Poster

Molecular ceramics of spin crossover materials by Cool-SPS for barocaloric refrigeration

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Climate change preoccupations motivate researching alternatives to energy-intensive vapor-compression thermodynamic machines, which use gases with tremendous greenhouse effect and are of limited thermodynamic efficiency. Roughly 3 billion systems (refrigeration, air-conditioning, heat pumps) consume around 1/6th of the whole global electricity production, with greenhouse gas emissions equivalent to the whole EU emissions. The mechanocaloric effect, which refers to adiabatic temperature changes induced by stress or pressure, is one of the most promising energy-saving new technology for cooling systems. Mechanocaloric research produced in the last decade highly performing materials, overcoming easily electrocaloric and magnetocaloric materials [1]. Most interestingly, mechanocaloric materials use non-critical, cheap, abundant and non-toxic elements. In 2016 a milestone paper identified molecular Spin CrossOver (SCO) complexes as showing promising mechanocaloric potential [2]. Following papers evidenced large to colossal barocaloric effects around the SCO temperatures, which were reviewed recently in a very favourable light as compared to other materials being investigated [3]. Indeed, SCO corresponds to a stimulus-induced (T, p, light,…) electronic configuration switch, which leads to a change of properties (optical, magnetic, electronic, structural), concomitant with important configurational, magnetic and phonon entropy changes exploitable for barocaloric refrigeration, all the more so since they may be sensitive to small pressure perturbations of a few kilobars or even less.

Crucially, any technological application of those materials, usually available only as polycrystalline powders, require their shaping into macroscopic (poly)centimetric forms. We have evidenced on various model systems that molecular ceramics [4,5], can be elaborated by Cool-SPS processing (SPS: Spark Plasma Sintering, $50 \leq T \leq 600°C$; $40 \leq p \leq 900$ MPa), with relative densities satisfyingly ranging from 85 to 95% of the corresponding crystal structures. Noteworthy differences have been evidenced with the morphology, phase identity (when confronted to polymorphs) and size distribution of the starting materials, be it in the sintering process itself or in the resulting ceramic properties. For one of those systems results obtained will be confronted to the (p,T) phase diagrams obtained through X-ray diffraction data. Indeed, the mapping of those complexes phase diagram, obtained mainly through diffraction studies on single crystals or polycrystalline powder to study and understand the nature of the species observed when combining pressure and temperature changes, is a fundamental tool to follow and control sintering processes.

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