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Infrared and Permittivity Studies on Alkali Perchlorates

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The infrared spectroscopic studies and the dielectric constant measurements during the orthorhombic to cubic transformation of $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ are reported here to investigate the possibility or not of rotation of ClO_4^- in the cubic form. The multiplicity of ν_3, the triply degenerate stretching frequency, change at T_t as it should go from a triplet to a singlet when the crystal structure changes from *Cmcm* to $F\bar{4}3m$. The symmetric stretching frequency of ClO_4^- is active in *Cmcm* but symmetry forbidden in $F\bar{4}3m$. At the respective transition temperature there is a sharp increase in the dielectric constants of these perchlorates proving the transition to be of order–disorder type with the possibility of rotation of ClO_4^- at least in $NaClO_4$ and $KClO_4$, but involves the discontinuity of properties characteristic of a first-order transition

Introduction

The alkali perchlorates, namely, $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ exist in dimorphic forms. The low temperature forms in all of these are of orthorhombic structure while the high temperature structures are cubic. The transformation from the orthorhombic to the cubic structures in $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ takes place at 310, 300, 278, and 221°C, respectively (*1*, *2*). Bredig (*3*), without any experimental evidence, suggested that these transformations are brought about due to the onset of rotation of ClO_4^- ions. The heats of transformation were estimated by DTA (*2*). No further information on these transformations is available. We have made an attempt to understand the mechanism of this structural transformation based on dielectric constant measurements and infrared spectroscopic investigations to consider the possibility or not of rotation of ClO_4^- in the cubic form.

Infrared spectroscopy has been fruitfully used for the study of the transformations of KNO_3, $NaNO_3$, KNO_2 and $K_2Cr_2O_7$ (*4–7*) as the absorption bands show marked variations during a transformation. So far no attempt was made to investigate the spectral changes during the transformation of alkali perchlorates from the orthorhombic to the cubic structure, although the infrared and Raman spectra of perchlorates have been studied and assignments made by Herzberg (*8*). Also, infrared spectra of polyatomic ions, such as CN^-, NO_2^-, NO_3^-, and OCN^-, isolated in alkali halides crystals have been studied by several authors (*9–12*).

Dielectric studies have been primarily responsible for revealing numerous exceptions whose importance is considerable in terms of both structural information and technical application. Although other physical properties such as specific heats, and especially heats and entropies of fusion, point clearly to molecular rotation, dielectric studies have perhaps contributed the greatest insight into this molecular behaviour. Dielectric constant measurements have been used for the transformation studies in solid HCl, HBr, HI (*13*), H_2S (*14*), $BaTiO_3$ (*15*), Rochelle Salt (*16*), NH_4Cl, NH_4Br, NH_4I (*17*, *18*), and NH_4NO_3 (*19*). Like the hydrogen halides, the organic

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rotator-phase molecules, e.g., camphor (*20*), thiourea (*21*), dimorphous solids as *n*-octadecane, *n*-octacosane, dicetyl, and dodecyl alcohol (*22*) etc. are also studied.

Experimental

Analar grade $NaClO_4$ and $KClO_4$ were twice recrystallized from distilled water. $RbClO_4$ and $CsClO_4$ were prepared from AR grade Rb_2CO_3 and Cs_2CO_3 by the action of 60% $HClO_4$ and the perchlorates were recrystallized four times with distilled water. The samples were dried at 180°C for 2 days. The materials were analysed by precipitation as nitron perchlorate (*23*) and the reagents were found to be better than 99.95% pure.

The infrared spectra of the specimens in the frequency range 4000–650 cm^{-1} were taken in the KBr matrix by holding the pellets in position by the retainer rings in the high-temperature cell for infrared spectroscopy, described earlier (*24*) for use in the Hilger and Watts H800.306 spectrophotometer.

For studying the variation of the real part of the dielectric constant with temperature during phase transformation studies the elimination of stray capacitance is of vital importance as the crystal capacitance is of the order of a few picofarads. A specially designed cell which permits measurements of even small capacitances over a range of temperatures was used. Wayne Kerr Universal Bridge B221A with Autobalance Adaptor AA221 was employed for measuring capacitances. A chromel–alumel thermocouple was used to measure the temperature of the specimen.

The samples were powdered and compressed into disc-shaped pellets, 1.6 cm in diameter and 0.15–0.25 cm in thickness, in the die of the hydraulic press under vacuum, and a pressure of 10 to 12 tons/in.^{2} was normally used. The thickness of the pellet was measured correct to 0.001 cm. Colloidal graphite (Aquadaq) obtained from Achenson colloids Ltd., London, was used as the electrode material and was coated on the two planar faces of the pellets to ensure good electrical contact with the electrodes. The electrode assembly was taken out by lifting the tube T_1 and the pellet was placed on the lower electrode *L*. The upper electrode was screwed down to form a good electrical contact with the upper surface between the electrodes, the tubes T_1 and T_2 were assembled. The temperature of the furnace was increased slowly by variation of applied voltage with dimerstat and the temperature of sample was measured with portable potentiometer of Toshniwal Instruments Pvt. Ltd., and at the same temperature the capacitance was measured with Wayne Kerr Universal Bridge B221A with Autovalance Adaptor AA221 fitted with frequency 1592 Hz.

Before measurements each sample was heated up to 350°C and cooled, 3–4 times through T_t, as this treatment was found necessary in order to obtain reproducible results. First the capacitance of cell was taken with air between the plates and then with the sample.

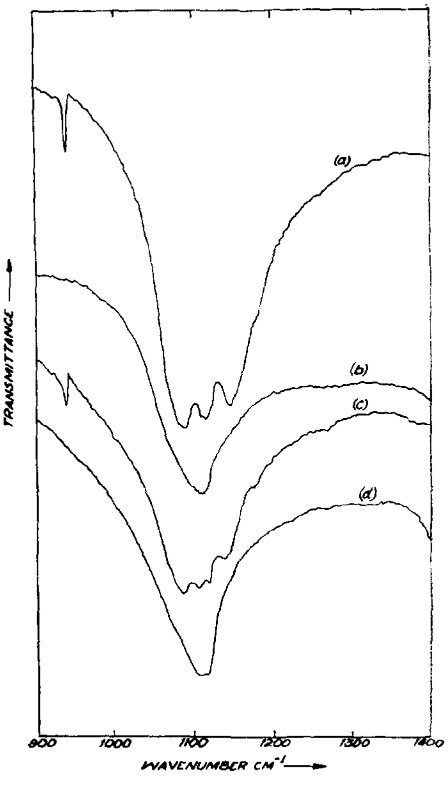


FIG. 1. Infrared spectra in KBr pellet of $NaClO_4$ at (a) 30°C; (b) 320°C; $KClO_4$ at (c) 30°C; (d) 320°C.

Results and Discussion

(a) IR Spectroscopic Investigation

The typical infrared spectra of $NaClO_4$, $KClO_4$, $RbClO_4$ and $CsClO_4$ in KBr pellet at temperatures below and above the transformation temperature are shown in Figs. 1 and 2. In the spectra of the low temperature orthorhombic form of all these perchlorates two bands are observed, namely one broad band in the frequency range 1080–1150 cm^{-1} which is ν_3, the triply degenerate stretching frequency of the ClO_4^- ion and the other one ground 935–940 cm^{-1} for ν_1, the symmetric stretching frequency of ClO_4^- (*8*). The spectra of the high temperature cubic forms of all these perchlorates have only one band around 1112–1114 cm^{-1}. An important feature is the disappearance of the band at 935–940 cm^{-1} at the transition temperature. The reversiblity of the transition can be seen from the reappearance of this band on cooling below the transition temperature though there is a slight temperature lag in accordance with our previous results by DTA studies (*2*). The multiplicity of ν_3 changes at T_t in accordance with the requirement that when the crystal structure changes from *Cmcm* to $F\bar{4}3m$, ν_3 goes from a triplet to a single (*25*). Thus, the disappearance of the triple degeneracy of the internal modes of the ClO_4^- ion, and the existence of the single band peaked around 1112–1114 cm^{-1} after the transformation, indicates the increase in the symmetry of the crystal. The increased symmetry presupposes that a rearrangement of all the axes takes place. The 935–940 cm^{-1} band in the orthorhombic phase is obviously active in the *Cmcm* but is symmetry forbidden in $F\bar{4}3m$ and it disappears in the cubic phase.

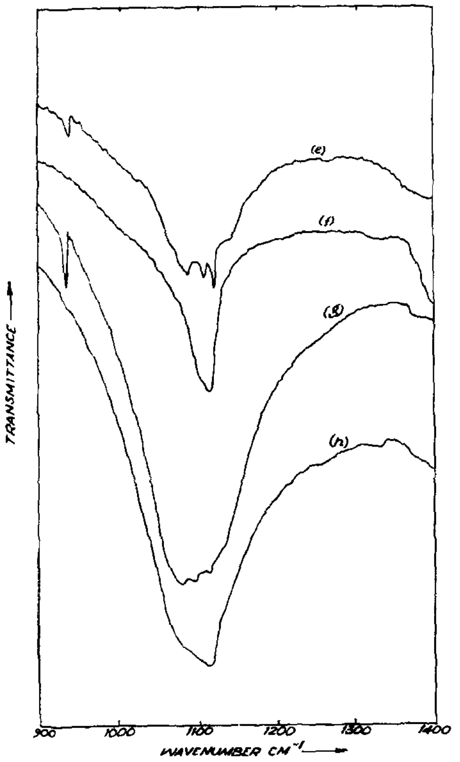


FIG. 2. Infrared Spectra in KBr pellet of $RbClO_4$ at (e) 30°C; (f) 300°C; $CsClO_4$ at (g) 30°C; (h) 300°C.

On increasing the temperature of the disc in the orthorhombic phase, every band became broader, its peak intensity decreased, and the position of the peak shifted slightly towards lower frequency, while after transition to the cubic form, no observable change in intensity and peak position is noticed. In orthorhombic form the shift in frequencies with temperature may be due to the shift of lattice constant of matrix, KBr, which is 6.60 at 25°C and increases to 6.65 at 200°C. Thus, the temperature dependence of the frequencies may be taken as one manifestation of a frequency–lattice constant relationship (*11*). The small variation of frequencies among different matrices has also been noted which also may have a similar origin.

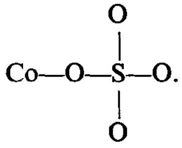
Ross (*26*), while studying the forbidden transitions in perchlorates, has given the ν_3 and ν_1 frequencies for $NaClO_4 \cdot 2H_2O$ and $KClO_4$ as (1081, 1111, 1124), 939 cm^{-1} and (1093, 1111, 1143), 941 cm^{-1} in solid perchlorates, and ν_3 for $NaClO_4$ in 0.2 *M* solution as 1105 cm^{-1}, ν_1 being absent. The free ClO_4^- of tetrahedral symmetry should have only 1102 band in ir spectra in the range 4000–650 cm^{-1}. Ross observed that the splitting of ν_3 is consistent with the loss of the T_d symmetry; there are three possible causes for this:

(i) distortion of the ClO_4^- tetrahedron in the crystal lattice;

(ii) covalent bonding of the perchlorate to the metal through one or more of the oxygen atoms,

(iii) a nonuniform field due to the water molecules round the cation.

Underhill (*28*) has observed ν_1 at 930 cm^{-1} and ν_3 as a doublet at 1025 and 1154 cm^{-1} in copper–perchlorate nitrate, and suggested that these features are due to covalent bonding of a type giving C_{3v} symmetry, with a possibility of some effect due to distortion of the perchlorate ion in the lattice. Ross (*26*) derived that in view of the known instability of covalent perchlorates (*29*, *30*) it seems unlikely that covalent bonding can contribute to any great extent; further, the observed spectra are not consistent with lowering of the symmetry merely to C_{3v}, when ν_3 would be doublets. In fact, a triplet is found for ν_3, which would imply the symmetry C_{2v}, and this would necessitate bonding of the perchlorate through two of its oxygen atoms. Nakamoto et al. (*27*) on comparing their spectra of free SO_4^{2-} and $[Co(NH_3)_5(SO_4)]Br$, attribute the appearance of ν_1 at 970 cm^{-1} to the perturbing effect of the ligand field and the splitting of ν_3 (1032–1044, 1117, 1143 cm^{-1}) to the covalent bonding with structures as



$$\mathrm{Co{-}O{-}}\overset{\displaystyle \mathrm{O}}{\underset{\displaystyle \mathrm{O}}{\mathrm{S}}}\mathrm{{-}O.}$$

Nakamoto et al. (*27*) in attributing the appearance of ν_1 to a perturbation caused by the ligand field, neglect the possibility of distortion in the crystal lattice. If the ligand field were entirely responsible for the lowering of symmetry, anhydrous perchlorates should show ν_3 as singlets and ν_1 should be absent. The presence of ν_3 as a triplet, and ν_1, in the spectra of anhydrous orthorhombic $NaClO_4$, $KClO_4$, $RbClO_4$, $CsClO_4$ show that some other factor must be involved.

Crystallographic evidence (*31*) shows that ClO_4^- tetrahedron is distorted in $KClO_4$ and other perchlorates to produce symmetry parallel to the *b*-axis and the two oxygen atoms (O_1,O_2) lying in this plane are nearer to the Cl than are the two equidistant oxygen atoms (O_3,O_4) which are not in the plane;

for $KClO_4$,	O_1–Cl	1.34 Å
	O_2–Cl	1.48 Å
	$O_3(O_4)$–Cl	1.51 Å

This shows considerable distortion compared with the value of 1.50 Å (*32*) for the Cl–O distance in regular tetrahedron.

I_{ν_1}/I_{ν_3}, the ratio of the intensities of ν_1 and ν_3, decreases with increase of temperature in the orthorhombic form till it is zero at the T_t (Fig. 3), and if distortion is directly related to the extent to which ν_1 is permitted, we can say that in the cubic form there is no distortion of the ClO_4^- tetrahedron. Thus, in orthorhombic form ClO_4^- is distorted and is bonded

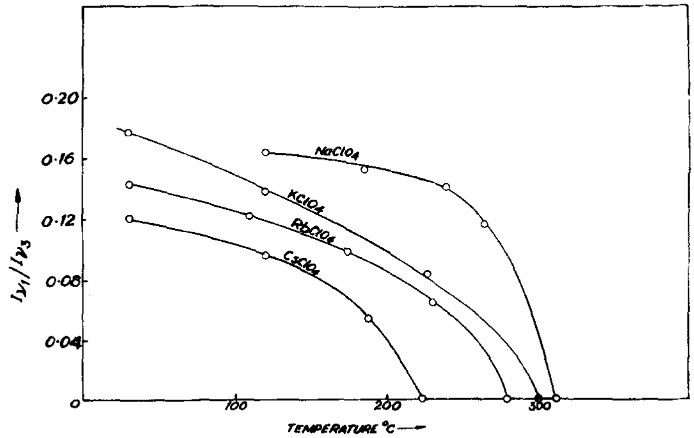


FIG. 3. Variation of $I_{\nu_1}|I_{\nu_3}$ with temperature.

to the cation (Na^+, K^+, Rb^+, Cs^+) through two of its oxygen atoms, while in the cubic form ClO_4^- is undistorted and free, thus giving the possibility of rotation of ClO_4^- in the cubic structure. As in the ir spectra of cubic form there is no change in the intensity or frequency value of ν_3 with increase of temperature, we can assume that there is free rotation of the ClO_4^- in the cubic structure of the alkali perchlorates. This is in agreement with the idea given for NO_3^- by Khanna (*4*) that if free rotation implies no interaction between NO_3^-, there should be no splitting of degeneracy and no activation of modes which are inactive for the free nitrate ion. The confirmation of this can be achieved by the dielectric constant studies as in the following section.

(*b*) *Permittivity Studies*

The capacity of a simple electric condenser of two parallel conducting plates, each of area A cm², at a distance d cm apart, is

$$C = \frac{\varepsilon A}{4\pi d}\,\text{esu} = 0.08854\frac{\varepsilon A}{d}\,\mu\mu\text{F}, \qquad (1)$$

where ε is the ratio of the dielectric constant of the medium between the plates to that of free space.

It may be determined by taking the capacitance of a condenser with vacuum (or air) between the plates as C_0 and the capacitance C of the condenser with material between the plates as εC_0, i.e.,

$$C = \varepsilon C_0 \quad \text{or} \quad \varepsilon = (C/C_0). \qquad (2)$$

Experimentally,

$$C_{\text{air}} = C_0 + C_{\text{cell}}$$

$$C_{\text{sample}} - C_{\text{air}} = C - C_0,$$

because the specially designed cell has one

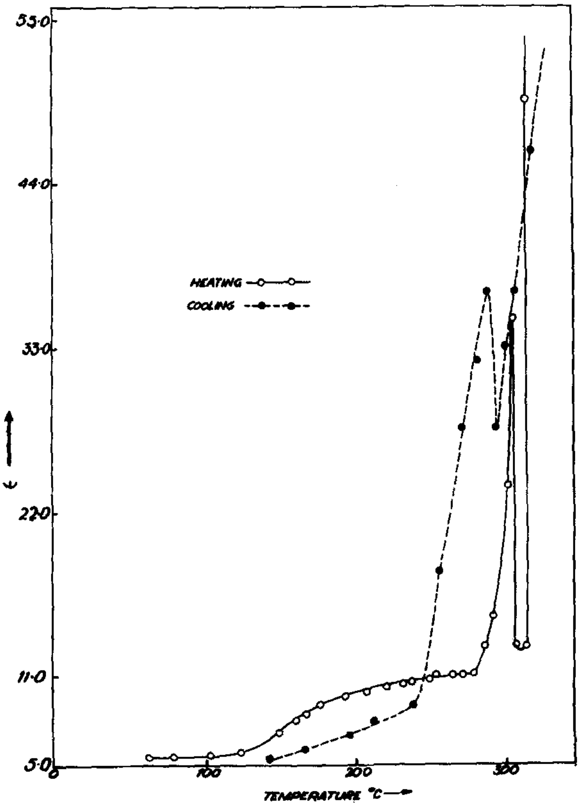


FIG. 4. Dielectric constant–temperature curve (at 1592 Hz) of $NaClO_4$ for forward and reverse transition.

pointed electrode; therefore, A is very small, d is high as compared to A; so C_0 is negligible.

$$C = C_{\text{sample}} - C_{\text{air}}. \qquad (3)$$

Thus, the difference of the capacitance values of the cell with air and sample as the medium, gives the capacitance of the condenser with sample as the dielectric.

The dielectric constant plots (ε vs T) $NaClO_4$, $KClO_4$, $RbClO_4$, and $CsClO_4$ for the temperatures below and above the transition point, T_t, are depicted in Figs. 4–7. It shows that in all these perchlorates there is a sharp increase in dielectric constant at T_t with a small increase just before T_t, though at lower temperature, the value is low and practically constant. After T_t, the nature of variation of ε with increase of temperature is found to be specific for each of the alkali perchlorates. On cooling from high temperatutes the ε of these perchlorates shows a sharp fall at T_t proving the transition to be reversible and of first-order.

Unless the molecule has spherical symmetry, one or more of its orientations in the field of force surrounding it are more stable than the other. Pauling (*38*) theoretically predicted that dielectric-constant measurements would show freedom of rotation above the transitions which are commenced by molecular rotation with rising temperature. Frenkel, Todes, and Ismailow (*34*) based an approximate treatment on the assumption that the transition from nonrotation to rotation is very sharp, so that a rotating phase and a nonrotating phase are in equilibrium at a definite transition temperature. But experimental facts gave little support to this treatment. This type of transition is sometimes called a second-order transition or lambda point, but involves the discontinuity of properties characteristic of a first order transition (*35*). Bartenev and Ramizova (*36*) suggested that the lambda curves are characteristic not only of second-order transitions but also of first-order transitions with processes of disordering. Majumdar and Roy (*37*) observed that there is superposition of second-order behaviour on many first-order transformations as in the transformations of alkali sulphates. As molecular rotation or a disordered arrangement of the molecule tends to lower the internal field, it is apt to give symmetry to a lattice. If the rotating molecule is fairly symmetric in form, the lattice is usually one which could be formed of close-packed spheres, commonly cubic or hexagonal. From the opposite point of view, if the crystal is isotropic, the potential energy of a molecule will tend to vary less with its

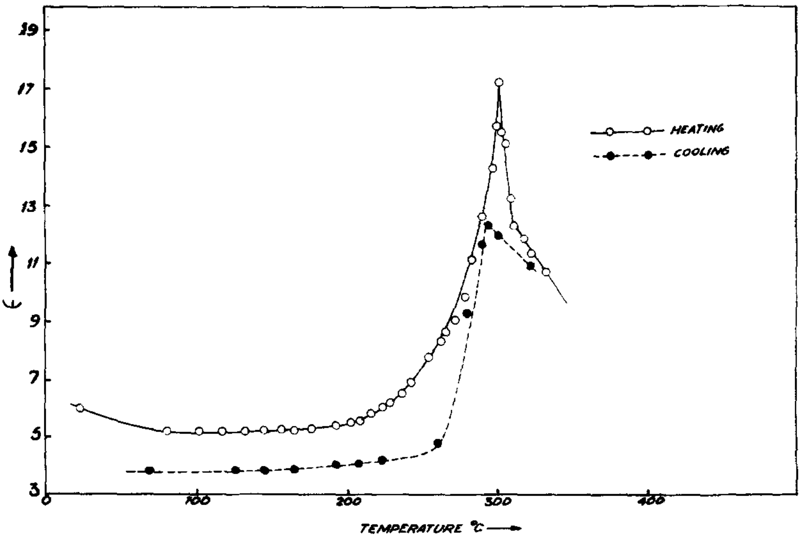


FIG. 5. Dielectric constant–temperature curve (at 1592 Hz) of $KClO_4$ for forward and reverse transition.

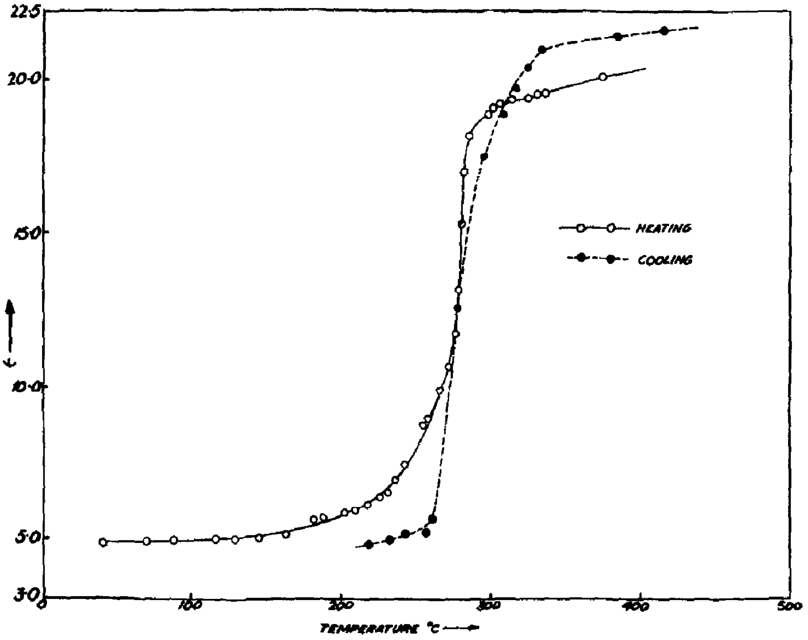


FIG. 6. Dielectric constant–temperature curve (at 1592 Hz) of $RbClO_4$ for forward and reverse transition.

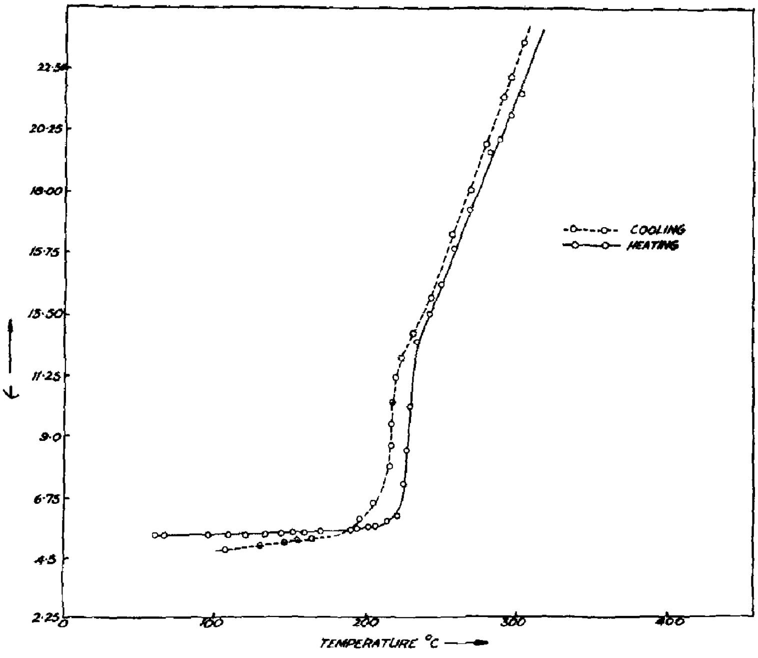


FIG. 7. Dielectric constant–temperature curve (at 1592 Hz) of $CsClO_4$ for forward and reverse transition.

orientations in the lattice, which means that the molecule is more apt to be able to rotate.

On comparing the ε vs T plots of the alkali perchlorates with those of the solid hydrogen halides (*13*), we observe that just before T_t a small increase in the value of ε is due to the prerotation caused by the loosening of the lattice structure. The λ-shape of the peak during transformation is in conformity with the idea of Bartenev and Ramizova (*36*) and Majumdar and Roy (*37*) characterizing it to be the first-order transition with processes of disordering. Since the infrared spectra of cubic forms shows that the cubic structure is isotropic, there is the possibility of the rotation of ClO_4^- in the cubic form. The sharp increase in the value of ε at T_t must be corresponding to the onset of rotation of ClO_4^- during the disordering of the lattice to the cubic structure.

The cubic structure of $NaClO_4$ and $KClO_4$ is found to have rotating ClO_4^- by the dielectric studies, while $RbClO_4$ and $CsClO_4$ are found not to agree to this idea. $NaClO_4$, in the cubic structure has such a high value which is comparable to the value of ε of ionic salts in dilute solutions, thus giving the possibility of free rotation to ClO_4^- ions. In $KClO_4$, above the transition the values are (approximately) $\varepsilon = 34.55 + 27416/T$ and the dependence upon $(1/T)$ qualitatively with the requirements of the Debye equation suggests molecular rotation in the solid (*38*, *39*).

$RbClO_4$ and $CsClO_4$ show the sharp increase at T_t which must be due to the transformation from ordered to the disordered arrangement of the molecules. As ε does not vary as $1/T$ after transition and also the value of ε at T_t is not as high as the value of ε for the ionic compounds in their dilute solutions, so there is no possibility of free rotation of ClO_4^- in the cubic forms of $RbClO_4$ and $CsClO_4$. This anomalous behaviour may be due to the large sizes of Rb^+ and Cs^+ as compared to Na^+ and K^+ ($r_{M^+} = 0.98$, 1.33, 1.49, and 1.65 Å, respectively, and $r_{ClO_4^-} = 2.2$ Å). In the cubic form of $RbClO_4$ and $CsClO_4$ there may be only a hindred rotation of the ClO_4^- in the lattice. As the temperature is increased, the degree of rotation goes on increasing causing a regular increase till it becomes almost constant in case of $RbClO_4$. At this temperature, they are possessed of sufficient energy to permit a fairly frequent passage over the potential energy barriers hindering rotation. In $CsClO_4$, ClO_4^- ions remain in hindered rotational form even at higher temperature as the potential energy barriers hindering rotation are not crossed even upto 350°C. On considering the ionic conductivity data of $CsClO_4$, we can say that in the cubic form not only Cs^+ migrate but ClO_4^- ions also migrate (40) thus possessing the tendency of translational motion; so, the energy required for free rotation of ClO_4^- in $CsClO_4$ will be very high, because it should be the sum of rotational as well as translational energies, which during heating of $CsClO_4$ does not seem to be possible.

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