Anomalous Dielectric Behavior and Thermal Motion of Water Molecules Confined in Channels of Porous Coordination Polymer Crystals

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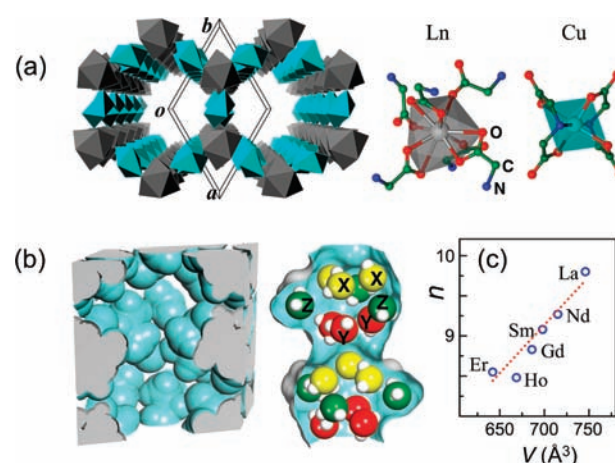[§]College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

S *Supporting Information*

ABSTRACT: Guest water molecules confined in channels of porous coordination polymer crystals $[Ln_2Cu_3(IDA)_6]\cdot nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, Er; IDA = $[NH(CH_2COO)_2]^{2-}$; $n \approx 9$) exhibited large dielectric constants (ε) and antiferroelectric behaviors at high temperatures (e.g., $\varepsilon(Sm) \approx 1300$ at 400 K). In addition, plots of the temperature dependence of ε showed broad peaks at ∼170 K, below which ε became very small. These puzzling temperature dependences of ε are consistent with the results of molecular dynamics simulations, suggesting the "freezing of thermal motion" of water molecules at ∼170 K.

Figure 1. (a) Crystal structure of $[Ln_2Cu_3(IDA)_6]\cdot nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, Er) viewed along the channel direction ($||c$) and the coordination structures around Ln and Cu atoms. (b) Schematic view of the inner region of the channel and a typical snapshot of the arrangement of water molecules determined by the molecular dynamics simulation. The positions occupied by yellow, red, and green water molecules are called positions X, Y, and Z, respectively. (c) Relation between n and the volume of porous space (V) of the unit cell of $[Ln_2Cu_3(IDA)_6]\cdot nH_2O$.

Recently, porous metal—organic framework crystals have attracted considerable attention for their uses in gas adsorption, separation, and storage.[1,2] These crystals also provide opportunities to investigate the physical properties of nanomolecular assemblies. We have previously examined the dielectric properties of ethanol molecules encapsulated in the channels of a crystal of $[Mn(HCOO)_2]$ and found a ferroelectric transition.[3] Recently, antiferro- and ferroelectric transitions have been discovered in similar metal—formate framework systems with ammonium cations, $[C][Zn(HCOO)_3]$ (C = $(CH_3)_2NH_2^+$, NH_4^+).[4,5] Water is an exceptionally polarizable material. Its dielectric constant (ε) increases with decreasing temperature to as much as 88 just above the freezing point, below which ε becomes very small.[3b,6]

We previously reported that the guest water molecules in the channels of the porous crystal $[La_2Cu_3(IDA)_6]\cdot nH_2O$ (IDA (iminodiacetate) = $[NH(CH_2COO)_2]^{2-}$) exhibited antiferroelectric behavior at high temperatures.[7]

We report here the dielectric behavior and thermal motion of guest water molecules in $[Ln_2Cu_3(IDA)_6]\cdot nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, Er; $n \approx 9$).[8] Because the guest water molecules tended to escape from the crystal above ∼315 K, we fabricated small Teflon-sealed cylindrical cells out of heat-resistant polyimide to store the sample crystal during the dielectric measurements. The decrease in ε observed at high temperatures in the previous measurements was completely suppressed.[7] X-ray diffraction experiments showed that all these crystals of $[Ln_2Cu_3(IDA)_6]\cdot nH_2O$ belong to the trigonal system with space group $P\bar{3}c1$ (Figure 1a). The guest water molecules are

accommodated in the channel along the c-axis. The diameter of the channel is not uniform. Large halls and small necks appear alternately along the channel (Figure 1b). Small water clusters, previously termed "Chinese lanterns", exist in the hall.[9] The n-value of $[Ln_2Cu_3(IDA)_6]\cdot nH_2O$ was determined from the weight loss of the single crystals after keeping the crystals in glass tubes evacuated at 395 K for 20 h. The obtained n-value decreased with increasing atomic number of Ln. The average value of n was 9.0 (Figure 1c).

We measured ε of $[Ln_2Cu_3(IDA)_6]\cdot nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, Er) at 80−400 K for an electric field (E = 0.2 V, 10 kHz) applied parallel ($||$) and perpendicular ($\perp$) to the c-axis (Figure 2a). Above room temperature, $\varepsilon_{||}$ increased rapidly with temperature. In contrast, $\varepsilon_\perp$ was small and exhibited featureless temperature dependence ($\varepsilon_\perp \approx 10$). When the sample cell was evacuated, $\varepsilon_{||}$ decreased sharply, clearly indicating that the large
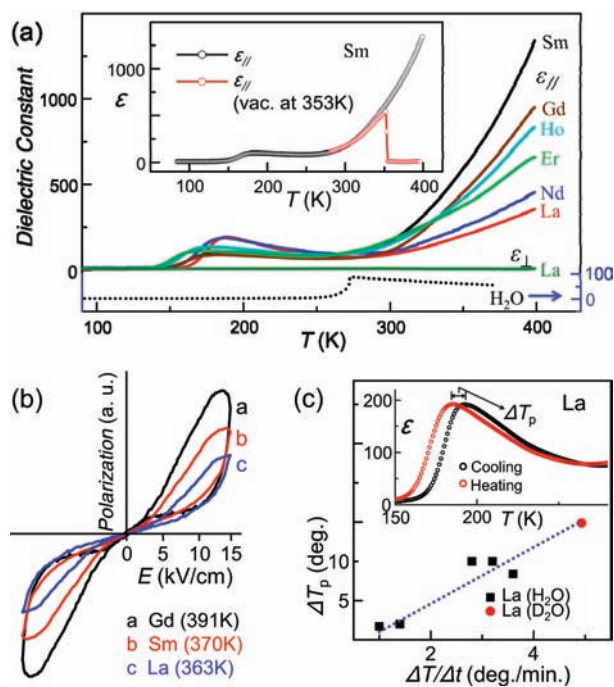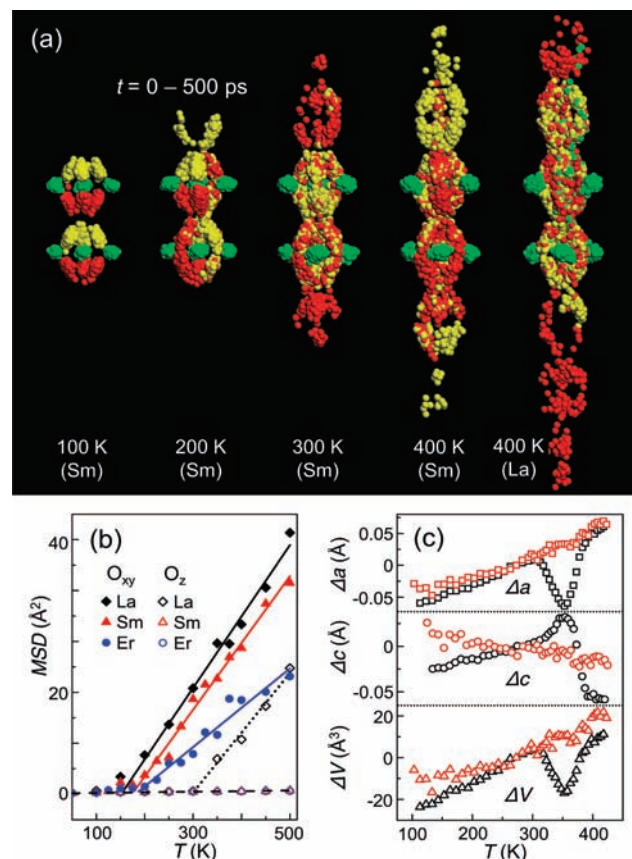
Figure 2. (a) Temperature dependences of dielectric constants (heating cycle) for $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, Er). The dark green line represents the temperature dependence of $\varepsilon_\perp$. The dotted black line represents the dielectric constant of bulk H_2O.[3b,6] The inset shows the comparison of $\varepsilon_\parallel$ for the Sm crystal (black circles) and for the Sm crystal evacuated at 353 K (red circles). (b) Hysteresis loops of $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ (Ln = La, Sm, Gd). (c) Relation between ΔT_p and the average speed of the temperature change at ~170 K ($\Delta T / \Delta t$) for $[La_2Cu_3(IDA)_6] \cdot nH_2O$ and $[La_2Cu_3(IDA)_6] \cdot nD_2O$. The inset shows the temperature dependence of $\varepsilon_\parallel$ for $[La_2Cu_3(IDA)_6] \cdot nH_2O$.

Figure 3. (a) MD simulation results for the thermal motion of guest water molecules of $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$. The distribution of oxygen atoms of guest water molecules initially located at sites X (yellow), Y (red), and Z (green) at 100, 200, 300, and 400 K is plotted every 5 ps between 0 and 500 ps (see Figure 1b). (b) Temperature dependences of MSD (Δ^2) for water molecules of $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ (Ln = La, Sm, Er; t = 100 ps). (c) Temperature dependences of the lattice constants of $[Gd_2Cu_3(IDA)_6] \cdot nH_2O$ (black) and the water-free La crystal $[La_2Cu_3(IDA)_6]$ (red). The ordinates are Δa ($= a(T) - a(273 K)$), Δc ($= c(T) - c(273 K)$), and ΔV ($= V(T) - V(273 K)$). Lattice constants at 273 K: Gd, a = 13.415(1) Å, c = 14.462(1) Å, V = 2253.9 Å^3; La (water-free), a = 13.461(1) Å, c = 14.881(1) Å, V = 2335.0 Å^3.

ε originated from guest water molecules (inset of Figure 2a). With an increase in the atomic number of Ln, the magnitude of $\varepsilon_\parallel$ at 400 K changed as La < Nd < Sm > Gd > Ho > Er (Figure 2a). $\varepsilon_\parallel$ of $[Sm_2Cu_3(IDA)_6] \cdot nH_2O$ (hereafter called the Sm crystal) became 1300, which is 15 times larger than the maximum dielectric constant of bulk water. Figure 2a also shows that $\varepsilon_\parallel$ of $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ exhibited a shallow minimum at ~240−280 K. $\varepsilon_\parallel$ then increased with a decrease in temperature and exhibited a drop at 150−190 K, below which $\varepsilon_\parallel$ became very small (<15). The La and Nd crystals with relatively small $\varepsilon_\parallel$ values at 400 K exhibited fairly large peaks at ~190 K ($\varepsilon_\parallel \approx 190$); however, the Sm and Gd crystals with large $\varepsilon_\parallel$ at 400 K exhibited inconspicuous minima and very small peaks. The Ho and Er crystals exhibited intermediate behaviors. At first sight, these dielectric behaviors appear very unusual. According to the well-known formula of the entropy (S) of a dielectric material, $\Delta S \propto (d\varepsilon / dT)E^2$, S increases with the application of E above room temperature because $d\varepsilon / dT$ is positive, suggesting that the guest water system is in a "dielectrically ordered state".[10] On the other hand, the negative $d\varepsilon / dT$ below 240 K suggests the existence of "disordered water molecules" besides the "ordered water system".

The dielectric hysteresis experiments were performed for La, Sm, and Gd crystals.[11a] Antiferroelectric hysteresis loops were observed at high temperatures (Figure 2b). Consequently, the rapid increase in ε above 350 K is ascribed to approaching the antiferroelectric transition with increasing temperature. At low temperature, the antiferroelectric susceptibility became small and the negative $d\varepsilon / dT$ became conspicuous. The resemblance between the dielectric behavior below 240 K and that of bulk water suggests that the drop of ε at ~170 K is due to the "freezing" of the positional freedom of guest water molecules (Figure 2a).

In order to understand the thermal behavior of the water molecules, we performed constant-volume, constant-temperature molecular dynamics (MD) simulations on $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ (Ln = La, Sm, Er).[12,13] We assumed $n = 9$ (or 18 molecules in the unit cell), because 9 is not only the average value of n (Figure 1c) but also a suitable number to realize "ordered water arrangement" consistent with the space group $P\bar{3}c1$. The atomic coordinates of the host lattice were fixed. As shown in Figure 3a, MD simulations suggested that the positions of all of the water molecules are well fixed at low temperatures. However, with increasing temperature, the molecules tended to move. The mean-squared displacement (MSD, Δ^2) indicated the existence of two types of water molecules (Figure 3b). For convenience of

explanation, nine molecules in one formula unit forming a small water cluster were tentatively classified into three groups (Figures 1b and 3a). One is the group of three green molecules occupying three crystallographically equivalent sites Z (Figure 1b). The other two groups are the groups of three yellow molecules and three red molecules. The six positions occupied by the yellow and red molecules (sites X and Y) are crystallographically equivalent. The three green molecules of the Sm, Gd, and Er crystals occupying three secluded positions in the large "hall" (site Z) naturally did not move within the temperature examined (<500 K). The green molecules in the La crystal with relatively large porous space began to move at ~300 K (Figure 3b). On the other hand, the crystallographically equivalent yellow and red molecules existing at narrower parts of the channel (sites X and Y) were fairly mobile and easily exchanged their positions. However, the average distribution of total water molecules was approximately identical to that at low temperature. MSD can be expressed as $\Delta^2 \approx 0$ at $T < T_c$, and $\Delta^2 \propto (T - T_c)$ at $T > T_c$, where $T_c = 150-185$ K for the molecules initially located at sites X and Y and $T_c = 300$ K for the molecules initially located at site Z of the La crystal (Figure 3b). These results, indicating the "freezing" of the positions of guest water molecules below T_c, are consistent with the drop of ε at ~170 K.

As mentioned before, the negative $d\varepsilon/dT$ below 240 K suggests the existence of disordered water molecules. Since the Sm and Gd crystals exhibited a large increase in ε at high temperatures and a very small increase below 240 K, they are considered to possess porous spaces suitable for accommodating an ordered water system, which is consistent with the experimentally determined n-value (~9) of these crystals (Figure 1c). Consequently, the antiferroelectric order is sufficiently developed, and the space to allow the existence of disordered water molecules is small. However, the porous spaces of the La and Nd crystals are larger than the optimal space to permit the existence of disordered molecules, producing the relatively large dielectric peak at ~180 K. In contrast, the porous spaces of the Ho and Er crystals are smaller than the optimal space, producing a less perfect molecular arrangement. The positional freedom of disordered molecules will be frozen at ~170 K, similar to the case of glass transition. In Figure 2c, the difference between the peak temperatures of ε in the cooling and heating cycles (ΔT_p) is plotted against the average speed of the temperature change at ~170 K ($\Delta T / \Delta t$) for $[La_2Cu_3(IDA)_6] \cdot nH_2O$ and $[La_2Cu_3(IDA)_6] \cdot nD_2O$. The relation $\Delta T_p \propto \Delta T / \Delta t$ was observed. When $\Delta T / \Delta t$ is large, it is plausible that the large disorder remains and ΔT_p becomes large. On the other hand, when $\Delta T / \Delta t$ is sufficiently small, the disorder is relaxed, reducing ΔT_p.

We also examined the temperature dependences of the lattice constants of $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ by using the crystals sealed in glass capillaries. All of the Ln crystals examined (Ln = La, Sm, Gd, Ho, Er) exhibited distinct anomalies at ~350 K (Figure 3c). However, no significant anomaly was observed at ~170 K. Since the lattice constants of the water-free La crystal $[La_2Cu_3(IDA)_6]$ showed no anomaly, the 350 K anomaly clearly originates from the structural change in the guest water system.

We performed X-ray structure determination of $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ (Ln = La, Sm, Er) at 113, 173, 233, 273, 313, 353, and 393 K. The oxygen (water) positions determined below 313 K were in good agreement with those obtained by MD simulation. On the other hand, the oxygen positions could not be determined above 353 K, which is consistent with previous results of the structure determination of the La crystal.[7] Because

antiferroelectric hysteresis was observed at high temperatures, the order of the arrangement of water molecules within the channel should be sufficiently developed even at 400 K. However, due to the strong one-dimensional nature of the guest water system, the interchannel correlation of water positions tends to be imperfect at high temperature, which will prevent the X-ray determination of water positions.[11b] The characteristic temperature dependence of the lattice constants at ~350 K is considered to reflect the temperature dependence of the development of the interchannel correlation between the water positions. Further studies are required to clarify the process of the ordering of water molecules in the channels of the porous crystals.

The guest water system encapsulated in the channels of the coordination polymer crystal $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, and Er) exhibited antiferroelectric behavior and very large enhancement of ε at high temperature. In particular, ε of the Sm crystal became as large as 1300 at ~400 K. In addition, the crystals exhibited broad dielectric peaks at ~170 K, below which ε became very small, indicating the freezing of the positional freedom of guest water molecules. These puzzling dielectric behaviors are consistent with the MD simulation results, showing the usefulness of MD simulations in the analyses of the dielectric properties of guest molecules in porous crystals.

ASSOCIATED CONTENT

S **Supporting Information.** Materials and methods; structural information (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. Science 2003, 300, 1127–1129. (b) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Belosludov, R. V.; Kobayashi, T. C.; Sakamoto, H.; Chiba, T.; Takata, M.; Kawazoe, Y.; Mita, Y. Nature 2005, 436, 238–241.

(2) (a) Kim, H.; Kim, Y.; Yoon, M.; Lim, S.; Park, S. M.; Seo, G.; Kim, K. J. Am. Chem. Soc. 2010, 132, 12200–12202. (b) Zheng, S. T.; Bu, J. T.; Li, Y. F.; Wu, T.; Zuo, F.; Feng, P. Y.; Bu, X. H. J. Am. Chem. Soc. 2010, 132, 17062–17064.

(3) (a) Cui, H. B.; Wang, Z. M.; Takahashi, K.; Okano, Y.; Kobayashi, H.; Kobayashi, A. J. Am. Chem. Soc. 2006, 128, 15074–15075. (b) Cui, H. B.; Takahashi, K.; Okano, Y.; Kobayashi, H.; Wang, Z. M.; Kobayashi, A. Angew. Chem. Int. Ed. 2005, 44, 6508–6512.

(4) Jain, P.; Dalal, N. S.; Toby, B. H.; Kroto, H. W.; Cheetham, A. K. J. Am. Chem. Soc. 2008, 130, 10450–10451.

(5) Xu, G. C.; Ma, X. M; Zhang, L.; Wang, Z. M.; Gao, S. J. Am. Chem. Soc. 2010, 132, 9588–9590.

(6) Archer, D. G.; Wang, P. M. *J. Phys. Chem. Ref. Data* **1990**, *19*, 371–411.

(7) Cui, H. B.; Zhou, B.; Long, L. S.; Okano, Y.; Kobayashi, H.; Kobayashi, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 3376–3380.

(8) The crystals of $[Ln_2Cu_3(IDA)_6] \cdot nH_2O$ (Ln = La, Nd, Sm, Gd, Ho, Er) were prepared according to the method described in ref 9. The unit cell volumes and volumes of porous spaces are given in the Supporting Information.

(9) Ren, Y. P.; Long, L. S.; Mao, B. W.; Yuan, Y. Z.; Huang, R. B.; Zheng, L. S. *Angew. Chem. Int. Ed.* **2003**, *42*, 532–535.

(10) Frohlich, H. *Theory of Dielectrics*; Oxford University Press: London, 1958.

(11) (a) We previously performed the hysteresis experiments on the La crystal,[7] but the hysteresis loop faded out at higher temperature because the measurements were made without using a polyimide cell. (b) We previously suggested that the guest water molecules are in the "1D liquid state" at high temperatures,[7] but the original idea must be modified because $d\varepsilon/dT$ was found to be positive up to 400 K.

(12) MD simulations were performed using the Material Studio Modeling v5.0 software package (Accelrys Inc., San Diego, CA), and the universal force field, as implemented in the Forcite Plus module.

(13) (a) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035. (b) Casewit, C. J.; Colwell, K. S.; Rappe, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 10035–10046. (c) Casewit, C. J.; Colwell, K. S.; Rappe, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 10046–10053.