapteijn, *Chem. Eur. J.* **2011**, *17*, 8832–8840.
- [36] R. Galvelis, B. Slater, R. Chaudret, B. Creton, C. Nieto-Draghi, C. Mellot-Draznieks, *CrystEngComm* **2013**, *15*, 9603–9612.
- [37] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [38] S. Grimme, *J. Comput. Chem.* **2006**, *27*, 1787–1799.
- [39] P. Vieillard, *Eur. J. Mineral.* **2010**, *22*, 823–836.
- [40] J. C. Tan, T. D. Bennett, A. K. Cheetham, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 9938–9943.
- [41] CCDC 1047055 and CCDC 1047056 (for the ZIF-4(Zn)-DS HT and LT phases, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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