Dielectric Behaviour of Hydrated Crystals. III. Potassium Tin (II) Chloride Monohydrate and Barium Nitrite Monohydrate[1]

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Introduction

The water of crystallization in potassium mercury (II) chloride monohydrate, $K_2HgCl_4 \cdot H_2O$, which is apparently zeolitic from the view point of the atomic arrangement in its crystal, is fixed tightly in the lattice and shows no orientation polarization of its dipole at a room temperature as reported in the previous paper.[2] The crystal structure of potassium tin (II) chloride monohydrate, $K_2SnCl_4 \cdot H_2O$ closely resembles to that of $K_2HgCl_4 \cdot H_2O$ and in both crystals, a pair of the water molecules which are crystallographically equivalent are enclosed in a cocoon-shaped space facing each other. Brasseur and Rassenfosse who analysed the crystal structure of $K_2SnCl_4 \cdot H_2O$ stated that the water of crystallization is zeolitic based on its continuous dehydration with temperature.[3] It is worth while to decide whether or not the water of crystallization of this crystal is truly zeolitic from the view point of the dielectric behaviour of single crystals as done on other salt hydrates previously reported by the present authors.[2,4]

Although the crystal structure of barium nitrite monohydrate, $Ba(NO_2)_2 \cdot H_2O$ has never been fully analysed, the position of the barium ion has been determined. From the consideration based on the corresponding space group of this crystal structure and the position of the barium ion, it was presumed that the water molecule of this monohydrate is enclosed in a tunnel structure coming from the hexagonal spiral configuration of the lattice and that the water is probably zeolitic.[5] Therefore, it is also interesting to investigate the behaviour of the dielectric properties of this crystal from the standpoint of the dipole orientation and to compare the result with those of the other related crystals.

Crystal, Specimen and Equipment

Transparent, large, single crystals of $K_2SnCl_4 \cdot H_2O$ could not be obtained until now owing to the fact that the effective velocity of crystal growth is exceedingly small. Thus usual crystals exhibit milky white appearance, are more brittle than the transparent ones obtained by us and contain more or less inclusions of the saturated solution between the bundle-shaped fragments parallel to the *c*-axis.

We have succeeded in obtaining these transparent crystals suitable for dielectric measurements (the area perpendicular to the crystallographic axes should be larger than $10 \times 10\,mm^2$) by careful regulation of the temperature of the water-thermostat and the composition of the aqueous solution of this double salt. The composition was maintained usually in excess of the stoichiometric amount of potassium chloride. Besides these, the solution contained a small amount of hydrochloric acid and several grains of metallic tin for the purpose preventing the stannous ion from oxidation. The time required was more than two months.

Frequently, translucent and opalescent crystals were obtained, probably because of a small fluctuation of the temperature of the thermostat or a slight deviation of the composition of the solution. Such crystals have also been investigated for the purpose of comparing the dielectric behaviour of the transparent crystal with that of this translucent one.

Barium nitrite was prepared from double decomposition of barium chloride and sodium nitrite or barium chloride and silver nitrite. The large, transparent, yellow-coloured, single crystal of barium nitrite monohydrate grew up easily from the seed crystal in its aqueous solution. The obtained crystal has the shape of a hexagonal prism with a pyramidal top, but belongs to the class of hexagonal trapezohedron, $\bar{6}2\text{-}D_3$ as the X-ray data show. Colourless crystal could not be obtained and the experiment has been performed using these yellow-coloured crystals.

Good crystals have been selected by a polarizing microscope beforehand, and the specimens for the dielectric measurements are made by cutting and grinding these crystals and pasted by tinfoils with vacuum-grease.

The equipment is the same as those in the previous papers.[2,4]

1) Parts of this investigation were separately read before the annual meeting of the Crystallographic Society of Japan in May, 1950, at that of the Chemical Society of Japan in April, 1951, and at the Second Congress of the International Union of Crystallography at Stockholm in July, 1951.

2) Part II: R. Kiriyama and H. Ibamoto, This Bulletin, **27**, 317 (1954).

3) H. Brasseur and A. de Rassenfosse, *Z. Krist.*, **101**, 389 (1939).

4) Part I: R. Kiriyama and H. Ibamoto, This Bulletin, **27**, 32 (1954).

5) A. Ferrari and L. Cavalca, *Periodico Mineral*, (Rome), **17**, 125 (1948); *Structure Reports* for 1947–1948, Vol. **11**, 355.

Result

(a) **$K_2SnCl_4 \cdot H_2O$**. The permittivities of this rhombic crystal are as follows: $\epsilon_a = 7.3$, $\epsilon_b = 10.1$, $\epsilon_c = 10.0$ (at 15°C; at 5 kc and 3 Mc). There are no dielectric dispersion at a room temperature on the transparent crystals, but a considerable dispersion along the *c*-direction and small dispersion along the *a*-direction are observed with the translucent crystals. Moreover, of the milky-white, opaque crystals the permittivities can not be measured in every direction of the principal axes owing to remarkable conduction.

Thus we have performed further measurements using the transparent crystals throughout the present experiment and the results for somewhat imperfect crystals will be quoted only in comparison with those for the perfect, that is, the transparent ones.

The temperature dependences of the permittivities and the dielectric losses are plotted in Fig. 1. While the values of permittivities

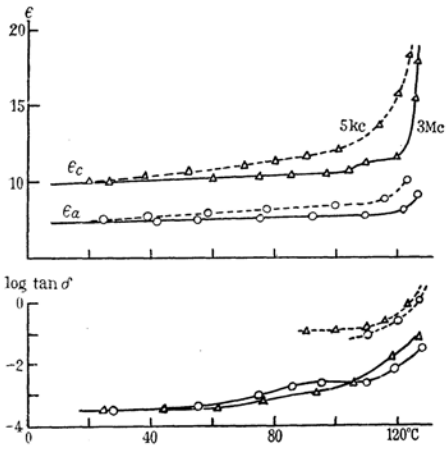


Fig. 1. The temperature dependences of the dielectric behaviour of $K_2SnCl_4 \cdot H_2O$.

are found reproducible in every repeated experiment, the temperature at which considerable dielectric losses appear becomes somewhat lower for every successive experiment. There are distinct dielectric dispersions at higher temperatures, a little along the *a*-axis and considerable along the *c*-axis, between 3 Mc and 5 kc as seen in Fig. 1.

The temperature coefficients of the permittivities $\frac{1}{\epsilon}\left(\frac{d\epsilon}{dT}\right)$ in the temperature range between 20° and 100°C are:

along *a* 6×10^{-4} (3 Mc), 14×10^{-4} (5 kc);
along *c* 6×10^{-4} (3 Mc), 23×10^{-4} (5 kc).

(b) **$Ba(NO_2)_2 \cdot H_2O$**. The room temperature permittivities at 3 Mc and 5 kc are: $\epsilon_a = 8.1$, $\epsilon_c = 7.4$. These values are equal in the limit of experimental error to those at 3 Mc previously reported.[6]

Their temperature coefficients are as follows: along *a* 3×10^{-4}, along *c* 6×10^{-4} in the temperature range between −170° and 80°C.

Up to about 90°C where the dehydration occurs, the permittivities increase monotonously and above 90° the slope of the ϵ-*T* curve becomes a little steeper than below and at about 100° the values increase rapidly owing to the surface conduction originated by the dehydrated water molecules. The temperature dependence at 3Mc, as an example, is shown in Fig. 2.

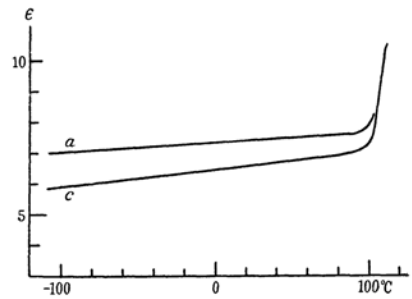


Fig. 2. The temperature dependences of the permittivities of $Ba(NO_2)_2 \cdot H_2O$.

Discussion

(a) **$K_2SnCl_4 \cdot H_2O$**. The anisotropy of the permittivities at room temperature is rather small and the direction of the maximum polarization is in the direction of the *b*-axis and not the *c*-axis. The refractive indices of this crystal were measured by us by means of the minimum deviation method using the prisms obtained by cutting and polishing the transparent, single crystals. The indices and other optical properties are listed in Table I.

TABLE I
OPTICAL CONSTANTS OF $K_2SnCl_4 \cdot H_2O$
Optically negative, axial plane—*b* (010), acute bisectrix—*a*-axis, (*a*-axis—*X*, *b*-axis—*Y*, *c*.axis—*Z*)[7]

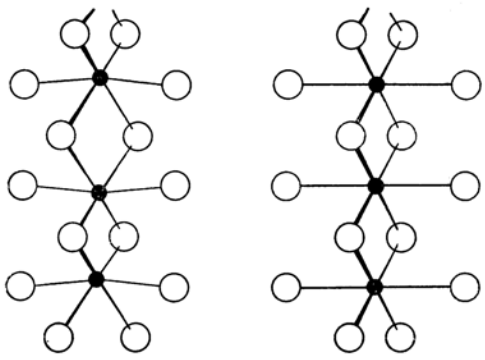
	589mμ	546mμ	436mμ	ε
n_a (α)	1.672	1.685	1.732	7.3
n_b (β)	1.693	1.707	1.752	10.1
n_c (γ)	1.749	1.757	1.798	10.0

It is probable that the direction of the maximum optical polarization coincides with that of the crystallographic *c*-axis because of the dense arrangement of chlorine atoms forming $(SnCl_4)_\infty$ chain along the *c*-axis. However, in spite of its chain-like arrangement of $(HgCl_4)_\infty$ along the *c*-axis, the crystal of $K_2HgCl_4 \cdot H_2O$ does not direct the

maximum optical polarization to that axis.[2] Moreover, it is noticeable that the maximum dielectric polarization of this tin salt occurs in the direction of the *b*-axis and not in the *c*-axis whereas in the case of the mercury salt its ϵ_c has much larger value than the others, ϵ_a and ϵ_b.

According to the analyses of the crystal structures, the mercury salt belongs to space group *Pbam*-V_h^9 but the tin salt to *Pbnm*-V_h^{16} in spite of the very similar atomic arrangements.[8,3] However, the results of the proton nuclear magnetic resonance absorption experiments of these crystals suggest that the space group of the tin salt is not *Pbnm* but *Pbam* which is identical with that of the mercury salt.[9] Therefore, it is confirmed that these two salts are not only isomorphous morphologically but also isostructural with each other.

The main difference of the atomic arrangements of these crystal structures is that the tin atom is surrounded by six chlorine atoms in a deformed octahedron; four are near and two in horizontal are distant, taking the *c*-axis as the vertical direction, while the chlorine octahedron surrounding the mercury atom in the mercury salt is much more deformed than that of the tin salt, namely the almost horizontal two chlorines are near, the other two are remote and the remaining two are more distant (Fig. 3).



$(HgCl_4)_\infty$ $(SnCl_4)_\infty$

Fig. 3. The difference of the atomic arrangements between $(HgCl_4)_\infty$ and $(SnCl_4)_\infty$ chain contained in $K_2HgCl_4 \cdot H_2O$ and $K_2SnCl_4 \cdot H_2O$ respectively.

From these different metal-chlorine distances, it may be concluded that, on the one hand, the two long horizontal Sn-Cl bonds in the $SnCl_6$-octahedron are almost purely ionic and the remaining four are much more covalent than these, and, on the other hand, two short horizontal Hg-Cl bonds in the deformed $HgCl_6$-octahedron are much more covalent than the remaining four Hg-Cl bonds which may be ionic. The electron cloud of a chlorine atom in such a partially ionic, covalent bond as in the oblique Sn-Cl or in the horizontal Hg-Cl may be much more polarizable than that in the purely ionic metal-chlorine binding. Owing to this polarizing effect, the electronic polarization of the tin salt in the vertical direction will become much larger than that expected simply from the dense arrangement of chlorine atoms along the *c*-axis in the form of $(SnCl_4)_\infty$-chain. On the contrary, the electron cloud of the chlorine atoms in the mercury salt may be more polarizable in the horizontal Hg-Cl direction and less in the oblique ones for light waves. As the result of this polarizing effect, the electronic polarization in the horizontal plane (the maximum refractive index γ is equal to 1.699, which lies along the *b*-axis) may become slightly superior to that in the direction perpendicular to this plane (along *c*, $\beta = 1.678$) overcoming the polarization effect of the dense arrangement of the chlorine atoms in $(HgCl_4)_\infty$-chain parallel to the *c*-axis. These are the principal causes of the essential difference of the optical anisotropies between two isostructural crystals.

By the way, it has been recognized generally that the more ionic the bond nature, the larger the atomic polarization or the infrared polarization. From this point of view, it may be assumed that the value of the atomic polarization of the tin atom in the tin salt may be maximum in the direction of the *b*-axis along which the largest component of the ionic Sn-Cl binding is directed. Owing to this large atomic polarization, the direction of the maximum deformation polarization will tend to the *b*-axis overcoming the considerably large electronic polarization along *c*. On the contrary, in the case of the mercury salt, the large atomic polarization of the mercury atom along the *c*-axis in the deformed chlorine-octahedron will contribute greatly to the deformation polarization as discussed in the previous paper[2] and the electronic polarization perpendicular to this axis will make less contribution to the whole deformation.

6) R. Kiriyama, *Kagaku*, **17**, 239 (1947) (in Japanese).
7) P. Groth, *Elemente d. physik. chem. Krystallogyaphie*, 171 (1921).
8) C. M. MacGillavry, J. H. de Wilde and J. M. Bijvoet, *Z. Krist.*, **100**, 212 (1938).
9) J. Itoh, R. Kusaka, Y. Yamagata, R, Kiriyama and H. Ibamoto, *J. Phys. Soc. Japan*, **8**, 293 (1953).

polarization, then the direction of the maximum deformation polarization will agree with the *c*-axis.

The temperature dependences of the permittivities of this tin salt are plotted in Fig. 1, where ϵ_b is omitted as its curve runs almost precisely on that of ϵ_c especially below 100°C. There are distinct dispersions of the permittivities above the room temperature, but there is no anomalous behaviour such as seen in the mercury salt, and the permittivities and the dielectric losses increase monotonously until the dehydration occurs, and at the dehydration temperature the permittivities increase suddenly as the ordinary hydrated salts.[4]

The result of the thermal analysis shows that there are no peaks up to the dehydration temperature 127°C, and this temperature is fairly coincident with that of the sudden increase of the permittivities 125°C. Moreover, the X-ray oscillation photographs taken at various temperature show that there are no structural changes between a room temperature and 125°C.

Thus we may conclude that the water molecules at the cocoon-shaped interstitial positions can move slightly as the temperature rises above about 105°C. This temperature corresponds to the point of inflection on the ϵ_c-T curves at 3 Mc (Fig. 1). And it is also concluded that from the temperature dependence and the frequency dependence of the permittivities and the dielectric losses the potential barrier against the dipole orientation of the water molecules will be lowered gradually as the temperature rises up to 125°C. And at this temperature the crystal lattice begins to collapse and then the dehydration through the breaking lattice takes place intensely.

In the case of the translucent crystal, the permittivities and the dielectric losses are much larger than those of the perfect, transparent crystal, especially in the *c*-direction. It may be also concluded that there are some lattice defects and the water molecules have some chances to form chain-like molecular clusters in the *c*-direction as assumed in the case of the high temperature form of $K_2HgCl_4 \cdot H_2O$.[2] The larger values of the permittivities along the *c*-axis and the irreproducibillity of them in the translucent crystal of the tin salt may be explained by this model. The remarkable conductivity found in the measurement for the opaque crystal of the tin salt may be attributed to the electrolytic conduction of the saturated solution contained in crystals as the form of liquid inclusion.

(b) $Ba(NO_2)_2 \cdot H_2O$. There are no appreciable dielectric dispersions up to the dehydration temperature in barium nitrite monohydrate. Moreover, the proton magnetic resonance absorption experiment using single crystals carried out by us shows that the water molecules are fixed in the crystal lattice at room temperature and no indications of the protonic movements in the lattice can be detected.[10] Thus, we may conclude from the results of the dielectric measurement that the water of crystallization in such monohydrates as $K_2HgCl_4 \cdot H_2O$, $(NH_4)_2HgCl_4 \cdot H_2O$ and $K_2SnCl_4 \cdot H_2O$ or $Ba(NO_2)_2 \cdot H_2O$ is not movable in the open space of the crystal lattice in spite of the zeolitic feature presumed from the position of the water-oxygen but that it orientates itself into a fixed direction stabilizing the crystalline field by its dipole moment. However, it is noticeable that the imperfect crystals of these substances have often tunnel-like capillaries and the water molecules enclosed in these capillaries will show various kinds of anomalous dielectric behaviour even at room temperature. From these considerations, it will be rather important to reexamine the behaviour of the so-called "zeolitic water" in the hydrated crystals, which might have been misjudged owing to some imperfections of their crystals used for the thermal or dielectric experiments.

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10) J. Itoh, R. Kusaka and R. Kiriyama, *J. Phys. Soc. Japan* (in press).