Oral presentation

Lamellar hybrid materials with solid-solid phase transitions for thermal energy storage: a multi-technique study

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Thermal energy storage has a major role to play in the energy transition, because of its potential and its various fields of application: recovery of the waste heat released during industrial processes, optimisation of battery operating points, heat dissipation in power electronics devices, and so on. The thermal storage using solid-solid phase change materials (SS-PCMs) appears interesting in this context. Organic-inorganic SS-PCMs such as 2D hybrid perovskites were identified as promising candidates as early as the 1980s [1]. Very recently, it has been shown that salts with the generic chemical formula (CnH2n+1NH3)2MIIX4 (where M is a divalent metal and X a halogen) are also interesting as heat transfer materials owing to their temperature and pressure induced phase changes, and can offer a high-performance alternative to current vapour compression systems that emit large quantities of highly polluting fluorocarbon refrigerants [2]. To date no systematic study has provided a global and multiscale description explaining the transitions of those lamellar materials, particularly with regard to the diversity of conformations within both the organic and inorganic layers [3]. We are seeking to establish relationships between compositions, average structures, local arrangements and thermal properties in order to identify the key parameters governing these phase transitions for ultimately designing new materials with optimised thermal properties. Compounds with M = Cu, Zn and Mn, X = Cl and n = 6, 7, 12, 13 and 16 were prepared by solution chemistry in the form of very thin crystalline platelets. Their crystal structures at room temperature could be determined by single-crystal XRD (SCXRD) allowing to rationalize their low temperature structural topologies and molecular conformations as a function of the nature of M and the value of n (Fig 1.a). The solid-solid phase transitions on heating are marked by a large increase of the inter-layer unit cell parameter and a dramatic increase of the crystal mosaicity, precluding their study by SCXRD. The in depth studies of these transitions then request a multitechnique approach combining complementary structural, microstructural and spectroscopic methods, Differential scanning calorimetry (DSC) have been first used to decipher the relationship between the energy and the transition temperature and both the length of the aliphatic chain and the nature of the cation (Fig 1.b). Vibrational spectroscopies (IR, Raman) has highlighted the impact of the phase transitions on dynamic response of the organic and inorganic moieties. Synchrotron radiation (BM31@ESRF) has been used on polycrystalline samples by combining simultaneously temperature dependent XRD with total scattering (PDF analysis) and X-ray absorption spectroscopy (XAS) in order to explain these phase transitions in terms of dynamic disorder, multiscale structural (incuding organic-inorganic and organic-organic interactions) and microstructural modifications.

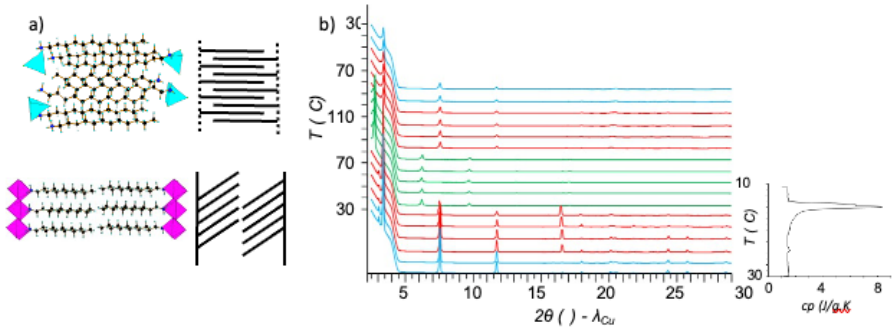

Figure 1. (a) Crystal structure (20°C) and relative arrangement of the aliphatic chains in $(C_{12}H_{25}NH_3)_2ZnCl_4$ (top) and $(C_{12}H_{25}NH_3)_2CuCl_4$ (bottom). (b) DSC curve and TD-PXRD of $(C_{12}H_{25}NH_3)_2ZnCl_4$ (each color corresponds to a different phase).

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