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Gel growth and dielectric studies of K, Rb and Cs perchlorates

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Single crystals of K, Rb and Cs perchlorates have been grown by the counter diffusion of the respective ions and ClO_4^- through the gel medium. Studies on nucleation, growth kinetics, morphological aspects and purity are discussed in this paper. The dielectric constant, ϵ_b, as well as loss measured along the longest axis, exhibits an anomaly at the transition temperature, T_t, in all the three crystals. It is found that the peak values of T_t are approximately 800, 100 and 53 in K, Rb and Cs perchlorates, respectively. The dielectric anomaly and the large value of ϵ_b in the cubic phase are discussed in terms of the degree of disorder of the ClO_4^- group and the possible contribution from defects.

1. Introduction

Crystals of alkali metal perchlorates, with the exception of $LiClO_4$, have been found to undergo structural phase transitions at elevated temperatures [1–4]. This is an order–disorder phase transition and is characterized by a disorder in the orientation of ClO_4^- ions. In the disordered phase the structure is described by the cubic space group $F\bar{4}3m$ if the positions of the oxygen atoms are not taken into account [5, 6]. Below the transition temperature, the structure is described by the orthorhombic space group $Pnma$ (except $NaClO_4$) [2, 7–10]. The phase change from orthorhombic to cubic has been extensively investigated by X-ray diffraction methods and by differential thermal analysis [3, 11, 12]. Many authors have also dealt with the vibrational spectra of perchlorates both in solution and solid forms, at both room temperature and at low temperatures [13–16]. The dielectric behaviour of these perchlorates in the pellet form has also been reported [5]. Since crystals of suitable size and quality of these perchlorates (especially $KClO_4$, $RbClO_4$ and $CsClO_4$) are difficult to grow, physical data on single crystals such as these is scarce. In this paper the growth of $KClO_4$, $RbClO_4$, $CsClO_4$ by the silica gel method and the temperature dependence of their dielectric properties is reported.

2. Crystal growth

The proper selection of a growth technique depends mainly on certain physical and chemical properties of the materials to be grown. Table I summarizes some of these properties, such as the melting points, decomposition, solubilities, which are relevant to the growth of these crystals [4].

As can be seen from Table I, the temperature interval between the fusion and the onset of rapid decomposition is of the following order

TABLE I Summary of some properties of the materials to be grown

Crystal	Crystallographic T_t (° C)	Fusion temperature (° C)	Onset of rapid decomposition (° C)	Polarizing power of cation charge/radius ratio	Solubility in water	
					Room temperature	Elevated temperature
$LiClO_4$	–	247	348	–	$59.7_{25°C}$	–
$NaClO_4$	309	468	525	2.275	Soluble	Very soluble
$KClO_4$	303	580	580	1.641	$0.75_{0°C}$	$21.8_{100°C}$
$RbClO_4$	284	597	597	1.472	$0.5_{0°C}$	$18_{100°C}$
$CsClO_4$	225	577	577	1.282	$0.8_{0°C}$	$30_{100°C}$

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$$\text{Li}(191^\circ\text{C}) > \text{Na}(57^\circ\text{C}) > \text{K, Rb, Cs}\ (0^\circ\text{C})$$

It is immediately apparent from Table I that crystals of $KClO_4$, $RbClO_4$ and $CsClO_4$ can therefore decompose during melting itself and hence cannot be grown by the normal melt techniques. Furthermore, because of their low solubility in water at room temperature, it has been difficult to grow single crystals of a suitable size and quality from an aqueous solution. However, the very fact that they are almost insoluble in water at room temperature allows them to be grown by the gel technique. The gel medium prevents turbulence and by remaining chemically inert it provides a three-dimensional structure which permits the reagent to diffuse at the desired controlled rate. In addition, its softness and the uniform nature of the constraining force that it exerts upon the growing crystals encourage orderly growth.

Recently crystals of $KClO_4$ have been grown from silica gel, and growth phenomenon has been studied in great detail [17–19]. However no previous literature exists on the growth of $RbClO_4$ and $CsClO_4$ from silica gel.

The system used by us to grow these crystals is the one developed by Patel *et al.* [20] which is commonly known as the beaker–single tube system. The density of the gel solution is varied from 1.05 to $1.04\,\text{g cm}^{-3}$. The best results were obtained with the gel density equal to $1.04\,\text{g cm}^{-3}$. The normal composition of the gel in the majority of the experiments was $45\,\text{cm}^3$ of Na_2SiO_3 solution + $50\,\text{cm}^3$ of 2 N acetic acid which took about 20 days for setting, and yielded a fairly transparent gel.

After setting, the nucleation was initiated by a counter diffusion of ions through the gel medium. When the proper feed solutions were added, tiny crystals were first sighted in about 4 to 5 days and subsequent growth proceeded over these crystallites. A number of experiments were attempted by changing the concentration as well as the composition of the starting materials. The results obtained are summarized in Table II.

The general chemical reaction taking place to give the required crystals is as follows

$$MX + HClO_4 \rightleftharpoons MClO_4 + HX$$

In all the cases ClO_4^- ions were obtained by adding 1 M $HClO_4$ solution.

Some general conclusions can be drawn from the above data:

(1) No nucleation occurs when the concentration of the cation is below 0.2 M;

(2) Good quality crystals can be obtained when the concentration is in the range from 0.2 to 0.3 M;

(3) No pronounced effect has been observed upon changing the cation solution (e.g. CsCl, CsBr, Cs_2SO_4).

2.1. Growth kinetics

With a view to studying the kinetics of growth of these crystals, their rate of growth was measured. The growth rates of these perchlorates were found to follow a parabolic relation between length, L, and time of growth, t, for all compositions of the gel such that

$$L^2 = Kt, \tag{1}$$

where K is called growth rate constant. A typical curve is shown in Fig. 1a for $RbClO_4$. When the square of length was plotted against time of growth a straight line was obtained as shown in Fig. 1b, from which the growth rate constant, K, was computed.

There are two main limitations to the application of Equation 1, one arising from the initial transient period during which steady state concentrations are established, and the other arising from exhaustion of the available solute. Both these factors can give rise to non-linearity. The fact that the straight line plot of L against t does not pass through the origin directly confirms the first limitation and the effect of the other limitation can be seen from the end region of the parabolic curve which is almost parallel to the t-axis.

2.2. Effect of gel ageing

For the results shown in Figs. 1 and 2 the gel was prepared by mixing $45\,\text{cm}^3$ of Na_2SiO_3 solution of specific gravity 1.04 and $50\,\text{cm}^3$ of 2 N acetic acid which took about 20 days for setting. In one case the growth was initiated immediately after the setting (Fig. 1) by adding the appropriate feed solution, whereas in the other case (Fig. 2), the growth was initiated after a lapse of 5 days. The difference produced as a result of this (because of gel ageing) can be seen as the change in growth rate constant (for Fig. 1, $K = 6.47 \times 10^{-4}\,\text{cm}^2\,\text{sec}^{-1}$ and for Fig. 2, $K = 4.44 \times 10^{-4}\,\text{cm}^2\,\text{sec}^{-1}$), and so the effect of gel ageing is only to decrease the growth rate.

In Fig. 2, the effect of addition of the cation

TABLE II Details of crystals growing using the gel technique

$KClO_4$			$RbClO_4$			$CsClO_4$		
Feed solution	Concentration (M)	Remarks	Feed solution	Concentration (M)	Remarks	Feed solution	Concentration (M)	Remarks
KCl	0.20	No nucleation	RbBr	0.20	A few nucleations and good quality crystals	CsCl	0.20	A few nucleations and good quality crystals
			RbBr	0.25		CsCl	0.25	
			RbBr	0.30				
KCl	0.25	A few nucleations and good quality crystals	RbBr	0.35	Too many nucleations	CsCl	0.50	Too many nucleations
KCl	0.30							
KCl	0.35	Too many nucleations	RbI	0.25	A few nucleations and good quality crystals	CaBr	0.25	A few nucleations and good quality crystals
						CsBr	0.35	Too many nucleations
						Cs_2SO_4	0.20	A few nucleations and good quality crystals

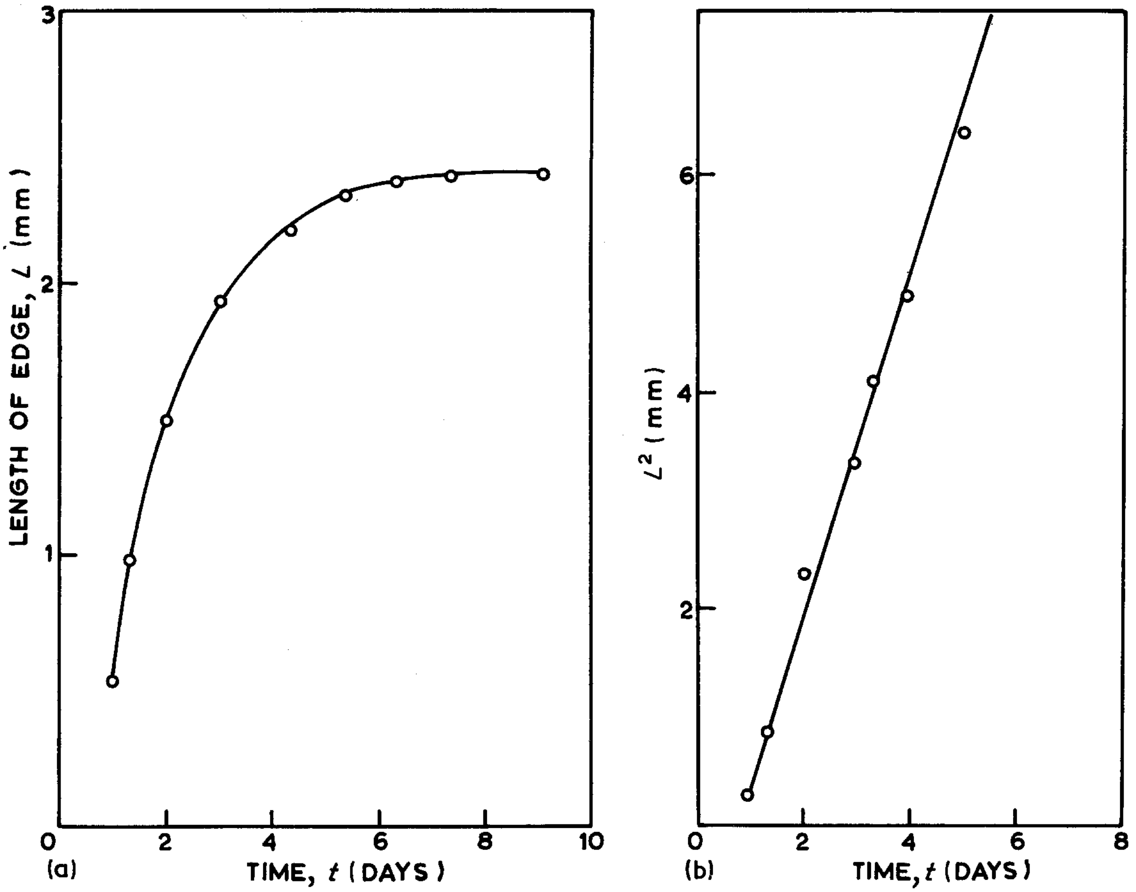


Figure 1 Plots of (a) length of the edge, L, against time, t, and (b) L^2 against t for $RbClO_4$.

solution again (after 5 days) is observed as another parabolic curve over the initial one. The change in the growth rate constant (from 4.44×10^{-4} cm² sec⁻¹ to 2.58×10^{-4} cm² sec⁻¹) is only due to the change in the concentration of the feed solution. From this it is concluded that the main factor governing gel growth is the diffusion process.

3. Characterization

The chemical analysis of these crystals indicated the presence of the respective alkali metal ions and perchlorate ions. The composition of these crystals, as determined by estimating the amount of the alkali metal ion, corresponded to the chemical formula $MClO_4$. The IR spectra of these samples compared well with the reported spectra. The crystals exhibited perfect cleavages parallel to (0 0 1) and (2 1 0) faces.

The impurity levels in the synthetic crystals have been determined by mass spectrometric analysis by using an AEI MS702 mass spectrometer (Mattauch–Hermony type fitted with electrostatic and magnetic analyser using a photographic method of detection). The result of a typical analysis is shown in Table III. The data reveal that the impurity levels of the crystals are quite low.

3.1. Morphology

Fig. 3 shows some typical crystals grown from silica gel. The morphologies of the crystals grown (see Fig. 4) are varied and similar to those of $KClO_4$ [17]. The most common habit faces observed in these crystals are however *c* {0 0 1}, *m* {2 1 0}, *r* {1 0 1} and *b* {0 1 0}. Further crystals of plate-like (tabular), needle shaped (acicular) and prismatic habits have been found to grow in the same growth run. These variations are naturally associated with variations of the local concentration of the feed solution around the various crystallites. However, no systematic change in the morphology was observed in the range of concentrations considered in this work. Also, no significant

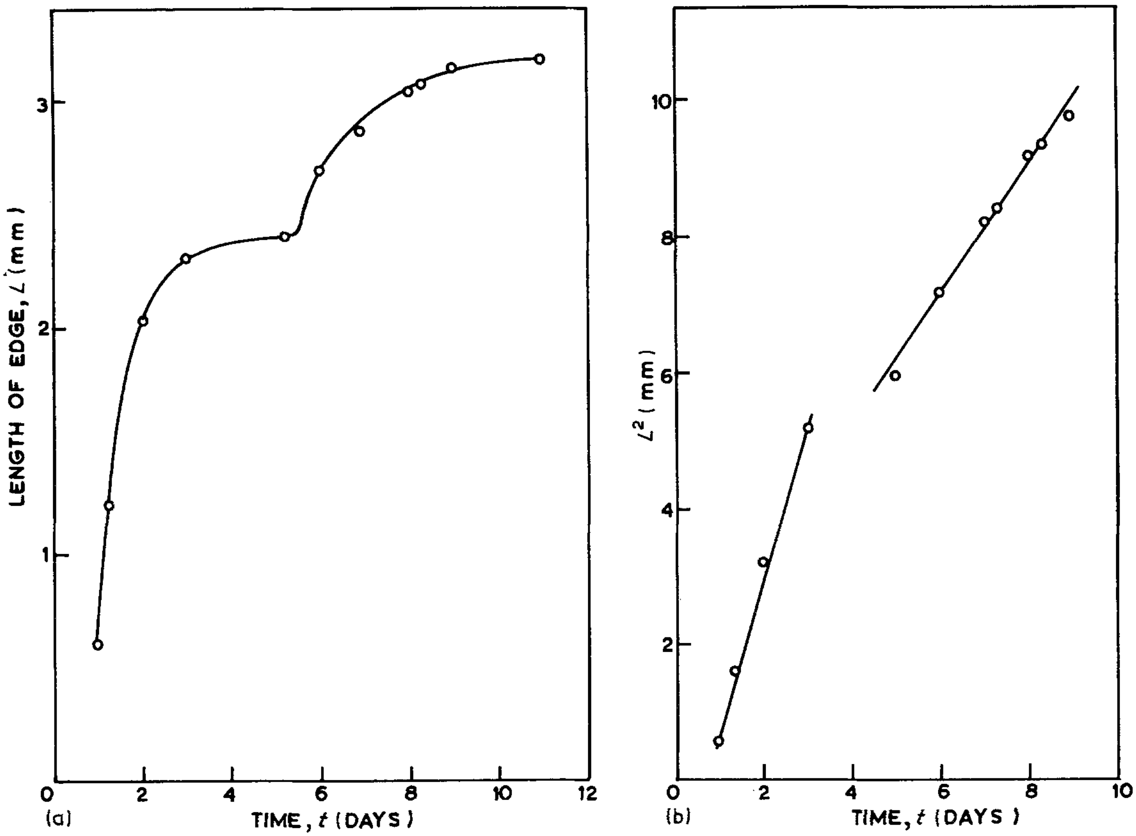


Figure 2 Plots of (a) L against t and (b) L^2 against t showing the effect of the addition of cation solution again after five days for $RbClO_4$.

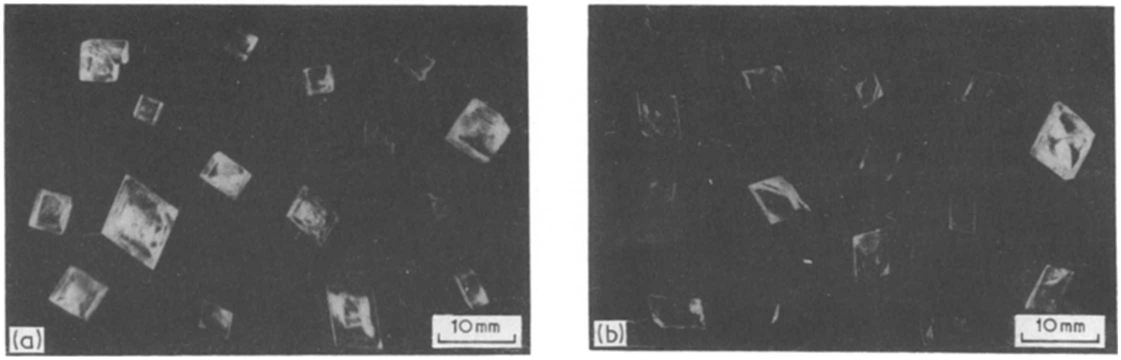
change in the morphology was observed with the change of starting material.

4. Dielectric studies

The alkali metal perchlorates, as mentioned earlier, undergo structural transitions from an orthorhombic to a cubic structure. Crystallographic evidence [9] shows that in the orthorhombic form, the ClO_4^- tetrahedron is distorted producing a two-fold symmetry parallel to the *b*-axis and two of the oxygen atoms are nearer to the Cl atom compared with the other two which are not in the plane. The ClO_4^- tetrahedra is bonded to the cation through two of its oxygen atoms. In the cubic form ClO_4^- is undistorted and is free, thus giving the possibility of rotation of ClO_4^- in a cubic structure. The effect of this change is reflected in the dielectric behaviour of these crystals. The temperature dependence of the dielectric constant of Na, K, Rb and Cs perchlorates have been studied by Syal and Yoganarasimhan [5]. They have observed a sharp increase in the dielectric constant for all these perchlorates as the transition temperature is approached. Their results show that the dielectric constant decreases after the transition temperature only in the case of Na and K perchlorates, whereas it continues to increase slowly for Rb and Cs perchlorates. This difference in the dielectric behaviour of these materials has been attributed to the different nature of the ClO_4^-

TABLE III Mass spectrometric analysis of crystals grown using the gel technique

Element	Impurity levels (wt ppm)		
	$KClO_4$	$RbClO_4$	$CsClO_4$
Na	34	8	15
Mg	4	2	3
Al	3	Nil	Nil
Si	20	12	18
K	–	2	2
Ca	6	16	17
Mn	3	21	13
Fe	9	11	13
Br	25	9	10
Rb	13	–	10
Cs	5	15	–



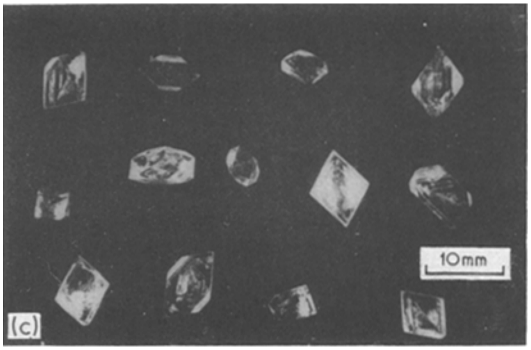


Figure 3 Photographs of typical crystals grown from the silica gel: (a) $KClO_4$; (b) $RbClO_4$; (c) $CsClO_4$.

motion. However, their IR spectroscopy studies predict similar behaviour of ClO_4^- in all the perchlorates. In the work reported here, a study of the dielectric behaviour of these materials in their single crystal form has been undertaken to try to understand better the role of the dynamics of ClO_4^- groups and the results obtained are discussed below. It should be noted that Syal and

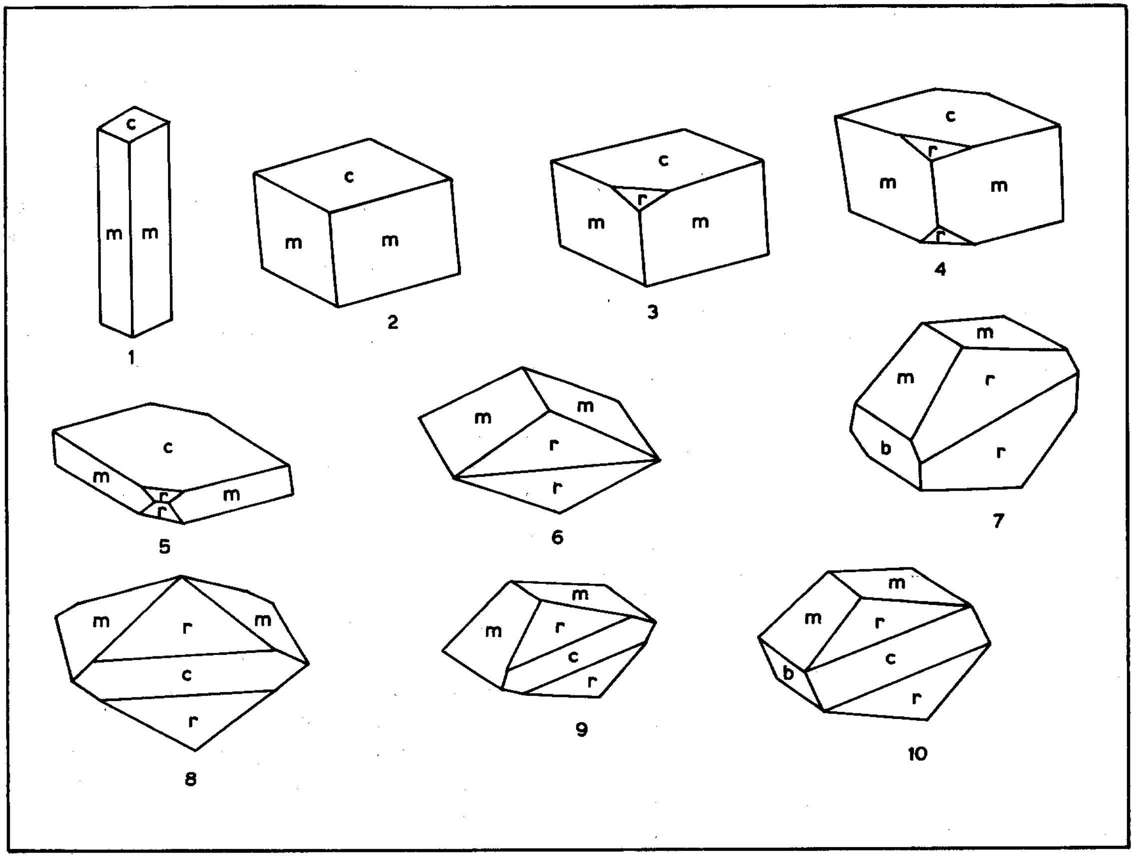


Figure 4 Typical habits exhibited by these crystals (according to the notation of Groth).

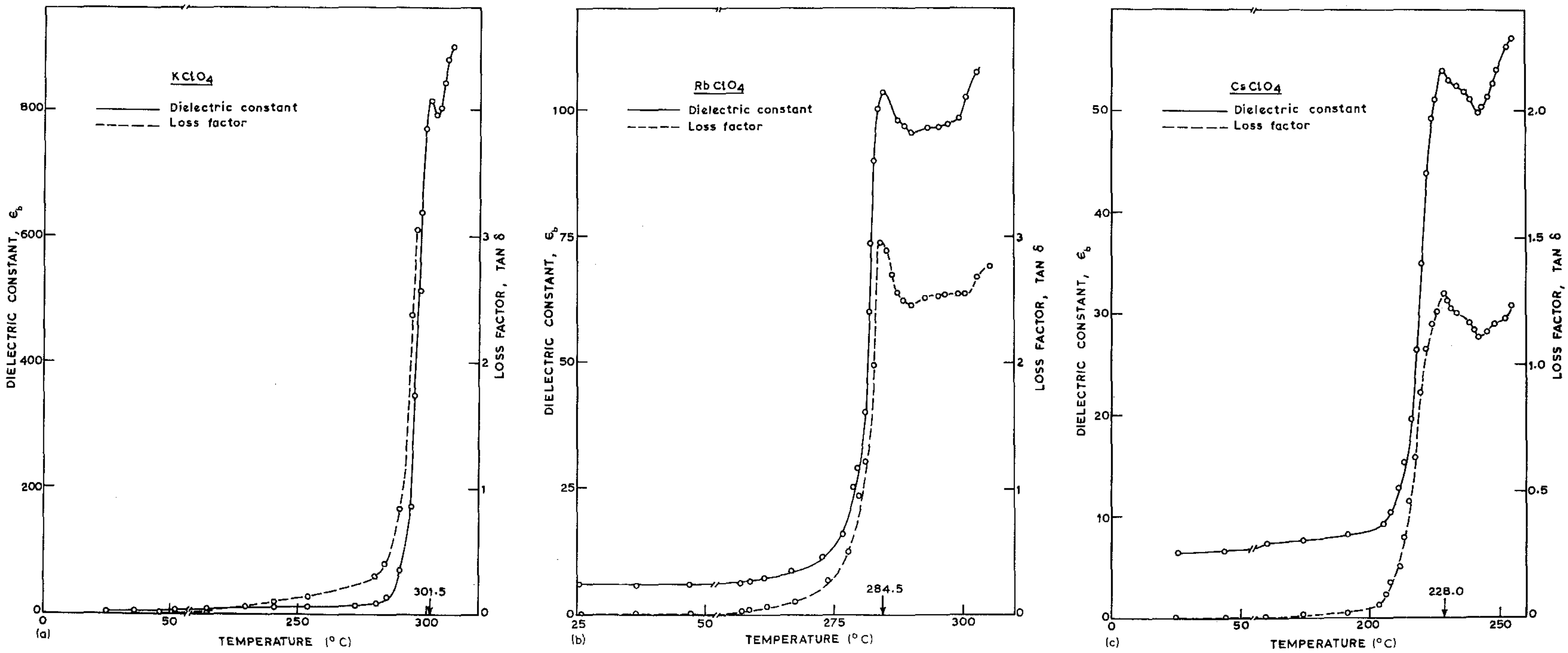


Figure 5 Temperature dependence of dielectric constant, ϵ_b, and dielectric loss, tan δ, for (a) $KClO_4$, (b) $RbClO_4$ and (c) $CsClO_4$.

TABLE IV Details of transition temperature, T_t, dielectric constant, ϵ_b, and dielectric loss, $\tan\delta$, for the crystal samples

Crystals	Room temperature value of ϵ_b	Transition temperature, T_t (° C)	Peak value	
			ϵ_b	$\tan\delta$
$KClO_4$	6.3	301.5	818	> 3
$RbClO_4$	5.4	284.5	104	2.96
$CsClO_4$	6.6	228.0	54	1.29

Yoganarasimhan [5] made their measurements on the polycrystalline samples.

Measurements of dielectric constant ϵ_b, as well as dielectric loss ($\tan\delta$), were made along the *b*-direction (long axis) which was identified from the morphology of the crystals. Samples of thickness about 0.5 mm and area about 10 to 30 mm^2 were prepared by wet polishing. On both sides of the specimens a thin coating of air drying silver paint was applied to ensure proper electrical contact. A suitably designed dielectric cell [21] capable of operating at 500° C was employed for this purpose. Both capacitance and loss were measured using a Marconi Instruments Universal bridge (TF 1313 A) operating at 1 kHz. The dielectric constant ϵ_b was computed by dividing the measured capacitance by the capacitance between the electrodes. The cell was first calibrated using standard samples of CaF_2, SrF_2 and BaF_2 obtained from the Harshaw chemical company.

4.1. Results and discussion

The high temperature behaviour of both the dielectric constant and $\tan\delta$ is shown in Fig. 5a, b and c as the function of temperature. The $KClO_4$ sample was found to be highly lossy at higher temperature and it was not possible to compensate for this with the measuring technique used. Both the dielectric constant and $\tan\delta$ remain almost constant until the phase transition temperature is nearly reached and both assume a high value as T_t is reached. After the transition temperature the values drop slightly and thereafter start increasing rapidly. When cooled the sample crystals regained their original properties, although it was observed that the crystals often shattered when heated to about 20° C above the transition temperature. The rapid increase of dielectric constant at higher temperature is expected of ionic salts and may be attributed to the activation and formation of defects. Table IV gives the values obtained for the dielectric constant, ϵ_b, at room temperature, peak values of both ϵ_b and $\tan\delta$ and values for the transition temperature. The Marconi bridge employed measures the impedance and therefore the capacitance measured is that of the equivalent *CR* network. The value of the dielectric constant obtained by taking the ratio of the capacitance of the sample holder with and without the crystal will be equal to the real part of the complex dielectric constant only when $\tan\delta$ is small. Near the phase transition this will not be so as $\tan\delta$ also shows an increase and consequently the numerical values of ϵ_b given in Table IV will differ from the real part of the complex dielectric constant. However, measurements at different frequencies [22] suggest that the large increase in $\tan\delta$ is confined to a small region just before the phase transition temperature and this may be a result of the relaxation associated with the motion of ClO_4^- ions. The increase noticed beyond the transition as the decomposition temperature is approached may be due to the increase in conductivity.

From Table IV it can be seen that the peak value of the dielectric constant decreases from $KClO_4$ to $RbClO_4$ to $CsClO_4$. This trend may be due to the increase in the size of the cation. The decrease in the dielectric constant after the transition could be due to the rapid rotation of the ClO_4^- groups as envisaged by Pauling [23] to explain phase transitions or could be due to increased disorder of the orientation of the ClO_4^- ions in the different units as suggested by Frenkel [24]. In addition, in the particular case of perchlorates studied, there is an increase in the symmetry from the *Pnma* space group to the one $F\bar{4}3m$ which implies that the site symmetry of ClO_4^- ion is enhanced from C_2 to T_d. Consequently, symmetry-wise the dielectric constants of the perchlorates in the cubic phase far away from transition temperature is of significance. However, the generation of defects producing a marked contribution to the dielectric behaviour at higher temperatures, as revealed by the dielectric loss, does not allow us, at this stage, differentiation of the different alternatives. It is clear, however, that the behaviour of the ClO_4^- ions is the same in all three perchlorates. A more detailed analysis of the dielectric behaviour of these perchlorates is in progress and will be reported elsewhere.

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