Metal substitution effect on a rubidium manganese hexacyanidoferrate showing a charge-transfer phase transition

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Cyanido-bridged metal assemblies show various phase transition derived from spin crossover, charge transfer, etc., by selecting metal ions. Rubidium manganese hexacyanidoferrates (**RbMnFe**), which have a three-dimensional cyanido-bridged Mn-Fe framework (Figure 1), show a charge-transfer-induced phase transition with a thermal hysteresis loop and also various physical properties such as ferroelectricity, second harmonic generation, and photo magnetism.[1] It is important for such compounds to have bistability at room temperature for practical applications as multifunctional materials. In some cyanido-bridged assemblies, the control of the transition temperature by metal substitution was reported.[2] Herein, we report partially-metal-substituted **RbMnFe** by cobalt or zinc ions (**Co 4%**, **Co 8%**, **Zn 4%** and **Zn 8%**).

Partially-metal-substituted **RbMnFe** were prepared by the modified method of the previous study.[3] Chemical formulas were determined by elemental analyses using CHN standard method and inductively coupled plasma mass spectroscopy (ICP-MS). Rietveld analyses for powder XRD patterns revealed not only crystal structures but also the tendency of decreasing lattice constants by increasing metal substitution ratio. The product of the molar magnetic susceptibility (χ_M) and temperature (T) vs. T plot of the compounds exhibited alternation of transition temperatures. By higher substitution, Zn-substituted **RbMnFe** have lower transition temperatures than that of the original compound while Co substituted **RbMnFe** show higher transition temperature. In particular, **Co 8%** shows room-temperature bistability and the transition temperatures are 254 and 340 K on cooling and heating, respectively (Figure 2).

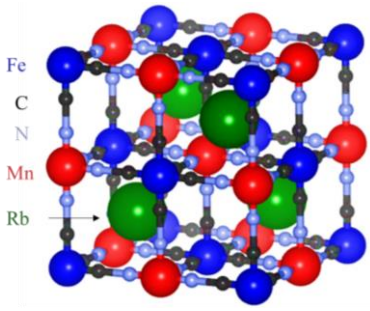

Fig. 1 The crystal structure of **RbMnFe**.

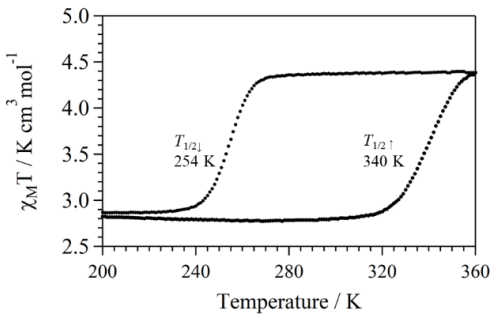

Fig. 2 $\chi_M T$ vs T plot of **Co 8%** under 5000 Oe.

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