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## Negative thermal expansion behavior in rubidium manganese hexacyanoferrate

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In recent years, cyano-bridged metal assemblies have been aggressively studied to demonstrate various magnetic functionalities.(1,2) Among them, rubidium manganese hexacyanoferrate is an attractive material since it shows a various functionalities, e.g., thermal-induced phase transition, electronic-field induced phase transition, ferroelectric ferromagnetism, second harmonic generation, photogmantic effect, and so on.(3-6) In the present work, we prepare plate-shaped microcrystals of rubidium manganese hexacyanoferrate,  $\text{Rb}_{0.97}\text{Mn}[\text{Fe}(\text{CN})_6]$  using a surfactant matrix (6).

The prepared microcrystals show a charge transfer induced phase transition between the cubic Mn(II)-NC-Fe(III) and tetragonal Mn(III)-NC-Fe(II) phases. The Mn(III)-NC-Fe(II) phase exhibits a small negative thermal expansion (NTE) along the  $a$ (LT) and  $c$ (LT) axes with a thermal expansion coefficient of  $\alpha_a(\text{LT}) = -1.40 \pm 0.12 \times 10^{-6} \text{ K}^{-1}$  and  $\alpha_c(\text{LT}) = -0.17 \pm 0.13 \times 10^{-6} \text{ K}^{-1}$  over a wide temperature range of 15 K–300 K. Such small  $|\alpha|$  materials are classified as ZTE materials. The far-infrared spectra show that NTE originates from the transverse modes  $\delta(\text{Fe}-\text{C}\equiv\text{N}-\text{Mn})$  of the transverse translational mode around  $304 \text{ cm}^{-1}$ , and transverse librational modes at 253 and  $503 \text{ cm}^{-1}$ , which are assigned according to first principle calculations. Molecular orbital calculations indicate that ZTE and the charge transfer phase transition both originate from the transverse mode. Additionally, an oriented film on  $\text{SiO}_2$  glass is prepared using a microcrystal dispersive methanol solution and a spin-coating technique. This is the first report of a ZTE film that maintains a constant film thickness over a wide temperature range of 300 K.

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