Charge-transfer phase transition and zero thermal expansion in caesium manganese hexacyanoferrates[†]

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A series of caesium manganese hexacyanoferrates is prepared; $Cs^{I}_{1.78}Mn^{II}[Fe^{II}(CN)_{6}]_{0.78}[Fe^{III}(CN)_{6}]_{0.22}$ (1), $Cs^{I}_{1.57}Mn^{II}[Fe^{II}(CN)_{6}]_{0.57}[Fe^{III}(CN)_{6}]_{0.43}$ (2), $Cs^{I}_{1.51}Mn^{II}[Fe^{II}(CN)_{6}]_{0.51}[Fe^{III}(CN)_{6}]_{0.49}$ (3), and $Cs^{I}_{0.94}Mn^{II}[Fe^{II}(CN)_{6}]_{0.21}[Fe^{III}(CN)_{6}]_{0.70} \cdot 0.8H_2O$ (4). 1–3 show charge-transfer phase transitions between the high-temperature (HT) and low-temperature (LT) phases with transition temperatures ($T_{1/24}$, $T_{1/27}$) of (207 K, 225 K) (1), (190 K, 231 K) (2), and (175 K, 233 K) (3) at a cooling and warming rates of 0.5 K min⁻¹. Variable temperature IR spectra indicate that the valence states of the LT phases of 1–3 are $Cs^{I}_{1.78}Mn^{II}_{0.78}Mn^{III}_{0.22}[Fe^{II}(CN)_{6}], Cs^{I}_{1.57}Mn^{II}_{0.57}Mn^{III}_{0.43}[Fe^{II}(CN)_{6}], and Cs^{I}_{1.51}Mn^{II}_{0.51}Mn^{III}_{0.49}$ [Fe^{II}(CN)₆], respectively. The XRD measurements for 1–3 show that crystal structures of the HT and LT phases are cubic structures ($Fm\bar{3}m$), but the lattice constants decrease from the HT phase to the LT phase; a =10.5446(17) \rightarrow 10.4280(7) Å (1), 10.5589(17) \rightarrow 10.3421(24) Å (2), and 10.5627(11) \rightarrow 10.3268(23) Å (3). The magnetization *vs.* temperature curves and the magnetization *vs.* external magnetic field curves show that the LT phases are ferromagnetic with Curie temperatures of 4.3 (1), 5.0 (2), and 5.6 K (3). At a cooling rate of -0.5 K min⁻¹, 4 does not show the charge-transfer phase transition, but does show a behavior of zero thermal expansion with a thermal expansivity of $+0.2 \times 10^{-6}$ K⁻¹ throughout the temperature range 300 and 20 K.

1. Introduction

Prussian Blue analogues^{1,2} are condensed matter with a strong cooperativity since the transition metal ions are bridged by ligands with a 3-D network structure. Various interesting properties have been reported with Prussian Blue analogues,³⁻¹¹ e.g., high Curie temperatures (T_c) ,³ humidity responses,⁴ photomagnetism,⁵ pressure-induced CN flip,6 and zero thermal expansion.7,8 Prussian Blue analogues have several types of crystal structure such as $M_A[M_B(CN)_6]_{2/3}$ · zH_2O (space group = $Fm\bar{3}m$), $AM_A[M_B(CN)_6]$ $(F\bar{4}3m)$, and $A_2M_A[M_B(CN)_6]$ $(Fm\bar{3}m)$ where M_A and M_B are transition metal ions, and A is an alkali metal ion in the interstitial site of the lattice.² The physical properties and functions of Prussian Blue analogues are influenced by the type of A^I incorporated. For example, Bleuzen et al. have reported that the position of the Cs⁺ ion in Cs_{0.7}Co₄[Fe(CN)₆]_{2.9}·16H₂O is displaced from the center of the interstitial site and the Co^{II}-NC-Fe^{III} entities are bent.¹⁰ In addition, we recently reported a chargetransfer phase transition with RbMn[Fe(CN)₆], which is caused by a metal-to-metal charge-transfer from Mn^{II} to Fe^{III} and a Jahn-Teller distortion of the produced Mn^{III}.11 In this work, instead of using the Rb⁺ ion, a series of $Cs_x Mn[Fe(CN)_6]_y \cdot zH_2O$ (x = 0.94-1.78, y = 0.92-1) was prepared. This article describes the synthesis, electronic states, crystal structures, and magnetic properties of this series.

2. Experimental

The target materials were prepared by reacting an aqueous solution of $MnCl_2$ (*a* mol dm⁻³) and CsCl (*b* mol dm⁻³) with a mixed aqueous solution of $K_3[Fe(CN)_6]$ (*a* mol dm⁻³) and CsCl (*b* mol dm⁻³): (*a*, *b*) = (0.01, 1) (condition I), (0.02, 1) (condition II), (0.025, 5) (condition III), and (0.02, 0.03) (condition IV).¹² The precipitates were filtered and dried, yielding powders. Caesium(1) manganese(II) hexacyanoferrate(II)¹³ was also prepared as a reference by reacting an aqueous solution of MnCl₂ (0.025 mol dm⁻³) and CsCl (1 mol dm⁻³) with a mixed aqueous solution of $K_4[Fe(CN)_6]$ (0.025 mol dm⁻³) and CsCl (1 mol dm⁻³).

Elemental analyses of the synthesized samples were performed by inductively coupled plasma mass spectrometry for Cs, Mn, and Fe and standard microanalytical methods for C and N. The infrared (IR) spectra were recorded on a Shimadzu FT-IR 8200PC spectrometer. The X-ray photoelectron spectroscopy (XPS) measurements were conducted by a Physical Electronics (PHI) model 5600 spectrometer equipped with a hemispherical capacitor analyzer. The X-ray powder diffraction (XRD) patterns were measured with a Rigaku RINT2100 instrument (Cu K α). The magnetic properties were investigated using a Quantum Design MPMS-5S superconducting quantum interference device magnetometer.

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[†] Electronic supplementary information (ESI) available: The phase transition temperatures of $Cs_xMn[Fe(CN)_s]_y$. zH₂O, O 1s XPS spectra for 1–4, IR spectra, magnetic susceptibility, and XRD patterns for 5, Weiss temperatures for 1–4, and magnetic properties of 4. See DOI: 10.1039/b605269j

3. Results and discussion

3.1. Materials

The precipitates under conditions I-III were dark brown powders. At 300 K, the CN stretching frequencies of Fe^{III}-CN-Mn^{II} and Fe^{II}-CN-Mn^{II} were observed in the IR spectra (Fig. 1, left). Elemental analyses showed that the formulas of the obtained compounds under conditions I-III were $Cs_{1.78}^{I}Mn^{II}[Fe^{II}(CN)_{6}]_{0.78}[Fe^{III}(CN)_{6}]_{0.22}$ (1) + 0.35MnO₂, $Cs_{1.57}^{I}Mn^{II}[Fe^{II}(CN)_{6}]_{0.57}[Fe^{III}(CN)_{6}]_{0.43}$ (2) + 0.24MnO₂, and $Cs_{1.51}^{I}Mn^{II}[Fe^{II}(CN)_{6}]_{0.51}[Fe^{III}(CN)_{6}]_{0.49}$ (3) + 0.19MnO₂, respectively: calculated wt% for the sum of 1 and 0.35MnO₂: Cs, 44.3; Mn, 13.9; Fe, 10.5; C, 13.5; N, 15.7%: found; Cs, 44.5; Mn, 14.1; Fe, 10.6; C, 13.5; N, 15.7%, calculated wt% for the sum of 2 and 0.24MnO₂: Cs, 42.0; Mn, 13.7; Fe, 11.3; C, 14.5; N, 16.9%: found; Cs, 42.0; Mn, 13.5; Fe, 11.0; C, 14.2; N, 16.7%, calculated wt% for the sum of 3 and 0.19MnO₂: Cs, 41.5; Mn, 13.5; Fe, 11.5; C, 14.9; N, 17.4%: found; Cs, 41.9; Mn, 13.5; Fe, 11.2; C, 14.4; N, 17.0%. To confirm the existence of MnO₂, XPS spectra were measured. The O 1s XPS spectra showed peaks at 533.3 eV and 529.9 eV (see ESI[†]). The peak at 533.3 eV is assigned to be oxygen of the water molecule in $Cs_x Mn[Fe(CN)_6]_v \cdot zH_2O$ and the substrate. The peak at 529.9 eV is assigned to MnO_2 , which is consistent with previous reports.¹⁴ The precipitate obtained under condition IV was a light brown powder. The observed CN stretching peaks in the IR spectrum at 2151 and 2078 cm⁻¹ were assigned to the CN groups of Fe^{III}-CN-Mn^{II} and Fe^{II}-CN-Mn^{II}, respectively. The formula was $Cs_{0.94}^{I}Mn^{II}[Fe^{II}(CN)_{6}]_{0.21}[Fe^{III}(CN)_{6}]_{0.70} \cdot 0.8H_{2}O$ (4): calculated: Cs, 32.3; Mn, 14.2; Fe, 13.1 C, 16.9; N, 19.8%:



Fig. 1 IR spectra for 1 (a), 2 (b), and 3 (c) at 300 (left) and 100 K (right).

found; Cs, 32.5; Mn, 14.7; Fe, 13.1; C, 16.5; N, 19.5%. The mixing of Fe^{II}(CN)₆ in **1–4** is due to the reduction of Fe^{III}(CN)₆ in the prepared solution. The observed densities of the samples were 2.8 (1), 2.6 (2), 2.5 (3), and 2.2 g cm⁻³ (4). These densities are almost consistent with the calculated densities of 2.93 (1), 2.74 (2), 2.68 (3), and 2.17 g cm⁻³ (4), considering the contamination by MnO₂. The reference sample, which was caesium(I) manganese(II) hexacyanoferrate(II), was pale green. The CN stretching peak of Fe^{II}–CN–Mn^{II} was observed at 2082 cm⁻¹ (see ESI†). The formula was Cs¹₂Mn^{II}[Fe^{II}(CN)₆]·3.5H₂O (5): calculated: Cs, 44.6; Mn, 9.2; Fe, 9.4; C, 12.1; N, 14.1%: found; Cs, 44.3; Mn, 9.2; Fe, 9.7; C, 11.9; N, 13.8%. Fig. 2 schematically illustrates the crystal structure of the obtained compounds.

$Cs_{x}Mn[Fe(CN)_{6}]_{v}$



Fig. 2 Schematic illustration of the crystal structures of $Cs_x Mn[Fe(CN)_6]_y$ for 1–3, 4, and 5.

3.2. Charge-transfer phase transition in 1–4

Fig. 3 shows the product of the molar magnetic susceptibility (χ_M) and temperature (T) vs. T plots. The $\chi_M T$ value of 1 decreased at 207 K $(T_{1/2\downarrow})$ as the temperature decreased at a cooling rate of -0.5 K min^{-1} , suggesting that 1 showed a temperature-induced phase transition. As the sample in the low-temperature (LT) phase was warmed, the $\chi_{\rm M}T$ value increased around 225 K $(T_{1/2\uparrow})$ and reached the high-temperature (HT) phase value (Fig. 3a). The width of the thermal hysteresis loop $\Delta T (= T_{1/2\uparrow} - T_{1/2\downarrow})$ was 18 K. Like 1, 2 and 3 also exhibited thermal phase transitions. The $\chi_{\rm M}T$ vs. T plots for **2** showed $T_{1/2\downarrow} = 190$ K, $T_{1/2\uparrow} = 231$ K, and $\Delta T = 41$ K (Fig. 3b), while the $\chi_M T$ vs. T plots for 3 showed $T_{1/2\downarrow} = 175$ K, $T_{1/2\uparrow} = 233$ K, and $\Delta T = 58$ K (Fig. 3c). 4 did not exhibit a phase transition over the entire temperature region at a cooling rate of -0.5 K min⁻¹ (Fig. 3d). Conversely, only at a very slow cooling rate of -0.01 K min⁻¹, 4 shows a small decrease in the $\chi_{\rm M}T$ value. Although the phase transition is not enough under the present condition, $T_{1/2\downarrow}$ and $T_{1/2\uparrow}$ are roughly estimated to be 140 and 230 K, respectively (Fig. 3d). However, 5 did not exhibit a phase transition over the entire temperature region (see ESI[†]).

The right hand side of Fig. 1 shows the CN stretching frequencies in the IR spectra for 1-3 at 100 K. The intensity



Fig. 3 Observed $\chi_M T vs. T$ plots for **1** (a), **2** (b), **3** (c), and **4** (d) in the cooling (\bullet) and warming (\bigcirc) processes at a cooling and warming rate of 0.5 K min⁻¹. The dotted line in (d) shows the $\chi_M T$ value for **4** measured at a very slow cooling rate, *i.e.*, -0.01 K min⁻¹ (165–120 K), -0.1 K min⁻¹ (200–165 K), -0.5 K min⁻¹ (300–200 K, 120–100 K), and +0.5 K min⁻¹ (100–300 K).

of the Fe^{III}–CN–Mn^{II} peak in **1–3** decreased as the temperature decreased and a broad Fe^{III}–CN–Mn^{III} peak appeared in the region 2020–2130 cm⁻¹ at 100 K. From the analyses of the IR changes, the electronic states of the LT phases for **1**, **2**, and **3** were assigned to $Cs^{I}_{1.78}Mn^{II}_{0.78}Mn^{III}_{0.22}[Fe^{II}(CN)_6], Cs^{I}_{1.57}Mn^{II}_{0.57}Mn^{III}_{0.43}[Fe^{II}(CN)_6],$ and $Cs^{I}_{1.51}Mn^{III}_{0.51}Mn^{III}_{0.49}[Fe^{II}(CN)_6]$, respectively.

The XRD patterns for 1–3 at 300 and 100 K were examined. Table 1 lists the *d*-values (lattice spacing) of the observed reflections. The XRD patterns in the HT and LT phases for 1 showed face-centred cubic structures ($Fm\bar{3}m$) with a = 10.5446(17) and 10.4280(7) Å, respectively, and the unit cell volume was reduced by 3.3%. The crystal structure returned to the original one upon warming. Similarly, the HT and LT phases of **2** showed a facecentred cubic structure with a = 10.5589(17) and 10.3421(24) Å, respectively, and the volume reduction was 6.0%. The HT and LT phases of **3** were face-centred cubic structures with a = 10.5627(11)and 10.3268(23) Å, respectively, and the volume reduction was 6.6%. In the light of the valence states of the HT and LT phases in **1–3**, the increased volume reduction is due to the increased chargetransfer sites of Fe^{III}–CN–Mn^{II}. The origins of the temperatureinduced phase transition with a thermal hysteresis loop is a metal-to-metal charge-transfer from Mn^{II} to Fe^{III} and a strong cooperativity in the cyano-bridged 3-D structure.

3.3. Zero thermal expansion of 4

The $\chi_{\rm M}T$ value of **4** at a cooling rate of -0.5 K min⁻¹ did not exhibit a phase transition as shown in Fig. 3d. The ratio between the IR intensities of Fe^{III}-CN-Mn^{II} and Fe^{II}-CN-Mn^{II} for 4 was constant over the entire temperature range. The lattice constants of 4 were nearly constant between a = 10.5764(18) (300 K) and 10.5759(25) Å (20 K) as the temperature changed, *i.e.*, the thermal expansivity of a_a (= d(ln a)/dT) was +0.2 × 10⁻⁶ K⁻¹, suggesting that 4 is a zero thermal expansion material (Fig. 4).¹⁵ Recently, Margadonna et al.⁷ reported that Fe^{III}[Co^{III}(CN)₆] shows zero thermal expansion behavior of $a_a = -1.47(1) \times 10^{-6} \text{ K}^{-1}$ between 300 and 4.2 K.⁷ 4 is also a good example of a zero thermal expansion material. The origin of the zero thermal expansion observed in 4 is considered to be the transverse vibrations which contract the lattice on heating. This explanation is used for the negative thermal expansion observed in the other Prussian Blue analogues.7,8



Fig. 4 (a) XRD patterns for **4** at 300 (upper) and 20 K (lower). (b) Lattice constant *vs.* temperature plots for **4**.

 Table 1
 The d values (Å) of the observed reflections for the HT (300 K) and LT (100 K) phases of 1–3

hkl	1				2				3			
	HT		LT		HT		LT		HT		LT	
	d (cal)	<i>d</i> (obs)	d (cal)	d (obs)								
220	3.7281	3.7265	3.6869	3.6859	3.7331	3.7312	3.6565	3.6581	3.7345	3.7330	3.6511	3.6514
222	3.0440	3.0444	3.0103	3.0114	3.0481	3.0481	2.9855	2.9852	3.0492	3.0488	2.9811	2.9804
400	2.6361	2.6360	2.6070	2.6058	2.6397	2.6396	2.5855	2.5849	2.6407	2.6406	2.5817	2.5815
422	2.1524	2.1538	2.1286	2.1287	2.1553	2.1563	2.1111	a	2.1561	2.1569	2.1080	a
440	1.8640	1.8651	1.8434	1.8425	1.8666	1.8661	1.8282	a	1.8672	1.8681	1.8255	a
620	1.6672	1.6675	1.6488	1.6491	1.6695	1.6705	1.6352	1.6339	1.6701	1.6701	1.6328	1.6333

3.4. Ferromagnetic ordering of the LT phase in 1–3

The left side of Fig. 5 shows the magnetization vs. temperature plots of the LT phase of 1-3 at 10 G. These phases exhibited spontaneous magnetization with magnetic phase transition temperatures of 4.3 (1), 5.0 (2), and 5.6 K (3). The magnetization as a function of the external magnetic field at 2 K showed that the



Fig. 5 (Left) Magnetization *vs.* temperature curves for **1** (a), **2** (b), and **3** (c): (\blacksquare) field-cooled magnetization (FCM) obtained as the temperature decreases in an external magnetic field of 10 G; (\bigcirc) remnant magnetization (RM) obtained as the temperature increases (2 K \rightarrow 15 K) after the temperature was initially lowered in an applied magnetic field of 10 G. (Right) Magnetization *vs.* external magnetic field curves at 2 K.

saturated magnetization (M_s) values were 4.5 (1), 4.2 (2), and 4.0 $\mu_{\rm B}$ (3) (Fig. 5, right side), which are close to the expected values of 4.8 (1), 4.6 (2), and 4.5 $\mu_{\rm B}$ (3) when the all magnetic spins on Mn^{II} and Mn^{III} have parallel ordering. In addition, the Weiss temperature (θ) values where the extrapolation of the $\chi_{\rm M}^{-1}$ vs. *T* curves intersects the abscissa were positive values of +2.3 (1), +3.9 (2), and +4.0 K (3) (see ESI†). The magnetic data indicated that the LT phases are ferromagnetic.

4. Conclusion

Cs_{1.78}Mn[Fe(CN)₆], Cs_{1.57}Mn[Fe(CN)₆], and Cs_{1.51}Mn[Fe(CN)₆] exhibit temperature-induced phase transitions with thermal hysteresis loops. These phase transitions are due to a metal-tometal charge-transfer from Mn^{II} to Fe^{III}, and a strong cooperativity in the 3-D structure. A material that exhibits a thermal phase transition with a thermal hysteresis loop is useful for applications such as memory devices. In addition, $Cs_{0.94}Mn[Fe(CN)_6]_{0.91} \cdot 0.8H_2O$ exhibits a zero thermal expansion behavior. Recently, Fe^{III}[Co^{III}(CN)₆] and M^{II}[Pt^{IV}(CN)₆]·*x*H₂O have been reported to show a zero (or negative) thermal expansion behavior.^{7,8} Cs_{0.94}Mn[Fe(CN)₆]_{0.91} · 0.8H₂O is also a good zero thermal expansion material, which is useful for resistance to thermal shock, *etc.*

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- 15 The Rietveld analysis of $Cs_{0.94}Mn[Fe(CN)_6]_{0.91} \cdot 0.8H_2O$ shows that the space group is $Fm\bar{3}m$, *i.e.*, the Cs⁺ ion randomly occupies the interstitial site. The displacement of Cs⁺ ion from the center of the interstitial site as reported in Cs_{0.7}Co₄[Fe(CN)_6]_{2.9} \cdot 16H_2O is not observed.¹⁰.