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Dielectric Properties of Water Chains Incorporated in Porous Coordination Polymer Crystal $[Cu(C_6H_4NO_2)_2]$

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The dielectric constant (ε) of "water chains" incorporated in the channel of porous coordination polymer crystal $[Cu(C_6H_4NO_2)_2]$ was small at low temperatures ($\varepsilon \approx 10$) but became as large as 250 at 370 K. These dielectric behaviors were consistent with the results of molecular dynamics simulation and indicated that a melting of hydrogen-bonded water chains occurred above 300 K.

Recently, the dielectric properties of molecular crystals have been attracting increasing attention.[1] In particular, the dielectric properties of supramolecular systems such as coordination polymer crystals incorporating polarizable guest molecules and ions have been reported frequently.[2] We have reported the temperature dependence of the dielectric constant (ε) of $[Mn_3(HCOO)_6](CH_3OH)(H_2O)$, which showed a dielectric anomaly associated with the freezing of the positional freedom of the guest molecules incorporated in the channels of the crystal.[2a] Besides the dielectric properties originating from the guest molecules, multifunctional molecular systems can be obtained by assembling guest molecules possessing dielectric functions and a host lattice exhibiting magnetic ordering. For example, $[Mn_3(HCOO)_6](C_2H_5OH)$ was reported to exhibit ferrimagnetic and ferroelectric transitions that originated from the Mn^{2+} ions at 10 K and guest ethanol molecules at 165 K, respectively.[3,4] To the best of our knowledge, this is the first possible example of a molecule-based *multiferroic* system.

Considering the exceptionally high polarizability of bulk water, the dielectric properties of "one-dimensional water" confined in the channels of coordination polymer crystals are of special interest. Recently, the ferroelectric behavior of one-dimensional water chains confined in the supramolecular architecture of $[Cu^I_2Cu^{II}(cdta)(4,4'\text{-bpy})_2]_n$ has been reported, where H_4cdta: *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid and 4,4′-bpy: 4,4′-bipyridine.[5] In previous studies, we observed antiferroelectric hysteresis and a very large dielectric constant (ε) of $[Ln_2Cu_3(ida)_6]\cdot nH_2O$, where Ln: lanthanide, ida (iminodiacetate): $[NH(CH_2COO)_2]^{2-}$, and $n \approx 9.0$, for the electric field applied parallel to the channel direction ($\varepsilon_{//} \approx 10^3$).[6,7] It was noted that the dielectric constant for the field perpendicular to the channel direction was very small ($\varepsilon_{\perp} < 15$). A sharp decrease in the value of $\varepsilon_{//}$ was indicative of the freezing of the positional freedom of guest water molecules at low temperatures, which was consistent with the results of a molecular dynamics (MD) simulation of guest water molecules.[7]

Since the magnitude of the dielectric constant of a molecular system is considered to reflect the degree of positional freedom of the molecules, the temperature dependence of dielectric constant of hydrogen-bonded water chains confined in the channel of coordination polymer crystal can provide useful information to clarify the nature of "one-dimensional water." Here, we report the temperature dependence of dielectric constants of $[Cu(in)_2]\cdot nH_2O$, where in: isonicotinate (i.e., $C_6H_4NO_2^-$).

The crystals of $[Cu(in)_2]\cdot nH_2O$ were prepared by hydrothermal synthesis. As reported by Lu and Babb,[8] the square-pyramidal copper atoms are linked by five two-connected tridentate in units to form channels along the *a* axis, where the guest water molecules are accommodated (Figure 1a). The free volume of the channel space was calculated to be 39% of the unit cell volume. The water molecules form a hydrogen-bonded chain where every two water molecules are bonded to the oxygen atoms of in of the host lattice. This suggests the existence of a stoichiometric amount of guest water molecules, which was confirmed by thermogravimetric analysis (TGA) and X-ray population refinements of oxygen atoms of guest water molecules performed by using freshly prepared crystals sealed in glass capillaries ($n = 2$).[9]

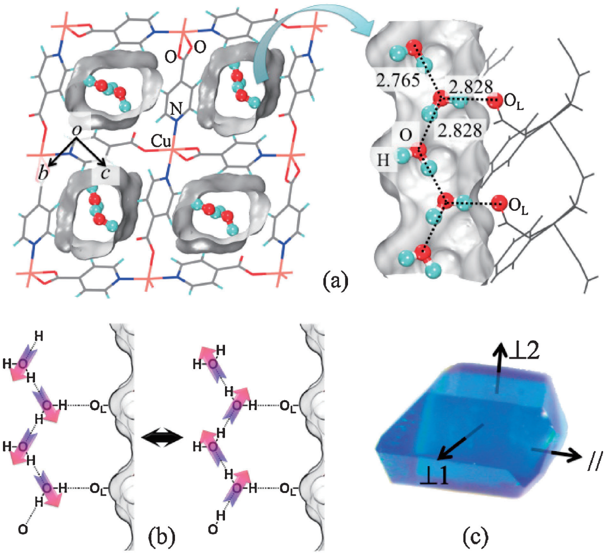

Figure 1. (a) Arrangement of channels in the crystal of $[Cu(in)_2]\cdot 2H_2O$ viewed along the *a* axis and the hydrogen-bonded water chain of guest water molecules. The O···O distances (Å) determined at 113 K are shown. O_L denotes the oxygen atom of the host lattice. (b) Schematic drawing of the possible collective structural change in the hydrogen-bonded water chain. The arrows represent the dipole moments of water molecules. (c) Typical crystal of $[Cu(in)_2]\cdot 2H_2O$. The directions of //, ⊥1, and ⊥2 are approximately parallel to the *a*, *b*, and *c* axes, respectively.

In order to check the possibility of magnetic order of the Cu^{2+} moments, the magnetic susceptibility was measured with a SQUID magnetometer down to 2 K. The Curie–Weiss behavior suggesting weak antiferromagnetic interaction between Cu^{2+} ions was observed ($\theta = -0.42\,K$). The χT value of 0.439 was consistent with the average g value of Cu^{2+} ($g_{av} = 2.16$) obtained by ESR measurements ($g_1 = 2.26$, $g_2 = 2.15$, and $g_3 = 2.08$).

Concerning the dielectric properties of $[Cu(in)_2]\cdot 2H_2O$, we considered three possible scenarios. (1) The dielectric constant (ε) is very small owing to a stable hydrogen-bonded water chain structure at high temperatures because of suppression of the orientation polarization of water molecules. (2) ε might possibly become very large if the orientation of hydrogen-bonded water molecules changes cooperatively at high temperatures (Figure 1b). (3) Similar to $[Ln_2Cu_3(ida)_6]\cdot nH_2O$, which exhibits antiferroelectric hysteresis,[6,7] ε will become fairly large if "melting of the water chain" occurs at high temperature and the water molecules become mobile in the channel.

The dielectric constants were measured in the temperature range of 83–373 K for the electric field (0.4 V, 1 kHz) applied approximately parallel to the a (//), b ($\perp 1$), and c ($\perp 2$) axes (Figures 1c and 2).[10] Conducting gold paste was applied to the crystal surface and used as an electrode. The typical size of the crystal used in dielectric constant measurements was $0.2 \times 0.4 \times 0.4\,mm^3$. In order to prevent the escape of guest water molecules at high temperatures, the sample crystals with gold leads ($30\,\mu m\,\phi$) were coated with epoxy resin (Araldite) and kept in a heat-resistant polyimide cell during the dielectric measurements. However, the loss of guest water molecules could not be suppressed completely at high temperatures even though the heating (or cooling) speed was relatively high ($>3\,°C\,min^{-1}$).

As shown in Figure 2, the dielectric constant was very small ($\varepsilon < 15$) and almost temperature independent at low temperatures. However, above room temperature, ε along the direction approximately parallel to c ($\varepsilon_{\perp 2}$) increased fairly rapidly with an increase in temperature. At around 370 K, ε became as large as 250, which is approximately three times the dielectric constant of bulk water (80 at 293 K). As shown in Figure 2, $\varepsilon_{\perp 2}$ decreased when the sample cell was evacuated. After the evacuation, $\varepsilon_{\perp 2}$ became very small (<15) and almost temperature independent, which clearly shows that the large dielectric constant was due to the polarizability of guest water molecules. These dielectric behaviors closely resembled those of $[La_2Cu_3(ida)_6]\cdot nH_2O$, which had large dielectric constants in the case of an electric field parallel to the channel direction ($\varepsilon_{//} \approx 270$ at 273 K) and antiferroelectric hysteresis loop at high temperatures.[7] These observations suggest the large positional freedom of the guest water molecules at high temperatures. As the positions of the water oxygen atoms could not be determined clearly by X-ray crystal structure refinement at 353 K, large thermal motion of the water molecules was believed to occur at this temperature. Thus, among the three above-mentioned scenarios for the thermal and dielectric behaviors of the guest water molecules in $[Cu(in)_2]\cdot 2H_2O$, the third scenario is the most plausible one. The dielectric constant along a ($\varepsilon_{//}$) was smaller than $\varepsilon_{\perp 2}$, but it exhibited similar temperature dependence. On the other hand, the dielectric constant for the field approximately parallel to the b direction ($\varepsilon_{\perp 1}$) was much smaller than $\varepsilon_{\perp 2}$ and $\varepsilon_{//}$. The large anisotropy of the dielectric constants is considered to be an inherent nature of one-dimensional water because similar large anisotropy has been observed in $[Ln_2Cu_3(ida)_6]\cdot nH_2O$.[7]

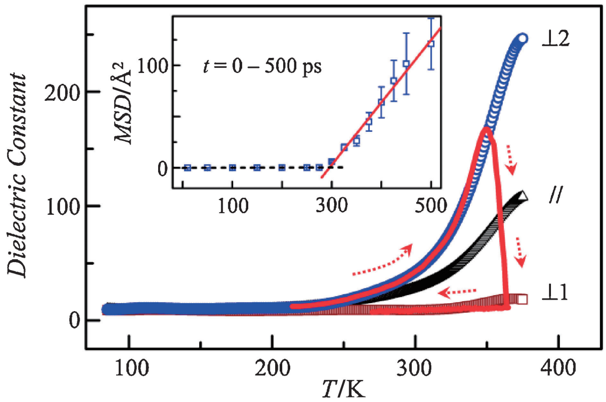

Figure 2. Temperature dependences of dielectric constants of $[Cu(in)_2]\cdot 2H_2O$ (see also Figure 1c). The red line shows the dielectric constant ($\varepsilon_{\perp 2}$) of the crystal evacuated for about 2 h at around 355 K. The arrows indicate the temperature change in the measurement. The inset shows the temperature dependence of the averaged *MSD* (Δ^2) of guest water molecules obtained by MD simulations.

According to the well-known formula of the entropy change (ΔS) of dielectric material under application of an external electric field (E), i.e., $\Delta S \propto (d\varepsilon/dT)E^2$, the positive $d\varepsilon/dT$ of $\varepsilon_{\perp 2}$ (or $\varepsilon_{//}$) at high temperatures shows that the disorder of the guest water system must be increased by the application of the electric field.[11] In other words, the water molecules are considered to be in a dielectrically ordered state. The trial to observe the dielectric hysteresis loop was performed at 353 K up to $E = 20\,kV\,cm^{-1}$ for the field parallel to $\perp 2$. However, no clear hysteresis loop was observed. It might be possible that the critical field required for observing the hysteresis loop is larger than $20\,kV\,cm^{-1}$ at 353 K.[12]

Since the large positional freedom of water molecules was suggested by the large increase in the dielectric constant above room temperature, constant–volume, constant–temperature MD simulations were performed for gaining a better understanding of the thermal behavior of guest water molecules.[13,14] It was initially thought that hydrogen bonding between the bound water molecules and the host lattice would have had an effect on the thermal behavior of water molecules (Figure 1a). However, the temperature dependence of the mean squared displacements (MSD, Δ^2) of two guest water molecules showed no significant difference. As shown in the inset of Figure 2, the water molecules were tightly bound below room temperature. But the water molecules were found to begin to move above room temperature. The values of Δ^2 can be assumed to be approximately 0 at $T < T_c$ and proportional to $(T - T_c)$ at $T > T_c$, where $T_c \approx 300\,K$. These results are consistent with the X-ray structure analyses. As expected, the dielectric constant of guest water molecules was very small when the positions of guest water molecules were fixed. However, with melting of the positional freedom of the water molecules, the dielectric constant began to increase rapidly. Similar results of the MD simulations and similar increase in ε were reported in $[Ln_2Cu_3(ida)_6]\cdot nH_2O$.[7]

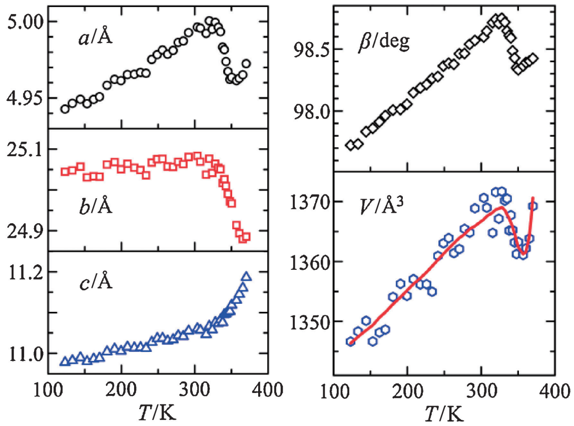

Figure 3. Temperature dependence of the lattice constants of $[Cu(in)_2]\cdot 2H_2O$.

The temperature dependence of dielectric constants and the results of MD simulations of $[Cu(in)_2]\cdot 2H_2O$ and $[Ln_2Cu_3(ida)_6]\cdot nH_2O$ will represent the dielectric and thermal behaviors characteristic of one-dimensional water systems incorporated in the channels of coordination polymer crystals.

In order to obtain more insight into the "melting of water chains," the temperature dependence of the lattice constants was studied in the temperature range of 123–370 K. As shown in Figure 3, the lattice constants *a* and *c* increased almost linearly with an increase in temperature between 123 and 323 K. On the other hand, the lattice constant *b* was almost constant within this temperature range. In the temperature range of 123–320 K, the thermal expansion coefficients were $\alpha_a = 5.5 \times 10^{-5}\,K^{-1}$, $\alpha_b = 0.3 \times 10^{-5}\,K^{-1}$, $\alpha_c = 4.2 \times 10^{-5}\,K^{-1}$, and $\alpha_v = 9.0 \times 10^{-5}\,K^{-1}$. The lattice constants showed anomalous temperature dependence above 323 K. The results of X-ray structure refinements and MD simulation indicated that these anomalies were induced by the thermal motion of water molecules (or "melting" of the water chain). A similar anomalous temperature dependence of the lattice constants was also observed in $[Ln_2Cu_3(ida)_6]\cdot nH_2O$.[6,7]

In conclusion, we have examined the dielectric properties of the water chain incorporated in the channel of the coordination polymer crystal $[Cu(in)_2]$. The dielectric constant of $[Cu(in)_2]\cdot 2H_2O$ was very small at low temperatures, where guest water molecules were locked by hydrogen bonds. However, with an increase in temperature, the dielectric constants along the *a* and *c* directions increased fairly rapidly. In contrast, the dielectric constant along the *b* direction remained small even at high temperatures. The results of MD simulation showed that the water molecules became mobile above room temperature, suggesting that the large increase in the dielectric constant at high temperature was due to the melting of the hydrogen-bonded water chain system. The results of the present work will contribute to better understand the microscopic process of the "melting of water chains" in the nanochannels and the origin of the large anisotropy of the dielectric constants, which is a future problem for the studies on one-dimensional water systems incorporated in porous coordination polymer crystals.

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9 The crystal belongs to the monoclinic system with the space group *Cc*. The room-temperature structure was reported by Lu and Babb (ref 8). The lattice constants at 113 K are $a = 4.938(2)$, $b = 25.001(8)$, $c = 10.964(4)$ Å, $\beta = 97.582(8)°$, and $V = 1341.7(8)$ Å^3. TGA and X-ray population refinement of oxygen atoms of guest water molecules gave the *n* value of 2.0 and showed a gradual loss of guest water molecules at 320–425 K, but the host lattice was stable up to about 570 K (see also ref 8).

10 The crystal of $[Cu(in)_2]\cdot nH_2O$ has a distorted hexagonal pillar-shape (Figure 1c). For the dielectric measurement along the *a* axis (//), the crystal was cut by the plane approximately perpendicular to the *a* direction (the distance between two electrodes was 0.2–0.4 mm). Accurate estimation of the dielectric constants was difficult because the crystal was not rectangular and the crystal was small. The error of the obtained dielectric constant was as large as ±30%. The measurements were performed up to about 385 K. Although ε showed a fairly sharp peak at around 375 K, the data above 373 K were omitted because the escape of guest water molecules seemed to be significant above 370 K.

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12 The nonideal shape of the antiferroelectric hysteresis loop of $[Ln_2Cu_3(ida)_6]\cdot nH_2O$ reported in ref 7 suggests that E_{crit} of the guest water system in this crystal was approximately 15 kV cm^{-1} at around 393 K, where E_{crit} is the critical electric field required to reverse the direction of the "polarization of the antiferroelectric domain." Since E_{crit} is believed to increase rapidly with decreasing temperature (for example, E_{crit} of the representative antiferroelectric material $PbZrO_3$ was 30 kV cm^{-1} at 220 K and 60 kV cm^{-1} at 200 K (E. Sawaguchi, T. Kittaka, *J. Phys. Soc. Jpn.* **1952**, *7*, 336)), it is considered that a fairly large electric field (>20 kV cm^{-1}) would be needed to observe the dielectric hysteresis loop of the guest water system of $[Cu(in)_2]\cdot 2H_2O$ at around 353 K. No attempt was made to observe the hysteresis loop at higher temperatures because the reliable experiments were considered to be difficult due to the possible escape of guest water molecules.

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