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Measurement of Dielectric Property of Calcium Carbonate under Hydrostatic High Pressure by Liquid-Solid Hybrid System

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The devices using gas or liquid compression have been usually adopted for the measurements of dielectric properties of solids under high pressure because of the hydrostatic pressure applied to samples and the fragility of samples.[1,2] Therefore, the magnitude of the pressure has been limited to about 20 kbar. The authors have successfully expanded the limit of the pressure up to 40 kbar by using liquid-solid hybrid system similar to those developed by Barnett *et al.*[3]

The purpose of this note is to introduce the techniques of measurement and to report the pressure dependence of dielectric constant for $CaCO_3$ obtained by this high pressure device.

A sample is a slab (*c*-plate) that was cut out perpendicular to *c*-axis from a natural calcite single crystal of good optical quality checked by a polarizing microscope and polished carefully with #1500 Al_2O_3 with some pure water, and its surfaces are painted with silver paste as electrodes. Each sample is 8 mm in diameter and 0.16 mm in thickness.

The used high pressure apparatus was a hexahedral press with six 600-ton capacity rams. A face of an anvil, being opposite to a ram, was a square with 20 mm length in edge dimension and was contacted with a pressure cell. As shown in Fig. 1, the pressure cell was a pyrophyllite cube with preformed gaskets ②, in which a capsule consisted of a body ④ and a cap ① was put. A sample ⑤ was immersed into a pressure transmitting fluid ⑪ filled in the capsule. The vaseline was employed as the transmitting fluid by reason of easiness in sealing compared with oil.

For calibration of oil pressure, the bismuth I-II, II-III and thallium phase transitions which occur at 25.5 kbar, 27.0 kbar and 37.0 kbar respectively were adopted.

The electrical capacitance C of samples was measured at 100 kHz under various pressures at room temperature with a Q-meter.

Usually, the negative electrode of a sample is grounded with one of the anvils, and the positive electrode of the sample is connected with another one. But, in our experiment, the negative electrode of a sample was grounded with all the anvils by a copper wire of 0.3 mm diameter ⑥ embedded in the pyrophyllite, while the positive electrode of the sample was connected directly with the Q-meter by a nichrome wire of 0.5 mm diameter ⑨ covered with a teflon tube ⑩ through the gasket to reduce the stray capacitance and leakage conductance. The reason why the nichrome was selected as the positive lead is its high tensile strength.

Since the solid-media gasket of the pressure cell was not well-formed at the pressure less than 4.5 kbar, the stability of the pressure was not good and the change of stray capacitance was different for each pressure cell below this pressure. Then, the measurements over a range of pressure less than 4.5 kbar were refrained. A typical result of measurements for the sample of $CaCO_3$ with initial capacitance 44pF is shown in Fig. 2, where the change of electrical capacitance ΔC is normalized at the pressure of 4.5 kbar.

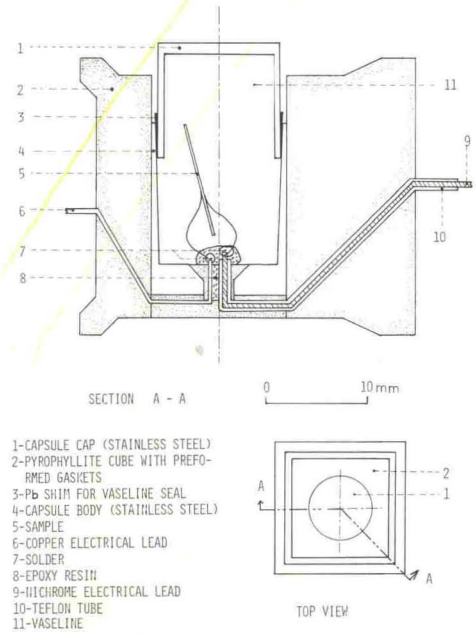

Fig. 1. Section of a pressure cell

The change of stray capacitance of the positive lead ΔC_s increased gradually with increasing pressure as seen in the curve ① in Fig. 2, and the change of the capacitance of the sample with the lead ΔC_a is shown in the curve ②. So, the net change of capacitance ΔC_n of the sample is obtained by subtracting the curve ① from the curve ②, and is given by the curve ③.

Now, the authors have formerly found that the relative dielectric constant (ε_{rc}) for a *c*-plate of $CaCO_3$ is 8.87 at 4.5 kbar at room temperature by using a piston-in-cylinder type high pressure apparatus.[4] So, the pressure dependence of ε_{rc} calculated with the above value is simultaneously given by the curve ③ using the right side scale. The dotted line in Fig. 2 shows the relative dielectric constant corrected by considering the change of the dimensions of the sample with pressure obtained from the result of X-ray diffraction measurement.[5]

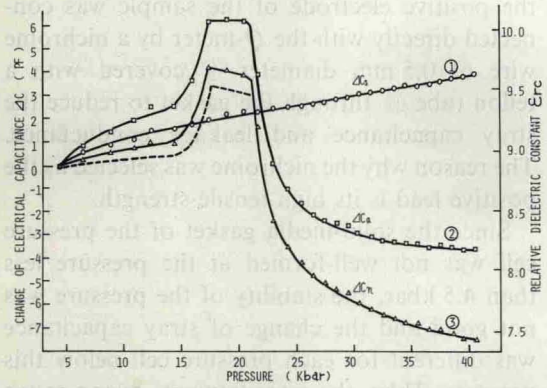

Fig. 2. The measurements of capacitance for a sample of $CaCO_3$ and the pressure dependence of relative dielectric constant along *c*-axis (ε_{rc}) at 24°C. Curve ①, ② and ③ show change ΔC of stray capacitance of the lead, capacitance of the sample with lead and the sample itself, respectively. The dotted line indicates a corrected curve of ③ in the phase I and II of $CaCO_3$. (The scale on the left side is available for all curves and the scale on the right side for the curve ③ only.)

It is found from Fig. 2 that the I-II and II-III phase transition are at about 17 kbar and at about 21 kbar respectively. These transition pressures are more reliable than those (14.6 kbar and 17.7 kbar) obtained by volume-discontinuity method[6] and those (15.5 kbar and 18.7 kbar) obtained by X-ray diffraction method,[5] because the pressure applied to the sample is more hydrostatic in our experiment.

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