Investigating the order-disorder phase transitions in solid-solid phase-change materials for latent heat storage applications

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Increasing use of renewable energy sources requires energy storage solutions to bridge the gap between energy supply and demand and facilitate large-scale adoption. As heating represents the largest use of energy in the UK, implementing thermal energy storage that captures and utilises waste heat offers a promising route to improved energy efficiency [1].

Phase-change materials (PCMs) can reversibly store and release large amounts of latent heat during phase transitions. Among these, solid-solid PCMs are emerging as promising candidates due to their inherent advantages over solid-liquid PCMs, including high energy-storage densities, retention of bulk solid properties and removing the need to contain hot liquids [2]. These materials undergo reversible structural reorganisation associated with order–disorder phase transitions, which are recognised as a key factor in achieving high enthalpy values required for effective latent heat storage. In systems containing tetrahedral anions, dynamic anion behaviour is often associated with these transitions, yet the relationship between anion dynamics and thermophysical performance remains poorly understood. To address this gap, selected solid–solid PCMs containing tetrahedral anions are investigated.

The two selected candidates, KBF_4 and Na_2MoO_4, exhibit phase transitions within the industrially relevant temperature range of 250 – 650°C. Although both salts contain tetrahedral anions, they display different properties, including the number of polymorphs, phase transition temperatures and reversibility. KBF_4 exhibits a single reversible solid-solid phase transition at 285°C from the ordered orthorhombic phase to the disordered cubic phase, where the BF_4^- anions gain rotational freedom. In contrast, Na_2Mo_4 is reported to undergo multiple solid-solid phase transitions between 460 – 650°C, which have been monitored using Differential Scanning Calorimetry (DSC) [3-5]. There is a need for more detailed characterisation of the crystal structures of these polymorphs. In this work, *in situ* X-Ray Powder Diffraction (XRPD) is used to monitor structural changes in KBF_4 and Na_2MoO_4. These findings provide insight into how tetrahedral anion disorder influences phase transitions, their reversibility, and heat-storage behaviour, establishing structure-property relationships that will guide the development of solid–solid PCMs for latent heat storage.

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