

“From Powder to Ceramic: Processing Spin Crossover Materials for Barocaloric Cooling”

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Environmental change is one of the most critical challenges of the 21st century. Everyday refrigeration devices (air conditioners, refrigerators, heat pumps) consumed up to 20% of the world's electricity production in 2025 and represented 7.5% of global CO₂ emission.^[1] More energy-efficient cooling systems need alternatives to vapor compression refrigeration. The mechanocaloric effect, that is adiabatic variations in temperature related to applied pressure (barocaloric) or stress (elastocaloric), is one of the most promising ones. In 2016, Spin CrossOver (SCO) materials were described as a promising candidates for barocaloric cooling devices.^[2] Molecular SCO complexes, are well-known for their stimulus-induced (*T*, *p*, light, etc.) variation in electronic configuration. This variation cause structural, entropic, mechanical, magnetic, optical, and electronic changes as well.^[3] Most interestingly, they may be sensitive to small pressure perturbations of a few kilobars or even less, due to volume changes of up to 11%.^[4]

Such materials, which are typically only available as polycrystalline powders, must be shaped into macroscopic (poly)centimetric forms in order to be used technologically. We have demonstrated on variety of representative samples that Cool-SPS processing (SPS: Spark Plasma Sintering, $50 \leq T \leq 600^\circ\text{C}$; $40 \leq P \leq 900 \text{ MPa}$) can sinter powders into “molecular ceramics”^[5], with relative densities that satisfactorily range from 85 to 95% of the corresponding crystal structures. Nevertheless, differences have been noticed regarding the morphology, phase identity (when dealing with polymorphs) and magnetic properties with the initial materials after the sintering process. A key tool for monitoring and managing sintering processes is the mapping 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.

[1] M. Baha, S. Hammami and J.-L. Dupont, 177 International institute of refrigeration/Institut international du froid, *The role of refrigeration in the global economy - 60. Informatory Note on Refrigeration Technologies*, International Institute Of Refrigeration/Institut International Du Froid, 177, Boulevard Malesherbes, 75017 Paris (France), **2025**.

[2] K. G. Sandeman, *APL Materials* **2016**, 4, 111102.

[3] P. Gülich, H. A. Goodwin, in *Spin Crossover in Transition Metal Compounds I* (Eds.: P. Gülich, H.A. Goodwin), Springer Berlin Heidelberg, Berlin, Heidelberg, **2004**, pp. 1–47.

[4] P. Guionneau, E. Collet, in *Spin-Crossover Materials* (Ed.: M.A. Halcrow), Wiley, **2013**, pp. 507–526. [5] T. Herisson De Beauvoir, V. Villemot, M. Josse, *Solid State Sciences* **2020**, 102, 106171.

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