Ferroelasticity in a Metal–Organic Framework Perovskite; Towards a New Class of Multiferroics

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Synopsis of the work[1]

$[(CH_2)_3NH_2][Mn(HCOO)_3]$ (1), A metal–organic framework perovskite, exhibits a weakly first order ferroelastic phase transition at ~272 K, from orthorhombic Pnma to monoclinic P21/n, and a further transition associated with antiferromagnetic ordering at ~8.5 K. The main structural changes, through the phase transition, are orientational ordering of the azetidium groups and associated changes in hydrogen bonding. In marked contrast to conventional improper ferroelastic oxide perovskites, the driving mechanism is associated with the X-point of the cubic Brillouin zone rather than being driven by R- and M-point octahedral tilting. The total ferroelastic shear strain of up to ~5% is substantially greater than found for typical oxide perovskites, and highlights the potential of the flexible framework to undergo large relaxations in response to local structural changes. Measurements of elastic and anelastic properties by resonant ultrasound spectroscopy show some of the characteristic features of ferroelastic materials. In particular, acoustic dissipation below the transition point can be understood in terms of mobility of twin walls under the influence of external stress with relaxation times on the order of ~10^{-7} s. Elastic softening as the transition is approached from above is interpreted in terms of coupling between acoustic modes and dynamic local ordering of the azetidium groups. Subsequent stiffening with further temperature reduction is interpreted in terms of classical strain–order parameter coupling at an improper ferroelastic transition which is close to being tricritical. By way of contrast, there are no overt changes in elastic or anelastic properties near 9 K, implying that any coupling of the antiferromagnetic order parameter with strain is weak or negligible.

Order parameter and entropy change of the phase transition

Variable temperature SCXRD measurements, from 120 to 300 K, show the orthorhombic to monoclinic phase transition between 270 and 280 K very clearly. The abrupt increase in β angle indicates the phase transition to be first order in character, and the decrease in β as the transition point is approached from below is consistent with a group/subgroup relationship for the two structures. DSC measurements showed an anomaly at ~273 K during heating and at ~272 K during cooling (Fig. 1a). This hysteresis is consistent with the first-order character deduced from the lattice parameter data. Further heat capacity measurements (at the magnet lab) showed a large peak at ~272 K as well as a small feature at the onset of magnetic ordering at ~8.5 K (Fig. 1b). In order to probe the excess entropy due to the ferroelastic transition, a baseline was fitted to the Cp data and the excess heat capacity, ΔCp, was taken to be the difference between this and the observed values. Integration of ΔCp/T yielded a value of ΔS for the phase transition of 3.39 $Jmol^{-1}K^{-1}$. Given that the measured heat capacity may not necessarily have included a small latent heat, and the possibility of short-range ordering above the transition point, this value is sufficiently close to Rln2 = 5.76 J mol^{-1} K^{-1} to be consistent with a twofold order/disorder transition.

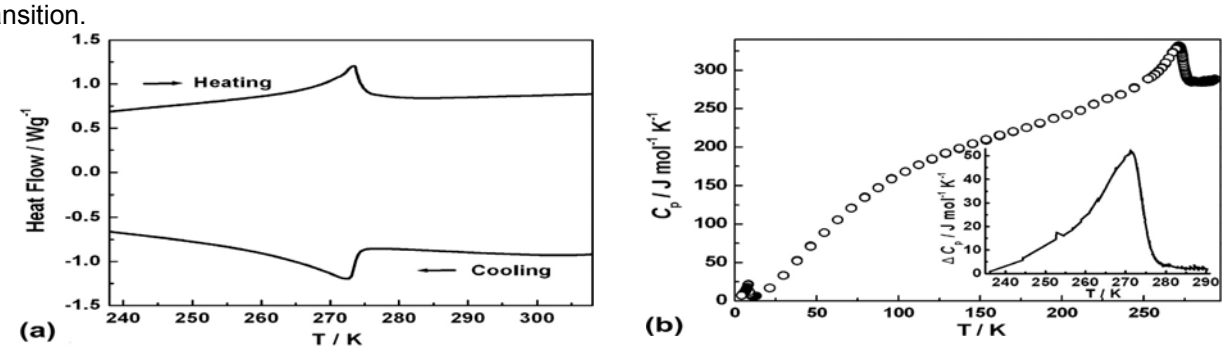

Fig. 1. (a) DSC trace of 1 upon cooling and warming. The bottom line is the cooling mode, the top line the warming mode. (b) Heat capacity of 1 as a function of temperature. The anomalies relating to azetidium group ordering and magnetic ordering are clearly visible. The inset shows the change in Cp related to the phase transition at ~272 K.