Alternating current breakdown voltage of ice electret

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Abstract. Ice has low environmental impact. Our research objectives are to study the availability of ice as a dielectric insulating material at cryogenic temperatures. We focus on ferroelectric ice (iceXI) at cryogenic temperatures. The properties of iceXI, including its formation, are not clear. We attempted to obtain the polarized ice that was similar to iceXI under the applied voltage and cooling to 77 K. The polarized ice have a wide range of engineering applications as electronic materials at cryogenic temperatures. This polarized ice is called ice electret. The structural difference between ice electret and normal ice is only the positions of protons. The effects of the proton arrangement on the breakdown voltage of ice electret were shown because electrical properties are influenced by the structure of ice. We observed an alternating current (ac) breakdown voltage of ice electret and normal ice at 77 K. The mean and minimum ac breakdown voltage values of ice electret were higher than those of normal ice. We considered that the electrically weak part of the normal ice was improved by applied a direct electric field.

1. Introduction
Ice has low environmental impact. The authors have been studying the behavior of ice as dielectrics or electrical insulating materials at cryogenic temperatures [1–5]. We focus on the dielectric properties of ferroelectric ice (iceXI) and normal ice (iceIh) at cryogenic temperatures. The properties of iceXI, including its formation procedure, are unclear and are under investigation [6–8]. The formation procedure for iceXI requires either specific techniques with added impurities, or a very long time (at least 624 hours [8]). We attempted to obtain polarized ice, which is similar to iceXI, with neither added impurities nor very long time. The polarized ice have a wide range of engineering applications as electronic materials at cryogenic temperatures. We obtained the polarized ice by controlling the movement of hydrogen ions (protons) in ice [4–5].

Proton (H⁺) movement depends on the temperature. Protons in normal ice can hop along lattice defects at relatively high temperatures, e.g. 253 K. The dependency of the proton movement on the temperature can be explained in terms of the dielectric constant. The relative permittivity of ice at 253 K is 45, and it is 3 at 77 K [9–10]. These results indicate that the responsible speed of a proton in an external electric field is low at 77 K and is high at 253 K. The proton movements can be controlled under an external electric field because the protons are positively charged. However, at cryogenic temperatures, such as 77 K, it is difficult to move protons in ice. Thus, the proton movements cannot be controlled by the electric field. The dipole moment of an H₂O molecule does not govern the
dielectric properties of ice, but the proton movement can govern it. These characteristics are responsible for the dielectric polarization of ice.

We successfully obtained the polarized ice as follows. A direct electric field was applied to normal ice at around 253 K, and the ice was cooled to 77 K. During this procedure, the protons moved toward the cathode because of the electric field application. Since the position of the protons was fixed at 77 K, the ice polarized without the electric field. This polarized ice is called ice electret [11]. Electret is a dielectric material possessing permanent and spontaneous polarization. In our previous paper, we obtained ice electret under the direct electric field application with cooling, and confirmed that ice electret was polarized based on the observation of the depolarization current of ice electret that was warmed from 77 K [4–5]. The protons in ice electret were fixed at the cathode side under the direct electric field application and cooling. On the other hand, the protons in normal ice are randomly fixed at 77 K.

Ice electrets and normal ice differ in their proton arrangements. We assumed that they also differed in their electrical properties. In this paper, we studied the effect of proton arrangement on ac breakdown voltage. Our research objective is to explore the availability of ice electret as a dielectric insulating materials at cryogenic temperatures.

2. Experimental procedure

2.1. Sample configuration

Figure 1 shows the parallel-plane electrode system used in the experiments. The electrodes were made of stainless steel. The diameters of the anode and the cathode electrode were 25 mm and 16 mm, respectively. The guard electrode configuration was ring-shaped. The internal and external diameters of the guard electrode were 18 mm and 26 mm, respectively. The guard electrode plays the role of a restraint leakage current. Only the bulk current between the anode and cathode can be observed because the surface current is released to ground from the guard electrode. The thicknesses of these electrodes were 10 mm. Each electrode was fixed on acryl plates.

Figure 2 shows a flowchart of the sample preparation. In procedure III and N-1 to N-2, all electrodes were grounded because deviations in the charge were prevented. In procedure E-3, the extra charge excluding the polarized charge (e.g. free charge) was released owing to the grounding of electrodes. The cooling rate from 253 K to 77 K was approximately 1 K/min.

The distilled water between the electrodes was renewed, and the surfaces of the electrodes were polished and washed for every experiment. The temperature of the sample was observed by a T-thermocouple inserted into a dummy sample, to which an electric field was not applied.

2.2. Observation procedure of depolarization current of ice electret and normal ice

A depolarization current was observed while the temperature of the sample was increased from 77 K to 253 K as follows. After the procedure in Subsection 2.1, the sample was moved from LN$_2$ to an electromagnetic shield at 253 K in a freezer. The electrode system with a sample was connected to a current measurement system. Figure 3 shows the measurement circuit for the depolarization current. The measurement equipment was an electrometer/high resistance meter (Keysight, B2985A). The
2.3. Observation procedure of ac breakdown voltage

After the procedure of Subsection 2.1, the sample was placed into LN$_2$ in a Dewar vessel made of stainless steel. The electrodes of the sample were connected to a circuit to observe the ac breakdown voltage, as shown in figure 4. Figure 4 shows a diagram of the experimental circuit. The sample was immersed in LN$_2$ at 77 K and 1,013 hPa with an ac voltage application of 60 Hz to the anode electrode. The cathode electrode was grounded. The voltage application was an ac ramp voltage with a rising rate of 240 Vrms/s. Vrms is the effective value of alternating voltage ($2^{-1/2}$ the amplitude of voltage). Equation (1) is the ac voltage application waveform:

$$V = 240t \sin(2\pi f t)$$  \hspace{1cm} (1)

where $t$ is the time of the application, and $f$ is the frequency.

In figure 4, the current control resistance prevents excessive currents in the circuit. The amplitude of the voltage applied to the sample was monitored with a high-voltage probe (EP-100K, NISSIN PULSE ELECTRONICS CO. LTD.) and an oscilloscope (DPO 4034, Tektronix). The waveform of the ac voltage was monitored from the start of the voltage application until the breakdown.
The occurrence of a breakdown of a sample can be judged by a rapid decrease in voltage. This is because once a breakdown occurs the electrodes of the sample are shortened. The amplitude of the voltage just before a breakdown is defined as a breakdown voltage. After the experiments, the electrodes were eliminated from the ice, and the position of the breakdown path was observed. A result was eliminated when the breakdown occurred through the outside of the anode and the cathode.

3. Results and Discussion

3.1. Depolarization current of ice electret and normal ice

The observation of a depolarization current indicates the presence or absence of polarization in a sample. Figure 5 shows the dependency of the depolarization current on time. The temperature was given by the dummy sample. The horizontal axis was a converted logarithmic axis. The depolarization current from 2 to 4 min was noise derived from the operation, which connected the electrode systems to measurement systems. For normal ice, positive values were observed at around 125 K and 251 K, and negative values were observed at around 168 K and 236 K in depolarization current. Because these values quickly increased and decreased repeatedly, the peak of depolarization current did not show clearly. For ice electret, the depolarization current peaked at approximately 105 K and 251 K, which was higher than that of normal ice.

We previously reported that the peak value around 105 K increased as the direct electric field increased during the ice electret procedure [5]. The relationship between the peak value at around 251 K and the electric field intensity is currently under consideration. The depolarization current peaks at around 105 K and 251 K higher than that of normal ice, and the peak around 105 K increased as the electric field increased in the procedure. These results indicate that the polarized charge fixed by protons was released at around 105 K and 251 K in ice electret.

The polarization was induced under a direct electric field application and cooling in ice electret. This result was a result of the release of protons fixed in ice electret at the cathode side. Protons began

![Figure 5. Dependency of depolarization current on time.](image-url)
to move with thermal stimulus when the temperature increased. Some protons moved at around 105 K, and others moved at around 251 K. The reason that the depolarization current of ice electret converged at 0 pA at around 172 K is currently under investigation.

3.2. AC breakdown voltage of ice electret and normal ice

Figure 6 shows the breakdown voltage of ice electret and normal ice. The vertical axis shows the effective value of the ac breakdown voltage. Numbers in brackets are the number of samples. The maximum values of ice electret and normal ice were almost the same. The minimum value of ice electret was 30 kVrms, which was 2.5 times larger than that of normal ice (12 kVrms). For these results of normal ice (iceIh), breakdowns occurred even in the range of 12–17 kVrms. Breakdown voltages in this range must have occurred in electrically weak parts of the samples. By contrast, breakdowns did not occur below 30 kVrms for ice electret.

In these results for ice electret, the distribution of the breakdown voltage was suppressed. Increases in the mean breakdown voltage were primarily caused by improving the minimum breakdown voltage value. The measured values around 30–44 kVrms of ice electret seemed to be slightly higher than those of normal ice. There is a possibility that the electrically weak part in the normal ice was improved because breakdowns at 12–17 kVrms did not occur in ice electret. The electrically weak part of the normal ice was improved owing to the change in proton arrangement of the ice under a direct electric field. Each proton arrangement of ice electret and normal ice was maintained as observing the breakdown voltage at 77 K. The temperature dependence of depolarization current peaks in figure 5 indicated maintenance of proton arrangement.

The structural difference between normal ice and ice electret is a result only of the position of protons because the direct electric field was applied to solid H₂O. Ice electret and normal ice have the same oxygen distribution. It is considered that the arrangement of protons in the ice electret is uniform because the characteristics of the proton arrangement are uniform in ice XI, which is similar to ice electret that holds its polarization at cryogenic temperatures. The positions of oxygen atoms in iceIh (normal ice) and iceXI are almost the same, and have a hexagonal arrangement. Figure 7 shows a
model of the crystal structure of iceXI. The protons always occupy the upper positions to oxygen atoms. It is easy to understand the characteristics of proton arrangement as shown in the white frame of figure 7. The structure of iceXI is known as the most stable structure of iceIh (normal ice). Figure 8 shows a model of the crystal structure of iceIh. There are no rules for proton distribution in iceIh. Protons exist at arbitrary locations. The crystal structure, including the proton distribution, in iceXI is regularly distributed compared with that of iceIh [6, 12]. Note the white frame inside of each figure. It easy to find the difference in proton arrangements between figure 7 and 8. We considered that the crystal structures of ice electret and iceXI are almost the same because the ice electret maintains a polarization similar to that of iceXI. Namely, the proton arrangement of normal ice and ice electret differ. Therefore, there is a possibility that the proton arrangement of ice influences the breakdown voltage.

4. Conclusions
We studied the effect of proton arrangement on the ac breakdown voltage of normal ice and ice electret at liquid nitrogen temperatures. The main results obtained are summarized as follows.

The maximum values of ice electret and normal ice were almost the same. By contrast, the minimum value of ice electret was 2.5 times larger than that of normal ice. For normal ice, a breakdown occurred even in the range of 12–17 kVrms, but the breakdown of ice electret did not occur below 30 kVrms. From these results, we considered that the electrically weak part of normal ice improved because changes in the proton arrangement of ice were made under a direct electric field application to normal ice.

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