

Ion-exchange synthesis and magneto-optical spectra of colored magnetic thin films composed of metal(II) hexacyanochromate(III)

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Magnetic thin films composed of hexacyanochromate-based magnets, $M^{II}_{1.5}[Cr^{III}(CN)_6] \cdot zH_2O$ ($M = Co, Ni, Cu$), were prepared on a transparent Nafion membrane by an ion-exchange process and their Faraday spectra were observed in the visible region.

Molecule-based magnets and metal complex-based magnets^{1,2} often show various bright colors. Hence, the film-type of molecule-based magnets would be useful for the study of magneto-optical effects³ in the visible region. For this purpose, we previously prepared $(Fe^{II}_xCr^{III}_{1-x})_{1.5}[Cr^{III}(CN)_6] \cdot zH_2O^4$ and $K^I_aV^{II/III}_xCr^{II}_{1-x}[Cr^{III}(CN)_6]_y \cdot zH_2O^{2,5}$ magnetic films by an electrochemical method and observed their Faraday spectra in the ferromagnetic region.⁶ In the present work, we tried to prepare molecule-based magnetic films according to an ion-exchange method.^{7,8} Here, we report the preparation of hexacyanochromate-based magnetic films, $M^{II}_{1.5}[Cr^{III}(CN)_6] \cdot zH_2O$ ($M = Co$ (1), Ni (2), Cu (3)), on a Nafion membrane and their Faraday spectra in the visible region.

The hexacyanochromate-based films were prepared by the following process.⁷ A Nafion[®] 117 membrane (2 × 4 cm) was immersed in an aqueous solution of $M^{II}Cl_2$ (10 mM) for 24 hours. It was then placed in an aqueous solution of $K_3[Cr^{III}(CN)_6]$ (10 mM) for 24 hours, to deposit Prussian blue analogs on both sides of the Nafion membrane. To remove M^{II} ions from the Nafion membrane, these films were dipped in an aqueous solution of KCl (1 M) for 20 minutes, rinsed with distilled water and dried under air.

Elemental analyses determined by an inductively coupled plasma (ICP) showed that the ratio of M^{II} to Cr^{III} in these films was 1.5 : 1.⁹ The prepared films showed various colors, *i.e.*, pink (film 1), yellowish green (film 2), and green (film 3). The CN stretching frequencies in the IR spectra were observed at 2178 cm^{-1} (film 1), 2176 cm^{-1} (film 2), and 2171 cm^{-1} (film 3). These CN frequencies correspond to those of powder-type of samples prepared by mixing MCl_2 and $K_3Cr^{III}(CN)_6$ aqueous solutions.^{4,10–12} Scanning electron microscopy (SEM) images showed that the sizes of the crystals were 150 ± 50 nm (film 1), 80 ± 20 nm (film 2), and 300 ± 100 nm (film 3). Their thicknesses determined by a laser profile micrometer were 320 nm (film 1), 350 nm (film 2), and 400 nm (film 3).

Fig. 1 shows the growth process of the $Cu^{II}_{1.5}[Cr^{III}(CN)_6] \cdot zH_2O$ film. After 1 second, the surface of Nafion membrane was covered with small crystals with a size of *ca.* 50 nm (Fig. 1a). After 30 minutes, the size of deposited crystals was *ca.* 100 nm (Fig. 1b). Then, the cubic-type of crystals were observed and the crystal size grew up to *ca.* 300 nm (Fig. 1c and 1d). In Fig. 1e, the growth process of the $M^{II}_{1.5}[Cr^{III}(CN)_6] \cdot zH_2O$ film is schematically illustrated; when a Nafion membrane containing M^{II} ion is dipped into a $K_3[Cr^{III}(CN)_6]$ solution, M^{II} ions coordinate with $[Cr^{III}(CN)_6]^{3-}$ ions depending on the diffusion rate of M^{II} ions in the Nafion membrane, to form $M^{II}_{1.5}[Cr^{III}(CN)_6] \cdot zH_2O$ microcrystals on the surface of the membrane.

Magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer. The

field-cooled magnetization *versus* temperature plots for the films in an external magnetic field (B_0) of 10 G showed abrupt breaks at magnetic critical phase transition temperatures (T_C) of 28 K (film 1), 70 K (film 2), and 70 K (film 3) (Fig. 2). These

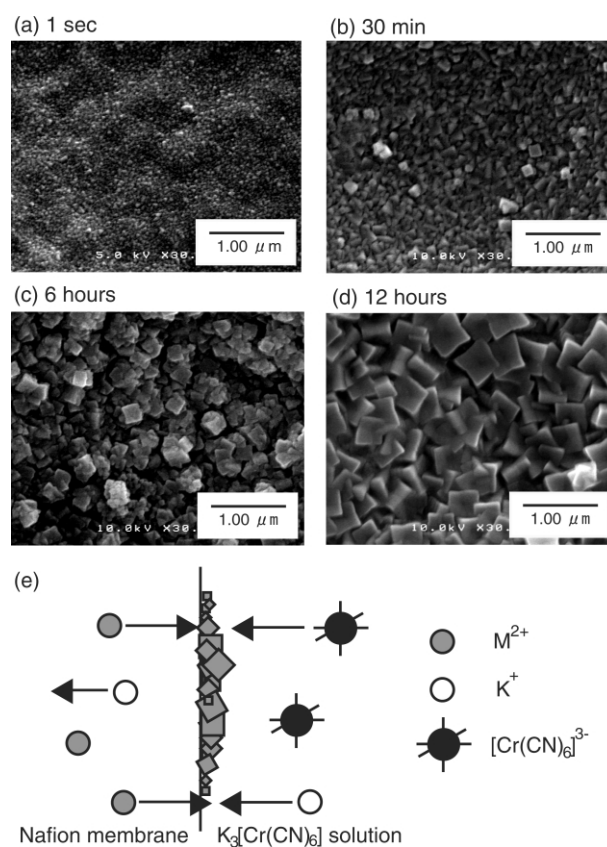


Fig. 1 SEM images of the growth process for $Cu^{II}_{1.5}[Cr^{III}(CN)_6] \cdot zH_2O$ film; (a) 1 second, (b) 30 minutes, (c) 6 hours, and (d) 12 hours. (e) is a schematic illustration of the growth process.

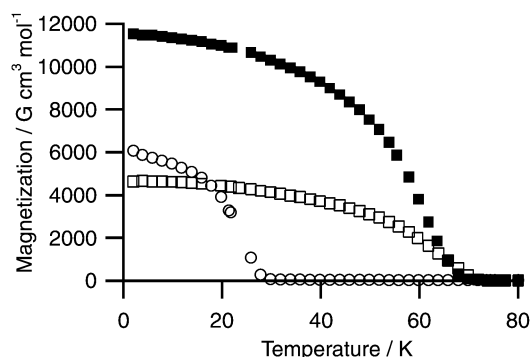


Fig. 2 Magnetization *versus* temperature plots for $M^{II}_{1.5}[Cr^{III}(CN)_6] \cdot zH_2O$ films in the external magnetic field of 10 G: (○) Co; (■) Ni; (□) Cu.

T_c values corresponded almost to values reported for powder-type samples, i.e., $T_c = 30$ K ($M = \text{Co}$)^{2,10}, 72 K ($M = \text{Ni}$)^{2,11,12} and 66 K ($M = \text{Cu}$)^{2,12}. Coercive fields of the films at 5 K were 250 G (**1**), 170 G (**2**), and 25 G (**3**). These values also corresponded to those of powder-type samples.

Magneto-optical effects of these films in the ferromagnetic region were measured using a magneto-optical meter. The Faraday ellipticity (FE) spectra for films at 7 K in $B_0 = 500$ G after the application of 1 T are shown in Fig. 3. For film **1**, the dispersive peak was observed around 470 nm with an intensity of ± 80 deg cm^{-1} (Fig. 3a). For film **2**, two broad peaks were observed with intensities of 200 and -200 deg cm^{-1} around 440 and 610 nm, respectively (Fig. 3b). For film **3**, a negative peak with an intensity of -210 deg cm^{-1} was observed around 550 nm (Fig. 3c). Moreover, the coercive fields determined by

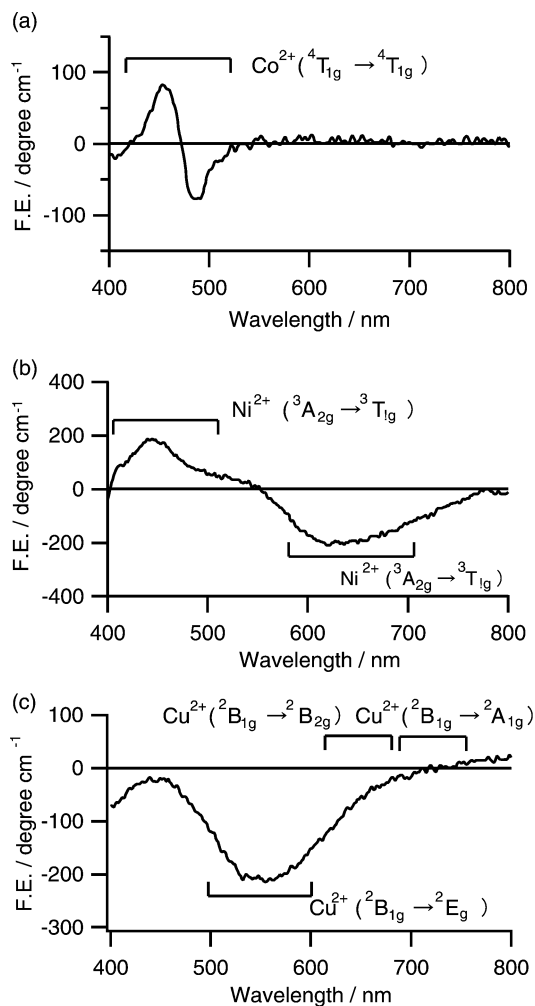


Fig. 3 Faraday ellipticity spectra for $\text{M}^{\text{II}}_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6]_z\text{H}_2\text{O}$ films at 7 K under 500 G after the application of 1 T: (a) $M = \text{Co}$; (b) Ni ; (c) Cu .

the hysteresis loops of the FE angle were 200 G (film **1**), 200 G (film **2**), and 50 G (film **3**) at 7 K. From the simulation of FE spectra based on the Faraday spectral analysis,¹³ the observed FE spectra could be assigned as follows: for film **1**, the dispersive peak around 470 nm is due to the ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}$ transition on an octahedrally coordinated Co^{II} ion; for film **2**, the peaks around 440 nm and 610 nm are due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (${}^3\text{P}$) and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (${}^3\text{F}$) transitions on an Ni^{II} ion, respectively; for film **3**, the peak around 550 nm is due to the sum of transitions ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ (556 nm), ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ (625 nm) and ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ (710 nm) on a Cu^{II} ion.

In summary, we have prepared transparent colored magnetic thin films composed of Prussian blue analogs¹⁴ by an ion-exchange method. These films made it possible to observe their Faraday spectra and we could assign their absorption bands in the visible region of these magnetic films.

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- The formula is $\text{M}^{\text{II}}_{1.5}[\text{Cr}^{\text{III}}(\text{CN})_6]_z\text{H}_2\text{O}$: For **1** $M = \text{Co}$ and $z = 17$; Calcd: Co, 14.7; Cr, 8.6. Found: Co, 14.2; Cr, 8.8. For **2** $M = \text{Ni}$ and $z = 9$; Calcd: Ni, 19.2; Cr, 11.3. Found: Ni, 19.6; Cr, 11.6. For **3** $M = \text{Cu}$ and $z = 11$; Calcd. Cu, 19.0; Cr, 10.4. Found: Cu, 19.2; Cr, 10.5.
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