

# 論文の要旨

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論文題目 Successive phase transitions in organic-inorganic layered perovskite  $(C_nH_{2n+1}NH_3)_2MeCl_4$  ( $Me$ : transition metal)

(有機無機層状ペロブスカイト  $(C_nH_{2n+1}NH_3)_2MeCl_4$  ( $Me$ :遷移金属)における逐次相転移)

In recent years, multiferroics, a compound that has cross-correlation of magnetic, electrical and elastic ordering, is expected as one of the ideal materials for constructing a faster and larger capacity information memory. In particular, metal-organic frameworks have attracted much attention as the new multiferroics. Among the frameworks, we focus on a family of  $(C_nH_{2n+1}NH_3)_2MeCl_4$  ( $Me$ :transition metal) with the  $A_2BX_4$  perovskite-type layered structure since  $(C_nH_{2n+1}NH_3)_2MeCl_4$  undergoes successive structural phase transitions accompanied by magnetic and dielectric orderings, and also ferroelastic ordering. In this study, we have performed single-crystalline X-ray diffraction, polarization microscopy, specific heat, relative permittivity, spontaneous electric polarization, ferroelectric loop, magnetic susceptibility and isothermal magnetizations measurements on the single crystals of  $(C_2H_5NH_3)_2CuCl_4$  and  $(C_3H_7NH_3)_2FeCl_4$ . The single crystals were grown by a slow evaporation method at room temperature from a stoichiometric aqueous solution of alkylamine hydrochloride  $C_nH_{2n+1}NH_2 \cdot HCl$  and metal chloride  $MeCl_2$  in a 2:1 molar ratio. Since they are highly deliquescent, preparations of all experiments were done in a glovebox of which the atmosphere gas was exchanged by pure nitrogen. In addition, the new sample cell to measure dielectric properties in vacuum was constructed to avoid the effect of the deliquescence. In the dielectric property measurements, the three terminal method is utilized to eliminate the stray capacitance in the electrical circuit. A new cryostat for the polarizing microscopy under a stress was also constructed to see the stress dependence of the ferroelastic domain structure.

From these experiments and corresponding analyses and discussion, we obtained the following results and conclusion for single-crystalline  $(C_2H_5NH_3)_2CuCl_4$  and  $(C_3H_7NH_3)_2FeCl_4$ .

## I. $(C_2H_5NH_3)_2CuCl_4$

I-1. Successive structural phase transitions, Structure determination of phases and Ferroelasticity

In the temperature dependence of specific heat in this work, anomalous peaks at 364 K, 356 K, 225 K, 37 K and the weak ferromagnetic transition temperature  $T_N = 10$  K

are detected, respectively. Since the transition temperatures 225 K and 37 K have not been reported so far, the single-crystalline X-ray diffraction at 273 K and 100 K was carried out. The crystal structures above and below 225 K are determined as *Abma* and *Pbca*, respectively. This result demonstrates that a structural phase transition undergoes at 225 K.

In the polarization microscopy at different temperatures, disappearance of the domain structure has been found at 360 K, indicating that the crystal structure above 364 K is the tetragonal (*I4/mmm*), which is the prototype structure of this compound.

#### I-2. Weak ferromagnetic transition

The magnetic susceptibility under the magnetic field along the *c*-axis shows the cusp-type anomaly at 10 K, which confirms that the weak ferromagnetic transition occurs at  $T_N = 10$  K.

#### I-3. Weak ferroelectric transition

We have found, for the first time, a remarkable anomaly at  $T_C = 25.8$  K in the temperature dependence of the relative permittivity under the magnetic field along the *c*-axis. In *D-E* hysteresis measurements, the ferroelectric loop opens below  $T_C$ , where *D* is the electric displacement field and *E* is the electric field (along the *c*-axis), respectively. The remnant polarization at 5 K reaches  $8 \mu\text{C}/\text{m}^2$ , that is almost one ten-thousandth of the remnant polarization of usual ferroelectrics. These results indicate that a weak ferroelectric ordering undergoes at  $T_C$ . The clear *D-E* hysteresis curve is detected below  $T_N$ , which is the weak ferromagnetic transition temperature, revealing that the weak ferroelectric and the weak ferromagnetic states coexist below  $T_N$ .

#### I-4. Main conclusion

The ferroelectric ordering of  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$  below  $T_C = 25.8$  K and, moreover the coexistence of the weak ferroelectric and weak ferromagnetic states are found for the first time. Consequently, we propose that  $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$  is one of potential multiferroics having a magnetoelectric effect.

## II. $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{FeCl}_4$

II-1. Successive structural phase transitions, Structure determination of phases and Ferroelasticity

Only the temperature dependence of magnetic susceptibility for a polycrystalline sample has been reported for  $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{FeCl}_4$ , which suggests an antiferromagnetic transition at 91.8 K. All data presented in this thesis are obtained for single crystals and newly reported physical properties.

The temperature dependence of specific heat shows anomalies at 181 K, 130 K and 89 K, respectively. The crystal structure of  $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{FeCl}_4$  at 290 K is determined to ferroelastic *Abma* with the reliability  $R_1 = 0.0363$ . In the polarization microscopy at room temperature, we have found a domain structure. When we apply the longitudinal stress along the *a*-axis of *Abma* phase, the domain structure disappears. The disappearance of the domain clearly indicates that the stress switches the spontaneous strain. This is the evidence of the ferroelasticity in the room temperature phase with *Abma* space group.

## II-2. Weak Ferromagnetic transition

The temperature dependence of magnetic susceptibility under the magnetic field perpendicular to the  $c$ -axis shows a cusp-type sharp peak at 89 K, confirming the antiferromagnetic transition. Moreover, the ferromagnetic loop under the magnetic field along the  $c$ -axis is detected at 5 K. The remnant magnetization is  $3.10 \times 10^{-3} \mu_B$  that is much smaller than the magnetic moment of  $\text{Fe}^{2+}$  ( $4 \mu_B$ ). Therefore, the weak ferromagnetism along the  $c$ -axis occurs below  $T_N = 89$  K.

## II-3. Conclusion

We succeeded in synthesizing the single crystals of  $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{FeCl}_4$  for the first time. Ferroelastic and weak ferromagnetic phases are found at room temperature and 89 K, respectively. Therefore,  $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{FeCl}_4$  may be a potential multiferroics.