Host–Guest Systems

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Dielectric Properties of Porous Molecular Crystals That Contain Polar Molecules

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Molecular materials with porous coordination frameworks have recently drawn considerable interest because of attractive properties arising from the synergy of the host lattice and the guest molecules. These properties include guest-switched spin-crossover transitions,[1] gas sorption,[2] molecular storage,[3] and magnetic solvent sensoring.[4] However, to our knowledge, reports on the dielectric properties of porous molecular materials are rare, although the ferroelectric properties of molecular materials have been studied.[5] As large charges can be induced in the highly polarizable materials upon application of a relatively low electric field, it may be useful to construct novel electronic devices such as

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ferroelectric field-effect transistors.[6] Except for ferroelectric (or antiferroelectric) materials, heavy-metal compounds such as $PbCl_2$ ($\varepsilon_r = 33.5$ at 20 °C), PbO ($\varepsilon_r = 25.9$ at 20 °C), and TlBr ($\varepsilon_r = 30.3$ at 25 °C) are typical materials with large dielectric constants, ε_r. It would be desirable to develop highly polarizable materials without pernicious heavy metal atoms, in particular, molecular materials with dielectric properties that switch between high and low dielectric states.

As most molecules do not have positional freedom in the crystalline state, the dielectric constants of molecular crystals are usually very small and almost independent of temperature. On the other hand, there exist polar molecules with fairly large polarizabilities in the liquid state. Considering that the guest molecules in the porous materials will have a large degree of positional freedom, molecular solids with large dielectric constants could be designed by the suitable combination of porous molecular materials and polar guest molecules. If the positions of the guest molecules are fixed at low temperature, the material will transform into a low dielectric system, thus allowing the desired variability between high and low dielectric states.

Water and methanol are typical solvents with high polarizabilities. The dielectric constants ε_r of H_2O, CH_3OH, and C_6H_6 measured down to 4.2 K are shown in Figure 1. In contrast to nonpolar benzene, which displays a very small and constant dielectric constant, the ε_r value of liquid H_2O was as high as 10^2 just above the freezing point and then dropped very sharply. At low temperature, H_2O became a nonpolarizable material like benzene ($\varepsilon_r \approx 2$ at 5 K). Similar behavior was observed for CH_3OH.

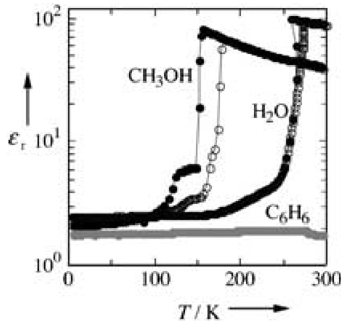

Figure 1. a) Plot of the dielectric constants ε_r of H_2O and CH_3OH as a function of temperature. The closed and open circles correspond to ε_r values of the cooling and heating processes, respectively. The dielectric constant of C_6H_6 is also presented for comparison.

We then measured the dielectric constants for $[Mn_3(HCOO)_6]$ and $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ in the temperature range 4.2–300 K. As reported before, $[Mn_3(HCOO)_6]$(guest) (guest = vacant; H_2O and CH_3OH;, acetic acid; *N*,*N*-dimethylformamide, furan; or benzene and iodine) is a porous ferrimagnet ($T_c = 5$–10 K).[7] Most guest molecules were removed below 100 °C and the open framework was thermally stable up to about 260 °C. The number of guest molecules was determined by elemental and thermogravimetric (TGA) analyses.[8] We reexamined the TGA results and confirmed a 10 % weight loss around 100 °C, which exactly corresponds to the weight percent of guest molecules in $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$. The dielectric constants of $[Mn_3(HCOO)_6]$ and $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ were measured for electric fields applied approximately parallel to the *a*, *b*, and *c* directions ($E = 1$ V, 10 kHz; Figure 2).

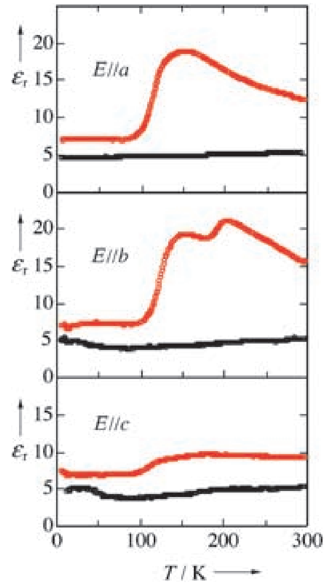

Figure 2. Plot of the dielectric constants ε_r of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ as a function of temperature (red) upon application of an electric field approximately parallel to the *a* (*E*//*a*), *b* (*E*//*b*), and *c* directions (*E*//*c*). The dielectric constants of $[Mn_3(HCOO)_6]$ without guest molecules are also presented (black).

The porous crystal $[Mn_3(HCOO)_6]$ without guest molecules showed a small dielectric constant that was basically independent of temperature. The difference between the maximum and minimum ε_r values in the temperature range 4.2–300 K was less than one for *E*//*a*, and about two for *E*//*b* and *E*//*c*. Although relatively large changes were observed for *E*//*b* and *E*//*c*, accurate measurements were difficult for these directions due to problems in cutting suitable rectangular parallelepipeds from small single crystals. The ε_r values of the guest-containing system $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ increased with lowering temperature to a maximum of $\varepsilon_r \approx 20$ around 150 K for *E*//*a*, and then decreased sharply to $\varepsilon_r = 7$. This sharp decrease resembles the large drop of ε_r associated with liquid↔solid phase transitions of H_2O and CH_3OH shown in Figure 1. Thus, the guest molecules seem to be free to some extent at high temperature and then almost fixed at low temperature, as indicated by the large decrease in ε_r; the movement of guest molecules is frozen fairly collectively around 120 K.

As expected, by insertion of polar molecules the porous molecular crystal could be changed into a novel system with high-temperature polarizable and low-temperature nonpolarizable states. Unlike the temperature dependencies of ε_r for H_2O and CH_3OH, no distinct hysteresis was observed. However, if it is considered that the guest molecules in the one-dimensional channel can contact with only a few other guest molecules arranged along the channel (parallel to the *b* direction; see Figure 3), the sharp drop in ε_r is surprising.

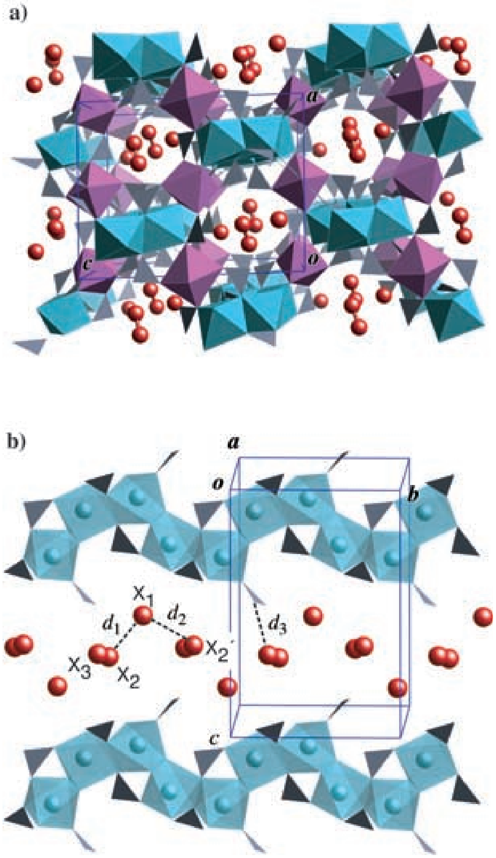

Figure 3. a) Perspective view of the crystal structure of $[Mn_3(HCOO)_6]$. The edge-sharing MnO_6 octahedrons (pale blue) form an infinite chain along the *b* axis, which are connected by apex-sharing MnO_6 octahedrons (purple) to produce the channel structure along *b*. The red spheres in the channel are non-hydrogen atoms (C, O) of water and methanol molecules. The gray triangles are HCOO ligands. b) The array of the edge-sharing MnO_6 octahedrons and the arrangement of water and methanol molecules along the *b* axis (at 155 K). The positions of the non-hydrogen atoms of the guest molecules (X_1, X_2, and X_3) were obtained from the structure refinements based on the main peaks in the difference Fourier maps. The distance (*d*) from X_2 to X_3 is about 1.5 Å, and the distances from X_1 to X_2 and X_2' are about 3.2 (d_1) and 3.5 Å (d_2) at 155 K, suggesting the alternating arrangement of water (X_1 or O) and methanol (X_2, X_3) molecules along the *b* axis. The short contact of 3.2 Å (d_3) between the O atom of ligand HCOO and X_1 is consistent with the expected compact molecular packing along the *c* axis.

The temperature dependence of ε_r for *E*//*b* showed two characteristic peaks around 200 K and 150 K followed by a sharp drop around 120 K; the latter peak seems to correspond to that observed for *E*//*a* (Figure 2). For *E*//*c*, ε_r exhibited only small changes. The difference between the maximum and minimum values of ε_r was only about three. If we take into account the difficulty associated with accurate shaping of the crystal, the small changes in ε_r for *E*//*c* around 120 K is insignificant. For *E*//*c*, there seems to be only a negligible contribution from the guest molecules. As the dielectric properties of a liquid cannot be anisotropic, the anisotropic behavior of the dielectric properties of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ cannot be explained by a simple liquid model of the guest molecules.

Similar measurements were made for $[Mn_3(HCOO)_6](CH_3OH)$ and $[Mn_3(HCOO)_6](C_2H_5OH)$ (Figure 4).[9] As CH_3OH (Figure 1) and $[Mn_3(HCOO)_6](CH_3OH)$ display a prominent peak around 150 K, the peak at 150 K for $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ (Figure 2) might be related to a change in the polarizability of the CH_3OH molecules. It seems surprising that CH_3OH molecules in very different environments exhibit dielectric anomalies around the temperature of the bulk liquid↔solid transition. As H_2O shows a peak around 250 K (Figure 1), this solvent may be responsible for the peak observed at 200 K for *E*//*b* (Figure 2). As shown in Figures 2 and 4, the polarizabilities of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$, $[Mn_3(HCOO)_6](CH_3OH)$, and $[Mn_3(HCOO)_6](C_2H_5OH)$ display a characteristic peak for *E*//*a*. Thus, guest molecules in $[Mn_3(HCOO)_6]$ seem to have a considerable amount of freedom along the *a* direction at high temperature. However, for *E*//*b*, only $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ gave the characteristic temperature dependence of ε_r. $[Mn_3(HCOO)_6](CH_3OH)$ and $[Mn_3(HCOO)_6](C_2H_5OH)$ showed small and featureless behaviors upon application of an electric field parallel to this direction. For *E*//*c*, every system demonstrated characterless dielectric behavior similar to that of $[Mn_3(HCOO)_6]$.

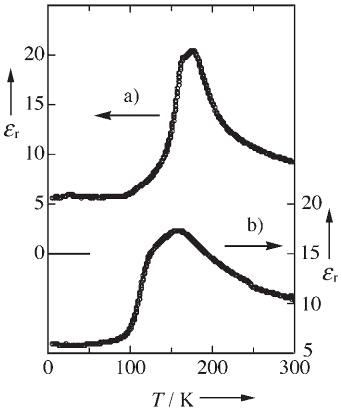

Figure 4. Plot of the dielectric constants of a) $[Mn_3(HCOO)_6](C_2H_5OH)$ and b) $[Mn_3(HCOO)_6](CH_3OH)$ for *E*//*a* as a function of temperature. The dielectric constants of both systems exhibited negligible temperature dependencies for *E*//*b* and *E*//*c*.

To obtain information on the thermal motion of guest molecules in the low and high polarizability states, we reexamined the crystal structures at 90, 155, and 230 K,[10] and calculated the channel spaces of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$. The unit cell volume ($V_{cell}$), the volume of the space occupied by the atoms of the host lattice (V_{host}, determined from the van der Waals radii), and the channel space ($V_{por} = V_{cell} - V_{host}$) were calculated to be $V_{cell} = 1769$, $V_{host} = 893$, and $V_{por} = 876$ Å^3 at 230 K (for all calculations, similar values were obtained at 90 and 155 K).[11] That is, about half of the volume of the unit cell is vacant. As the "van der Waals volumes" (the volume occupied by the atoms based on the van der Waals radii) of CH_3OH and H_2O are 35.0 and 17.5 Å^3, respectively, V_{guest} is 210 Å^3 ($= (35.0 + 17.5) \times 4$) for the unit cell containing four CH_3OH and four H_2O molecules. Therefore, the guest molecules occupy only 24% of the vacant space (V_{por}) and have a large degree of positional freedom in the channel.

We first imagined the possibility of a "1D liquidlike state" for the guest molecules along the channel at high temperature, but the results of the dielectric measurements suggest that the packing of the guest molecules in the channel tends to be loose along the *a* direction (and not the *b* direction). Due to the heavy disorder of the guest molecules, it was very difficult to determine accurately their atomic positions, although the reliability factor of the structure refinement could be reduced significantly by including solvent molecules. The difference Fourier syntheses based on the host lattice atoms gave similar peak distributions at 230, 155, and 90 K. The peaks become relatively large at lower temperatures. The carbon and oxygen atoms of the CH_3OH molecules could not be located uniquely. However, the distribution of the large peaks suggested that the water and methanol molecules are arranged alternately along the channel (parallel to *b*; Figure 3b). The structure refinements gave extremely large temperature factors for the guest molecules (the average B_{eq} value of the non-hydrogen atoms was about 15 at 155 K); the temperature factors reflect not only the large thermal motion but also the broad distribution of the guest molecules in the channel. Examination of the distribution of the main peaks in the difference Fourier maps and the results of the subsequent structure refinements did not provide information on the distribution of the guest molecules. As for the roughly refined positions of the non-hydrogen atoms, there are no contacts shorter than 3.3 Å between guest molecules and the host lattice. The positions of the non-hydrogen atoms X_1, X_2, and X_3 (Figure 3) showed only slight changes between 230 and 155 K. However, the positions of X_2 and X_3 changed significantly between 155 and 90 K, suggesting an alteration in the molecular orientation of CH_3OH. Thus, the change in the orientation polarization due to the CH_3OH molecules is expected below 155 K, which is consistent with the assumption that the peak at 150 K is related to the change of polarizability of the CH_3OH molecules. It is suggested that the non-hydrogen atoms of the guest molecules are arranged along the *b* axis with very short contacts (3.2, 3.5 Å at 155 K; broken lines in Figure 3b). Therefore, the guest molecules do not appear to be as free along this direction. It is possible that the peak at 200 K for $E//b$ (Figure 2b) is related to the formation of weak O(methanol)···O(water) hydrogen bonds. However, due to the absence of information on the hydrogen atoms, clear structural evidence for the expected role of H_2O in the appearance of a peak at 200 K for $E//b$ was not obtainable. As seen from Figures 3a and b, the distribution of the guest molecules is fairly compact along the *c* direction (transverse direction of the channel). In contrast, the guest molecule seems to have a large open space along the *a* direction. These structural features then cause the anisotropic dielectric behavior of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$.

Although the desired dielectric properties could be realized by the combination of porous molecular crystals and polar guest molecules, these properties do not originate from the simple 1D liquidlike behavior of the guest molecules. It is nonetheless interesting that molecules confined in the narrow 1D channel show sharp "transition-like behavior", because systems with strong a 1D nature generally do not exhibit this phase transition. As shown in Figure 4, $[Mn_3(HCOO)_6](C_2H_5OH)$ demonstrates a surprisingly steep increase in the dielectric constant around 175 K. Such a strong temperature dependence of ε_r was quite unexpected. This behavior indicates the possibility of a collective freezing of guest molecules, which will be studied in the future. Other than porous molecular crystals with 1D channel structures, there are many interesting capsule-type molecular complexes.[12] Can guest molecules confined in zero-dimensional nanocapsules exhibit characteristic dielectric behaviors? The dielectric properties of such cluster complexes that contain water molecules will be examined in the near future.

Experimental Section

The samples were synthesized according to a reported method.[7] Freshly distilled water, methanol, ethanol, and benzene were used. The guest-containing crystals were obtained by soaking $[Mn_3(HCOO)_6]$ crystals in these solvents. The temperature dependencies of the dielectric constants of H_2O, CH_3OH, C_6H_6, and $[Mn_3(HCOO)_6]$(guest) (guest = vacant, CH_3OH, H_2O, CH_3OH, C_2H_5OH) were measured in the temperature range 4.2–300 K with an LCR meter (Precision Component Analyzer 6440B of Wayne Kerr Electronics). The liquid samples were measured by using a small cylindrical platinum cell with a cell volume of about 0.25 cm^3 (the liquid samples were frozen at low temperatures). The single-crystal measurements were made with crystals cut into rectangular parallelepipeds (ca. $2.2 \times 1.5 \times 0.5$ mm^3). Silver conduction paste painted on the crystal surfaces was used as the electrodes. A 10-kHz electric field of 0.1 V (for the liquid sample) or 1 V (for the single crystal) was applied. Owing to the difficulties in shaping the small crystal, the accuracy of the dielectric constant obtained was not so high (especially for $E//b$ and $E//c$ because of the small size of the crystal along the *a* direction). However, the temperature dependencies were determined fairly precisely.

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[8] As reported in the supplementary data of reference [7a], the composition of $[Mn(HCOO)_3](H_2O)(CH_3OH)$ was determined by elemental analysis and TGA measurements. We reexamined the TGA and confirmed the previous results. The chemical compositions of $[Mn_3(HCOO)_6](CH_3OH)_x$ and $[Mn_3(HCOO)_6](C_2H_5OH)_y$ were also determined by elemental analyses and TGA experiments. Although the content of CH_3OH could be larger than 1.0, these experiments indicated that both x and y were approximately equal to 1.0.

[9] As the crystals of $[Mn_3(HCOO)_6]$ were destroyed upon placement in water, the susceptibility of $[Mn_3(HCOO)_6](H_2O)_x$ could not be examined.

[10] Although the details of the structural data of $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$ were reported in reference [7], we reexamined the crystal structures at 230, 155, and 90 K. We previously reported that the crystal has the space group $P2_1/c$, with β ≈ 127°. However, here we adopted the space group $P2_1/n$ in order for β to be approximately 90° so that it was easier to adjust the direction of the electric field E to each crystal axis: $[Mn_3(HCOO)_6](H_2O)(CH_3OH)$, monoclinic, $P2_1/n$, $a = 11.683(1)$ Å, $b = 10.166(1)$, $c = 14.904(2)$, $\beta = 91.674(3)°$, $V = 1769$ Å^3, $Z = 4$, $R = 0.030$, $R_w = 0.033$ at 230 K ($R = 0.032$, $R_w = 0.036$ at 155 K and $R = 0.039$, $R_w = 0.047$ at 90 K).

[11] Pauling's van der Waals radii were used.

[12] For example, see: A. Lützen, *Angew. Chem.* **2005**, *117*, 1022 – 1025; *Angew. Chem. Int. Ed.* **2005**, *44*, 1000 – 1002.