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MLZ Heinz Maier-Leibnitz Zentrum

SNSB Mineralogische Staatssammlung München

MS19: Solid State and Materials Chemistry II

In-situ recrystallization of elastically bendable cocrystals of caffeine post partial desolvation

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The system of 1:1:1 cocrystal solvate of caffeine, 4-chloro-3-nitrobenzoic acid and methanol is the first reported example of molecular crystal that exhibits reversible elastic flexibility [1]. The compound crystallizes in orthorhombic space group symmetry $Fdd2$ [T = 100 K: a = 32.784(9) Å, b = 55.541(15) Å, c = 3.9564(12) Å, V = 7191(4) Å^3]. Elastic bending in these crystals has been determined to be governed by changing distances between molecules within stacks and molecular rotations [2]. The crystals have been demonstrated to lose flexibility at high temperatures which is attributed to partial loss of solvent from their structure (irreversible phase transformation at T_c = 388 K) [1]. While combination of weak dispersive interactions *viz.* C–H ···O hydrogen bonds, π-stacking and van der Waals forces between pseudo spherical functional groups aids flexibility, permanent plastic deformation in these crystals has been argued to be prevented by "interlocking"/ steric barriers in the supramolecular architecture [1,2].

High temperature *in-situ* powder X-ray diffraction studies confirm the phase transformation around T_c. Upon cooling down to room temperature, long acicular crystals were observed after few days. These crystals demonstrate excellent elastic flexibility. Single crystal X-ray diffraction experiments employing synchrotron radiation revealed that the *in-situ* recrystallized crystals have identical space group symmetry but a unit cell volume significantly larger than as grown crystals [T = 100 K: $V_{in\text{-}situ}$ = 7444.7(3) Å^3]. Interestingly, the large a and b axes are found to be slightly shorter as compared to the as grown crystals while the significantly larger c-axis [= 4.15160(10) Å] accounts for such increased unit cell volume of the regrown crystals.

Here we present the atomic level studies of the regrown crystals in comparison to the as grown crystals. The reversibility post partial desolvation is governed by the re-inclusion of methanol albeit different electron counts at the site of the solvent that is suggested to be ~ 1.3-1.4 times larger than the as synthesized crystals from structure refinements. Increased content in the structure enhances the solvent channels that concomitantly result in larger distances between molecules within stacks thus stabilizing the lattice with a larger **c**-axis. The apparent reconstruction of the molecular stacks is accompanied by tilting of the molecules and reorientation between hydrogen bonded tapes different to as synthesized crystals. While in the present case, inherent disorder of the solvent possibly aids in such inclusion of molecular entities, such *in-situ* recrystallization could be employed to manipulate overall structure to tune in variable and/or revive mechanical response in molecular crystals.

[1] Ghosh S, Reddy C. M. Elastic and bendable caffeine cocrystals: Implications for the design of flexible organic crystals. Angew. Chem. Int. Ed., 51, 10319-10323 (2012)

[2] Thompson A. J., Price J. R., McMurtrie J. C., Clegg J. K. The mechanism of bending in co-crystals of caffeine and 4-chloro-3-nitrobenzoic acid. Nat. Commun., 12, 5983, (2021)

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