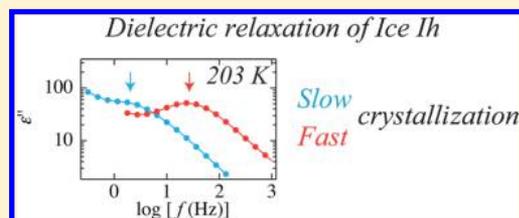


Dielectric Relaxation Time of Ice-Ih with Different Preparation

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ABSTRACT: Dielectric relaxation process of ice-Ih has been investigated by many researchers. Pioneering studies focused on the temperature dependence of the dielectric relaxation time, τ_{ice} , were reported by Auty in 1952 [Auty, R. P.; Cole, R. H. *J. Chem. Phys.* **1952**, *120*, 1309] and Johari in 1981 [Johari, G. P.; Whalley, E. *J. Chem. Phys.* **1981**, *75*, 1333]. However, the temperature dependences of τ_{ice} found in these studies are not in agreement. While Auty et al. reported a single Arrhenius temperature dependence of τ_{ice} for the entire 207–273 K temperature range, Johari et al. reported changes in the temperature dependence of τ_{ice} at 230 and 140 K. In this study, the temperature dependence of τ_{ice} is investigated by broadband dielectric spectroscopy for ice prepared by three different procedures. For all investigated ices, a dielectric relaxation process is observed, and τ_{ice} decreases with increasing temperature. Temperature dependence of τ_{ice} with rapid crystallization shows the same properties at temperatures down to 140 K as that reported by Johari et al. On the other hand, ice obtained by slow crystallization exhibits the same temperature dependence of τ_{ice} as those reported by Auty et al. We suggest that the difference between the temperature dependences of τ_{ice} found by Auty et al. and Johari et al. can be controlled by preparation conditions. That is, the growth rate of the ice crystal can affect τ_{ice} because a slow growth speed of the ice crystal induces a smaller impurity content of ice, giving rise to an Arrhenius temperature dependence of τ_{ice} .



INTRODUCTION

The dynamics of solid states of water have been intensely studied due to their importance in several scientific fields. For example, the dynamics of water in the glassy state has been recently examined by many researchers using various techniques.¹ For the crystalline state of water, polymorphism and transition between different polymorphic states of ice have been widely investigated. The dielectric relaxation process of hexagonal ice, i.e., ice-Ih, has also been investigated experimentally^{2–8} and theoretically.^{9–11} Following the pioneering study of Auty and Cole (referred to as sample Auty-1952)² that focused on the dielectric relaxation process of ice-Ih in the 207–273 K temperature range, the dielectric properties of ice-Ih were investigated at various conditions, as summarized in Table 1.^{3–7} Previous studies have demonstrated that the temperature dependence of the dielectric relaxation time of ice-Ih, τ_{ice} , does not show any anisotropy⁵ and is independent of the probe for measurement at higher temperatures^{2–4} with good agreement between the τ_{ice} values obtained in different studies. However, at lower temperatures, there is a disagreement between the temperature dependences of τ_{ice} obtained in previous studies. A detailed study on the temperature dependence of τ_{ice} in a wide temperature (272–133 K) and frequency range was reported by Johari and Whalley (Johari-1981).⁸ With the exception of Auty-1952,² for all the studies listed in Table 1,^{3–7} the temperature dependences of τ_{ice} exhibit the features found in Johari-1981.⁸ Additionally, the literature data for single crystal ice^{3,5,6} show the same temperature dependence of τ_{ice} as that of polycrystal ice-Ih reported by Johari in 1981.⁸ Thus, the crystal size and/or metastable crystal surface do not seem to contribute to the temperature dependence of τ_{ice} . It was suggested that the different τ_{ice}

behavior found by Auty-1952² is caused by either a narrow temperature range of the measurement⁴ or measurement error.³

The recent development of precise and automatic temperature control and dielectric measurements has enabled investigations of partially crystallized aqueous solutions.^{12–19} Several studies reported the investigation of the relaxation process of ice in the partially crystallized aqueous mixtures containing proteins^{13–16} and glycerol^{17,18} as solutes. As per these studies, τ_{ice} values in partially crystallized aqueous mixtures are often between τ_{ice} (Johari-1981) and τ_{ice} (Auty-1952).^{13,14} The τ_{ice} values of such mixtures appear to be largely governed by the growth properties of the ice in the mixture. However, in all of these studies, τ_{ice} (Auty-1952)² and/or τ_{ice} (Johari-1981)⁸ are used merely to determine the molecular origin of the unknown relaxation process that appears at a similar frequency range in aqueous systems at subzero temperatures.^{13–19} An explanation of the mechanism underlying the difference between the τ_{ice} (Auty-1952)² and τ_{ice} (Johari-1981)⁸ would enable the use of τ_{ice} observed in aqueous systems to be utilized effectively not only for understanding ice dynamics but also as a probe of the dynamic viscoelastic behavior of water and solute molecules through ice growth.

Thus, it is essential to understand the details of the relaxation process and preparation conditions of ice observed in Auty-1952.² However, as mentioned above, for more than half a century, τ_{ice} values (Auty-1952)² have not been reproduced. This study was undertaken in order to reproduce the τ_{ice} (Auty-

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Table 1. Crossover Temperature, T_c , of Ice-Ih

| sample ID | polycrystal or single crystal | T_c (K) | preparation condition | temp range (K) | ref |
|--------------------------|-------------------------------------|-----------|--|-------------------|-----|
| Literature | | | | | |
| Auty-1952 | poly | none | formed in cell | 207–273 | 2 |
| Wörz-1969 | single | 233 | formed in cell | 93–273 | 3 |
| Gough-1970 | poly | 243 | freezing liquid water | 174–273 | 4 |
| Kawada-1978 | single | 223 | bridgeman method | 123–268 | 5 |
| at above 253 K | | | | | |
| Johari-1978 | single | 210 | zone-refining at 263 K | 125–274 | 6 |
| Johari-1981 ^a | poly | 242 | pour into cell at 263 K | 113–272 | 8 |
| Murthy-2002 | poly | 220 | formed in cell with cooling 1 K/min | 203–265 | 7 |
| This Work | | | | | |
| ice-Ih _a | | 250 | formed in cell with cooling 5 K/min | 123–273 | |
| ice-Ih _b | | 230 | formed in beaker at 265 K | 123–273 | |
| ice-Ih _c | | none | formed in beaker at 265 K with stirring | 123–273 | |

^aData of D₂O ice.

1952)² data, focusing on (I) the preparation condition of ice-Ih and (II) the temperature dependence of τ_{ice} (Auty-1952)² at several temperatures and frequencies to reproduce the temperature dependences of τ_{ice} (Auty-1952)² and τ_{ice} (Johari-1981).⁸

EXPERIMENTAL SECTION

Pure ices, i.e., ice-Ih_a, ice-Ih_b, and ice-Ih_c, were prepared from pure water (H₂O) by three different procedures. For the original material of the pure ice, we used pure water obtained by the following procedure. Tap water was distilled by a distiller (EYELA, steel ace), and this distilled water was purified by pure water products (Milli-Q Lab., Simplicity UV) and was then deionized and filtered to obtain an electrical resistivity of approximately 18.2 MΩ cm. Pure water is degassed immediately before the ice preparation by stirring with a magnetic stirrer in vacuum under 1 kPa for 1 h until no more bubbles are generated by decompression. Ice-Ih_a was formed within coaxial type electrode cell by cooling from 298 K down to 133 K at the rate of 5 K/min without any special treatment. Ice-Ih_b was prepared from a half liter of pure water in a beaker with the temperature controlled by an environmental testing machine (KATO, SE-22ORN-A) at 265 K for 5 h. Ice-Ih_c was prepared using the same conditions but with stirring by magnetic stirrer to avoid containing bubbles and rapid ice crystallization. The obtained block of ice-Ih_c is approximately 3 cm thick; thus, the growth rate of the ice crystal was approximately 6 mm/h. The blocks of ice-Ih_b and ice-Ih_c are cut into approximately 5-mm-thick samples to place the ice between the parallel plate electrode. All of the equipment in direct contact with pure water or ice was cleaned by ultrasonic cleaner with the same pure water used as the original material

of the ices. Dielectric measurements were performed in the 10 mHz to 10 MHz frequency range at temperatures between 123 and 263 K at every 10 K on heating for ice-Ih_a and on both cooling and heating for ice-Ih_b and ice-Ih_c. We used an Alpha-A analyzer (Novocontrol) with a coaxial capacitor with 24 and 19 mm outer and inner diameters, respectively, for ice-Ih_a and a flat parallel plate capacitor with 20 mm diameter for ice-Ih_b and ice-Ih_c. For both ice phases, the temperature was controlled with a Quatro cryosystem (Novocontrol) with the temperature error within 0.01 K.

RESULTS AND DISCUSSION

Isothermal dielectric spectra for ice-Ih_a and ice-Ih_b obtained in 20 K temperature steps are shown in Figure 1a,b, respectively.

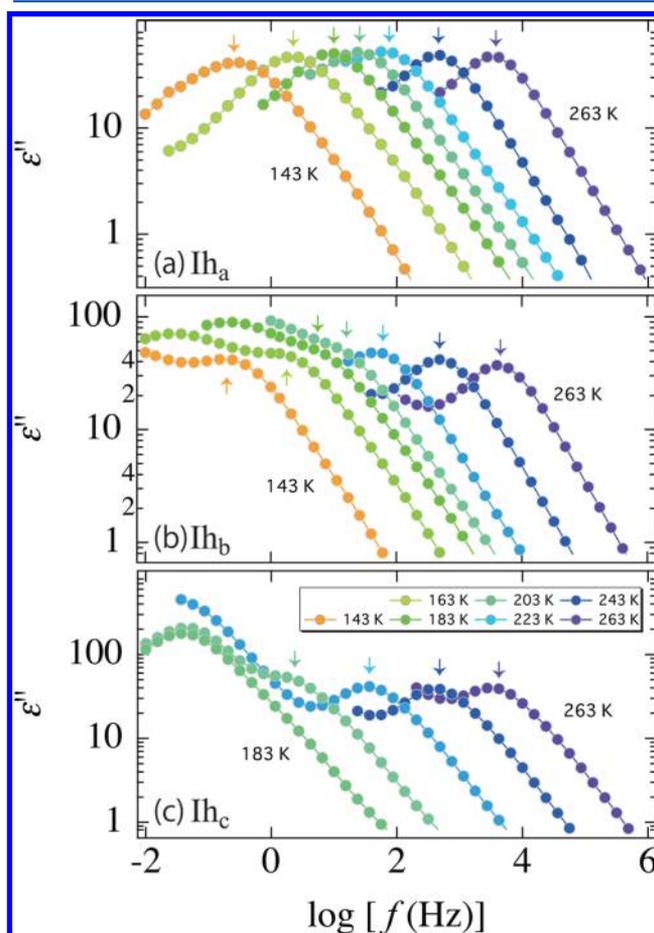


Figure 1. Frequency dependences of the imaginary parts of dielectric permittivity for ice-Ih_a (a), ice-Ih_b (b), and ice-Ih_c (c) at various temperatures and frequencies between 10 mHz and 1 MHz. The dielectric data are shown at temperatures from 143 to 263 K (ice-Ih_a and ice-Ih_b) and 183 to 263 K (ice-Ih_c) in steps of 20 K. The arrows indicate the peak of the relaxation process of ices.

All spectra are dominated by the well-known Cole–Cole type process, and the presence of complex temperature-dependent shifts indicates the change in the apparent activation energy. In addition, especially for ice-Ih_b, at frequencies lower than the loss peak, a contribution of interfacial polarization (IP) is clearly observed. Isothermal data of the dielectric spectra of ice-Ih_c are also shown in Figure 1c. All spectra are dominated by a Cole–Cole type peak, and the constant shift of loss peak frequency appears to obey Arrhenius law with a temperature-

independent activation energy. Below 183 K, the peak is hidden by the IP contribution.

To characterize the relaxation process, a curve fitting procedure has been performed for each isothermal spectrum. The frequency dependence of complex permittivity, ϵ^* , can be described by a simple sum of dc conductivity and two Cole–Cole equations given by

$$\epsilon^* = \epsilon_\infty + \sum_k^{\text{ice,IP}} \frac{\Delta\epsilon_k}{1 + (i\omega\tau_k)^\beta} + \frac{\sigma}{i\omega\epsilon_0} \quad (1)$$

where ω is the angular frequency, i is the imaginary unit given by $i^2 = -1$, ϵ_0 (F/m) is the dielectric constant in vacuum, ϵ_∞ is the limiting high frequency permittivity, $\Delta\epsilon$ is the relaxation strength, τ (s) is the relaxation time, β is the symmetric broadening parameter ($0 < \beta \leq 1$), σ (S/m) is the dc conductivity, and the superscripts ice and IP refer to the relaxation process of the ice and the contribution of interfacial polarization, respectively. Temperature dependences of τ_{ice} for ice-Ih_a, ice-Ih_b, and ice-Ih_c are shown in Figure 2 together with

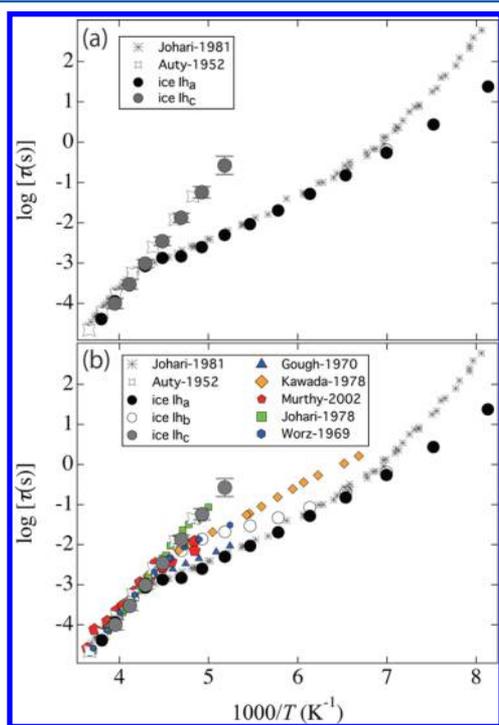


Figure 2. Temperature dependences of relaxation times of ice-Ih_a, ice-Ih_b, and ice-Ih_c. For comparison, relaxation times obtained by Johari in 1981⁸ (black star, D₂O) and in 1978⁶ (green square), Auty² (open gray star), Murthy⁷ (red pentagon), Gough⁴ (purple triangle), Kawada⁵ (orange diamond), and Wörz³ (blue hexagon) are plotted together. For the ease of viewing, the top panel (a) shows the relaxation times of ice-Ih_a and ice-Ih_c together with that of ice obtained by Johari⁸ in 1981 (black star) and Auty² (open gray star) in 1952. Error bars for ice-Ih_c are given by standard deviation with four times measurements.

the data from previous studies listed in Table 1. Literature values were obtained for H₂O ice except that of Johari-1981⁸, which was obtained for D₂O ice. The temperature dependences of τ_{ice} for ice-Ih_b and ice-Ih_c have no difference between heating and cooling measurement. To avoid confusion, the top panel (panel a) of Figure 2 shows our data and τ_{ice} values from Johari-1981⁸ and Auty-1952,² while the bottom panel (panel b) shows

our data and τ_{ice} values obtained in all the studies listed in Table 1.

The temperature dependence of τ_{ice} (Johari-1981)⁸ was divided into three temperature regions: the high temperature region at temperatures higher than 230 K, the intermediate region at temperatures between 140 and 230 K, and the low temperature region at temperatures below 140 K.^{8,9,11} The activation energy, E_a , values of temperature dependence of τ_{ice} were 53, 19, and 46 kJ/mol for the high, intermediate, and low temperature regions, respectively.⁸ The two changes in E_a at 230 and 140 K indicate the changes in the relaxation mechanism of ice-Ih. In this study, we define temperature of the τ_{ice} change at the higher temperature as T_c . In general, E_a of the high temperature region is considered to be dominated by two well-known types of orientational defects, i.e., Bjerrum's D- and L-defects.^{3–11,20,21} The dielectric relaxation in the intermediate temperature region is considered to be dominated by ionic-induced^{11,22} or impurity-induced^{3–10,20,21} defects. Recently, Popov et al. succeeded in describing not only the change of the temperature dependence of τ_{ice} but the temperature dependence of broadening of the relaxation time of ice as well.¹¹ The examination of the literature data shows that τ_{ice} and T_c of Gough-1970⁴ agree with those of Johari-1981,⁸ while τ_{ice} values of Murthy-2002,⁷ Kawada-1978,⁵ and Wörz-1969³ are between the τ_{ice} of Auty-1952² and Johari-1981⁸ and exhibit a crossover in the temperature dependence of τ_{ice} at approximately 230 K.^{3,5,7} τ_{ice} of Johari-1978⁶ agrees with τ_{ice} of Auty-1952² for temperatures down to 210 K. However, below 210 K, τ_{ice} (Johari-1978)⁶ deviates from τ_{ice} (Auty-1952).² It is clearly shown that the temperature dependence of τ_{ice} (Auty-1952)² remains the same. Before the present study, τ_{ice} (Johari-1978)⁶ exhibited the lowest T_c value in the literature. According to the several investigations of τ_{ice} , it has been reported that the concentration of impurities influences T_c , with lower amounts of impurities leading to lower T_c values.^{3–11,20,21}

All the τ_{ice} values shown in Figure 2 are almost on the one common line at temperatures above 230 K. The temperature dependence of τ_{ice} (Ih_a) agrees with the data of Johari-1981⁸ at temperatures between 263 and 153 K. At temperatures lower than 153 K, τ_{ice} (Ih_a) deviates from τ_{ice} (Johari-1981).⁸ The deviation of τ_{ice} (Ih_a) from τ_{ice} (Johari-1981)⁸ was also observed in previous studies on aqueous solutions.^{13,14} The most recent discussion on the relaxation process of pure ice by Popov et al.¹¹ suggests that, in the low temperature region below 153 K, τ_{ice} depends on the experimental details of the sample preparation and the temperature protocol of the dielectric study. As shown in Figure 2, τ_{ice} (Ih_b) is found between the τ_{ice} of Auty-1952² and that of Johari-1981⁸ and shows a complicated temperature dependence. For temperatures above 203 K, τ_{ice} (Ih_b) values agree with those of Kawada-1978⁵ and Wörz-1969.³ Between 203 and 173 K, τ_{ice} (Ih_b) values deviate from those of Kawada-1978⁵ and Wörz-1969.³ Below 173 K, τ_{ice} (Ih_b) data are in agreement with τ_{ice} (Ih_a). In other words, for ice-Ih, the lowest E_a is observed in the intermediate range of temperature between 203 and 173 K. Conversely, the temperature dependence of τ_{ice} (Ih_c) agrees with that of τ_{ice} (Auty-1952).² Moreover, the Arrhenius behavior of τ_{ice} (Ih_c) extends to 193 K, which is lower than the lowest temperature of τ_{ice} (Auty-1952).² Such an extension of the Arrhenius temperature dependence of τ_{ice} to temperatures lower than τ_{ice} (Auty-1952)² has not been reported in any previous study. These results indicate that the nature of the

relaxation process in ice must be considered for results with and without crossover T_c .

According to these results, the temperature dependence of τ_{ice} depends on the preparation procedure. Among the three ices, i.e., ice-Ih_a, ice-Ih_b, and ice-Ih_c, ice-Ih_c appears to be the most pure on the basis of τ_{ice} and the preparation methods. Ice-Ih_c was created without the rapid crystallization from the supercooled state. This procedure is expected to produce highly purified ice crystals because the growth of the ice crystal lattice during slow crystallization excludes impurities. The change of the temperature dependence of the relaxation time has been discussed in terms of an "impurity-produced orientational defect". Unfortunately, we do not show any direct evidence for the models. However, our result suggests that a remarkable difference between the relaxation time of ices reported by Auty (1952) and Johari (1981) results from the different preparation method of ice. Our result implies that the growth speed of ice in an aqueous system is expected to influence the relaxation time of ice, and we hope such information will be utilized for understanding microscopic viscoelastic property of water in materials.

CONCLUSION

We now summarize our findings on the dielectric relaxation process of two types of ice-Ih. (1) τ_{ice} can be controlled by the preparation method. (2) τ_{ice} (Auty-1952) can be reproduced by our preparation method. (3) Temperature dependence of τ_{ice} (Ih_c), which is the same as that of Auty-1952 above 207 K, extends to lower temperatures down to 193 K. (4) The relaxation mechanism of the dielectric relaxation of ice must be considered for two types of ices, i.e., ice-Ih_a and ice-Ih_c. (5) Ice-Ih_c is expected to contain fewer impurity-produced orientational defects than any other ice reported in the literature. (6) The relaxation process of ice in partially crystallized aqueous mixtures could be evaluated by comparing with two types of ices, i.e., ice-Ih_a and ice-Ih_c.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Debenedetti, P. G. Supercooled and Glassy Water. *J. Phys.: Condens. Matter* **2003**, *15*, R1669–R1726.
- (2) Auty, R. P.; Cole, R. H. Dielectric Properties of Ice and Solid D₂O. *J. Chem. Phys.* **1952**, *20*, 1309–1314.
- (3) Wörz, O.; Cole, R. H. Dielectric Properties of Ice I. *J. Chem. Phys.* **1969**, *51*, 1546–1551.
- (4) Gough, S. R.; Davidson, D. W. Dielectric Behavior of Cubic and Hexagonal Ices at Low Temperature. *J. Chem. Phys.* **1970**, *52*, 5442–5449.
- (5) Kawada, S. Dielectric Anisotropy in Ice Ih. *J. Phys. Soc. Jpn.* **1978**, *44*, 1881–1886.
- (6) Johari, G. P.; Jones, S. J. The Orientation Polarization in Hexagonal Ice Parallel and Perpendicular to the c-axis. *J. Glaciol.* **1978**, *21*, 259–276.
- (7) Murthy, S. S. N. Slow Relaxation in Ice and Ice Clathrates and its Connection to the Low-Temperature Phase Transition Induced by Dopants. *Phase Transitions* **2002**, *75*, 487–506.
- (8) Johari, G. P.; Whalley, E. The Dielectric Properties of Ice Ih in the Range 272–133 K. *J. Chem. Phys.* **1981**, *75*, 1333–1340.
- (9) Johari, G. P.; Whalley, E. The Dielectric Relaxation Time of Ice V, its Partial Anti-Ferroelectric Ordering and the Role of Bjerrum Defects. *J. Chem. Phys.* **2001**, *115*, 3274–3280.
- (10) Bjerrum, N. Structure and Properties of Ice. *Science* **1952**, *115*, 385–390.
- (11) Popov, I.; Puzenko, A.; Khamzin, A.; Feldman, Y. The Dynamics Crossover in Dielectric Relaxation Behavior of Ice Ih. *Phys. Chem. Chem. Phys.* **2015**, *17*, 1489–1497.
- (12) Shinyashiki, N.; Shimomura, M.; Ushiyama, T.; Miyagawa, T.; Yagihara, S. Dynamics of Water in Partially Crystallized Polymer/Water Mixtures Studied by Dielectric Spectroscopy. *J. Phys. Chem. B* **2007**, *111*, 10079–10087.
- (13) Sasaki, K.; Kita, R.; Shinyashiki, N.; Yagihara, S. Glass Transition of Partially Crystallized Gelatin-Water Mixtures Studied by Broadband Dielectric Spectroscopy. *J. Chem. Phys.* **2014**, *140*, 124506–7.
- (14) Shinyashiki, N.; Yamamoto, W.; Yokoyama, A.; Yoshinari, T.; Yagihara, S.; Kita, R.; Ngai, K. L.; Capaccioli, S. Glass Transitions in Aqueous Solutions of Protein (Bovine Serum Albumin). *J. Phys. Chem. B* **2009**, *113*, 14448–14456.
- (15) Nakanishi, M.; Sokolov, A. P. Protein Dynamics in a Broad Frequency Range: Dielectric Spectroscopy Studies. *J. Non-Cryst. Solids* **2015**, *407*, 478–485.
- (16) Panagopoulou, A.; Kyritsis, A.; Shinyashiki, N.; Pissis, P. Protein and Water Dynamics in Bovine Serum Albumin-Water Mixtures over Wide Ranges of Composition. *J. Phys. Chem. B* **2012**, *116*, 4593–4602.
- (17) Hayashi, Y.; Oshige, I.; Katsumoto, Y.; Omori, S.; Yasuda, A. Protein-Solvent Interaction in Urea-Water Systems Studied by Dielectric Spectroscopy. *J. Non-Cryst. Solids* **2007**, *353*, 4492–4496.
- (18) Hayashi, Y.; Puzenko, A.; Feldman, Y. Slow and Fast Dynamics in Glycerol-Water Mixtures. *J. Non-Cryst. Solids* **2006**, *352*, 4696–4703.
- (19) Cervený, S.; Ouchiar, S.; Schwartz, G. A.; Alegria, A.; Colmenero, J. Water Dynamics in Poly(vinyl pyrrolidone)-Water Solution Before and After Isothermal Crystallization. *J. Non-Cryst. Solids* **2010**, *356*, 3037–3041.
- (20) Kawada, S. A. Phenomenological Interpretation of Anomalous Quickening of Dielectric Relaxation by Doping of KOH in Ice Ih. *J. Phys. Soc. Jpn.* **1988**, *57*, 3694–3697.
- (21) Bruni, F.; Consolini, G.; Careri, G. Temperature Dependence of Dielectric Relaxation in H₂O and D₂O Ice. A Dissipative Quantum Tunneling Approach. *J. Chem. Phys.* **1993**, *99*, 538–547.
- (22) Bilgram, J. H.; Granicher, H. Defect Equilibria and Conduction Mechanisms in Ice. *Eur. Phys. J. B* **1974**, *18*, 275–291.