

Complex dielectric permittivity spectroscopy using ACROSS measurement system III. dielectric properties of bulk and interface

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Slight wetting of rocks yields strong dielectric dispersion at low frequencies, in particular. The remote observation of this dielectric dispersion is expected to provide us with important information on H₂O and its tectonic roles in the Earth's crust. However, existing laboratory data are so much diversified in their results, the measurement conditions and also the extent of reliability. The purpose of this work is to make reliable laboratory measurements and clarify the physics of this type of dielectric dispersion on the basis of laboratory measurements.

We have devised a reliable system of laboratory measurement by (1) using ACROSS (a reliable measurement method of a linear system) to obtain the high quality data with an evaluation of reliability extent, and also by (2) combining two electrode method and four electrode method to determine the bulk property and interface property separately. Using this system, we have measured the dielectric dispersion of water with different impurity level and several solid ionic conductors such as glass, quartz, onyx, etc at low frequency below 1 kHz. We present the experimental results on complex dielectric permittivity, $\epsilon^* = \epsilon + s / i\omega$, where ϵ is a dielectric permittivity and s is electric conductivity. Further we propose our theory of electrochemical reactions associated with the presence of interfaces between the different ionic conductors with different charge carriers.

The dielectric dispersion of water with different NaCl content showed the following results: (a) Whereas the s is constant over the whole range of frequency, the dielectric permittivity ϵ , $\sim 80\epsilon_0$ at high frequency, shows the peculiar frequency dependence at low frequency. (b) The ϵ with interface involvement (two-electrode method) is proportional to $f^{-1.5}$ and it switches to f^{-1} in millihertz range. (c) The ϵ of bulk water (4 electrode method) is proportional to $f^{-0.5}$ and it switches to f^{-1} at lower frequency. We confirmed that (c) does not depend on applied voltage of measurement, whereas (b) depends on the voltage indicating the electro-dissociation of water. The overall pattern of frequency dependence of s and ϵ does not appear to change with the change in impurity content, indicating that only the shift of characteristic frequency takes place by the conductivity change caused by the impurity content.

Dielectric dispersion of solid ionic conductors, quartz, onyx and glass, showed quite similar frequency dependence to that of water. The activation energy of ϵ^* was measured to be of the order of 10-1 eV for all samples, suggesting that the dominant charge carrier may be Li⁺ or probably H⁺ originated from very small amount of H₂O contained in the samples. Further, the extrapolation to higher temperature suggests that ϵ in the deep crust is expected to be very large.

No reasonable explanation has been presented to account for the features mentioned above to our knowledge so far. Summarizing the data obtained here and reported somewhere, we propose a theory of large dielectric dispersion at very low frequency in terms of electrochemical processes and the associated diffusion of neutral atoms or molecules in ionic conductors. The frequency dependent factor of f^{-1} for ϵ is caused by the electro-chemical reaction leading to the energy storage in proportion to time (reciprocal frequency), and the factor $f^{-1/2}$ is related to the generation of compositional gradient by diffusion, which has a time scale of square root of time.