Dielectric Behaviour of Crystalline Pentaerythritol

By Ryoiti KIRIYAMA, Shigeru YABUMOTO and Isamu NITTA

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Introduction

The crystal structure of tetragonal pentaerythritol shows a particular arrangement of hydrogen bonds, these lying in the plane perpendicular to the tetragonal axis and forming a closed square configuration.[1] Owing to this arrangement, exceptionally perfect cleavage parallel to this plane appears.

Therefore, this crystal seems to be an adequate case where the dielectric behavior of a hydrogen bond might be elucidated in respect to its anisotropic nature. Moreover, this tetragonal modification transforms at 188°C. to a cubic one, which is looked upon as an example of the so-called plastic crystals and it has been assumed that the hydrogen bonds in a closed square configuration of the low modification are likely to be broken suddenly, at least partly, at transformation temperature.

From the X-ray and thermal studies,[2] it has been concluded that in the high modification, pentaerythritol molecules will rotate about their centers of gravity with some internal rotations of constituting radicals. If such radical and molecular rotations will occur in the crystal lattice, they must be observable in some dielectric behaviours, in addition to the existence of the non-zero dipole moment of the molecule revealed by the molecular beam method carried out by Estermann.[3] Thus we have studied the dielectric behaviours of pentaerythritol in both low and high modifications.

This paper contains the results of the experiment together with some discussion about the nature of the so-called atomic polarization of the hydrogen atom in hydrogen bond and the role of rotating hydroxyl radicals in the dielectrical phenomena.

Material

About 1 kg. of fairly pure pentaerythritol powder was purified by recrystallization several times from its aqueous solution and we obtained about 500 g. of a sufficiently pure sample with melting point 257°C.

The growth of a large single crystal suitable for the anisotropy measurement of its dielectric properties was difficult to achieve to a certain extent on account of spontaneous nucleation or germination of conidiospore frequently occurring in its solution during the growth-process. After various attempts, we have succeeded in obtaining single crystals suitable for these measurements by slow cooling of a supersaturated aqueous solution filled in a sealed glass-vessel, on the bottom of which a seed crystal had been laid beforehand. The optimum temperature region was 60~65°C. and the cooling-rate was several degrees in 3—4 weeks. We have successfully obtained single crystals more easily than the above mentioned by improving a thermostat as seen in Fig. 1. The temperature of this thermostat was maintained constantly at a point between 60~65°C. and the upper end of the copper rod dipped in an ice-filled Dewar vessel was brought into contact with the bottom of the solution vessel in such a way that the seed placed inside came just above the upper end. This then gave rise to some slow convection currents downwards meeting onto the seed, thus the crystal grows up satisfactorily several times faster than in the case of the above procedure.

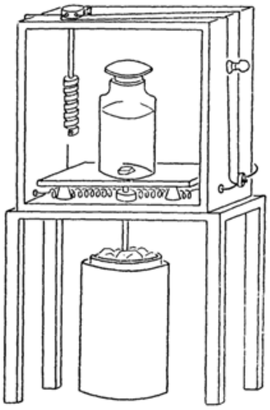

Fig. 1. The thermostat for preparing a large single crystal of pentaerythritol using convection current arised in the solution by strong temperature gradient at the bottom of the glass vessel

The specimens have been prepared from such crystals by cutting and grinding to plates of 1.1~1.8 mm. thick and 1.2~2.0 cm². in area and affixing aluminum or tin foils of 1×1 cm². on both their

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[1] I. Nitta and T. Watanabé, *Sci. Papers Inst. Phys. Chem, Research* (*Tokyo*), **34**, 1669 (1938); E. G. Cox, F. J. Llewellyn and T. H. Goodwin, *J. Chem. Soc.*, **1937**, 882.

[2] I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26** (9), 25 (1950); I. Nitta, S. Seki, M. Momotani, K. Suzuki and S. Nakagawa, ibid (10) 11; I. Nitta, T. Watanabe, S. Seki and M. Momotani, ibid (10) 19).

[3] J. Estermann, *Z. physik. Chem.*, B**2** 287 (1929), B**20** 195 (1933).

sides using vacuum grease or vaseline or sometimes coating with aquadag.

Apparata and Measurements

In the high frequency region two sorts of resonance circuits were used in the present experiment. The one is constructed of a push-pull oscillator of 30 Mc and a variable precision-condenser of 50pF in the resonance circuit in which the current is measured by means of a crystal detector and a microammeter. The other is composed of either quartz oscillator of 600 kc or 3 Mc and a coupling resonance circuit with a variable precision-condenser of 500 pF, the resonance being detected as above. In order to follow quickly the change of temperature, we read equivalent resistance from the lowering of the microammeter reading calibrated previously by substitution method.

In audio-frequencies, a capacity-resistance bridge was constructed suitable for the measurements, especially for high dielectric losses in the high temperature modification. In this bridge, the oscillator is an RC type one and the balancing is attained by a variable precision-condenser of 1500 pF, a set of variable non-inductance dial type resistance and a number of fixed condensers and resistances which are used to change arm-ratios. To detect the balancing, a set of crystal detector and galvanometer or a Brown-tube oscilloscope with preamplifier was used, the dielectric losses being calculated from the observed data.

The crystal condenser used for the accurate capacity measurement at room temperature was carefully constructed to have almost no stray capacity. The dielectric constant was determined from the ratio of the capacity of the sample to that of rock salt plate with the same thickness. This rock salt single crystal was made by Stockbarger's method in this laboratory. The standard dielectric constant adopted for rock salt was 5.62 throughout this study.

The cell for the measurement of the temperature dependence was made of a copper cylinder and a small-stray-capacity crystal condenser as shown in Fig. 2. The temperature was measured by a copper-constantan thermocouple with a millivoltmeter.

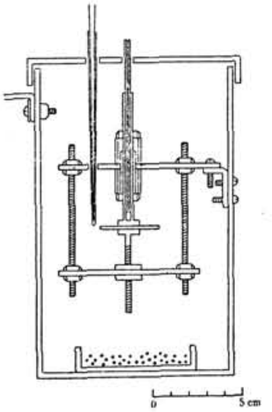

Fig. 2. The measuring cell for the dielectric constant and loss of the high-temperature modification of pentaerythritol

In order to avoid sublimation and decomposition of the sample at high temperatures, we have covered the bottom of the cylinder with pentaerythritol powder and raised the temperature somewhat rapidly, the rate being about 0.7°C. per minute.

For the measurement of direct current (D. C.) conductivity, the specimen was coated with aquadag, then dried at about 110°C., and the measurement carried out using a Wheatstone bridge with a battery of 4V. For the purpose of avoiding the effect of electrolytic polarization in the specimen, the successive readings were at longer intervals and the field direction was altered every time.

Results

The dielectric constants at room temperature for the respective field directions parallel to the *c*- and *a*-axes of the crystal are as follows:

$$\epsilon_c = 2.89, \text{ and } \epsilon_a = 3.7,$$

at frequencies from 5 kc to 30 Mc and at 17°C., where ϵ_a is calculated from the value 3.37 of the plate measured perpendicular to the natural *o*(111) plane. Thus these values show no appreciable dispersion. It may be added that the dielectric losses are too small to be observed in our experiments for the mentioned region of frequencies at room temperature.

Up to the transition point, there is no appreciable temperature dependence of these dielectric phenomena at every frequency. Even at about 130°C. where a small anomaly of its specific heat curve has been reported in a previous paper,[2] there is observed nothing anomalous in the present dielectric study.

On heating a single crystal specimen through and above the transition point, its dielectric constant and loss both increase suddenly as shown in Fig. 3.

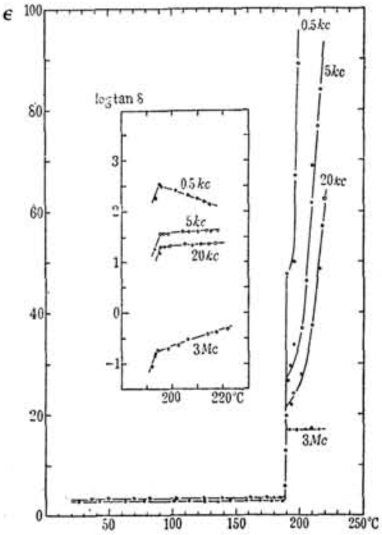

Fig. 3. Temperature dependences of the dielectric constants and losses of pentaerythritol in both low- and high- temperature modifications

The dielectric behaviour of the high temperature modification was carefully measured up to 220°C. at the above-mentioned frequencies except for 0.5kc, at the latter frequency the measurement became somewhat uncertain because of the scaling out of the instrument. As seen in Fig. 3 a remarkable dielectric dispersion in the audio-frequency region appears. And, it is worth noticing that the measured capacities of the specimens with the metal foils are always considerably larger than those coated with aquadag at every temperature as well as frequency.

At the transition point, dielectric losses appear suddenly at every frequency used, and above it they increase rapidly with temperature. In audio frequencies, the loss of a metal-foiled plate is higher than that of an aquadag-coated plate but in high frequencies such a phenomenon was not observed. The frequency dependence of the dielectric constants and losses is shown in Fig. 4.

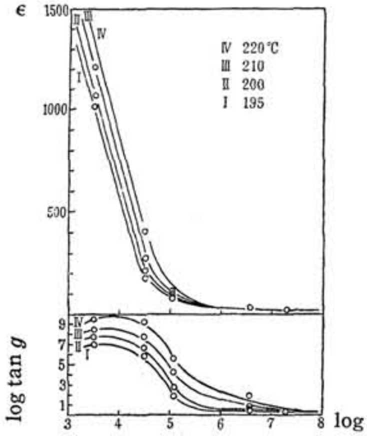

Fig. 4. Frequency dependences of the dielectric constant and loss of the high-temperature modification of pentaerythritol

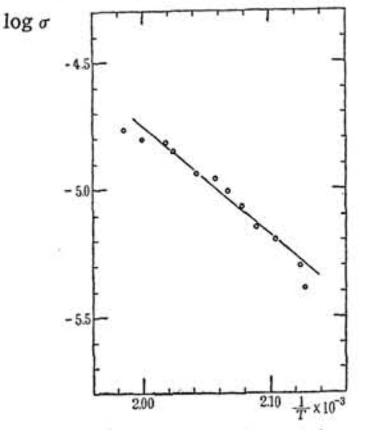

Fig. 5. Specific conductivities of pentaerythritol crystal at various temperatures

The specific conductivities at various temperatures are plotted against reciprocals of absolute temperatures in Fig. 5. In spite of inaccuracy of the D.C. conductivity measurements, many points are distributed in the form of a straight line. The value of the conductivities are unexpectedly large compared with those of ordinary molecular crystals.

Discussion

I. The Low Temperature Modification (tetragonal form)

Refractive indices and their temperature dependences were measured formerly by one of the authors (Kiriyama).[4] The values at room temperature, listed in Table I,[4] agree fairly well with those quoted in Groth's Chemische Krystallographie. This crystal is optically negative, refractive indices n_ω and n_ϵ corresponding to n_a and n_c repectively, of which their suffixes respresent the directions of the electric field of the light wave. In Table II the squares of the refractive indices, extrapolated to infinitely long wave length by Cauchy's dispersion formula, are given in comparison with corresponding dielectric constants. The latter are appreciably larger than the former in both directions. These differences may be attributed chiefly to the socalled atomic polarization of a hydrogen bond, the O-H···O system, or roughly speaking, ionic polarization of a proton of the system.

TABLE I

REFRACTIVE INDICES OF PENTAERYTHRITOL

λ(mμ)	n_ω	n_ε
486	1.5628	1.5218
589	1.5559	1.5146
659	1.5537	1.5109

TABLE II

DIELECTRIC CONSTANTS AND SQARES OF REFRACTIVE INDICES OF PENTAERYTHRITOL

ε_a	3.7	n_a^2	2.38
ε_c	2.89	n_c^2	2.24

From our previous studies on the double refraction of the tetragonal molecular crystal (Nitta)[5] and the above-mentioned temperature dependence of the double refraction of the present crystal (Kiriyama)[4], it was found that the Lorentz-Lorenz relation held approximately for the present crystal and the observed temperature dependence was primarily due to the anisotropic thermal expansion of the lattice, there being no evidence that the electronic polarization of the molecule itself had changed with the temperature.

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[4] Read before the annual meeting of the Chemical Society of Japan (1939).

[5] I. Nitta, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **37**, 114 (1940).

Thus assuming that the Lorentz-Lorenz and Clausius-Mosotti formulae hold goods, we obtain somewhat formally the two components of the atomic polarization per mole to be approximately,

$$P_{Ac}=9.1\,\text{cc.} \quad \text{and} \quad P_{Aa}=15\,\text{cc.}$$

which correspond to 24 % and 34 % of the total polarization P_T($P_{Tc}=38$, $P_{Ta}=46$ cc.) in each direction. The fact that we have still a considerable amount of P_{Ac} and P_{Aa} will imply that the hydrogen bond is largely of the ionic nature and relative displacement of the hydrogen atoms or protons induced by the external field will be considerable, being more in the case of P_{Aa}. In this connection it will be interesting to reexamine the experimental result of the infra-red study carried out by Ellis and Bath for this crystal.[6]

The temperature dependence of the dielectric constants up to the transition point is negligibly small in spite of the large expansion coefficient along the *c*-axis.[2] This may be explained by the cancellation of the decrease of the dielectric constants due to decreasing density by the increase of ionic polarization due to the increasing thermal loosening of the lattice. It may be added that, according to Bayley's low temperature observation,[7] this substance shows no significant dielectric change in the region from -100° to 0°C. which is outside of the region of our experiment.

II. The High Temperature Modification (cubic form)

The high temperature form is isotropic and it is one example of the so-called plastic crystals, resembling the liquid state in many points. The molecule possesses statistically a mean shape of cubic or spherical symmetry owing to the internal rotation around the C–C and C–O bonds as well as finite or infinite possible molecular orientations.

At higher temperatures than the transition point, the dielectric phenomena are somewhat unusual. The large dielectric constant and losses as well as their remarkable temperature dependences at audio frequencies are evidently due to the D.C. conduction, as confirmed by the directly observed large D.C. conductivity. Similar phenomena have been observed with long chain alcohols and monoglycerides.[8] Their abnormally high dielectric constants with dispersion in the solid phase decrease by a considerable amount at the melting points and show no dispersion effects in the molten state. However, in the present case of pentaerythritol we could not extend such measurement because of the considerably rapid decomposition as well as sublimation near the melting point.

The observed conductivity must be due to a kind of protonic transfer. From the temperature dependence of the D.C. conductivity σ, the activation energy E is estimated to be roughly 20kcal./mole assuming the usual relation $\sigma=A\exp(\text{-}E/RT)$. This energy value is appreciably larger than that of ice which is estimated to be about 10 kcal./mole. It is interesting to notice that, while the latter is approximately equal to the heat of sublimation, the former value, 20 kcal./mole, is again nearly equal to the heat of sublimation of pentaerythritol in the high temperature modification as has been measured in this laboratory.[9] Thus, formally speaking, in regard to the electrical conduction it seems as if the molecule which has approximately the same energy as in the vapour state plays some role in transporting the protonic charge. It should be added that in the measurement of the dielectric constant we obtained greater values in the case of the specimen plate metal-foild with vaseline or vacuum grease than in the case when it was coated with aquadag. The higher value is thus due to the interfacial polarization of accumulated protons caused by the high resistance of vaseline or vacuum grease.

The appreciable dispersion effect in these audio frequency regions is not observed any more in the high frequency region (600kc to 30Mc). This will mean that the time of relaxation concerning the transport of the protonic charge is by far larger than the period of these alternating fields. Nevertheless the dielectric constant of the high temperature modification at these high frequencies is still considerably greater than that of the low temperature modification. This fact is due to the acquisition of a dipole moment of pentaerythritol molecule arising from the internal molecular rotation above the transition point, the molecule in the tetragonal from having the symmetry of S_4-$\bar{4}$, and thus no dipole moment. This supports qualitatively the conclusion of the X-ray study already mentioned. Moreover the time of relaxation for the dipole orientation may have something to do with that of the internal rotation and be considerably shorter than the applied high frequencies. It is also interesting to notice

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[6] J. W. Ellis and J. Bath, *J. Chem. Phys.*, **7**, 862 (1939); *cf.* E. F. Westrum, Jr. and K. S. Pitzer, *J. Amer. Chem. Soc.*, **71** 1940 (1949).

[7] S. T. Bayley, *Trans. Faraday Soc.*, **47**, 518 (1951).

[8] Y. Kakiuchi, *Proc. Japan Acad.*, **23**, (6) 65 (1947); J. D. Hoffman and C. P. Smyth, *J. Amer. Chem. Soc.*, **71**, 431 (1949); R. W. Crowe and C. P. Smyth, ibid., **72** 4427 (1950).

[9] I. Nitta, S. Seki and K. Suzuki, This Bulletin, **24**, 63 (1951); P. G. Owsten, *Quart. Rev.*, **5**, 344 (1951).

that as far as our measurement covers the dielectric constant it remains almost unchanged at various temperatures.

From the formal application of the well-known Debye formula[10] for the orientation polarization using the dielectric constant 16.7 and the refractive index 1.439 calculated from the average refractive index of the low temperature form and the volume change at the transition point, the dipole moment of the molecule in the crystal at 200°C. was calculated to be 1.8D, which agrees fairly well with Estermann's value 2D obtained by the molecular beam method, though these should not be compared with the other directly. Another formal application of the Debye formula for hindered dipole rotation,[11] assuming the Estermann value 2D we obtain for the hindering potential $U=1.3$kcal./mole so as to be able to account for the peculiar behaviour when the dielectric constant remains approximately the same in the high temperature region.

Evidently the two Debye formulae used above are not satisfactory in respect to the consideration of the reaction field. If we next use the formula of Onsager[12] we obtain the moment in vacuum $\mu_v=3.9$D which is by far greater than Estermann's and will mean that all the local dipole moments in the molecule orientate themselves to a considerable extent in the same direction. This difficulty comes out of course from the neglect of the short range interaction. Thus we come now to the Kirkwood formula for polar liquid.[13]

$$\epsilon_s-n^2=\frac{3\epsilon_s}{2\epsilon_s+n^2}\left(\frac{n^2+2}{3}\right)^2\frac{4\pi}{3}\frac{\mu^2{}_vN_0}{kT}(1+z\cos\gamma)$$

where $\cos\gamma$ is the averaged cosine of angles between nieghbouring dipoles and z is the number of the nearest nieghbours which is in the present case equal to 12. Substituting the following numerical values for the static dielectric constant $\epsilon_s=16.7$ and $\mu_v=2\times10^{-18}$, we obtain $\cos\gamma=0.244$. In the case of water the value of $\cos\gamma$ is equal to 1/3, assuming the free rotation of one of the OH bonds of water molecule about the other OH bond which is fixed in a direction towards the neighbouring oxygen atom.[14] Hence the value 1/4 would mean that the short range interaction can not be neglected. It would be better not to go further in detail because of the difficulties as follows; the molecules in the cubic form carrying out complicated internal rotations which cause the dipole moment of the molecule as a whole change from time to time, thus the theories of Onsager and Kirkwood are not directly applicable to the present case, in which the statistical average of short range interactions due to changing dipole moment is very difficult to compute with accuracy.

Department of Chemistry, Faculty of
Science, Osaka University,
Nakanoshima, Osaka

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10) P. Debye, "Polare Molekeln" Leipzig, 1929, p. 27.

11) P. Debye, *Physik. Z.*, **36**, 160 (1935); *Chem. Rev.* **19**, 171 (1936).

12) L. Onsager, *J. Amer. Chem. Soc.*, **58**, 1486 (1936).

13) J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

14) J. G. Kirkwood, *Trans. Faraday Soc.*, **42**, 7 (1946); *cf.* H. Fröhlich, "Theory of Dielectrics", Oxford, 1949, P. 140.