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DIELECTRIC PROPERTIES OF NaCl-DOPED ICE AT 9.7 GHz

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Abstract: The relative complex dielectric permittivity of NaCl-doped ice was measured at 9.7 GHz in order to clarify the doping effect of the salt component in the microwave frequency range. It was found that over a wide range of NaCl concentrations between 6×10^{-5} M and 1×10^{-2} M the loss tangent and conductivity of NaCl-doped ice increased linearly with increasing NaCl concentration at temperatures above the eutectic point of NaCl solution (−21.3°C). The conductivity of NaCl-doped ice was compared with those of artificial ice containing sea salt and natural sea ice at X-band frequencies reported in the literature.

1. Introduction

The knowledge of the relative complex dielectric permittivity, $\varepsilon^*=\varepsilon'-i\varepsilon''$, of ice at microwave frequencies is important for the analysis of remote sensing data of the cryosphere. In the microwave frequency range, at X-band frequencies in particular, dielectric properties of ice have been reported by several investigators (LAMB, 1946; CUMMING, 1952; VANT *et al.*, 1974; MÄTZLER and WEGMÜLLER, 1987; FUJITA *et al.*, 1992a, b). It has been accepted that the real part of permittivity (ε') was reasonably constant around 3.17 (earlier reviewed by EVANS, 1965) with a very slight temperature dependence. Recently, dielectric anisotropy was found by the present authors (FUJITA *et al.*, 1993). The real part of permittivity parallel to the *c*-axis is larger than that perpendicular to the *c*-axis by 0.037 (±0.007) or about 1.2 %. Although the values of ε' reported by previous investigations are scattered within a similar range to the anisotropy, basically they agree well with each other. In contrast, the reported values of the loss tangent ($\tan\delta=\varepsilon''/\varepsilon'$) were contradictory with each other by factors larger than 10 (reviewed by WARREN, 1984). One possible reason for the discrepancies was that the $\tan\delta$ at microwave frequencies was too small to be measured precisely. In addition, it was considered that small impurities might have a significant influence on the absorption of electromagnetic waves (MÄTZLER and WEGMÜLLER, 1987). In fact, MÄTZLER and WEGMÜLLER (1987) showed that slightly saline ice had a larger value of $\tan\delta$ than pure ice by the precise measurement of the complex permittivity of pure and saline ice containing 1.9×10^{-4} M (13 ppm) sea salt (M is molarity, $molL^{-1}$) with both the cavity resonator method and radiometric method. In addition, FUJITA *et al.* (1992b) showed that ice containing strong acids (H_2SO_4, HCl, HNO_3) had a larger $\tan\delta$ than pure ice. The increase of $\tan\delta$ caused by acid impurity was about twice as large as that by the same molarity of sea salt at 9.7 GHz.

In 1992, the present authors performed a new measurement of dielectric properties of artificial NaCl-doped ice by the standing wave technique. The aim of the measurement was to clarify the influence of NaCl on the dielectric properties of ice over a wide range of concentrations between those typical for meteoric ice (of the order of 10^{-5} M) and those typical for multi-year sea ice (of the order of 10^{-2} M). Thus the concentration of doped NaCl in ice samples prepared for measurement was between 6×10^{-5} M and 1×10^{-2} M. The saline ice sample investigated by MÄTZLER and WEGMÜLLER (1987) was only a single sample with sea salt concentration of 1.9×10^{-4} M. A large body of work also exists on the microwave properties of sea ice (VANT *et al.*, 1974, 1978) which contains far higher impurities (more than 10^{-2} M) than meteoric ice. However few data are available at intermediate concentrations and at concentrations below 1.9×10^{-4} M. Therefore, the new measurement was performed in order to fill in the gap over these concentration ranges. Although sea salt contains not only NaCl but also other salts, only the effect of NaCl was investigated in order to extract the pure effect of NaCl, because NaCl is the dominant component of salts in ice containing sea salt such as sea ice and ice in the polar ice sheets. The role of the different salts in sea ice can be understood by comparing the dielectric properties of NaCl-doped ice with those of ice containing sea salt.

In the present paper, we report the results of the measurements and comparison with the results of previous investigations on the dielectric properties of ice containing NaCl and sea salt at X-band frequencies.

2. Experiments

2.1. *Method*

The measurement method was a standing wave "two-point method" (SUCHER and FOX, 1963). Figure 1 shows, schematically, the experimental arrangement for measuring dielectric permittivity of ice. The ice sample was set in an empty rectangular waveguide terminated by a short circuit. Input impedance of the short-circuited waveguide was measured. Special modifications of this method used here are described in FUJITA *et al.* (1992a). The measurements were carried out at temperatures between -5°C and -50°C. The experimental error with this system was at most ±0.01 for the real parts and $\pm2\times10^{-4}$ for the loss tangents. It has been confirmed that the present system could be used for measuring other low loss materials such as Teflon and polyethylene (FUJITA *et al.*, 1992a). The frequency used for this measurement was 9.7 GHz.

2.2. *Ice samples*

The ice samples studied were made from deionized water containing NaCl. The solutions were frozen inside plastic bags at -20°C. The samples contained bubbles and were polycrystalline with densities between 910 and 916 kgm^{-3}. Impurity distributions within the samples were probably not homogeneous since ice rejects impurities as it freezes, so that the remaining solution becomes

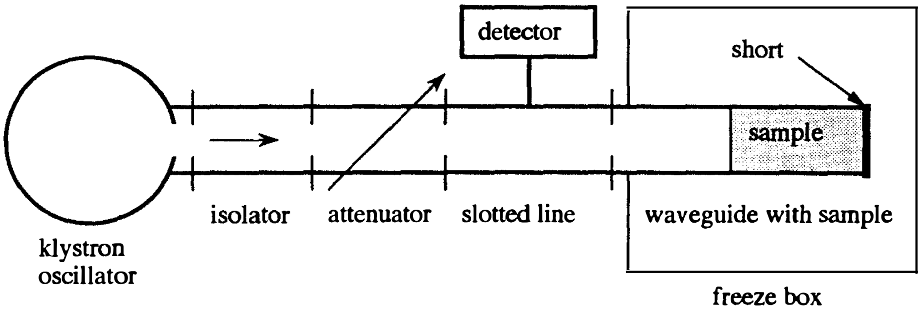

Fig. 1. Experimental arrangement for measuring the dielectric constants in a waveguide.

increasingly concentrated. A range of samples containing NaCl concentrations between 6×10^{-5} M and 1×10^{-2} M was prepared. NaCl concentrations were found by measuring the electrical conductivity of the melted sample after experimentation. The samples were rectangular prisms with cross section 10.2×22.9 mm^2 and length of 30.0 mm. The dimension of the cross section was the same as the inner dimension of a waveguide whose standard was WRJ-10. Seven samples were prepared for measurement in all.

3. Results

Figures 2 and 3 show the temperature dependence of the real part of the permittivity (ε') and the loss tangent ($\tan\delta$), respectively. In both figures, the measured values of only four samples with different concentrations of NaCl are shown to show the general trend of the results. Each result in Figs. 2 and 3 is the corrected value for density at 917 kgm^{-3} in order to eliminate the effect of

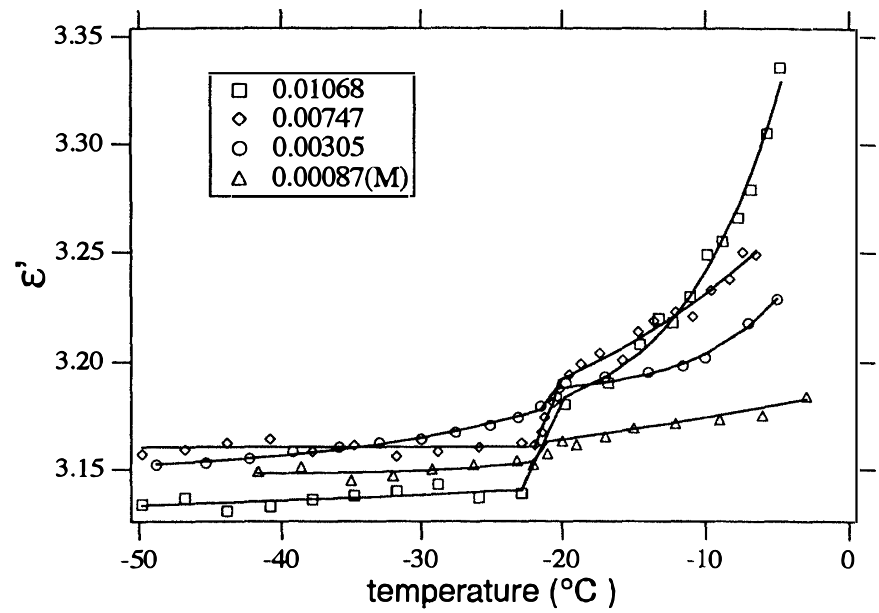

Fig. 2. The real part of the complex permittivity of the NaCl-doped ice versus temperature. Molarity concentrations of NaCl are given in the figure.

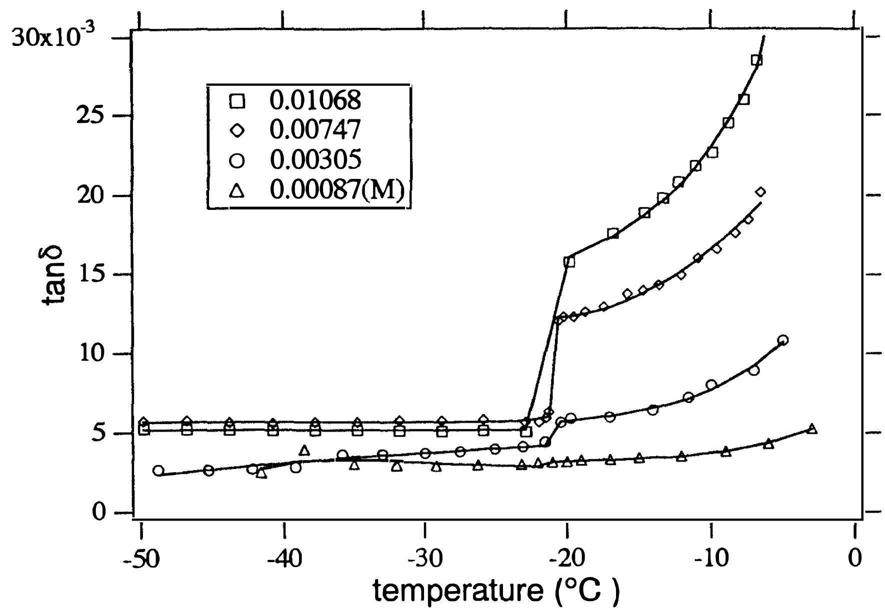

Fig. 3. The loss tangent of the complex permittivity of NaCl-doped ice versus temperature.

density from the data because the purpose of this study is to investigate the effect of NaCl on the complex permittivity (ε^*). For the correction, the density dependence of ε^* for dry snow derived by TIURI *et al.* (1984) was used for ice. They are

$$\varepsilon'_d=1+1.7\rho+0.7\rho^2, \tag{1}$$

for the real part, and

$$\tan\delta=D(0.52\rho+0.62\rho^2)/\varepsilon'_d, \tag{2}$$

for the loss tangent where ρ is the relative density of the dry snow compared to water. D is a number which depends on frequency and temperature. The correction of ε^* with respect to density using eqs. (1) and (2) was carried out only for the purpose of comparison. Thus only the gradient determined from eqs. (1) and (2) was used to estimate the effect of density variation.

A sudden sharp increase was found at about -21°C in the results of all samples both for ε' and $\tan\delta$. This temperature agrees with the eutectic point of NaCl solution, -21.3°C. Above the eutectic point, the gradients of ε' and $\tan\delta$ *versus* temperature, $(d\varepsilon'/dT)$ and $(d\tan\delta/dT)$ respectively, increase as NaCl concentration increases.

Figure 4 shows $\tan\delta$ versus NaCl concentration. The result at -15°C is shown as an example. It was found that $\tan\delta$ of NaCl-doped ice increases linearly with the concentration of NaCl at temperatures between the eutectic point and -5°C. That is,

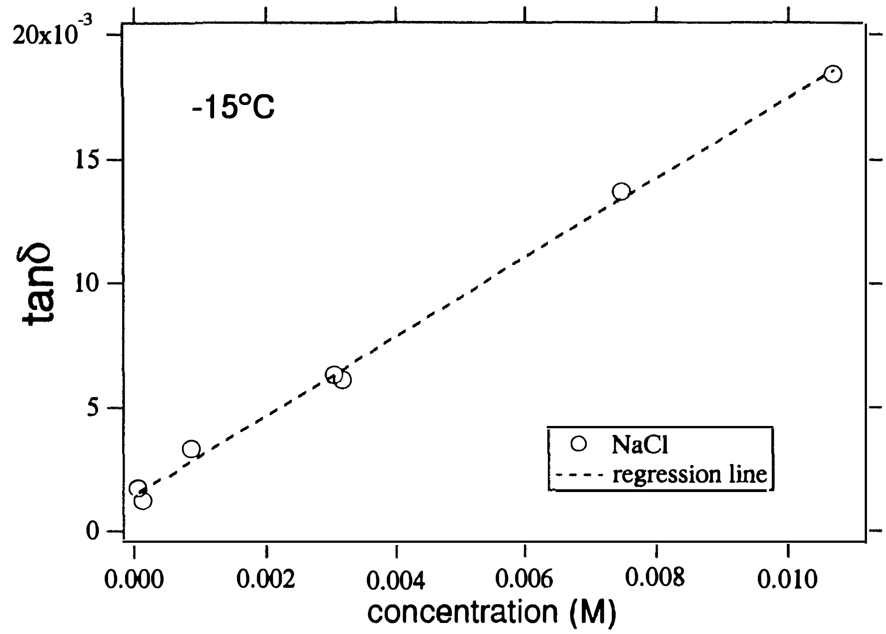

Fig. 4. The loss tangent of the complex permittivity at −15°C versus concentration of NaCl.

$$\tan\delta = \tan\delta_p + A[\mathrm{NaCl}], \qquad (3a)$$

where $\tan\delta_p$ is the loss tangent of pure ice. A is the temperature dependent factor. [NaCl] is the chemical concentration of NaCl expressed by molarity. In the case of −15°C, as an example, A is 1.60. A at temperatures between −20°C and −5°C is shown in Table 1.

Table 1. Values of A and μ_{NaCl}

Temperature(°C)	A	μ_{NaCl}
−5.0	2.80	4.79
−7.5	2.35	4.01
−10.0	2.01	3.44
−12.5	1.77	3.02
−15.0	1.60	2.72
−17.5	1.47	2.51
−20.0	1.38	2.35

In the following discussions, we present the experimental results in terms of conductivity although the dielectric properties of ice at microwave frequencies have been traditionally presented in terms of real and imaginary permittivities and loss tangents. This is because it is somewhat easier to compare dielectric results that are measured at different frequencies when they are presented in terms of conductivity. We can rewrite eq. (3a) in terms of conductivity $\sigma = \varepsilon_0 \varepsilon' 2\pi f \tan\delta$, where f is the frequency and ε_0 is the permittivity of free space.

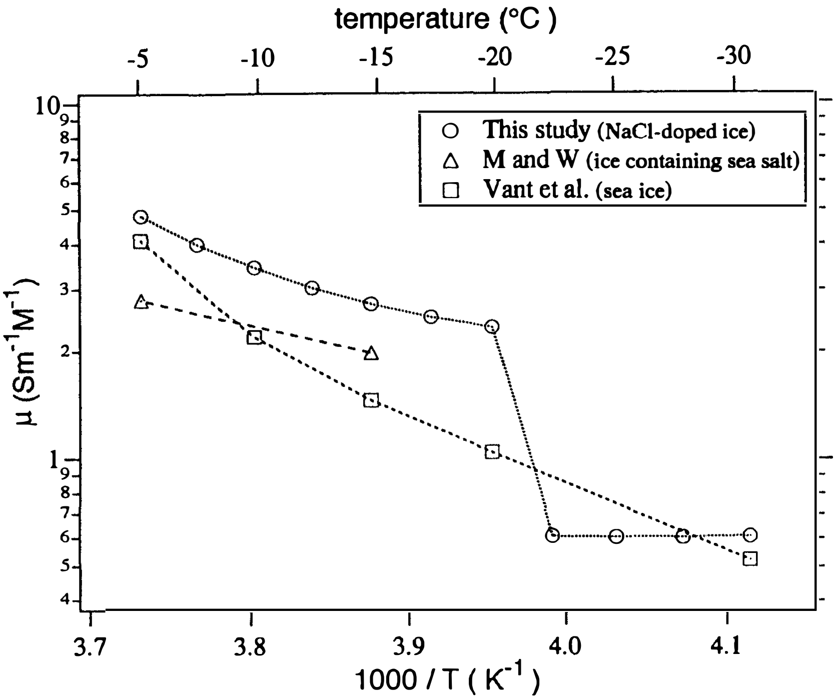

Fig. 5. Arrhenius plot of the molar conductivity against reciprocal temperature for experimental results measured in X-band. The data denoted by M and W are those at 10 GHz from MÄTZLER *and* WEGMÜLLER *(1987) on ice sample containing 1.9×10^{-4}M sea salt. The data from* VANT *et al. (1974) are on natural sea ice containing 1.0×10^{-2} M~7.5×10^{-2}M sea salt.*

Therefore,

$$\sigma=\sigma_p+\mu_{NaCl}[NaCl], \tag{3b}$$

where $\mu=\varepsilon_0\,\varepsilon'2\pi fA$ and the unit of σ is Sm^{-1}. Thus the unit of μ is $Sm^{-1}M^{-1}$. This is called molar conductivity. The temperature dependence of molar conductivity, μ_{NaCl} , is shown in Fig. 5 and in Table 1. The standard errors of μ_{NaCl} are smaller than 0.15 at temperatures between −30°C and −5°C. In Fig. 5, μ_{NaCl} is plotted *versus* reciprocal temperature because the Arrhenius equation,

$$\mu_{NaCl}=\sigma_0\exp(\frac{-E}{RT_K}), \tag{4}$$

is assumed to hold. Here R is the gas constant, E is an activation energy and T_K is the absolute temperature. In Fig. 5, the slopes of the lines show the activation energies, E. At temperatures below the eutectic point, E of μ_{NaCl} is almost zero. At temperatures above the eutectic point, E of μ_{NaCl} gradually increases as the temperature increases. Average activation energy is 26.6 kJ M^{-1} or 0.28 eV at temperatures between −20°C and −5°C.

4. Discussion

The critical decrease in the conductivities and the loss tangents observed at the eutectic temperature can be attributed to disappearing of the liquid phase. Since the liquid has a three dimensional network of the channels along the intersections of the grain boundaries, the conductivity is considerably increased by the small amount of liquid included in the ice sample above the eutectic point. Similar results were reported by HOEKSTRA and CAPPILLINO (1971). They measured the dielectric loss of two NaCl-doped ice samples with 0.125 M (7.3 ppt) and 0.250 M (14.6 ppt) at X-band frequencies. Their result on the 0.250 M sample was in good agreement with the present result. The value of A derived at -15°C was approximately equal to 1.6, which is roughly equal to the data shown in Table 1. It can be said that the value of A derived in this study can apply to a high concentration sample of 0.250 M.

We then compared the result of our study with the results of previous investigations on the dielectric properties of ice containing sea salt. VANT *et al.* (1974) studied the dielectric properties of natural sea ice samples at 10 GHz. The samples were from multi-year sea ice with salinities around 1.0×10^{-2} M, and columnar and frazil ice with salinities up to 7.5×10^{-2} M. MÄTZLER and WEGMÜLLER (1987) measured the dielectric properties of a single ice sample containing a higher concentration of salt than found in normal meteoric ice at microwave frequencies from 2 to 100 GHz. The ice sample containing sea salt was made by freezing a solution of melted snow which lay on the top of the sea ice near Spitzbergen. The salinity of the sample was 1.9×10^{-4} M.

Using eqs. (3a) and (3b), their results were expressed as the molar conductivities, μ_V and μ_{MW}. Here, μ_V and μ_{MW} are the molar conductivity of four sea ice samples from VANT *et al.* (1974) and that of saline ice sample from MÄTZLER and WEGMÜLLER (1987), respectively (Fig. 5) at 10 GHz. μ_{MW} increases with increasing frequency; *i.e.* μ_{MW} shows frequency dispersion at microwave frequencies; μ_{MW} at 10 GHz was calculated as μ_{MW}. In Fig. 5, it is seen that a noticeable eutectic point does not exist in the case of sea ice samples of VANT *et al.* (1974). Figure 5 also shows that at temperatures above the eutectic point of NaCl-doped ice, the value of μ_{NaCl} is larger than the value of μ_V and μ_{MW}. These differences may be attributed to the fact that the sea ice samples contain other sea salt chlorides, such as KCl and $MgCl_2$. Since they remain in solution below the eutectic point of NaCl solution, the conductivity in ice containing sea salt decreases more gradually than that of NaCl-doped ice. This point was discussed earlier by HOEKSTRA and CAPPILLINO (1971). However, it is not clear why μ_{NaCl} is larger than μ_V and μ_{MW}.

In this paper, the authors report μ_{NaCl} only at 9.7 GHz. To further clarify and discuss μ_{NaCl}, the authors are presently measuring μ_{NaCl} at frequencies between 10 MHz and 35 GHz. Publication of these results is forthcoming.

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