The Role of Hydrogen Bond Competition in the Colossal Barocaloric Response of Choline-based Plastic Crystals

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Solid-state refrigerants, known as caloric materials, exhibit temperature changes upon the application of external fields such as hydrostatic pressure and hold the potential to replace the environmentally harmful refrigerants with large global warming potentials currently ubiquitously used in cooling processes.

Plastic crystals, compounds which exhibit solid phases characterized by large degrees of orientational disorder, have been shown to exhibit colossal barocaloric effects (ΔS > 100 J kg^{-1} K^{-1}) on par with commercial hydrofluorocarbon refrigerants [1]. The exceptionally large barocaloric response found in plastic crystals originates from structural phase transitions from an ordered state to an orientationally disordered state.

In this work, we explore the structural and barocaloric properties of the [choline]$_2$MX$_4$ family (M = Co, Zn; X = Cl, Br, I). Using pressure- and temperature-variable single crystal and powder x-ray diffraction [2,3] together with differential scanning calorimetry and *ab initio* Molecular Dynamics simulations, we map the P-T phase diagram and systematically study the structural changes that drive the colossal barocaloric response. The chlorinated compounds exhibit a first-order phase transitions with small thermal hysteresis (~2 K) around room temperature. A colossal and competitive reversible isothermal entropy change of $\Delta S_{it,rev}^{max}$ = 139 J kg^{-1} K^{-1} and reversible adiabatic temperature change of $\Delta T_{ad,rev}^{max}$ = 6.1 K are obtained for ΔP = 100 MPa.

We demonstrate that through halide substitution the transition temperature can be tuned over an 80 K temperature range. We find that hydrogen bonding competition plays a central role in the stability of the observed crystallographic phases and underlies the evolution of the barocaloric properties observed with halide substitution. The results of this work illustrate the potential of chemical exchange for tuning barocaloric properties and can be used to inform the design of future solid-state refrigerants.

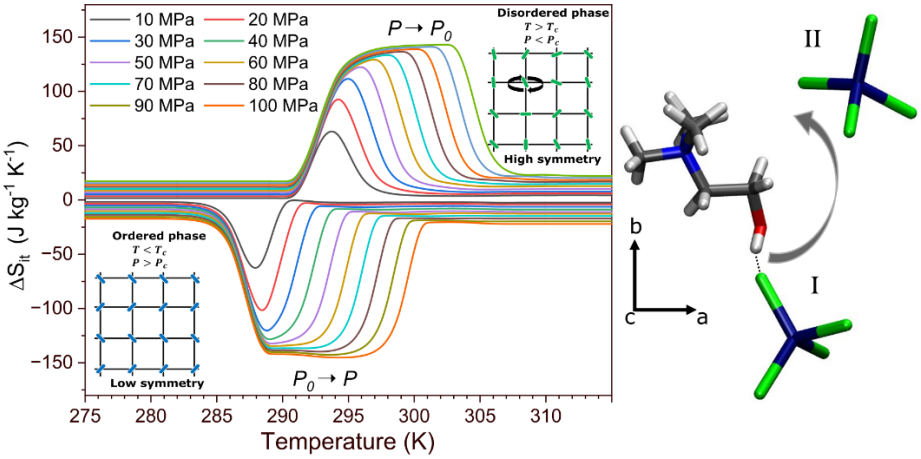


Figure 1. *(left) Isothermal entropy changes as a function of pressure. (right) Reorientation of choline ion in the high-temperature phase.*

[1] B. Li et al., Colossal barocaloric effects in plastic crystals, Nature **567**, 506 (2019).

[2] C. J. McMonagle, et al., High-pressure sapphire capillary cell for synchrotron single-crystal X-ray diffraction measurements to 1500 bar, J. Appl. Crystallogr. **53**, 1519 (2020).

[3] N. J. Brooks, et al., Automated high pressure cell for pressure jump x-ray diffraction, Rev. Sci. Instrum. **81**, 064103 (2010).