

Development of Functional Single Crystal Materials with Flexible Structure

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博士論文の要約

Development of Functional Single Crystal Materials with Flexible Structure

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Molecular-based single crystals, which are built up from molecules via weak interactions, such as hydrogen bonding, van der Waals forces, and π - π interactions, possess a relatively low energy barrier, allowing distinctive molecular degrees of freedom in the solid state. These flexible features impart molecular-based single crystal materials with numerous types of functionality, including magnetism, electricity, mechanology, and photology. The geometrical transformation of photoresponsive molecules in the solid state can give rise to bending and stretching motions in single crystals, which can also be achieved via modification of the molecular packing arrangements. In this study, the latter method was adopted. Specifically, molecular rearrangement motion derived from 90° rotation of uniaxially aligned oxalate molecules during an atypical order-disorder phase transition of Ni^{II} and Co^{II} complexes was found to trigger an abrupt and a reversible shape change of the single crystals. The large magnitude of the molecular motion may influence the magnetic properties of the materials through modification of the magnetic exchanging pathway or orbital angular momentum contribution. Notably, tuning of the magnetic properties of the $\text{Co}(\text{II})$ complex was successfully achieved by modifying the orbital angular momentum contribution. Furthermore, motion of the flexible components in the solid, which is a prerequisite for materials with interesting dielectric and ferroelectric properties, was demonstrated in a pure organic single crystal.

Chapter 2, A single crystal of the Ni complex $[\text{Ni}^{\text{II}}(\text{en})_3](\text{ox})$ (en = ethylenediamine; ox^{2-} = oxalate anion) was depicted. The rod-like crystal, in which the $[\text{Ni}^{\text{II}}(\text{en})_3]^{2+}$ cations and ox^{2-} anions are linked via weak $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds and ionic interactions, shows abrupt and reversible shape changes in response to thermal changes around room temperature. At the crystal deformation phase transition temperature, the oxalate molecules atypically rotate by 90° . Such molecular rotation induces a size change of the order of several angstroms per molecule. This sub-nanometer scale change is amplified by the collective motion of cooperatively interacting molecules in the entire crystal, resulting in micrometer-scale contractions-expansions that manifest as biaxial positive and uniaxial negative thermal expansions. At the critical

temperature, the long axis (i.e., the crystallographic c direction) of the rod-like crystal expands/contracts by 5% and exhibits thermal hysteresis. This novel molecular rearrangement motion is highly dependent on the symmetry, crystal packing, and molecular interactions of the molecule. A similar phenomenon occurs in a Zn analog, which was also described in this chapter.

Chapter 3, To achieve switchable magnetic properties, Ni(II) in the above complex cation was substituted with Co(II), because high-spin Co(II) complexes typically possess large orbital angular momentum. A large orbital angular momentum contributes to the magnetic momentum of a complex and is readily modulated by distortion of the ligand field. The Co(II) complex prepared via hydrothermal reaction exhibits an abrupt anisotropic shape change induced by a 90° rotation of uniaxially aligned oxalate molecules at the phase transition temperature; this behavior is similar to that of the previously described [Ni^{II}(en)₃](ox) complex. Because the orbital angular momentum is modulated by a ligand field distortion in response to the oxalate reorientation, the rod-like single crystal exhibits anisotropic magnetic bistability at the phase transition temperature. More interestingly, because a large orbital moment is essential for the preparation of a single-molecule-magnet, the Co(II) complex exhibits a slow relaxation of magnetization at temperatures less than 10 K.

Chapter 4, A pure organic single crystal [H₂dabco]·[2CB]₂ ([H₂dabco]²⁺ = diprotonated 1,4-diazabicyclo[2.2.2]octane, 2CB⁻ = 2-chlorobenzoate), which exhibits ferroelectricity above room temperature, was discussed. The crystal is constructed from trimer units in which two 2CB⁻ anions are bridged by one diprotonated [H₂dabco]²⁺ cation through N–H···O hydrogen bonds. The [H₂dabco]²⁺ cation undergoes an order–disorder phase transition above room temperature (*ca.* 326 K upon heating). In the high temperature phase, the [H₂dabco]²⁺ cation located at the middle position of the trimer is rotated with disorder about its N···N axis and lies at the center of inversion. When the temperature drops below the phase transition temperature, the [H₂dabco]²⁺ cation is frozen such that it is ordered and deviates from the center of the trimer unit. This displacement of the cation leads to symmetry breaking (nonpolar space group *Pbca*

to polar space group $Pna2_1$) and generates a spontaneous polarization along the crystallographic c axis. The paraelectric-to-ferroelectric phase transition was further confirmed by temperature-dependent second harmonic generation measurements.

By studying single crystal materials with flexible structures, several novel results have been demonstrated in this thesis. Research in this area is on the rise and great prospects are expected.