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学 位 論 文 内 容 の 要 旨

博士 (環境科学)

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学 位 論 文 題 名

Development of multifunctional ferromagnets based on supramolecular structures and bimetallic oxalate complexes

(超分子構造とシュウ酸金属錯体塩に基づいた多機能強磁性体の開拓)

The molecular-based magnetic networks of $[\text{MnCr}(\text{oxalate})_3]^-$ not only exhibit interesting magnetic ordering like ferromagnetism, but also can accommodate other functional cations to design novel multifunctional materials such as ferromagnetic conductors, chiral magnets, optical-active magnets, or multiferroics. The coexistence of more than two ferroic properties (ferroelectricity, ferromagnetism, and ferroelasticity), known as multiferroics, has attracted much attention in the field of novel electronic devices. Especially the coexistence of ferroelectricity and ferromagnetism, the most focusing multiferroics, could be used as magnetoelectric (ME) materials in memory devices to overcome the slow writing problem of ferroelectric memory and the high energy consumption drawback of magnetic random access memory.

In Chapter 2, to realize molecular multiferroic crystals, a series of two-dimensional polar crystals were obtained by introducing supramolecular cations composed of anilinium derivatives and benzo[18]crown-6 into the $[\text{MnCr}(\text{oxalate})_3]^-$ system, denoted as $(x\text{-anilinium}^+)(\text{benzo}[18]\text{crown-6})[\text{MnCr}(\text{oxalate})_3]^-$, where $x = \text{H}$, *o*-fluoro, *m*-fluoro, and *p*-fluoro, for **1**, **2**, **3**, and **4**. To obtain the polar space group essential for ferroelectricity, benzo[18]crown-6 with low symmetry was used as a crown ether. All anilinium derivatives gave crystals with polar space groups. Among these crystals, $(o\text{-fluoroanilinium}^+)(\text{benzo}[18]\text{crown-6})[\text{MnCr}(\text{oxalate})_3]^-$ (**2**) crystallized in the *Cc* space group exhibited a ferroelectric transition at 470 K. In the paraelectric phase of the space group $P2_1/n$, both *o*-fluoroanilinium and benzo[18]crown-6 were observed to be disordered, canceling the dipole moments in the crystal. The molecular motion of $(o\text{-fluoroanilinium}^+)(\text{benzo}[18]\text{crown-6})$ supramolecule is the origin of the ferroelectric-paraelectric phase transition. The ferroelectricity is proved by the fact that the sign of the pyroelectric current is inverted by the external electric field. The honeycomb layers of $[\text{MnCr}(\text{oxalate})_3]^-$ exhibited ferromagnetic ordering below 5 K. The crystal is the first example of type-I multiferroic based on $[\text{MnCr}(\text{oxalate})_3]^-$ layer structure. Flip-flop motion of *m*-fluoroanilinium was observed in crystal **3**. The crystal did not show long-range order of dipole moments, but fluctuations in dipole moments due to rotation of aryl groups were clearly observed as dielectric relaxation, with an activation

energy of 34.1 kJ/mol.

In Chapter 3, the supramolecular motion associated with solvent desorption from $[\text{MnCr}(\text{oxalate})_3]^-$ crystals was investigated. The majority of the network structure consisting of $[\text{MnCr}(\text{oxalate})_3]^-$ readily incorporates crystalline solvents during crystallization. Due to crystal disintegration associated with desolvation, it is often difficult to evaluate the physical properties of the crystals. A polar crystal $(\text{CBA}^+)([\text{18}]\text{crown-6})[\text{MnCr}(\text{oxalate})_3]^- (\text{CH}_3\text{OH})$ (**5**• CH_3OH) ($\text{CBA}^+ = 4\text{-carboxybutan-1-aminium}$) was synthesized. Upon desolvation, crystal **5**• CH_3OH underwent a crystal-to-crystal transformation to form $(\text{CBA}^+)([\text{18}]\text{crown-6})[\text{MnCr}(\text{oxalate})_3]^-$ (**5**). Both crystals exhibited ferromagnetic ordering at approximately 5 K. The structural transformation was accompanied by a reorganization of hydrogen bonds in the $(\text{CBA}^+)([\text{18}]\text{crown-6})$ supramolecular assembly. In crystal **5**, a "merry-go-round" motion of $[\text{18}]\text{crown-6}$ was observed, with a relatively small activation energy of 9.57 kJ/mol. The motion of $[\text{18}]\text{crown-6}$ was observed as dielectric relaxation. This crystal-to-crystal structural transformation provides a design strategy for multifunctional hybrid materials that can add new functions based on molecular motion.

$[\text{MnCr}(\text{oxalate})_3]^-$ gives diverse network structures depending on the valence and shape of the counter cation. Gyroid structure, which is strongly isotropic and induces exotic physical and electronic properties, is one of the most important examples. In Chapter 4, supramolecular cations were used to induce diverse three-dimensional network structures of $[\text{MnCr}(\text{oxalate})_3]^-$. By using the achiral supramolecular cation $(\text{ethanaminium}^+)(\text{benzo}[\text{18}]\text{crown-6})$, a chiral network of $[\text{MnCr}(\text{oxalate})_3]^-$ was successfully achieved in the crystal $(\text{ethanaminium}^+)(\text{benzo}[\text{18}]\text{crown-6})[\text{MnCr}(\text{oxalate})_3]^- (1.5\text{CH}_3\text{OH})$ (**6**) crystallized in orthorhombic space group $Pna2_1$. Using chiral cations $(1S,2S)\text{-1,2-diphenylethan-1,2-diaminium}$ ($S\text{-DPEDA}^{2+}$) and $[\text{18}]\text{crown-6}$, another chiral crystal $(S\text{-DPEDA}^{2+})[\text{18}]\text{crown-6}\{[\text{MnCr}(\text{oxalate})_3]^- \}_2(1.5\text{CH}_3\text{OH})(0.5\text{CH}_3\text{COCH}_3)$ (**7**) was obtained. In crystals **6**, a homochiral arrangement of the oxalate ligands was observed, similar to the Gyroid network of $[\text{MnCr}(\text{oxalate})_3]^-$. In crystal **7**, the stereochemistry of the ligands around each transition metal cation exhibits $A\text{-}A\text{-}A\text{-}A$ combinations, forming an achiral three-dimensional network, but the projected structure of the bc and ac planes closely resembled a strongly isotropic Gyroid structure. In crystal **7** adjacent four folded screw axes were clockwise or anticlockwise to each other, while in Gyroid all four folded screw axes are the same (either clockwise or anticlockwise). The structure is interesting as a gyroid-like structure from the viewpoint of magnetic properties, and this result demonstrates the usefulness of supramolecular structures to construct novel network structures with interesting physical properties.