Shaping Spin-Crossover Molecular Ceramics through Cool-SPS for Efficient Barocaloric Refrigeration

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Abstract

As the global demand for energy-efficient cooling solutions grows in response to climate change, tranditional vapor-compression system, responsible for significant energy consumption and greenhouse gas emission, are under increasing scrunity. Everyday refrigeration devices (air conditioners, refrigerators, heat pumps) accounted for up to 20% of the world's electricity production in 2025 and 7.5% of its greenhouse gas emission[1]. One of the most promising new energy-saving technologies for cooling systems used the mechanocaloric effect, which describes adiabatic temperature variations brought on vy pressure (barocaloric) or stress (elastocaloric). Using non-critical, inexpensive, pleintiful, and non-toxic elements, mechanocaloric research has created advanced materials in the past ten years that can readily overcome electrocaloric and magnetocaloric materials[2]. In molecular Spin Crossover (SCO) complexes, a stimulus-induced (*T*, *p*, light,etc.) variation in electronic configuration triggers a transition in properties (mechanical, magnetic, optical, electronic) along with structural and entropy changes[3]. Most interestingly, this transition can be triggers by low pressure stimuli of less than few kilobars, due to volume changes of up to 11%[4]. These characteristics position SCO materials as highly promising canditates for barocaloric application as anticipated in breakthrough reserach published on 2016[5].

Such materials, which are typically only availble as polycrystalline powders, must be shaped into macroscopic (poly)centrimetric forms in order to be used technologically. We have demostrated on variety of respresentative samples that Cool-SPS processing (SPS : Spark Plasma Sintering, 50 ≤ T ≤ 600°C ; 40 ≤ p ≤ 900 MPa) can sinter powders into "molecular ceramics"[6], with relative densities that satisfactorily range from 85 to 95% of the corresponding crystal structures. Singnificant differences have been observed regarding the morphology, phase identity (when dealing with polymorphs) with the initial materials, whether during the sintering process or in the properties of the resulting ceramics. For molecular materials, the results will be compared with the (*p,T*) phase diagrams derived from X-ray diffraction data. In fact, a key tool for monitoring and managing sintering processes is the maping of those complexes phase diagram, which is primarily accomplished through spectroscopic and diffraction studies on single crystals or polycrystalline powder to examine and comprehend the nature of the species seen when combining pressure and temperature changes.

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Gratefully acknowledge funding from the European Innovation Council Pathfinder challenge Clean and Efficient Cooling under the FROSTBIT project (Grant Agreement No. 101161137).