論文の内容の要旨

Structure, photo-magnetism, and dielectric relaxation of a copper-octacyanidomolybdate film

(銅-オクタシアノモリブデン錯体薄膜の構造、光磁性、および誘電緩和)

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Molecular-based magnets have been extensively studied due to their interesting properties, such as long-range magnetic ordering, non-linear magnetooptical effects, and ionic conduction. Cyanido-bridged bimetallic assemblies are promising molecular-based magnets because of their magnetic properties and external-stimuli responsivities. Among the various functionalities of cyanido-bridged bimetallic assemblies, photo-induced magnetization has attracted much attention. The copper(II)-octacyanidomolybdate(IV) bimetallic assembly (**CuMo**) is one of cyanido-bridged bimetallic assemblies and the powder sample has been reported to be a photo-reversible ferromagnet with a Curie temperature of 25 K and ferroelectric around 150 K. However, the crystal structure of **CuMo** has not yet been determined. The previous results of X-ray absorption spectra and wide-angle X-ray scattering patterns suggest that the structure of **CuMo** could be analogous to $M^{II}_2[Mo^{IV}(CN)_8]\cdot nH_2O$ (M^{II}=Mn^{II}, Fe^{II}, Co^{II}). In addition, though the crystal structures of two **CuMo** analogues have been revealed, both of them barely show photo-responsivity. Therefore, it is important to determine the structure of **CuMo** showing photo-induced magnetization. Since **CuMo** can be synthesized electrochemically and the growth rate of crystals can be controlled by this method, this study aimed to synthesize **CuMo** as electrochemical thin films and to identify its structure. In this study, the synthesis of **CuMo** films with good quantity, the crystal structure of **CuMo** films, and the photo-reversible ferromagnetism and dielectric relaxation observed in **CuMo** films are reported.

Synthesis and characterization

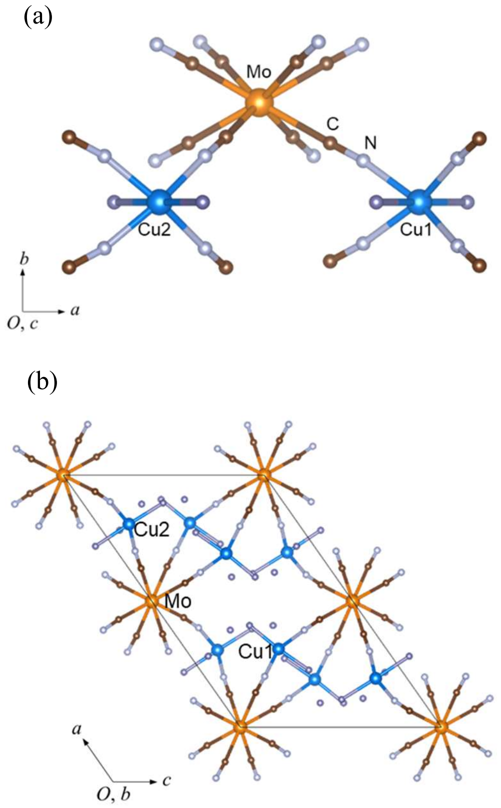

Figure 1. (a) Coordination geometry, (b) crystal structure of **CuMo** film.

The thin film of **CuMo** was synthesized on an indium-tin-oxide (ITO)-coated glass substrate by a constant potential electrolysis. The electrolyte solution was prepared by mixing two nitric acid solutions (pH = 3) of $Cu^{II}(NO_3)_2·3H_2O$ (36.2 mg, 0.15 mmol) and $Na_3[Mo^{V}(CN)_8]·4H_2O$ (33.4 mg, 0.075 mmol). The electrolysis was carried out at +500 mV vs an Ag/AgCl reference electrode, using ITO-coated glasses as both working and counter electrodes. The target material was deposited and obtained as a purple film. Elemental analyses revealed that the chemical formula is $Cu^{II}_2[Mo^{IV}(CN)_8]·8H_2O$. Scanning electron microscope (SEM) images showed that the **CuMo** film is composed of small crystals. The infrared (IR) spectrum shows a $\nu(C\equiv N)$ stretching band around 2169 cm^{-1}, while the ultraviolet-visible (UV-vis) spectrum of the **CuMo** film indicates a charge transfer band from Mo^{IV} to Cu^{II} around 510 nm. Powder X-ray diffraction (PXRD) measurements were performed on the **CuMo** film and the powder scratched from the film. X-ray absorption fine structure (XAFS) measurements were conducted with the **CuMo** film and the powder scratched from the film as well. The radial distribution functions (RDF) around Cu^{II} and Mo^{IV} were obtained from the Cu K-edge and Mo K-edge extended X-ray absorption fine structure (EXAFS) spectra. The valence states of Cu and Mo in the **CuMo** film was confirmed to be Cu^{II} and Mo^{IV} from the Cu K-edge and Mo K-edge X-ray absorption near edge structure (XANES) spectra. To determine the structure more accurately, the iterative analysis of between PXRD patterns and EXAFS spectra were conducted: first, Rietveld analysis of the PXRD pattern was performed based on the previously reported structure of $Mn^{II}_2[Mo^{IV}(CN)_8]·8H_2O$, then EXAFS spectra were analyzed based on the results of this Rietveld analysis, and the next Rietveld analysis was performed based on the results of EXAFS analysis. This cycle was repeated three times. The result of Rietveld analyses and EXAFS analysis revealed that the crystal structure of **CuMo** have a monoclinic structure with a space group of $C2/m$ (Figure 1). The cell parameters are a = 17.2461 Å, b = 11.1681 Å, c = 11.2618 Å, β = 125.1089°, and V = 1774.44 $Å^3$. The Cu^{II} site is coordinated to four nitrogen atoms of the cyanido bridges and two oxygen atoms of water molecules. All eight cyanido ligands that are coordinated to Mo^{IV} sites bridge to eight neighboring Cu^{II} sites. These cyanido bridges between Cu^{II} and Mo^{IV} sites construct a three-dimensional coordination network which is analogous to the structure of $M^{II}_2[Mo^{IV}(CN)_8]\cdot nH_2O$ (M^{II}=Mn^{II}, Fe^{II}, Co^{II}). The distance between the coordinated and crystal water molecules indicates the existence of a hydrogen bonding network among the water molecules.

Magnetic properties

Magnetic properties of the **CuMo** film before and after photo-irradiation were examined. The film shows paramagnetism before photo-irradiation, and after the irradiation of 473 nm light at 2 K, the magnetization was significantly increased. On heating to 250 K, the **CuMo** film returned to the paramagnetic state. Additionally, the phase photo-induced by 473 nm light changed to the paramagnetic phase by 840 nm light (Figure 2). These photomagnetic phenomena can be explained as follows. The initial state has Cu^{II}(S = 1/2) and Mo^{IV}(S = 0) sites, showing paramagnetism. After photo-irradiation with the blue light, a charge transfer between the Cu^{II} and Mo^{IV} sites occurs, resulting in Cu^{I}(S = 0) and Mo^{V}(S = 1/2) states. Therefore, the spins on the Mo^{V} sites and the remaining Cu^{II} sites ferromagnetically interact and produce long-range magnetic ordering.

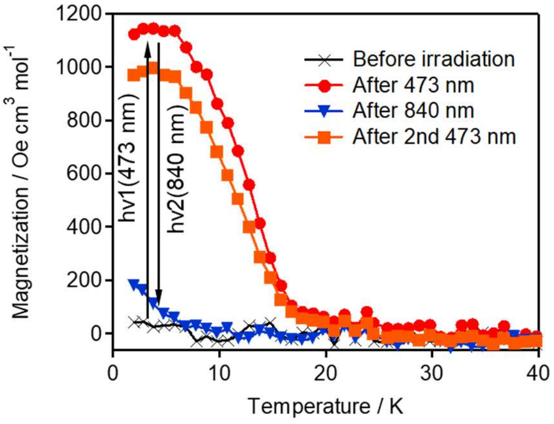

Figure 2. Magnetization vs. temperature plots before and after the photo-irradiations.

Dielectric properties

Dielectric constant (ε) measurements were carried out with the **CuMo** film. Figure 3 shows the temperature dependences of the imaginary part (ε”) of the dielectric constant. The peaks around 100-190 K shift to lower temperatures with decreasing frequency, indicating a relaxation behavior of the permanent electric dipoles. The ln(τ) vs T^{-1} plots, which are extracted from the peaks of the ε” plots have linear relations with an inflection point around 157 K. Therefore, using the Arrhenius equation: $\tau = \tau_0\exp(E_a/k_BT)$, the activation energies are estimated to be 49.9 kJ/mol in the range of 182-157 K and 27.3 kJ/mol in the range of 157-145 K (Figure 4). These activation energies are reasonable for typical hydrogen bonding. Thus, the variation of the activation energy implies a change in the hydrogen bonding network around 157 K. The temperature dependence of IR spectra was measured to study the origin of the dielectric

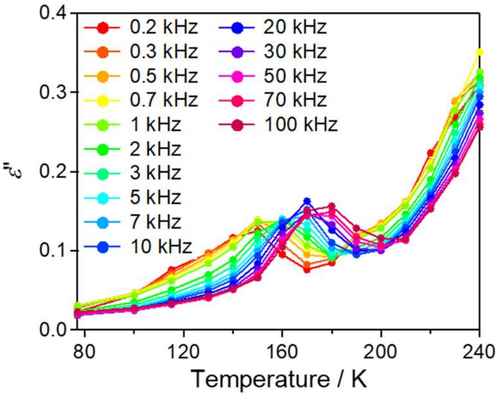

Figure 3. Imaginary part of dielectric constants.

relaxation. A change in the O−H stretching band for the water molecules was observed with decreasing temperature. This change indicates freezing of the water molecules accompanied with strengthening of the hydrogen bonding among the crystal and coordinated water molecules. Additionally, in the differential scanning calorimetry (DSC) measurements, peaks of heat flow were observed which shifted depending on the cooling rate in the temperature range of 230-190 K, suggesting a glass transition by freezing. Also, another dielectric relaxation in low frequency region around 1-1000 Hz is observed from 230-190 K, corroborating the existence of the glass transition. Considering the results from the dielectric constants, IR spectra, and DSC measurements, a glass transition of water molecules occurs in 230-190 K, and the vitrified water molecules causes the change in the dielectric relaxation as the dipoles of the water molecules are modulated by the transition around 157 K.

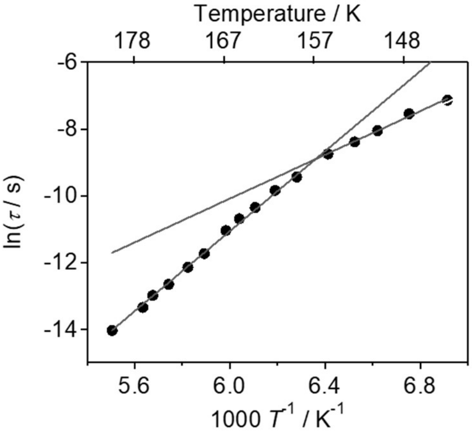

Figure 4. ln(τ) vs T^{-1} plots. The lines are linear fittings using the Arrhenius equation.

Conclusion

In this work, films of a copper(II)-octacyanidomolybdate(IV) assembly was synthesized, and the crystal structure was determined. The structure proved to be a monoclinic crystal system different from the structure of reported octacyanidomolybdate(IV) assemblies of $M^{II}_2[Mo^{IV}(CN)_8]\cdot nH_2O$ (M^{II}=Mn^{II}, Fe^{II}, Co^{II}). The film showed photo-reversible magnetization by irradiation with blue light and red light, and dielectric relaxation caused by the glass transition of water molecules within the crystal structure. The structural, magnetic, and electric studies in this work will contribute to further developments in functional photo magnets.