Discovering formation of ice 0 by low-frequency measurement data

A O Orlov¹ and S V Tsyrenzhapov
Institute of Natural Resources, Ecology and Cryology Siberian Branch of RAS, 16a, Nedorezova Street, Chita, 672014, Russian Federation

¹E-mail: Orlov_A_O@mail.ru

Abstract. In this work, low-frequency characteristics of wetted nanoporous silicate materials were measured, as well as the specimen’s own low-frequency electric fluctuations at the frequencies of 1…100 Hz. The measurements at low frequencies were conducted at different voltages of the probing signal. A capacity cell was used in making the measurements. In the experiments, at the temperatures below −25…−30 °C, non-linearity of the medium was discovered. The experiments on the study of the specimen’s own electric fluctuations at these temperatures revealed their essential increase. These temperatures are below the point of phase transition of supercooled water to recently discovered ferroelectric ice 0. Based on the measurements made, a conclusion was made regarding formation of this modification of ice in the nanosize pores of the wetted materials under study. Ice 0 is a ferroelectric; therefore, its formation from deeply supercooled water may have a significant impact on the electric parameters of wetted bodies at the temperatures below −23 °C. At the interface of such ice with another dielectric, a thin layer with practically metallic conductivity emerges. Such a layer influences not only the non-linear dependence of dielectric permittivity but also increases attenuation of electromagnetic radiation in a medium.

1. Introduction
At normal atmospheric pressure and the temperatures from 0 to −100 °C, three crystalline modifications of ice may exist. Ice Ih is hexagonal, ice Ic is cubic and ice 0, discovered by way of numerical modeling, is metastable [1]. Ice 0 is formed only from supercooled water at the temperatures below −23 °C [2]. Supercooling of water to temperatures lower than −20 °C is a rather serious problem. To solve it, nanoporous silicate materials were used in this work. Nanosize pores containing water allow supercooling at 90 °C, with the pore diameter ~1 nm [3]. With the pore diameter in a silicate matrix being greater than 3 nm, only the monomolecular layer of water will be connected with the surface. The rest of the water remains to be close for its properties to volume water [4].

Previously we made measurements of permittivity of electromagnetic radiation in the optical band through specimens of transparent dielectrics with a thin layer of ice 0 of the nanometric thickness on their surface [5]. Ice 0 was obtained by deposition of water vapor at the temperatures from −170 to −23 °C.

This study had an objective to discover ice 0 by the data of low-frequency measurements. For this purpose, conditions were created for formation of ice 0 and dielectric measurements were made, which allowed the signs of its emergence at the temperatures below −23 °C to be discovered. In addition, the
special property of ice 0 was taken into consideration – its ferroelectric state, at which strong low-frequency electric fluctuations emerge in the medium. In the study, wetted nanoporous silicate material MSM-41 was used, with the pore diameter 3.5 nm, allowing supercooling of water to the temperatures –60…–70 °C.

2. The measurement technique
Measurements of the specimen’s parameters at the frequency of 20 Hz were made using a capacity cell having a square cross section with the plates sized 40х40 mm². The cell’s capacitance and resistance were measured. The configuration of the experimental setup is shown in figure 1.

![Figure 1. The configuration of the setup for measuring low-frequency dielectric parameters of a specimen. 1 – a capacity cell with the specimen; 2 – a thermostat; 3 – a thermocouple; 4 – a Dewar flask with liquid nitrogen; 5 – a resistor evaporator; 6 – a stabilized power source; 7 – a thermo-resistor; 8 – an LCR meter; 9 – a data acquisition system; 10 – computer.](image)

The powder specimen was saturated with water vapor in the exicator to reach the required wetness and was then placed into the cell (1). The measurement cell was placed into a thermostat chamber (2). Cold nitrogen vapor was fed into the thermostat from the Dewar flask when the resistor was heated (5). A thermal resistor was used to control delivery of the cold vapor in the system (7). Cooling ensured the temperature of ~95 °C. The characteristics of the specimen at low frequencies were measured with an LCR-meter (8). The temperature of the specimen was measured with the thermocouple with the accuracy of ~1 °C (3). The thermocouple was switched to the Agilent data acquisition system (9). All the data were fed onto the computer (10). The data of the data acquisition system and of the LCR-meter were synchronized in time.

The specimen’s own electric fluctuations were measured in a similar way, only in a cylindrical cell with the diameter of ~10 mm. The configuration of the setup for measuring the specimen’s own electric fluctuations is shown in figure 2.

In the experiments on the study of the specimen’s electric noise, wetted MSM-41 specimens were also used. The specimens were put into a cell (1), at the edges of which there were flat metal electrodes. Voltage of the specimen’s own noise from the electrodes passed through the amplifier with the frequency band from 1 to 100 Hz (7), was detected (8) and fed to the filter of the low frequencies (9). The choice of the band for passing the amplifying signal was determined by the characteristics of the ferroelectric phase. Abrupt transformation of the electric domain structure may be observed in it when external parameter change (pressure, temperature, external electric fields). Such electric fluctuations are observed in the range of 1…100 Hz and are called Barkhausen noise [6].
Figure 2. The configuration of the setup for measuring the specimen’s own low-frequency electric fluctuations. 1 – a capacity cell with the specimen; 2 – a thermostat; 3 – a thermocouple; 4 – a Dewar flask with liquid nitrogen; 5 – a resistor evaporator; 6 – a stabilized power source; 7 – an amplifier; 8 – a detector; 9 – a filtration system; 10 – a data acquisition system; 11 – computer.

The dielectric parameters of the specimen at the frequency of 20 Hz were measured in the following range of voltages of the probing signal (U): 0.01 V; 0.1 V; 0.2 V; 0.5 V; 1 V and 2 V.

3. Measurement results and discussion
The results of measuring electric resistance at the frequency of 20 Hz at different voltages of the probing signal for the MSM-41 specimen with the moisture content of ~50% are shown in figure 3.
Figure 3. Dependence of the electric resistance of a cell containing a wetted specimen MSM-41 on temperature at the frequency of 20 Hz at different ranges of the voltage of the probing signal in the process of cooling (a) and heating (b).

As seen from the curves, resistance depends much on temperature, and for the temperatures below –25…–30 °C, also on the voltage amplitude. For U equal to 10 mV, the curves diverge in their course at these temperatures. As the temperature decreased further, the resistance values decreased nearly 100 times, compared to the voltage of 0.5…1 V. The maximum difference was observed at the temperatures below –60 °C. At the same time, fluctuations in the measured value rose sharply. A similar process was observed for the measured cell capacitance, but capacitance for the voltage of 10 mV was higher than that for higher voltage amplitudes – figure 4.
Figure 4. Dependence of the capacitance of a cell containing a wetted specimen MSM-41 on temperature at the frequency of 20 Hz at different amplitudes of the voltage of the probing signal in the process of cooling (a) and heating (b).

If a ferroelectric phase emerges in a medium and the electric domain structure becomes exposed to abrupt transformations when the external parameters change, the emerging noise should be manifested during measurements at the same frequencies and, to a greater extent, at low values of the voltage of the probing signal. This is related to the fact that at greater voltages in the measurement setup, the noise becomes suppressed due to the relatively low values of the fluctuation voltages.

The provided measurement results demonstrate that at the temperatures below –20 °C, fluctuations of the measured parameters emerge in the medium. The less the voltage of the measurement signal is, the greater are the fluctuations. Based on that, a conclusion can be made that Barkhausen noise appears in the specimen. Formation of the ferroelectric state leads to emergence of a ferroelectric state in the medium.

In studying the MSM-41 specimen’s own electric fluctuations, they were shown to rise in the range of the temperatures below –25 °C. An example of the temperature dependence of the amplitude of the specimen’s own low-frequency electric fluctuations \( U_n \) is shown in figure 5.

Figure 5. Dependence of the amplitude of intense electric noise voltage of the cell with MSM-41 in the band 1–100 Hz on temperature during its cooling. The moisture content of the specimen is 56%. Voltage is presented in relative units.
In measuring the amplitude of noise voltage, a bell-like curve of its dependence on temperature with the maximum at the temperature of –46 °C (at cooling of the medium) and –39 °C (at its heating). The characteristic feature is the sharp change in the curve’s slant at the temperature of ~26 °C. Such growth may suggest emergence of the ferroelectric phase in the medium.

4. Conclusions
1. Measurements of the dielectric characteristics of the cell with wetted nanoporous sorbent at different amplitudes of the signal emitted by the measuring setup revealed intense non-linearity of the capacitance and of the resistance at the temperatures below –25…–30 °C. This non-linearity may be related of the ferroelectric state in the medium.
2. The measurements of the medium’s own low-frequency electric fluctuations show the increase of noise at the temperatures below –23 °C, which may be related to Barkhausen noise (i.e., with the ferroelectric state).
3. It is known that at the temperatures below –23 °C, ferroelectric ice 0 should be formed from supercooled water; therefore, a conclusion has been made regarding formation of the given crystalline modification of ice in the medium.

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