COMPOSITIONAL INHOMONOGEITY IN MIXED-METAL MOFS

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Compositional heterogeneity is an essential ingredient in a number of functional materials,[1] with mixed-metal and mixed-linker metal–organic frameworks (MOFs) emerging as an important class of compositionally-complex materials. Making use of a wide range of complementary techniques (variable-temperature X-ray powder diffraction, scanning electron microscopy (SEM) and a combination of infrared spectroscopy, non-negative matrix factorisation (NMF) and reverse Monte Carlo refinement) we show that two MOF families support inhomogeneous distributions of cations – mixed-metal formate perovskites with general formula $[C(NH_2)_3]M_{1-x}Cu_x(HCOO)_3$ (M = Mn, Zn, Mg)[2] and $Zn_{1-x}Cd_x(mIm)_2$ (HmIm = 2-methylimidazole).[3]

For the formate perovskites we have studied, the observation of Cu clustering has important implications for the formation of polar nanoregions and hence relaxor behaviour. Cd doping in the ZIF-8 framework drives a fivefold reduction in the magnitude of thermal expansion behaviour. We interpret this effect in terms of an increased density of negative thermal expansion modes in the more flexible Cd-rich frameworks.

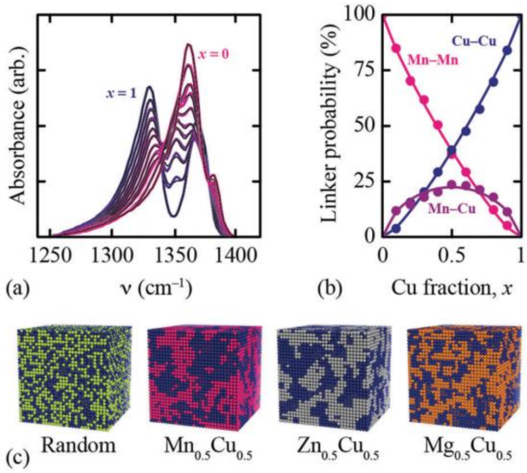

Figure 1. (a) Normalised IR absorption spectra of $[C(NH_2)_3]Cu_xMn_{1-x}(HCOO)_3$ in the formate C–O stretching region (coloured lines) with NMF fits in black. (b) NMF linker distributions (data points) with equilibrium fit (Δ_{Hmix} = 3.1 kJ mol^{-1}) as a solid line. (c) Representative x = 0.5 RMC configurations for M = Mn, Zn, and Mg, showing nanoscale clustering of Cu-rich regions (dark blue).

REFERENCES

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