Electrical Engineering in Japan, Vol. 75, No. 3, 1975
Translated from Denki Gakkai Ronbunshi, Vol. 95A, No. 5, May 1975, pp. 187-193

Dielectric Properties of Inorganic Salts (KNO_2, $NaNO_2$, $CaCO_3$) under High Pressure by Liquid-Solid Hybrid Systems

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1. Introduction

Because of the difficulty in applying the static pressure on the sample and also because of the fragility of the sample itself, the physical properties of solid materials have been investigated by high-pressure apparatus [1, 2] employing gas or liquid media which can withstand higher pressure than solid media.

The liquid-media, tapered-cylindrical, high-pressure apparatus which was developed by Bridgman and later improved by Birch produces the pressure up to 20 kbar and suffers from a crack of the cylinder wall if higher pressure is required.

We have developed a liquid-solid hybrid system which was first proposed by Barett [4], and measured dielectric properties of salts (KNO_2, $NaNO_2$ and $CaCO_3$) under high pressure up to 40 kbar at 100 kHz. It was found that the permittivity increases with the pressure and the logarithmic dielectric conductivity decreases in an inverse proportion to the pressure.

This paper reports the construction of a liquid-solid hybrid high-pressure apparatus and presents the experimental results on the dielectric properties of salts under high pressure. So far, no papers have reported the pressure dependence of the permittivity of salts except Rochelle salts [2], barium titanate [5] and nitric soda [6].

2. Sample and High-Pressure Device

2.1 Selection of samples

A number of papers has reported ferroelectric behaviors of inorganic salts which change their center-symmetric phase at transition temperature. However, the effect of high pressure on their ferroelectric behaviors is not well known.

Under high pressure, some salts exhibit ferroelectric properties after the transition from center-symmetric phase to noncenter-symmetric phase. Other salts reveal ordinary electric properties after the transition from noncenter-symmetric phase to center-symmetric phase. The former includes $NaK\,C_4H_4O_6 \cdot 4\,H_2O$ (Rochelle salt), $NaNO_3$ [6], etc., while the latter includes $BaTiO_3$, KH_2PO_4, $LiH_3(SeO_3)_2$ (lithium hydroxide in selenious acid), etc.

Based on data of crystalline symmetry in the X-ray diffraction measurement, the temperature versus pressure diagram in the thermal analysis, and anomalous permittivity in the dielectric measurement, we selected ClO_3, NO_2, NO_3, SO_4, CrO_4, etc. Further, eliminating absorptive, unstable and low-conductivity samples, we finally selected three kinds of inorganic salts, i.e., KNO_2, $NaNO_2$ and $CaCO_3$.

2.2 Sample preparation

(1) KNO_2

The 85% KNO_2 powder was refined from the solution by the recrystallization method. The KNO_2 powder thus obtained was poured into a shaping machine with the mirror surface polished by No. 1500 Al_2O_3 powder to form a disk (thickness 0.7 mm, and diameter 10 mm) under the pressure of 1500 kg/cm^2. The silver paste applied to the disk surface was used as an electrode.

Since KNO_2 is highly sensitive to moisture, the sample was kept in a high-temperature bath for one day and then yellow wax was applied to its surface to protect the sample from moisture penetration.

(2) $NaNO_2$

The 98% $NaNO_2$ powder was poured into a pyrex glass crucible (inner diameter 2.3 cm and length