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Ferroelectric Porous Molecular Crystal, $[Mn_3(HCOO)_6](C_2H_5OH)$, Exhibiting Ferrimagnetic Transition

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Weak interactions are the most characteristic feature in the assembling of the molecules. A typical example is the host−guest interaction in the porous materials, which have recently attracted large attention because of the high potentialities in the design of new functional materials.[1−3] Since the guest molecules are loosely confined in the porous space, the porous material will be easily converted to the highly polarizable system. If the polarized guest molecules are three-dimensionally ordered, a ferro- (or antiferro-) electric state will be realized. Furthermore, if we can combine the ferroelectrically polarizable guest molecules and the porous host lattice exhibiting magnetic order, we can obtain a new type of "*multiferroic*" molecular materials where ferroelectricity and ferromagnetism coexist. Such multifunctional materials have recently aroused an increasing interest from the viewpoint of the development of new materials with very large magnetoelectric effects.[4]

We have recently reported the temperature dependences of the magnetic and dielectric properties of the porous molecular crystal $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$, where H_2O and CH_3OH are guest molecules.[5,6] $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ is a porous molecular ferrimagnet ($T_c = 8.1$ K).[5] Of course, the magnetic properties come from the Mn^{2+} ions ($S = {}^5/_2$) incorporated in the host lattice, which was interpreted on the basis of the Goodenough−Kanamori rule.[7] We have also reported the temperature dependence of the dielectric constant (ϵ_r) of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ which is governed by the electric properties of guest molecules.[6] For $E//a$ and $E//b$, ϵ_r shows a transition between high-temperature polarizable ($\epsilon_r \approx 20$) and low-temperature nonpolarizable ($\epsilon_r \approx 7$) states at around 150 K. The guest molecules are easily removed under vacuum and/or by heating. But the vacant host lattice remains stable up to about 280 °C. The guest-free crystal $[Mn_3(HCOO)_6]$ shows a very small and almost temperature-independent dielectric constant ($\epsilon_r \approx 5$) irrespective of the direction of the electric field.[6] We have also reported the preliminary dielectric data of the ethanol-containing crystal, $[Mn_3(HCOO)_6](C_2H_5OH)$. However, it was recently found that reexamination is needed because of the large escaping tendency of the guest ethanol molecule at around room temperature. We report here the ferroelectric and ferrimagnetic properties of $[Mn_3(HCOO)_6](C_2H_5OH)$.

$[Mn_3(HCOO)_6](C_2H_5OH)$ crystals were obtained by keeping $[Mn_3(HCOO)_6]$ crystals in the ethanol vapor for several days. The TGA measurement exhibited a gradual weight loss between 30−100 °C (Figure S1). The observed 9.7% weight loss well corresponds to the calculated weight loss (9.6%) of one ethanol molecule ($[Mn_3(HCOO)_6](C_2H_5OH) \rightarrow [Mn_3(HCOO)_6]$). The crystal structure of $[Mn_3(HCOO)_6](C_2H_5OH)$ was determined at 90, 190, and 230 K (Figure 1).[8] $[Mn_3(HCOO)_6](C_2H_5OH)$ is isostructural to $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$. The crystal belongs to the monoclinic system with the space group of $P2_1/n$ and has one-dimensional channels along the b-axis.[5,6]

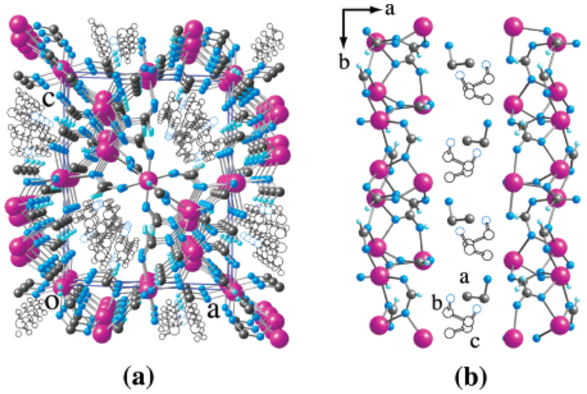

Figure 1. (a) Crystal structure of $[Mn_3(HCOO)_6](C_2H_5OH)$ viewed along the b-axis: Mn, pink; C, gray; O, blue; H, pale sky blue. The C and O atoms of guest C_2H_5OH molecules are shown by open circles. (b) The arrangement of guest ethanol molecules along the channel at 90 K. Fourier peaks gave three possible positions of C_2H_5OH molecules (two colorless positions and one colored positions). In the structure refinement, the occupancy probabilities of C and O of the guest molecule were assumed to be 33%.

In order to confirm the magnetic transition of Mn^{2+} spin ($S = {}^5/_2$) system at low temperature, the magnetic measurements of $[Mn_3(HCOO)_6](C_2H_5OH)$ were performed by SQUID magnetometer at 2−300 K. As shown in Figure 2a, a ferrimagnetic transition was observed at 8.5 K, which was slightly higher than the ferrimagnetic transition temperatures of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ ($T_c = 8.1$ K) and $[Mn_3(HCOO)_6]$ ($T_c = 8.0$ K).[5]

At the beginning of the dielectric experiments, we used the crystalline powder sample. But the obtained ϵ_r was anomalously high around the room temperature and increased with increasing temperature. Similar dielectric behaviors were also observed for various crystalline powder samples including representative ferroelectric material such as KH_2PO_4 (KDP), although its single crystal gave the expected dielectric behavior. Therefore, we used single crystals in spite of the small sizes of the crystals. The crystals of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ were cut into rectangular parallelepipeds with dimensions of about 2.0 × 1.5 × 0.5 mm^3 so as to make each crystal face approximately parallel to the ab, ac, or bc planes. Then H_2O and CH_3OH molecules were removed, and C_2H_5OH molecules were inserted.

The dielectric measurements were performed at 4.2−310 K. The silver conducting paste painted on the crystal surfaces was used as

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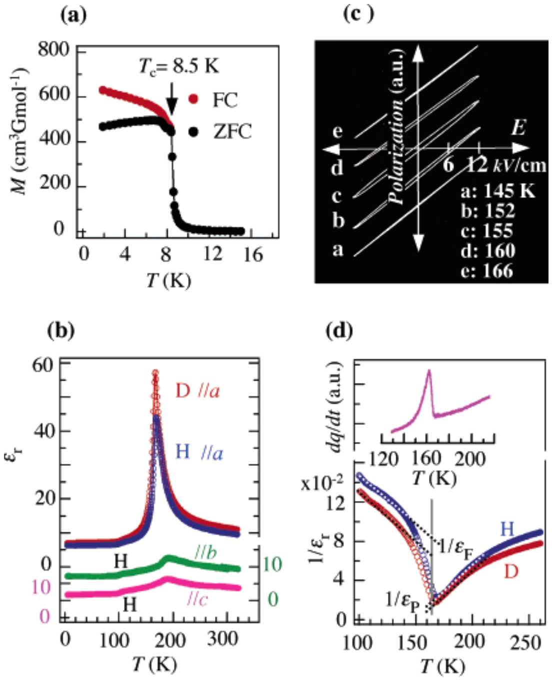

Figure 2. (a) Temperature dependence of the magnetization of [Mn(HCOO)$_6$](C$_2$H$_5$OH) (H = 5 Oe). (b) Dielectric constants (ϵ_r) of [Mn(HCOO)$_6$](C$_2$H$_5$OH) for the field E//a (blue), b (green), and c (pink). The red line represents ϵ_r (E//a) of the crystal with deuterated ethanol, [Mn(HCOO)$_6$](C$_2$H$_5$OD). (c) The hysteresis loop of [Mn(HCOO)$_6$](C$_2$H$_5$OH) (E//a). (d) The 1/ϵ_r vs T curve of [Mn(HCOO)$_6$](C$_2$H$_5$OH). In the dielectric measurements, the relatively high speed of the temperature change (2−3°/min) was adopted to avoid the escaping of guest molecules, which will be the main reason of the gradual temperature change of 1/ϵ_r just below T_c. The DSC curve is also presented. In (b) and (d), D and H represent the dielectric data of [Mn(HCOO)$_6$](C$_2$H$_5$OH) and [Mn(HCOO)$_6$](C$_2$H$_5$OD), respectively.

the electrode. As shown in Figure 2b, ϵ_r showed featureless temperature dependences for E//b and E//c, except for small anomalies at 160−200 K which will be related to the difficulties in the accurate cutting of the small crystal, while ϵ_r for E//a showed a very sharp peak at 165 K. The maximum ϵ_r was about 45. This behavior quite resembles that of CH$_3$NH$_3$Al(SO$_4$)$_2$•12H$_2$O showing the first-order ferroelectric transition (T_c = 177 K and ϵ_{max} = 56).[9] Similar to the case of NH$_4$Fe(SO$_4$)$_2$•12H$_2$O,[9] a small hysteresis loop was observed just below T_c (Figure 2c). The differential scanning calorimetry (DSC) experiment gave a peak indicating the phase transition at around 163 K (Figure 2d). The ferroelectric properties are considered to come mainly from the guest molecules because the guest-free [Mn$_3$(HCOO)$_6$] crystal showed the temperature-independent small ϵ_r (≈5) as mentioned before. The dielectric transition suggests the important role of the interaction between host lattice and C$_2$H$_5$OH molecules. With the expectation of the deuteration effect on T_c,[10] the dielectric constants of [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OD) were also examined. However, the dielectric behavior was almost unchanged (Figure 2b), and a sharp peak was observed at 164 K (ϵ_{max} = 57). It is well-known that in the first-order ferroelectric transition, the relation of $\epsilon_P = 4\epsilon_F$ is satisfied at $T = T_c$, where ϵ_P and ϵ_F are the dielectric constants of paraelectric and ferroelectric phases, respectively. As shown in Figure 2d, ϵ_P/ϵ_F at $T = T_c$ was 4.1 for [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OH) and 4.0 for [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OD). Thus, to our best knowledge, [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OH) (and [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OD)) is considered to be the first ferroelectric, porous molecular crystal. The crystal structure analyses at 90, 190, and 230 K showed that the temperature change of the structure of the host lattice is very small. The Fourier peaks corresponding to C and O atoms of guest molecules were very broad at 190 and 230 K, but the Fourier peaks became sharp at 90 K, and the distribution of the peaks suggested three possible positions of C$_2$H$_5$OH (Figure S2). Thus, there seems to be a significant change in the arrangement of guest molecules between 90 and 190 K. Below T_c, the space group of each ferroelectric domain should be changed from $P2_1/n$. In fact, the X-ray intensity data collected at 90 K suggested the absence of screw (2$_1$) and glide (n) symmetries. However, the intensities of the symmetry-breaking reflections were very weak, and the structure determined by assuming the space group of $P\bar{1}$ gave the structure almost the same as the structure with centrosymmetric space group $P2_1/n$. Further detailed structural information on the guest molecules was hardly obtained. As seen from Figure 2b, ϵ_r showed no distinct anomaly at low temperature, suggesting that the ferrimagnetic order and the ferroelectric order coexist below 8.5 K. [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OH) will give a hint to design "*multiferroic*" molecular materials where ferroelectric and ferromagnetic orders coexist.

In conclusion, we have obtained the porous molecular crystal, [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OH) exhibiting the ferroelectric transition at 165 K and the ferrimagnetic transition at 8.5 K. The ferroelectric order suggests the important role of the host−guest interaction, which remains to be clarified for future studies.

Supporting Information Available: TGA curve of [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OH); difference Fourier peaks of C$_2$H$_5$OH in [Mn$_3$(HCOO)$_6$](C$_2$H$_5$OH) at 230, 190, and 90 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The lattice constants and R-values were: at 230 K, a = 11.6954 Å, b = 10.1510 Å, c = 14.9162 Å, β = 91.642°, V = 1770.1 Å^3, R = 0.025, and R_w = 0.029; at 190 K, a = 11.6829 Å, b = 10.1309 Å, c = 14.8952 Å, β = 91.625°, V = 1762.3 Å^3, R = 0.030, and R_w = 0.046; at 90 K, a = 11.6575 Å, b = 10.1053 Å, c = 14.8790 Å, β = 91.633°, V = 1752.1 Å^3, R = 0.038, and R_w = 0.046.
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(10) T_c is usually used for both magnetic and dielectric transition temperatures. Although it will be better to distinguish them in the *multiferroic* crystal, T_c is used for both transitions in this paper.

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