Solvent Dependence of Molecular Motion in Ferromagnetic [Mn(II)Cr(III)(oxalate)₃]⁻ Salt

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Two-dimensional oxalate-bridged complexes exhibiting diverse magnetic properties can accommodate a variety of functional cations between the two-dimensional layers, giving rise to interesting multifunctional magnets.^[1] We are developing type-I multiferroics by introducing a supramolecular rotor structure that exhibits ferroelectricity^[2] into the oxalate-bridged complex network. However, oxalate-bridged complexes often form voids and are often crystallize with solvent molecules, especially at the cavities of honeycomb layers. It is difficult to measure the physical properties of the crystals above room temperature because the crystals become unstable and collapse due to desolvation.^[3]

In this study, we report on the polar crystal (CBA⁺)([18]crown-6)[MnCr(oxalate)₃](CH₃OH) (CBA⁺ = 4-carboxybutan-1-aminium) (**1**-CH₃OH) of space group *Cc*. The crystals remain in a single-crystal state even when the solvent is removed by heating. The solvent-free crystal (CBA⁺)([18]crown-6)[MnCr(oxalate)₃] (**1**) has the space group *C*2 retaining the polarity of the crystal. It is noteworthy that crystal **1** after desolvation showed a clear dielectric relaxation in the temperature range from 100 K to 300 K with disorder of [18]-crown-6. The dielectric and magnetic properties of the crystals before and after desolvation will be discussed in detail.



Fig. 1. Crystal structure before (a)(c) and (b)(d) after desolvation. Temperature- and frequency dependent dielectric constants before (e)(g) and (f)(h) after desolvation.

References

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