Crystallographic insights into the solid-solid phase change of pentaglycerine

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Phase-change materials (PCMs) can store and release energy by undergoing a phase transition and can be used for latent heat thermal energy storage (LHTES). The most common type of PCM exploits the solid-liquid transition and is exemplified by sodium acetate trihydrate, which is used in commercially available heat batteries for domestic heating applications [1]. By contrast solid-solid PCMs can store and release heat via solid-solid phase transitions that typically involve order-disorder changes in crystal structures. This approach has the advantages of avoiding issues such as leakage of high-temperature liquids, difficulties in containment of liquids, and the large volume changes associated with melting and freezing of solid-liquid PCMs.

This work focuses on the solid-solid PCM pentaglycerine, an organic polyalcohol [$CH_3C(CH_2OH)_3$] that undergoes an order–disorder phase transition at 82 °C with an enthalpy change of approximately 165 J g^{-1} (201 J cm^{-3}) [2]. Despite its large-scale industrial production and widespread use in resins, coatings [3], and energetic plasticisers [4], the crystallographic behaviour and phase-transition mechanism of pentaglycerine remains poorly understood. In this study, we address this gap by characterising pentaglycerine using powder, single-crystal and *in-situ* X-ray diffraction, as well as differential scanning calorimetry.

Single-crystal X-ray diffraction was used in this work to determine the low-temperature crystal structure of pentaglycerine, revealing an ordered body centred tetragonal phase (a = 6.054 Å, c = 8.610 Å at 100 K). This structure undergoes an order–disorder transition at 82 °C to a previously reported high-temperature face-centred cubic phase (a = 8.86 Å at 373 K) [5]. The increase in crystallographic symmetry observed across the transition is indicative of molecular orientational disorder developing within the solid crystal framework.

Powder X-ray diffraction patterns were also recorded and used for refinements of the room temperature structure. Preliminary results show a different structure of pentaglycerine at room temperature compared to its low and high temperature ones, indicating the presence of another phase transition between 100K and 293K. This suggests a more complex phase behaviour for pentaglycerine than previously thought and highlights the importance of further investigation into its crystallographic properties.

This study presents the first detailed crystallographic characterisation of the solid–solid phase transition in pentaglycerine, providing a structural basis for understanding its thermal behaviour and advancing its potential deployment in thermal energy storage technologies.

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