

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/49767062>

Thermal Expansivity of Ionic Clathrate Hydrates Including Gaseous Guest Molecules

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY B · FEBRUARY 2011

Impact Factor: 3.3 · DOI: 10.1021/jp110737q · Source: PubMed

CITATIONS

5

READS

18

9 AUTHORS, INCLUDING:



Dong-Yeun Koh

Georgia Institute of Technology

31 PUBLICATIONS 179 CITATIONS

SEE PROFILE



Yong Nam Choi

Korea Atomic Energy Research Institute (KA...)

59 PUBLICATIONS 454 CITATIONS

SEE PROFILE



Baesoon Son

Samsung Electro-Mechanics

21 PUBLICATIONS 41 CITATIONS

SEE PROFILE



Seongsu Lee

Korea Atomic Energy Research Institute (KA...)

98 PUBLICATIONS 2,224 CITATIONS

SEE PROFILE

Thermal Expansivity of Ionic Clathrate Hydrates Including Gaseous Guest Molecules

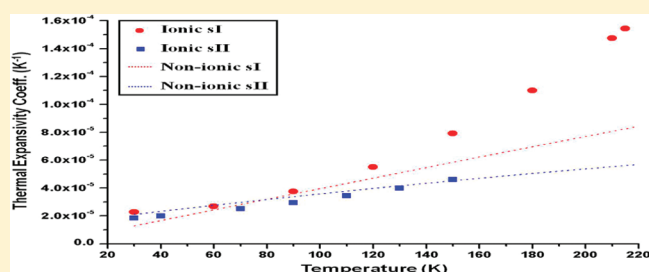
Kyuchul Shin,^{†,§} Wonhee Lee,[†] Minjun Cha,[†] Dong-Yeun Koh,[†] Yong Nam Choi,[‡] Heeju Lee,[‡] Bae Soon Son,[‡] Seongsu Lee,[‡] and Huen Lee^{*,†}

[†]Department of Chemical and Biomolecular Engineering (BK21 Program) and Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

[‡]Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong-gu, Daejeon 305-600, Republic of Korea

[§] Supporting Information

ABSTRACT: Although thermal expansion is a key factor in relation to the host–guest interaction of clathrate hydrates, few studies have investigated the thermal behavior of ionic clathrate hydrates. The existence of ionic species in these hydrates creates a unique host–guest interaction compared to that of nonionic clathrate hydrates. It was revealed that X-ray diffraction cannot be used for research of tetramethylammonium hydroxide clathrate hydrates due to damage of the cations by the X-ray, which results in abnormal thermal expansion of the ionic clathrate hydrates. Hence, in the present work, the thermal expansivities of binary sII $\text{Me}_4\text{NOD} \cdot 16\text{D}_2\text{O}$ and sI $\text{DClO}_4 \cdot 5.5\text{D}_2\text{O}$ were measured by neutron powder diffraction (NPD) in order to shed light on their thermal behavior. General correlations for the thermal behaviors of given structures were established and lattice expansions depending on the guests were compared between ionic and nonionic clathrate hydrates. The peculiar change in the thermal expansivity of binary $\text{DClO}_4 \cdot 5.5\text{D}_2\text{O}$ was also considered in relation to the host–guest configuration.



1. INTRODUCTION

Ionic clathrate hydrates are known to form various crystal structures by encaging hydrophobic cations or anions into confined cavities and incorporating counterions into the water host lattice.^{1,2} Due to the ionic interaction between the ionic guest and host, ionic clathrate hydrates exhibit discrete magnetic behavior, metal ion encagement, cohost inclusion, and excellent thermal stability and proton conductivity.^{3–8} The thermal expansivity of both nonionic and ionic clathrate hydrates and a close comparison between these two cases can provide valuable information concerning the interaction between the guest and host lattice.

Diffraction studies are essential for calculation of the lattice parameter and determination of the volume change of hydrates depending on temperature. A variety of nonionic clathrate hydrates have been explored using the X-ray diffraction technique to reveal their thermal properties. Tse et al. reported that the larger thermal expansion of the sI ethylene oxide hydrate relative to that of hexagonal ice is profoundly affected by the greater anharmonicity of the clathrate lattice.⁹ Takeya et al. revealed that the lattice parameter and volume expansion of sI, sII, and sHI mixed gas hydrates are strongly affected by the physicochemical properties of the guest molecules.^{10,11} Natural gas and air clathrate hydrates from sediments and ice cores were also studied to elucidate their thermal properties.^{12,13} Recently, Hester et al. measured the thermal expansivity of sI and sII gas hydrates at

various gas concentrations and constructed general correlations for thermal expansivity.¹⁴

While diffraction studies have yielded the aforementioned findings, it is very difficult to identify light atoms in the presence of heavy atoms by X-ray diffraction, because X-ray scattering originates from the interaction of X-ray photons with electron clouds. Furthermore, X-ray diffraction may not be appropriate for some types of ionic clathrate hydrates in that, in the case of peralkylammonium hydroxide clathrate hydrates, X-irradiation splits the tetraalkylammonium cations into alkyl radicals.^{15,16} Hence, X-ray scattering can only be used for determination of the crystal structure for peralkylammonium hydroxide hydrates, while measurement of the cell parameters or thermal properties of these compounds with X-ray diffraction technique leads to unreliable results.

In contrast, the neutron diffraction technique shows high sensitivity to light atoms such as D due to interaction of the neutrons with nuclei instead of with electron clouds. Furthermore, neutron scattering does not damage peralkylammonium cations, and consequently measurement results of the lattice parameter and thermal properties of ionic clathrate hydrates are more reliable. Despite this advantage, the neutron approach has not been used

Received: November 10, 2010

Revised: January 3, 2011

Published: January 19, 2011

to research ionic clathrate hydrates, but rather has been applied only to the study of nonionic clathrate hydrates. Ikeda et al. studied the effects of the types of guests on a hydrogen-bonded D_2O host lattice using neutron powder diffraction (NPD) data.¹⁷ Jones et al. revealed the lattice structure of a THF- d_8 clathrate hydrate and considered the thermal expansion and the atomic configuration of the compound depending on the temperature by neutron scattering.¹⁸ Park et al. also used this technique in order to address how the guest size and the thermal history influence the host lattice expansion of the THF sII clathrate hydrate.¹⁹

In this study, we examined the structure-dependent lattice expansion of ionic clathrate hydrates encaging small gaseous molecules over a temperature range of 30–215 K. $Me_4NOD \cdot 16D_2O$ and $DClO_4 \cdot 5.5D_2O$ were selected as sI and sII ionic clathrate hydrates, respectively, and H_2 , D_2 , N_2 , O_2 , and CH_4 as secondary guests. The general correlation in thermal expansivity for each ionic clathrate hydrate system was constructed from the lattice parameter data obtained by the neutron scattering technique, and the peculiar thermal behaviors of the hydrates were considered by investigation of the host–guest interactions and configurations.

2. EXPERIMENTAL METHODS

Tetramethylammonium hydroxide pentahydrate ($Me_4NOH \cdot 5H_2O$, $\geq 97\%$), deuterated perchloric acid ($DClO_4$, 68 wt % in D_2O), and deuterium oxide (D_2O , 99.9 atom % D) were purchased from Sigma Aldrich Inc. All gases (N_2 , O_2 , H_2 , D_2 , and CH_4) were supplied by Special Gas (Korea), with a stated minimum purity of 99.995 mol %. For high-resolution neutron powder diffractometer (neutron HRPD) experiments, $Me_4NOH \cdot 5H_2O$ was dissolved into an excess amount of D_2O and the solution was evaporated in an oven in order to remove H_2O . The addition of excess D_2O and evaporation of the solution were repeated several times for deuteration of the samples. The produced $Me_4NOD \cdot 16D_2O$ solution through stoichiometric calculation at each step was frozen at 213 K for at least 1 day and was then powdered to 200 μm under liquid nitrogen. The powder sample was placed in a high-pressure cell and exposed to N_2 , O_2 , H_2 , or D_2 (120 bar) at 203 K for at least 1 week to synthesize double sII ionic clathrate hydrates. The formed hydrate samples were stored in liquid nitrogen. For synthesis of the sI acid clathrate hydrate, a stoichiometric $DClO_4$ solution was prepared and frozen at 213 K for at least 1 day. In this hydrate, N_2 , O_2 , and CH_4 were used as secondary guests but H_2 and D_2 were excluded due to their extremely high pressure condition for enclathration. Nondeuterated samples for both sI and sII were also prepared in order to obtain high-resolution synchrotron X-ray powder diffraction (X-ray HRPD) patterns and Raman spectra. All synthesizing procedures followed the same recipe used for Me_4NOD hydrates.

The neutron diffraction experiments were carried out on a high-resolution neutron diffractometer ($\lambda = 1.83429$ Å), installed at horizontal channel ST2 of the 30 MW reactor “HANARO” of the Korea Atomic Energy Research Institute (KAERI). The deuterated samples were packed into thin vanadium cylinders, and each cylinder was mounted in a closed-cycle refrigerator (CCR). The resolution of the diffractometer was variable as any of the four Soller collimators with angular divergences $\alpha_1 = 20'$. The divergence $\alpha_2 = 30'$ of the second collimator, and the divergence $\alpha_3 = 10'$ of the third collimator, were fixed.

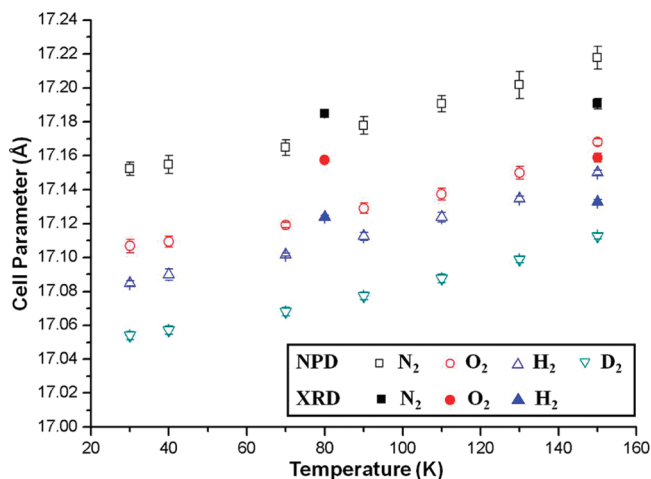


Figure 1. Temperature-dependent lattice parameters for sII $Me_4NOD \cdot 16D_2O$ + various gases using neutron powder diffraction (NPD) and for sII $Me_4NOH \cdot 16H_2O$ + various gases using synchrotron X-ray diffraction (XRD).

Low-temperature neutron diffraction measurements were performed using a CCR with cooling power of 0.5 w and a Si-diode sensor installed on the neutron beam. Although the background signals of the obtained diffraction patterns of the Me_4NOD hydrate samples were not negligible due to the H atoms of the methyl groups in Me_4N^+ ions, the coherent scattering signal intensities were sufficiently high to determine the lattice parameter of each sample (see the Supporting Information for the diffraction patterns). For comparison, X-ray diffraction patterns of Me_4NOH hydrates were also obtained using the high-resolution powder diffractometer equipped at the Pohang Accelerator Laboratory (PAL) Synchrotron. During the measurements, a $\theta/2\theta$ scan mode with a fixed time of 2 s and a step size of 0.01° for $2\theta = 0^\circ - 120^\circ$ and the beamline with a wavelength of 1.549 50 Å were used for each sample. Loading of the samples was performed at 80 K to minimize possible sample damage. The neutron and X-ray HRPD patterns were indexed by the Check-Cell program to obtain the lattice parameters of the clathrate structures.²⁰ A high-resolution dispersive Raman microscope (Horiba Jobin Yvon, France) was also used for confirmation of the gas uptake of $HClO_4 \cdot 5.5H_2O$. The Raman spectra were recorded at 93 K using an Ar ion laser (514.5 nm, 25 mW) with an electrically cooled ($-70^\circ C$) CCD detector.

3. RESULTS AND DISCUSSION

The ionic Me_4NOH clathrate hydrate forms three different crystalline structures: cubic β - $Me_4NOH \cdot 5H_2O$, tetragonal β - $Me_4NOH \cdot 7.5H_2O$, and orthorhombic $Me_4NOH \cdot 10H_2O$ stabilized by the ionic interaction between Me_4N^+ and OH^- .²¹ In a previous work, we confirmed the structure transformation of Me_4NOH ionic clathrate hydrate into cubic $Fd3m$ (sII) by coinclusion of nonionic guest molecules.^{3,22} In particular, the proton-deficient cage framework of Me_4NOH clathrate hydrate is induced by inclusion of OH^- instead of a water molecule, where Me_4N^+ cations and small gas molecules occupy $5^{12}6^4$ and vacant 5^{12} cavities, respectively.^{3,22} Four sII ionic clathrate hydrates of $Me_4NOD \cdot 16D_2O$ + H_2 , D_2 , N_2 , and O_2 were prepared to measure their lattice parameters using neutron HRPD, and the results are presented in Figure 1.²³ Here, one interesting feature

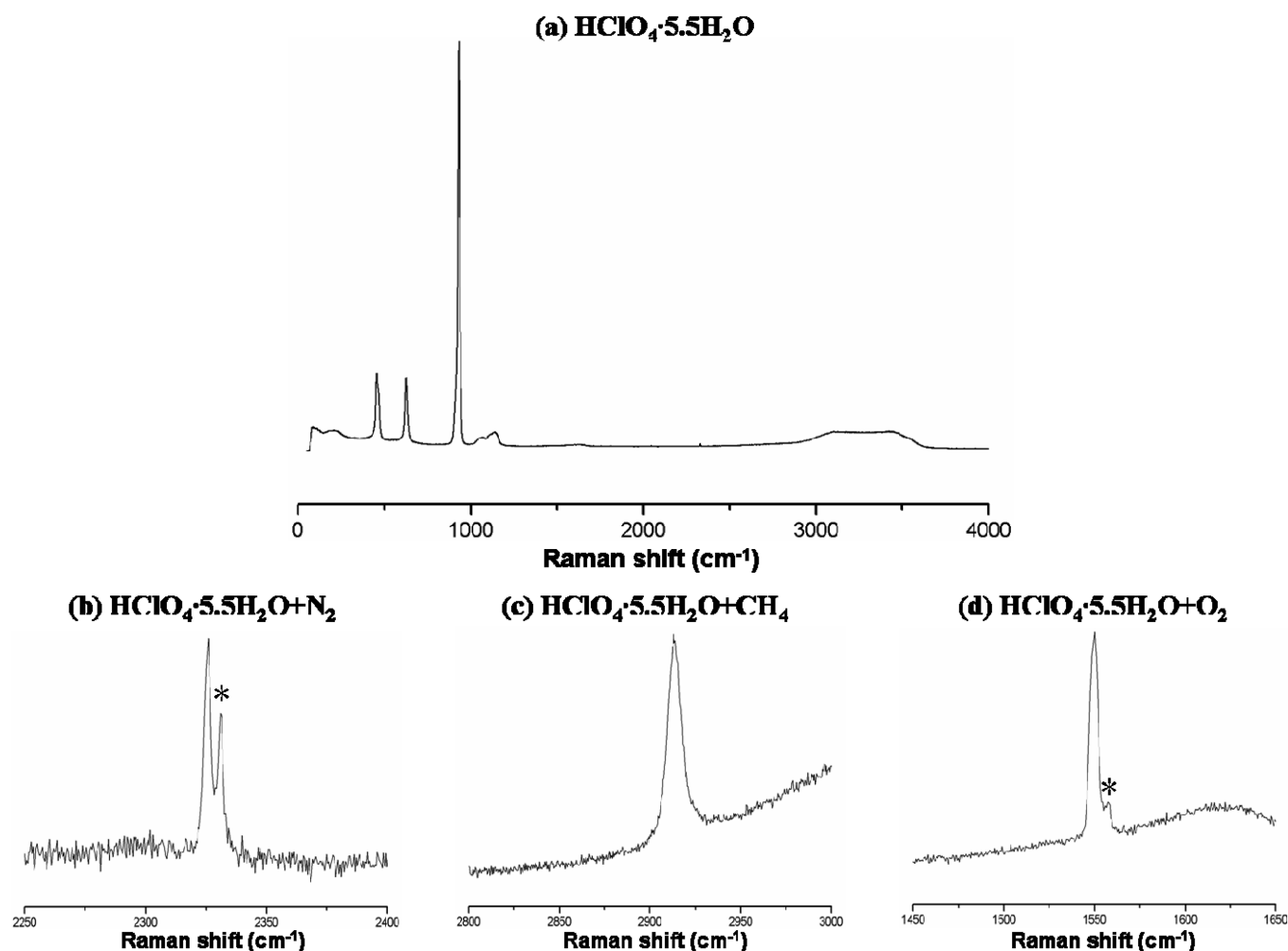


Figure 2. Raman spectra of (a) pure $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ in the entire range of the spectrum, (b) $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O} + \text{N}_2$, (c) $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O} + \text{CH}_4$, and (d) $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O} + \text{O}_2$ in the range of the detection region of the gas included in the clathrate hydrates. The peaks of N_2 and O_2 from air are marked by asterisks (*).

is that the X-ray HRPD patterns of $\text{Me}_4\text{NOH} \cdot 16\text{H}_2\text{O} + \text{N}_2$, O_2 , and H_2 show a lattice parameter increase of less than 0.01 Å with a temperature increase of 70 K (from 80 to 150 K), while the NPD results show a 0.04 Å increase with a temperature increase of 90 to 150 K (Figure 1). This abnormally small thermal expansion of sII ionic hydrates might be due to damage of Me_4N^+ occupying the large cage by the X-ray, which would ultimately lead to prevention of the normal host–guest interaction. Accordingly, the NPD appears to be a more powerful and reliable tool than XRD for diffraction studies of ionic clathrate hydrates.

The sI ionic clathrate hydrates of pure $\text{DClO}_4 \cdot 5.5\text{D}_2\text{O}$ and binary $\text{DClO}_4 \cdot 5.5\text{D}_2\text{O} + \text{N}_2$, O_2 , and CH_4 were also examined in this work. Unlike $\text{Me}_4\text{NOD} \cdot 16\text{D}_2\text{O}$, $\text{DClO}_4 \cdot 5.5\text{D}_2\text{O}$ generates an anionic guest of ClO_4^- and could potentially occupy both $5^{12}6^2$ and 5^{12} cavities composed by the protonated sI host lattice.²⁴ However, the hydration number of 5.5 for $\text{DClO}_4 \cdot 5.5\text{D}_2\text{O}$ is slightly lower than that of the ideal sI clathrate hydrate, (5.75). This reduction of the hydration number from 5.75 to 5.5 could be attributed to some of oxygen atoms in ClO_4^- being incorporated in the protonated water host framework by hydrogen bonding, resulting in a small transformation from the ideal sI water host structure.²⁴ We also recognize that ionic clathrate hydrates having a hydration number of 5.75 would cause the melting

temperature to be much lower than -45°C , the mp of $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$.²⁴ Owing to this depression of the melting point, we chose $\text{DClO}_4 \cdot 5.5\text{D}_2\text{O}$ for the synthesis of binary clathrate hydrates enclosing secondary gaseous guest molecules. The high-pressure condition enables small nonionic molecules to occupy the 5^{12} cavities over ClO_4^- under a favorable host–guest interaction. The Raman spectra of both pure and binary $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ clathrate hydrates given in Figure 2 show N–N, C–H, and O–O stretching modes at around 2330, 2910, and 1550 cm^{-1} , respectively. The corresponding lattice parameters obtained from neutron diffraction patterns are also given in Figure 3.

One interesting feature concerning the lattice parameters of both sI and sII ionic hydrates (Figures 1 and 3) is that the ionic systems do not obey a general trend of lattice size with guest size. Larger guest molecules generally increase the lattice parameter in nonionic clathrate hydrates.²⁵ With the ionic clathrate hydrates, however, the lattice parameter is considered to be strongly affected by guest–host interactions, especially related to molecular properties of the guest such as molecular electron or proton affinities besides the guest size.^{3,22,26}

In order to investigate thermal expansion behavior of the ionic clathrate hydrates, we followed the previous study reported by Hester et al. for nonionic system.¹⁴ The thermal expansivity

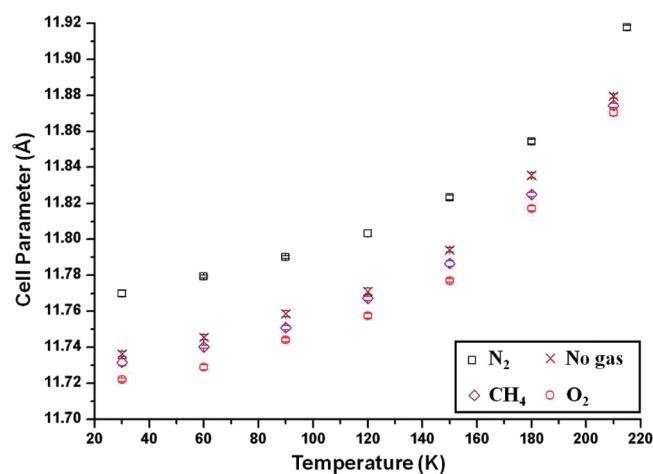


Figure 3. Temperature-dependent lattice parameters for sI $\text{DCIO}_4 \cdot 5.5\text{D}_2\text{O}$ + various gases.

coefficient is defined as the product of the reciprocal of the lattice parameter a and the partial derivative of a with respect to the temperature.²⁷

$$\alpha = \frac{1}{a} \left(\frac{\partial a}{\partial T} \right)_{p,n} \quad (1)$$

The thermal expansivity coefficient α is large when the change in the volume of the material is highly dependent on the temperature. Because α is a function of the temperature T , it can also be expressed as

$$\alpha = a_1 + a_2(T - T_0) + a_3(T - T_0)^2 \quad (2)$$

where T_0 is the reference temperature of 30 K in this study. Separating and integrating, we can obtain

$$\frac{a - a_0}{a_0} = \exp \left\{ a_1(T - T_0) + \frac{a_2}{2}(T - T_0)^2 + \frac{a_3}{3}(T - T_0)^3 \right\} - 1 \quad (3)$$

where a_0 is the lattice parameter at T_0 .

For both sI and sII ionic clathrate hydrates, it is predicted that there exist general and structure-dependent correlations due to the similar trends of the lattice parameter versus temperature and all of the data for given structure should be fit to eq 3. The coefficients a_1 , a_2 , and a_3 of eq 3 can be obtained by using the least-squares regression method for completion of the equations describing the thermal behavior of each system.

The normalized lattice parameters of the sII ionic clathrate hydrates can be expressed as

$$\frac{a_{\text{sII}} - a_{\text{sII},0}}{a_{\text{sII},0}} = \exp \{ (1.83282 \times 10^{-5})(T - T_0) + (6.98231 \times 10^{-8})(T - T_0)^2 + (2.53724 \times 10^{-10})(T - T_0)^3 \} - 1 \quad (4)$$

where T_0 is the reference temperature, 30 K. Figure 4 shows the temperature-dependent normalized lattice parameters of sII $\text{Me}_4\text{NOD} \cdot 16\text{D}_2\text{O}$ + secondary gases systems. Equation 4 fits all of the experimental data for sII hydrates in this study quite well.

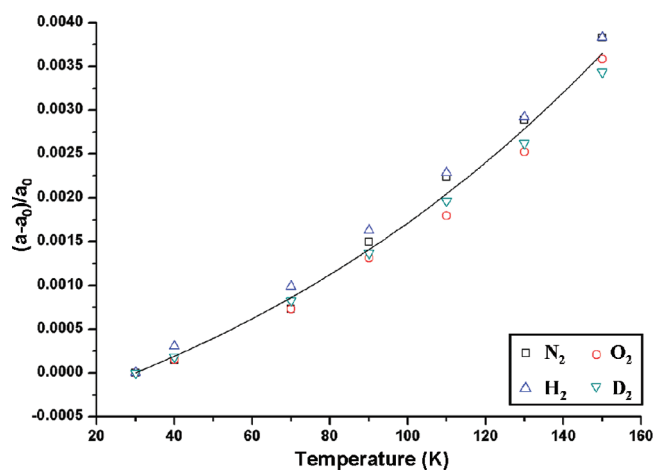


Figure 4. Temperature-dependent normalized lattice parameters for sII $\text{Me}_4\text{NOD} \cdot 16\text{D}_2\text{O}$ + various gases.

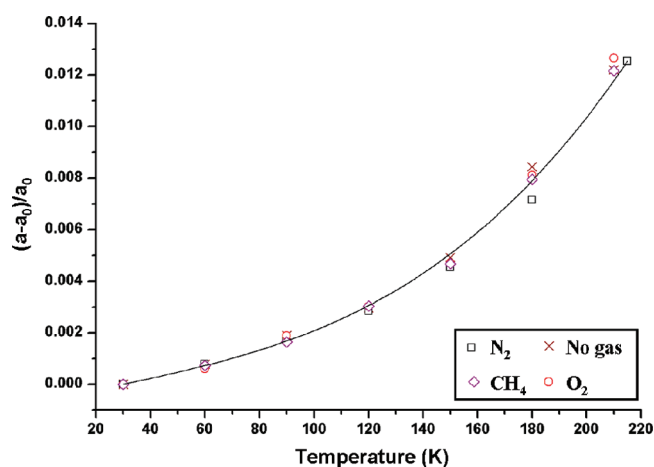


Figure 5. Temperature-dependent normalized lattice parameters for sI $\text{DCIO}_4 \cdot 5.5\text{D}_2\text{O}$ + various gases.

Similarly, the normalized lattice parameters of the sI ionic clathrate hydrates with the reference temperature of 30 K can be expressed as

$$\begin{aligned} \frac{a_{\text{sI}} - a_{\text{sI},0}}{a_{\text{sI},0}} &= \exp \{ (2.26838 \times 10^{-5})(T - T_0) \\ &+ (1.35214 \times 10^{-8})(T - T_0)^2 \\ &+ (1.23294 \times 10^{-9})(T - T_0)^3 \} - 1 \end{aligned} \quad (5)$$

The normalized lattice parameters as a function of temperature for sI acid clathrate hydrates are shown in Figure 5. The linear thermal expansion coefficient from eq 1 can be obtained by substitution of the coefficients of given structures into eq 2. As shown in Figure 6, the linear thermal expansion coefficient of sII binary $\text{Me}_4\text{NOD} \cdot 16\text{D}_2\text{O}$ is proportional to the temperature, as in the case of nonionic clathrate hydrates studied by Hester et al.¹⁴ In contrast, the thermal expansivity of sI ionic hydrates follows a monotonously increasing curve as the temperature rises. Additionally, it is observed that the linear thermal expansion of sI ionic clathrate hydrates is larger than that of sII ionic

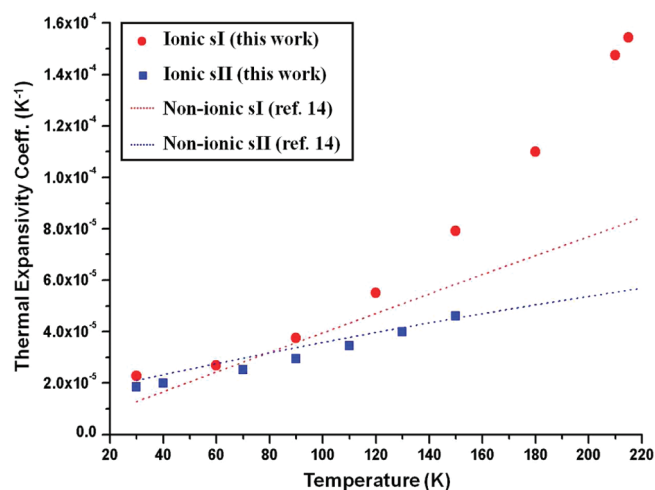


Figure 6. Linear thermal expansion coefficient of sI and sII ionic clathrate hydrates.

systems, similar to the case of nonionic systems, as reported previously.¹⁴ This implies that the volume of sI hydrates is more temperature-sensitive than that of sII, especially at the higher temperature range in this study. The reason for the large difference in the thermal expansivity between sI and sII for nonionic and ionic clathrate hydrates remains unclear.¹⁴

At this stage, the thermal expansion behavior of ionic and nonionic clathrate hydrates should be compared in order to elucidate the peculiar host–guest interaction in ionic clathrate hydrates. In a previous study, it was reported that the lattice expansion is strongly affected by the internal pressure originating from mass-dependent thermal energy of the secondary diatomic guests in the binary THF clathrate hydrates.¹⁹ In this study, on the other hand, the results indicate that the ionic sII system is not profoundly affected by the size and mass of the secondary guest, as shown in Figure 4. In particular, the smaller lattice expansion of the $\text{Me}_4\text{NOD} + \text{O}_2$ hydrate than that anticipated from the size and mass of O_2 molecule implies that the strong interaction between the OH^- incorporated host and electronegative O_2 guest, as confirmed from the magnetic patterns of O_2 hydrates in previous studies,^{19,22} affects the thermal expansion behavior. Similar effects of O_2 guest on smaller lattice parameter and compressibility compared to N_2 guest in pure O_2 and N_2 sII hydrates were observed by Chazallon and Kuhs,²⁸ but the difference of lattice parameter between N_2 and O_2 hydrates was significantly smaller than that of the ionic sII system. Therefore, this kind of interaction should be additionally considered to predict the thermal expansion behavior of ionic clathrate hydrates.

In contrast to the sII clathrate hydrates, the lattice expansion of sI ionic clathrate hydrates is not thought to be influenced by the kind of secondary guest (Figure 5). This might be due to the small number of 5^{12} cages of sI hydrate, compared with the sII structure. Instead, the thermal expansivity of DClO_4 clathrate hydrates is considerably higher than that of nonionic sI hydrates predicted by Hester et al.¹⁴ This discrepancy might arise from the peculiar inclusion of ClO_4^- in the hydrate phase. The partial connection between some of the oxygen atoms in ClO_4^- and the water molecules via hydrogen bonding²⁴ changes the occupation sites of the guests and might cause an extraordinary host–guest interaction, unlike other sI clathrate hydrates.

4. CONCLUSIONS

As ionic clathrate hydrates are considered for their potential in practical application fields, including those that involve solid electrolytes, gas sensor, and energy storage,^{2,29} in-depth investigations of their physicochemical properties are required. In this study, we explored the lattice expansion of the sI and sII ionic clathrate hydrates depending on temperature, one of those important physicochemical properties. To this end, instead of XRD, we utilized NPD in order to avoid damage to the guest ion, which causes deviation of the real thermal behavior of the ionic hydrate phases. The lattice expansion of binary sII Me_4NOD hydrates is dominantly affected by the charge interaction between the OH^- included host and the secondary guest. This finding contrasts with the case of nonionic binary THF clathrate hydrates, where the mass and the size of the guest molecules affect the thermal expansion behavior. The larger thermal expansivity coefficients of sI DClO_4 hydrates relative to those of ordinary sI systems might be due to partial incorporation of ClO_4^- into the host lattice through hydrogen bonding. The present study on the thermal expansion of ionic clathrate hydrates provides important information for better understanding of the nature of the host–guest interaction in ionic clathrate systems. Furthermore, the experimental results provide important physicochemical data needed to open up practical application fields such as solid electrolytes and other energy devices.

■ ASSOCIATED CONTENT

S Supporting Information. The NPD patterns and the table of lattice parameters details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +82-42-350-3910. Tel: +82-42-350-3917. E-mail: hlee@kaist.ac.kr

Present Addresses

[§]Current address: National Research Council of Canada, 100 Sussex Drive, Ottawa K1A 0R6, Canada.

■ ACKNOWLEDGMENT

This work was supported by the National Research Foundation of Korea (NRF) grants [Leading Research Support Program, 2010-0029176; WCU program, 31-2008-000-10055-0] funded by the Ministry of Education and Science & Technology (MEST). This research was also funded from the Ministry of Knowledge Economy through Recovery/Production of Natural Gas Hydrate using Swapping Technique [KIGAM—Gas Hydrate R&D Organization]. High-resolution X-ray diffraction experiments at PLS (8C2) were supported in part by MEST and POSTECH. We thank the Korea Atomic Energy Research Institute for granting beam time and support.

■ REFERENCES

- (1) Jeffery, G. A. *Inclusion Compounds*; Academic Press: London, 1984; Vol. 1.
- (2) Shin, K.; Cha, J.-H.; Seo, Y.; Lee, H. *Chem. Asian J.* **2010**, *5*, 22–34.
- (3) Shin, K.; Cha, M.; Choi, S.; Dho, J.; Lee, H. *J. Am. Chem. Soc.* **2008**, *130*, 17234–17235.

- (4) Mootz, D.; Stabel, D. *J. Am. Chem. Soc.* **1994**, *116*, 4141–4142.
- (5) Cha, J.-H.; Lee, W.; Lee, H. *J. Mater. Chem.* **2009**, *19*, 6542–6547.
- (6) Shin, K.; Choi, S.; Cha, J.-H.; Lee, H. *J. Am. Chem. Soc.* **2008**, *130*, 7180–7181.
- (7) Cha, J.-H.; Shin, K.; Choi, S.; Lee, H. *J. Phys. Chem. C* **2008**, *112*, 10573–10578.
- (8) Cha, J.-H.; Shin, K.; Choi, S.; Lee, S.; Lee, H. *J. Phys. Chem. C* **2008**, *112*, 13332–13335.
- (9) Tse, J. S.; McKinnon, W. R.; Marchi, M. *J. Phys. Chem.* **1987**, *91*, 4188–4193.
- (10) Takeya, S.; Uchida, T.; Kamata, Y.; Nagao, J.; Kida, M.; Minami, H.; Sakagami, H.; Hachikubo, A.; Takahashi, N.; Shoji, H.; Khlystov, O.; Grachev, M.; Soloviev, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 6928–6931.
- (11) Takeya, S.; Hori, A.; Uchida, T.; Ohmura, R. *J. Phys. Chem. B* **2006**, *110*, 12943–12947.
- (12) Takeya, S.; Nagaya, H.; Matsuyama, T.; Hondoh, T.; Lipenkov, V. Y. *J. Phys. Chem. B* **2000**, *104*, 668–670.
- (13) Takeya, S.; Kida, M.; Minami, H.; Sakagami, H.; Hachikubo, A.; Takahashi, N.; Shoji, H.; Soloviev, V.; Wallmann, K.; Biebow, N.; Obzhairov, A.; Saloatin, A.; Poort, J. *Chem. Eng. Sci.* **2006**, *61*, 2670–2674.
- (14) Hester, K. C.; Huo, Z.; Ballard, A. L.; Koh, C. A.; Miller, K. T.; Sloan, E. D. *J. Phys. Chem. B* **2007**, *111*, 8830–8835.
- (15) Bednarek, J.; Erickson, R.; Lund, A.; Schlick, S. *J. Am. Chem. Soc.* **1991**, *113*, 8990–8991.
- (16) Bednarek, J.; Lund, A.; Schlick, S. *J. Phys. Chem.* **1996**, *100*, 3910–3916.
- (17) Ikeda, T.; Mea, S.; Yamamuro, O.; Matsuo, T.; Ikeda, S.; Ibberson, R. M. *J. Phys. Chem. A* **2000**, *104*, 10623–10630.
- (18) Jones, C. Y.; Marshall, S. L.; Chakoumakos, B. C.; Rawn, C. J.; Ishii, Y. *J. Phys. Chem. B* **2003**, *107*, 6026–6031.
- (19) Park, Y.; Choi, Y.-N.; Yeon, S.-H.; Lee, H. *J. Phys. Chem. B* **2008**, *112*, 6897–6899.
- (20) The PXRD patterns were indexed using the CheckCell program. LMGPSuite Suite of Programs for the interpretation of X-ray experiments, by Jean laugier and Bernard Bochu, ENSP/Laboratoire des Matériaux et du Génie Physique, BP 46. 38042 Saint Martin d'Herès, France (<http://www.inpg.fr/LMGP> and <http://www.ccp14.ac.uk/tutorial/lmgp/>).
- (21) Mootz, D.; Seidel, R. *J. Inclusion Phenom.* **1990**, *8*, 139–157.
- (22) Cha, M.; Shin, K.; Kwon, M.; Koh, D.-Y.; Sung, B.; Lee, H. *J. Am. Chem. Soc.* **2010**, *132*, 3694–3696.
- (23) For minimizing sII hydrate phase to retransform into orthorhombic decahydrate phase, the experimental temperature for Me₄NOD hydrates did not exceed 150 K.
- (24) Mootz, D.; Oellers, E.-J.; Wiebcke, M. *J. Am. Chem. Soc.* **1987**, *109*, 1200–1202.
- (25) Udachin, K. A.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Supramol. Chem.* **2002**, *2*, 405–408.
- (26) Shin, K.; Cha, M.; Kim, H.; Jung, Y.; Kang, Y. S.; Lee, H. *Chem. Commun.* **2011**, *47*, 674–676.
- (27) Touloukian, Y. S. *Thermal Expansion: Nonmetallic Solids*; Plenum Publishing Corp.: New York, 1977; Vol. 13.
- (28) Chazallon, B.; Kuhs, W. F. *J. Chem. Phys.* **2002**, *117*, 308–320.
- (29) Cha, J.-H.; Lee, W.; Lee, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 8687–8690.