

MS27-2-10 Understanding the behaviour of spin crossover materials for barocaloric applications: (P,T) phase diagrams

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Abstract

Climate change preoccupations motivates researching alternatives to energy-intensive vapour-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 roughly about 1/6th of the whole global electricity production, with greenhouse gas emissions equivalent to the whole EU emissions.[1] 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.[2] 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.[3] Following papers evidenced large to colossal barocaloric effects around the SCO temperatures,[4] which were reviewed recently in a very favourable light as compared to other materials being investigated.[5] Indeed SCO corresponds to a stimulus-induced (T, P, light,...) electronic configuration change, leading to a switch of optical/magnetic/electronic/structural properties concomitant with configurational, magnetic and phonon entropy changes[6] that may be sensitive to very small pressure perturbations of a few kilobars or even less.

Understanding the properties of such systems is of interest for the design of improved systems. To do so it is most informative to cross data gathered from structural determinations under varied conditions (temperature, light irradiation or pressure) and properties determination under similar conditions (magnetism, spectroscopy,...). We will present studies on two spin crossover complexes. SCO compounds show a change of spin state under application of an external stimuli (pressure, temperature, photoexcitation). This change goes together with modification of the population of molecular orbitals, with anti-bonding orbitals corresponding to longer metal-ligand bond lengths being populated in the High Spin (HS) state. Pressure is thus naturally one of the relevant thermodynamic constraints to consider: in SCO materials based on Fe²⁺ (d6) ions, it usually favors the diamagnetic low-spin (LS) state, which has a lower volume than the paramagnetic HS state. Diffraction studies, on single crystals or polycrystalline powder, are a powerful tool to study and understand the nature of the species observed when combining pressure and temperature changes (Fig. 1), allowing the mapping of the phase diagram of those complexes.

References

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Fig. 1 Diffraction pattern evolution up to 2.2 GPa

