Coexistence of Ferroelectricity and Ferromagnetism in a Rubidium Manganese Hexacyanoferrate

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(ix) Synthesis and valence states of Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}^{-}$·0.4H$_2$O, Rb$_{0.28}$Mn[Fe(CN)$_6$]$_{0.76}^{-}$·3.6H$_2$O, and K$_{0.10}$Mn[Fe(CN)$_6$]$_{0.70}^{-}$·4.5H$_2$O.
(x) P-E curve at 77 K and schematically structural illustration of K$_{0.10}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$[Fe$^{III}$(CN)$_6$]$_{0.70}^{-}$·4.5H$_2$O, Rb$_{0.28}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$[Fe$^{III}$(CN)$_6$]$_{0.76}^{-}$·3.6H$_2$O, Rb$_{0.28}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$[Fe$^{III}$(CN)$_6$]$_{0.70}^{-}$·3.6H$_2$O, and Rb$_{0.94}$Mn$^{II}_{0.02}$Mn$^{III}_{0.98}$[Fe$^{II}$(CN)$_6$]$_{0.98}^{-}$·0.4H$_2$O.
(xi) $P$ vs. $E$ plots for reference samples of SiO$_2$, Mn$^{II}$(Cr$^{III}$(CN)$_6$)$_{2/3}^{-}$·5H$_2$O, Co$^{II}$(Cr$^{III}$(CN)$_6$)$_{2/3}^{-}$·5H$_2$O, and Cs$^1$Co$^{II}$(Cr$^{III}$(CN)$_6$)$_{1/3}^{-}$·0.5H$_2$O at 77 K.
(i) \( \chi_{MT-T} \) plots of Rb\(_{0.82}\)Mn[Fe(CN)\(_6\)]\(_{0.94}\)·H\(_2\)O under an external field of 5000 Oe:

![Graph](image1)

Fig. S1 \( \chi_{MT-T} \) plots of Rb\(_{0.82}\)Mn[Fe(CN)\(_6\)]\(_{0.94}\)·H\(_2\)O under an external field of 5000 Oe.

(ii) IR spectra of Rb\(_{0.82}\)Mn[Fe(CN)\(_6\)]\(_{0.94}\)·H\(_2\)O at 300 and 100 K:

The CN stretching peaks at 2152 cm\(^{-1}\) and 2095 cm\(^{-1}\) are Fe\(^{III}\)–CN–Mn\(^{II}\) and Fe\(^{II}\)–CN–Mn\(^{III}\), and the ratio between these two peak intensities is 1:1.05\(^{[6a]}\). Since only Fe\(^{III}\)–CN–Mn\(^{II}\) peak was observed at 300 K, HT phase is Rb\(_{0.82}\)Mn\(^{II}\)[Fe\(^{III}\)(CN)\(_6\)]\(_{0.94}\)·H\(_2\)O. The IR spectrum observed at 100 K indicates that the LT phase contains Fe\(^{II}\), Fe\(^{III}\), Mn\(^{II}\), and Mn\(^{III}\) and the valence state is Rb\(_{0.82}\)Mn\(_{1-a}\)Mn\(_{a}\)[Fe\(^{II}\)(CN)\(_6\)]\(_a\)[Fe\(^{III}\)(CN)\(_6\)]\(_{(0.94-a)}\) (\(a = \text{Mn}^{III}/(\text{Mn}^{II} + \text{Mn}^{III})\)). Considering that the peak intensity of Fe\(^{II}\)–CN–Mn\(^{III}\) is proportional to \(a^2\), the valence state of LT phase is determined to be Rb\(_{0.82}\)Mn\(_{0.20}\)Mn\(_{0.80}\)[Fe\(^{II}\)(CN)\(_6\)]\(_{0.80}\)[Fe\(^{III}\)(CN)\(_6\)]\(_{0.14}\)·H\(_2\)O from the IR peak intensity ratio (Fig. S3).

![Graph](image2)

Fig. S2 IR spectra of Rb\(_{0.82}\)Mn[Fe(CN)\(_6\)]\(_{0.94}\)·H\(_2\)O at 300 K (dotted line) and 100 K (solid line).
(iii) XRD patterns of $\text{Rb}_{0.82}\text{Mn}[\text{Fe(CN)}_6]_{0.94}\cdot\text{H}_2\text{O}$ at 300 and 100 K:

![XRD patterns of $\text{Rb}_{0.82}\text{Mn}[\text{Fe(CN)}_6]_{0.94}\cdot\text{H}_2\text{O}$ at 300 and 100 K. (*: Silicon.)](image)

Fig. S3 XRD patterns of $\text{Rb}_{0.82}\text{Mn}[\text{Fe(CN)}_6]_{0.94}\cdot\text{H}_2\text{O}$ at 300 K and 100 K. (*: Silicon.)

(iv) Magnetization vs. external magnetic field plots of $\text{Rb}^I_{0.82}\text{Mn}^{II}_{0.20}\text{Mn}^{III}_{0.80}[\text{Fe}^{II}(\text{CN})_6]_{0.80-}[\text{Fe}^{III}(\text{CN})_6]_{0.14}\cdot\text{H}_2\text{O}$:

![Magnetization vs. external magnetic field plots of $\text{Rb}^I_{0.82}\text{Mn}^{II}_{0.20}\text{Mn}^{III}_{0.80}[\text{Fe}^{II}(\text{CN})_6]_{0.80-}[\text{Fe}^{III}(\text{CN})_6]_{0.14}\cdot\text{H}_2\text{O}$.](image)

Fig. S4 Magnetization vs. external magnetic field plots at 2 K of $\text{Rb}^I_{0.82}\text{Mn}^{II}_{0.20}\text{Mn}^{III}_{0.80-}[\text{Fe}^{II}(\text{CN})_6]_{0.80}[\text{Fe}^{III}(\text{CN})_6]_{0.14}\cdot\text{H}_2\text{O}$. 

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(v) Leakage current vs. electric field at 77 K of Rb$_{0.82}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$[Fe$^{II}$(CN)$_6$]$_{0.80}$[Fe$^{III}$(CN)$_6$]$_{0.14}$·H$_2$O:

The leakage current is extremely low (less than $10^{-10}$ A cm$^{-2}$). Measuring limitation in the present equipment is $10^{-9}$ A cm$^{-2}$.

![Leakage current vs. electric field at 77 K of Rb$_{0.82}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$[Fe$^{II}$(CN)$_6$]$_{0.80}$[Fe$^{III}$(CN)$_6$]$_{0.14}$·H$_2$O.](image)

Fig. S5 Leakage current vs. electric field at 77 K of Rb$_{0.82}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$[Fe$^{II}$(CN)$_6$]$_{0.80}$[Fe$^{III}$(CN)$_6$]$_{0.14}$·H$_2$O.

(vi) Temperature dependence of $P_r$ and $E_c$ values of Rb$_{0.82}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$[Fe$^{II}$(CN)$_6$]$_{0.80}$-[Fe$^{III}$(CN)$_6$]$_{0.14}$·H$_2$O:

![Temperature dependence of $P_r$ and $E_c$ values of Rb$_{0.82}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$[Fe$^{II}$(CN)$_6$]$_{0.80}$-[Fe$^{III}$(CN)$_6$]$_{0.14}$·H$_2$O.](image)

Fig. S6 Temperature dependence of $P_r$ (a) and $E_c$ (b) values of Rb$_{0.82}$Mn$^{II}_{0.20}$Mn$^{III}_{0.80}$-[Fe$^{II}$(CN)$_6$]$_{0.80}$-[Fe$^{III}$(CN)$_6$]$_{0.14}$·H$_2$O.
(vii) Leakage current vs. temperature plots for Rb$_{0.82}$Mn[Fe(CN)$_6$]$_{0.94}$·H$_2$O:

The leakage current is observed above 160 K by the application of +100 kV cm$^{-1}$.

![Leakage current vs. temperature plots for Rb$_{0.82}$Mn[Fe(CN)$_6$]$_{0.94}$·H$_2$O](image)

Fig. S7 Leakage current vs. temperature plots for Rb$_{0.82}$Mn[Fe(CN)$_6$]$_{0.94}$·H$_2$O by the application of +100 kV cm$^{-1}$.

(xiii) Temperature dependence of the dielectric constant of Rb$^+$$_{0.82}$Mn$^{II}$$_{0.20}$Mn$^{III}$$_{0.80}$-[Fe$^{II}$(CN)$_6$]$_{0.80}$[Fe$^{III}$(CN)$_6$]$_{0.14}$·H$_2$O:

![Temperature dependence of the dielectric constant](image)

Fig. S8 Temperature dependence of the dielectric constant ($\varepsilon$) of Rb$^+$$_{0.82}$Mn$^{II}$$_{0.20}$Mn$^{III}$$_{0.80}$-[Fe$^{II}$(CN)$_6$]$_{0.80}$[Fe$^{III}$(CN)$_6$]$_{0.14}$·H$_2$O ($E = \pm 25$ V cm$^{-1}$ and $f = 500$ Hz). $\varepsilon$ of the LT phase vs. temperature plots show that the increase of $\varepsilon$ is observed above 200 K in the warming process. Although the peak of $\varepsilon$ can not be observed due to phase transition from LT phase to HT phase above 260 K, we are considering that the ferroelectric phase transition occurs at higher temperature.
(ix) Synthesis and valence states of Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$·0.4H$_2$O, Rb$_{0.28}$Mn[Fe(CN)$_6$]$_{0.76}$·3.6H$_2$O, and K$_{0.10}$Mn[Fe(CN)$_6$]$_{0.70}$·4.5H$_2$O:

Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$·0.4H$_2$O

The compound was prepared by reacting an aqueous solution of MnCl$_2$ (0.1 mol dm$^{-3}$) with a mixed aqueous solution of RbCl (1.5 mol dm$^{-3}$) and K$_3$[Fe(CN)$_6$] (0.1 mol dm$^{-3}$) to yield a precipitate. Elemental analyses showed that the formula was Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$·0.4H$_2$O, Calcd, Rb; 22.94, Mn; 15.69, Fe; 15.63, C; 20.16, N; 23.52%, Found, Rb; 22.96, Mn; 15.86, Fe; 15.62, C; 19.97, N; 23.47%. The magnetic susceptibility ($\chi_M$) decreased at 225 K ($T_{1/2}$), but abruptly increased at 306 K ($T_{1/2}$) in the cooling and warming processes, respectively (Fig. S9a). Variable-temperature IR spectroscopy indicated that the formulas of the high-temperature (HT) and the low-temperature (LT) phases were composed of Rb$_1^{0.94}$Mn$_{0.02}$Mn$^{III}$[Fe$^{III}$]$_{0.98}$·0.4H$_2$O and Rb$_{0.94}$Mn$^{II}$[Fe$^{III}$]$_{0.76}$·3.6H$_2$O, respectively (Fig. S9b).

Rb$_{0.28}$Mn[Fe(CN)$_6$]$_{0.76}$·3.6H$_2$O

The compound was prepared by reacting an aqueous solution of MnCl$_2$ (0.1 mol dm$^{-3}$) with a mixed aqueous solution of RbCl (0.05 mol dm$^{-3}$) and K$_3$[Fe(CN)$_6$] (0.1 mol dm$^{-3}$) to yield a precipitate. Elemental analyses showed that the formula was Rb$_{0.28}$Mn[Fe(CN)$_6$]$_{0.76}$·3.6H$_2$O, Calcd, Rb; 7.85, Mn; 18.02, Fe; 13.92, C; 17.97, N; 20.96%, Found, Rb; 7.74, Mn; 18.26, Fe; 14.10, C; 17.69, N; 20.82%. The $\chi_M$ value did not exhibit a phase transition (Fig. S9c). In this compound, the phase transition was not observed and HT phase (Rb$_1^{0.28}$Mn$_{0.02}$Mn$^{III}$[Fe$^{III}$]$_{0.76}$·3.6H$_2$O) was maintained in the whole temperature.

K$_{0.10}$Mn[Fe(CN)$_6$]$_{0.70}$·4.5H$_2$O

The compound was prepared by reacting an aqueous solution of MnCl$_2$ (0.1 mol dm$^{-3}$) with a mixed aqueous solution and K$_3$[Fe(CN)$_6$] (0.1 mol dm$^{-3}$) to yield a precipitate. Elemental analyses showed that the formula was K$_{0.10}$Mn[Fe(CN)$_6$]$_{0.70}$·4.5H$_2$O, Calcd, K; 1.36, Mn; 19.06, Fe; 13.56, C; 17.50, N; 20.41%, Found, K; 1.13, Mn; 18.80, Fe; 13.73, C; 17.27, N; 20.48%. The $\chi_M$ value did not exhibit a phase transition (Fig. S9d). In this compound, the phase transition was not observed and HT phase (K$_1^{0.10}$Mn$_{0.02}$Mn$^{III}$[Fe$^{III}$]$_{0.70}$·4.5H$_2$O) was maintained in the whole temperature.

The temperature dependence of the IR spectra and the magnetic susceptibilities of these compounds show that the charge-transfer phase transition in Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$·0.4H$_2$O is completely achieved, i.e., Mn$^{III}$ abundance ratio (ratio$_{Mn}^{III} = Mn^{III}/(Mn^{II}+Mn^{III}) =98\%$, but in Rb$_{0.28}$Mn[Fe(CN)$_6$]$_{0.76}$·3.6H$_2$O and Rb$_{0.82}$Mn[Fe(CN)$_6$]$_{0.94}$·H$_2$O, phase transitions do not occur, ratio$_{Mn}^{III} = 0\%$, and their HT phases are maintained even at low temperatures.
Fig. S9  a) $\chi_M T$–$T$ plots of Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$·0.4H$_2$O. b) IR spectra of Rb$_{0.94}$Mn[Fe(CN)$_6$]$_{0.98}$·0.4H$_2$O at 300 K (dotted line) and 100 K (solid line). c) $\chi_M T$–$T$ plots of Rb$_{0.28}$Mn[Fe(CN)$_6$]$_{0.76}$·3.6H$_2$O. d) $\chi_M T$–$T$ plots of K$_{0.10}$Mn[Fe(CN)$_6$]$_{0.70}$·4.5H$_2$O.

The valence states of the rubidium manganese hexacyanoferrates

<table>
<thead>
<tr>
<th></th>
<th>HT phase</th>
<th>LT phase</th>
<th>ratio$_{Mn^{III}}$ $^a$</th>
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<tbody>
<tr>
<td>Rb$_{0.94}$Mn$^{II}$[Fe$^{III}$(CN)$<em>6$]$</em>{0.98}$·0.4H$_2$O</td>
<td>Rb$_{0.94}$Mn$^{II}$[Fe$^{III}$(CN)$<em>6$]$</em>{0.98}$·0.4H$_2$O</td>
<td>98%</td>
<td></td>
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<tr>
<td>Rb$_{0.82}$Mn$^{II}$[Fe$^{III}$(CN)$<em>6$]$</em>{0.94}$·H$_2$O</td>
<td>Rb$_{0.82}$Mn$^{II}$[Fe$^{III}$(CN)$<em>6$]$</em>{0.80}$[Fe$^{II}$(CN)$<em>6$]$</em>{0.14}$·H$_2$O</td>
<td>80%</td>
<td></td>
</tr>
<tr>
<td>Rb$_{0.28}$Mn$^{II}$[Fe$^{III}$(CN)$<em>6$]$</em>{0.76}$·3.6H$_2$O</td>
<td></td>
<td>[b]</td>
<td></td>
</tr>
<tr>
<td>K$_{0.10}$Mn$^{II}$[Fe$^{III}$(CN)$<em>6$]$</em>{0.70}$·4.5H$_2$O</td>
<td></td>
<td>[b]</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ ratio$_{Mn^{III}}$ is Mn$^{III}$ abundance ratio ($=\text{Mn}^{III}/(\text{Mn}^{II}+\text{Mn}^{III})$).

$^b$ the sample does not exhibit a phase transition.
(x) P-E curve at 77 K and schematically structural illustration of K\textsubscript{0.10}Mn\textsuperscript{II}[Fe\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{0.70}·4.5H\textsubscript{2}O, Rb\textsubscript{0.28}Mn\textsuperscript{II}[Fe\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{0.76}·3.6H\textsubscript{2}O, Rb\textsubscript{0.82}Mn\textsuperscript{II}0.20Mn\textsuperscript{III}0.80[Fe\textsuperscript{II}(CN)\textsubscript{6}]0.80[Fe\textsuperscript{III}(CN)\textsubscript{6}]0.14·H\textsubscript{2}O, and Rb\textsubscript{0.94}Mn\textsuperscript{II}0.02Mn\textsuperscript{III}0.98[Fe\textsuperscript{II}(CN)\textsubscript{6}]0.98·0.4H\textsubscript{2}O:

\[
\text{A}_{3x-2}\text{Mn[Fe(CN)]}_x\cdot z\text{H}_2\text{O} \quad (A = \text{K or Rb})
\]

<table>
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<th>x</th>
<th>ratio\textsubscript{Mn\textsuperscript{III}}</th>
</tr>
</thead>
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<td>0%</td>
</tr>
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<td>80%</td>
</tr>
<tr>
<td>0.94</td>
<td>98%</td>
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</table>

Fig. S10  (upper) P-E curve at 77 K of (from left to right) K\textsubscript{0.10}Mn\textsuperscript{II}[Fe\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{0.70}·4.5H\textsubscript{2}O, Rb\textsubscript{0.28}Mn\textsuperscript{II}[Fe\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{0.76}·3.6H\textsubscript{2}O, Rb\textsubscript{0.82}Mn\textsuperscript{II}0.20Mn\textsuperscript{III}0.80[Fe\textsuperscript{II}(CN)\textsubscript{6}]0.80[Fe\textsuperscript{III}(CN)\textsubscript{6}]0.14·H\textsubscript{2}O, and Rb\textsubscript{0.94}Mn\textsuperscript{II}0.02Mn\textsuperscript{III}0.98[Fe\textsuperscript{II}(CN)\textsubscript{6}]0.98·0.4H\textsubscript{2}O. (lower) Schematically structural illustration of A\textsubscript{3x-2}Mn[Fe(CN)]\textsubscript{x}·zH\textsubscript{2}O (A = K or Rb) at 77K, (from left to right) K\textsubscript{0.10}Mn\textsuperscript{II}[Fe\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{0.70}·4.5H\textsubscript{2}O, Rb\textsubscript{0.28}Mn\textsuperscript{II}[Fe\textsuperscript{III}(CN)\textsubscript{6}]\textsubscript{0.76}·3.6H\textsubscript{2}O, Rb\textsubscript{0.82}Mn\textsuperscript{II}0.20Mn\textsuperscript{III}0.80[Fe\textsuperscript{II}(CN)\textsubscript{6}]0.80[Fe\textsuperscript{III}(CN)\textsubscript{6}]0.14·H\textsubscript{2}O, and Rb\textsubscript{0.94}Mn\textsuperscript{II}0.02Mn\textsuperscript{III}0.98[Fe\textsuperscript{II}(CN)\textsubscript{6}]0.98·0.4H\textsubscript{2}O. The positions of Mn\textsuperscript{II}–Fe\textsuperscript{III} site, Mn\textsuperscript{III}–Fe\textsuperscript{II} site, and Fe vacancy are chosen by computing with random numbers. Red octahedron is Mn\textsuperscript{II}, red sphere is Fe\textsuperscript{III}, blue octahedron is Mn\textsuperscript{III}, blue sphere is Fe\textsuperscript{II}, and blank is Fe vacancy.
(xi) \( P \) vs. \( E \) plots for reference samples of SiO\(_2\), Mn\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_{2/3}\cdot5\)H\(_2\)O, Co\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_{2/3}\cdot5\)H\(_2\)O, and Cs\(^{I}\)Co\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_0.5\)H\(_2\)O at 77 K:

As reference experiments, SiO\(_2\) glass, Mn\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_{2/3}\cdot5\)H\(_2\)O, Co\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_{2/3}\cdot5\)H\(_2\)O, and Cs\(^{I}\)Co\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_0.5\)H\(_2\)O were measured in similar manners at 77 K. The \( P \) vs. \( E \) plots of these reference samples show straight lines without hysteresis loops. These observations indicate that Rb\(_{0.82}\)Mn\(_{0.20}\)Mn\(_{0.80}\)[Fe\(^{II}\)(CN)\(_6\)]\(_{0.80}\)[Fe\(^{III}\)(CN)\(_6\)]\(_{0.14}\)H\(_2\)O has an intrinsic ferroelectric origin.

Fig. S11 \( P \) vs. \( E \) plots at 77 K for SiO\(_2\) (black line), Mn\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_{2/3}\cdot5\)H\(_2\)O (green line), Co\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_{2/3}\cdot5\)H\(_2\)O (red line), and Cs\(^{I}\)Co\(^{II}\)[Cr\(^{III}\)(CN)\(_6\)]\(_0.5\)H\(_2\)O (blue line).