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ELECTRIC CONDUCTIVITY OF POWDERED FERROELECTRIC SUBSTANCES UNDER PRESSURES

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Introduction

The alternating-current conductivity of powdered potassium ferrocyanide as an example of hydrous crystals was previously[1] measured up to a pressure of 14,100kg/cm^2 at room temperature. In the present experiment the direct-current conductivity of powdered ferroelectric substances, such as rochelle salt, potassium dihydrogen phosphate(KDP), ammonium dihydrogen phosphate(ADP) and barium titanate, has been measured in the pressure range from 1,400 to 21,000kg/cm^2 at room temperature.

Experimentals

Preparation of materials

a) Rochelle salt was of c. p. reagent quality and recrystallized from water and smashed into fine powder smaller than 250 meshes. The powder was preserved in a desiccator with the relative humidity of 70% at room temperature in order to keep it stable[2].

b) KDP and ADP were of c. p. reagent quality and of reagent quality respectively. Each material was recrystallized from water and smashed into fine powder smaller than 250 meshes. The powder was preserved over phosphorous pentoxide.

c) Barium titanate was prepared by the following method. The equi-mole of TiO_2 and $BaCO_3$ were mixed, ground and then sintered at 1350°C for an hour. The soluble impurities contained, such as barium oxide and barium carbonate, were washed with hot water and cold 0.5N-acetic acid successively. The purified barium titanate was dried at 200°C for three hours and smashed into fine powder smaller than 200 meshes. The powder was preserved over phosphorous pentoxide.

High pressure apparatus and electrodes

The high pressure apparatus and electrodes used for the present experiment were previously reported[1),3)]. The electrode was made of tungsten carbide and its surface was 8mm in diameter. In the course of compression up to 21,000kg/cm^2 the deformation of electrodes could not be detected in the measurement down to 0.001mm by means of a micrometer.

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1) T. Yanagimoto, *This Journal*, **23**, 30 (1953)
2) W. P. Mason, *Piezoelectric Crystals and Their Application to Ultrasonics*, p. 116 (1950)
3) R. Kiyama and T. Yanagimoto, *This Journal*, **21**, 32 (1951)

Operations

In all cases the electric conductivity measurements were made on the disk prepared by compressing the powdered material in the cylindrical pressure vessel[3] at 900 kg/cm^2 for 30 minutes. The disk was placed between the two electrodes and then gradually compressed to a desired pressure*. The direct-current conductivity of the disk which was kept at a definite pressure for 30 minutes was measured by the potential drop method as a function of pressure at room temperature. Since a continuous direct-current causes the electrolysis by the transport of ions, the actual current was kept in a minimum and was allowed to flow through the disk just long enough (a few seconds for each reading) to obtain the necessary data.

During the course of the experiments the circumference of the electrodes and disk was covered with "Electron compound" as used in the previous work[1] in order to avoid the influence of atmospheric moisture. The thickness of the disk was measured by means of a micrometer after the pressure had been released and its value was about 0.2~0.4 mm. The difference between the thickness of the disk under the applied pressure and that measured after the pressure had been released, was within 0.01mm.

Experimental Results

The variation of specific conductivity with pressure is shown in Figs. 1, 2, 3 and 4. The conductivities measured for a few different disks are plotted in each figure. An inspection of the curves in these figures reveals the following two features.

(1) The conductivity of rochelle salt increases with increasing pressure and reaches a maximum point at about 3,000 kg/cm^2 and above that pressure it decreases with increasing pressure. The conductivity of KDP and ADP decreases and that of barium titanate increases with increasing pressure in the range of applied pressure.

(2) Rochelle salt, KDP and ADP at the pressure lower than about 5,000 kg/cm^2 and barium titanate at the whole applied pressure, have not the reproducible values for different disks.

The compressed disks of rochelle salt, KDP and ADP became translucent at 7,000 kg/cm^2 and almost transparent at 15,000 kg/cm^2 in appearance. On the other hand, barium titanate did not yet become transparent at 20,000 kg/cm^2, but like a powder cake.

Considerations

It is known that the electric conduction of solid dielectrics at a low (viz. room) temperature is essentially a surface conduction[4),5),6)]. In the disks formed from the

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* When the disk was compressed by this method, it was believed by Bridgman that a large central part of the disk would be under fairly uniform pressure. *cf.* P. W. Bridgman, *Phys. Rev.*, **48**, 825 (1935); P. F. Chester and G. O. Jones, *Phil. Mag.*, **44**, 1281 (1953)

4) A. Smekal, *Handbuch der Physik*, 24 (part 2), 881 (1933)

5) I. Shapiro and I. M. Kolthoff, *J. Chem. Phys.*, **15**, 41 (1947)

6) I. Shapiro and I. M. Kolthoff, *J. Phys. Colloid Chem.*, **52**, 1319 (1948)

powder there exist many internal surfaces originating from pores, cracks and grain boundaries. The continuous paths of these internal surfaces, namely the conducting surfaces, contribute to the conduction. The experimental results can be explained on the basis of such conducting surface.

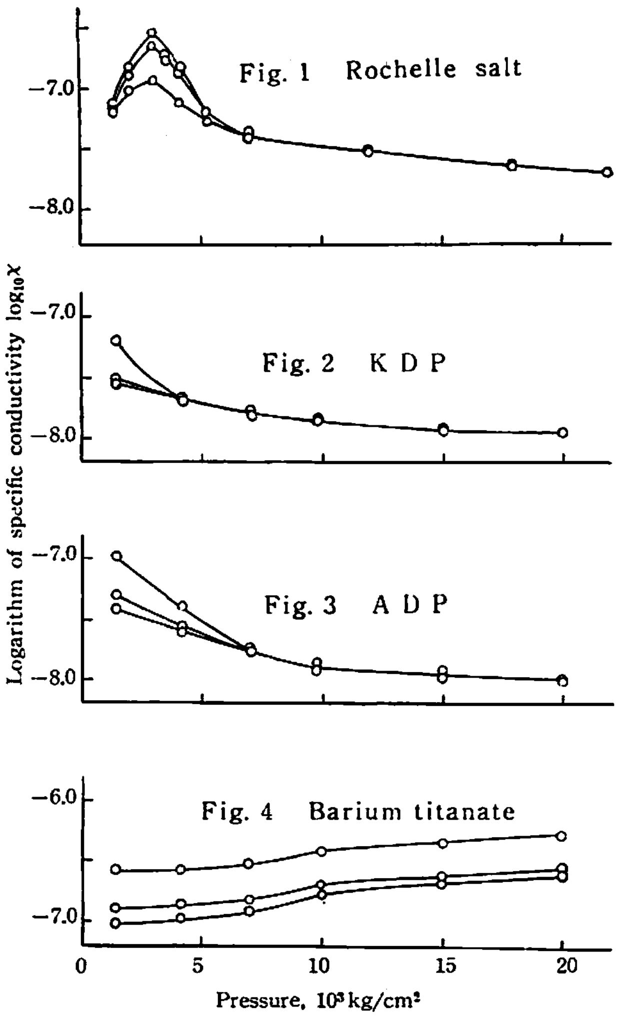

Fig. 1 Rochelle salt

Fig. 2 K D P

Fig. 3 A D P

Fig. 4 Barium titanate

(1) With increasing pressure the conductivity increases as a result of the better contacts between separated grains, while at higher pressures the conductivity decreases as a result of the decrease of conducting surface. These two contrary tendencies may cause the maximum point of conductivity at a certain pressure. In the case of rochelle salt, the maximum point was found at about 3,000 kg/cm^2. In KDP, ADP and barium titanate the maximum point was not found in the pressure range from 1,400 to 21,000 kg/cm^2. Considering the above-mentioned two contrary tendencies, however, it is expected that KDP and ADP may give the maximum point at the pressure lower than 1,400 kg/cm^2 and barium titanate at the pressure higher than 20,000 kg/cm^2.

(2) The result that another disk formed from the same material has a different conductivity, may be attributed to the dissimilarity of the amount of the conducting surface which is caused by the irregularity of grain size. In rochelle salt, KDP and ADP, however, all curves for different disks merge into one curve at the pressure higher than about 5,000 kg/cm^2. In this case it seems plausible to conclude that the pores, cracks and grain boundaries decreases with increasing pressure and all disks reach such a similar state as contains the same amount of conducting surface at a fixed pressure higher than 5,000 kg/cm^2. On the other hand, in barium titanate the discrepancy among the curves does not disappear even at 20,000 kg/cm^2. These distinctive features of barium titanate may be attributed to the property of its powder

that the pores, cracks and grain boundaries are difficult to diminish by compression. The propriety of these considerations is supported by the transparency of the compressed disks.

Moreover, the result that the specific conductivity of all materials in the present experiment was larger than the values for their single crystals[7),8),9),10)] or ceramics [11),12)], may be understood by considering that the disk made of powder contains more conducting surfaces caused by the pores, cracks and grain boundaries[4),5),6),13)].

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