Dielectric Properties of Disodium Monohydrogen Phosphate Dodecahydrate, $Na_2HPO_4 \cdot 12H_2O$

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Using large single crystals we measured the temperature and frequency dependences of the dielectric constants and losses of several hydrated salts. The region of the temperatures measured is from −170°C to the temperature of dehydration and that of frequencies is from 0.3 kc to 3 Mc. For disodium monohydrogen phosphate dodecahydrate, $Na_2HPO_4 \cdot 12H_2O$ (crystal class, C_{2h}), no appreciable anisotropy in its dielectric behaviour is observed. At 3 Mc the dielectric constant perpendicular to (001) is 5.2, monotonously increasing with temperature coefficient 3×10^{-3}. At 0.5 kc, as temperature rises the dielectric dispersion becomes appreciable from about 10°C upward, and ε' reaches a value twice as great as that measured at 3 Mc, accompanying a large conductivity when the temperature is raised to its dehydration temperature 35°C. These are the results obtained with the tin-foiled specimen. On the other hand, in the case of the sandwiched specimen by mica-foils for avoiding the d.c. conductivity, the temperature and frequency dependences of ε' become considerably greater and at 0.5 kc ε' attains to a value of about 70 at 35°C as shown in Fig. 1. The ε' and ε'' values fit in with the Cole-Cole diagram in this dispersion region with distribution parameter α of about 10° (Fig. 2). From the relaxation time and its temperature variation, the free energy of activation is obtained to be $\Delta F = 13$ kcal/mole and the enthalpy $\Delta H = 27$ kcal/mole. For the single crystals of $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO \cdot 10H_2O$, we obtained similar results and the single crystal of $Na_2S_2O_3 \cdot 5H_2O$ shows a similar behaviour but to a less extent, and that of $Na_2B_4O_7 \cdot 10H_2O$ no appreciable effects.

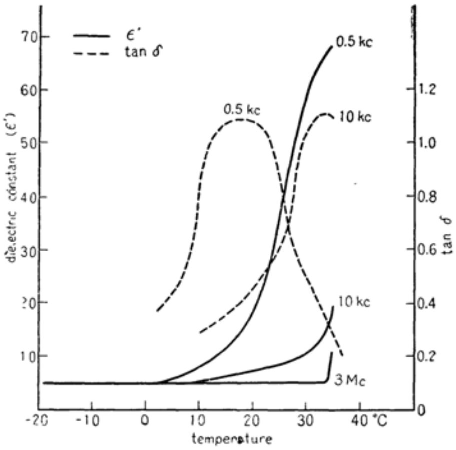

Fig. 1.
Dielectric constant-temperature and loss tangent-temperature curves for $Na_2HPO_4 \cdot 12H_2O$ (perpendicular to (001))

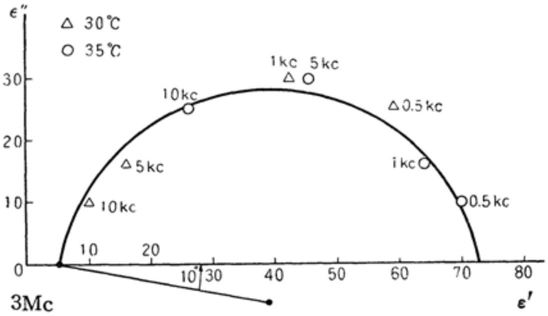

Fig. 2.
Cole-Cole diagram for $Na_2HPO_4 \cdot 12H_2O$ (perpendicular to (001))

All these crystals are very efflorescent, and the dehydrated water molecules are set free from the crystal surfaces and affect the dielectric properties considerably. In the above experiments, we have taken precaution by passing dry air through the measuring cell in order to avoid these effects of dehydrated water as far as possible.

From these measurements and our previous experiments about such behaviours of water of crystallization, it may be concluded that water molecules in these hydrated phosphate, sulphate and carbonate crystals are linked to oxygen atoms in a manner somewhat similar to the water molecules in ice and further the observed dielectric phenomena due to rotation of the water molecules may be originated at some points of lattice defects.

Detailed discussion will be published in this Bulletin.

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