Charge transport mechanism and low temperature phase transitions in KIO₃

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Abstract. Our report deals with the measurement of some electrical properties, namely the ac conductivity \( \sigma(\omega, T) \) and the complex dielectric permittivity \( \varepsilon^*(\omega, T) \) in the temperature interval 95K < T < 280K and at some selected frequencies (0.7kHz – 20kHz) for polycrystalline samples of potassium iodate KIO₃ using a computerized RLC meter. The improper character of the ferroelectricity over the mentioned temperature range has been achieved by recording the ferroelectric hysteresis loops. The temperature dependence of each electrical parameter reveals that the compound undergoes two phase transitions at \( T \approx 258K \) and at \( T \approx 110K \). The frequency dependent conductivity seems to be in accordance with the power law \( \sigma(\omega, T) \propto \omega^{s(\omega, T)} \) and the trend of temperature dependence of the frequency exponent \( s(0< s < 1) \) suggests that the quantum mechanical tunneling (QMT) model is the main mechanism of the charge transport. Comparison with the behavior of the NH₄IO₃ in the same temperature range was outlined.

1. Introduction
Potassium iodate KIO₃ is a member of the monovalent metal iodate series of the general molecular formula MIO₃ where M stands for Li, Cs, Na, K… and/or NH₄. This series of compounds attracted the attention of investigators due to their interesting properties. For example, the improper ferroelectric hydrogen-bonded NH₄IO₃ undergoes a ferroelectric phase transition at \( \approx 368K \) [1-3]. Moreover, since the compound behaves as a proton conductor, therefore it has some practical applications such as chemical sensors, electrochromic displays and supercapacitors [3-4]. Furthermore, LiIIO₃ undergo successive phase transitions and the high temperature phase behaves as a superionic conductor [5-6]. Properties such as piezoelectric, pyroelectric and non-linear optical effects are common for some members of this series [7-11].

For KIO₃, which is the subject of this article, it is known that most of the physical properties of the crystals of this compound such as, (dc) dielectric constant [12] piezoelectric and pyroelectric effects [13,14], electro-optical behavior [13], non-linear optical properties [7,14], ferroelectricity...
in addition to nuclear quadruple resonance (NQR) [12] and Raman scattering experiment [17], have been investigated previously. Later on, some of these properties were discussed [18]. Due to the increasing interest of these properties and the expected applications of such a material in laser technology, it is logical to re-examine these properties using more advanced techniques. For example, a somewhat recent work dealing with the temperature dependence for piezoelectric and ferroelastic properties, using resonance – antiresonance method [19], has been reported. The data indicate that the compound undergoes successive five phase transitions (I-II, II-III, III-IV, IV-V, V-VI ) at the transition temperatures: $T_1 = 485K$, $T_2 = 345.5K$, $T_3 = 258K$, $T_4= 113K$ and $T_5 = 33K$ respectively. Similar behavior was observed earlier [12] with somewhat slight different in the value of the transition temperature for some phases. The anomaly that has been observed around 150°C (423K) by Crane [14], and by others [12,19] and more recently at (428±2)K by the present authors [20] has been already explained as a change in electrical conduction between extrinsic and intrinsic mechanisms [20]. It is not related to any phase transition [19,20].

Among other things, KIO$_3$ single crystal exhibits noble non-linear optical properties in all phases [7]. Furthermore, its non-linear optical coefficient in the room temperature phase (phase III), is the largest between monovalent metal iodates (MIO$_3$) [7,21] and is also greater than those of KH$_2$PO$_4$ (KDP), BaB$_2$O$_4$ (BBO) and LiBrO$_5$ (LBO), which are known as double frequency materials in the ultraviolet wavelength [22]. Although the presence of ferroelectric domains and twins at room temperature (phase III) prevents or at least hinders practical applications, yet using the poling technique and specially after detwening and domain removal, it can be used for fabrication of non-linear optical devices [22].

Another point of interest is that the static piezoelectric constants of the single crystals of KIO$_3$ in phase III are about 50 times greater than those of α-quartz [23]. Due to this large piezoelectric effect, KIO$_3$ is a promising candidate for the fabrication of piezoelectric sensors [24]. Furthermore, the thermal characterization including specific heat and thermal decomposition in the temperature interval 260K< $T$ < 600K were investigated [25] using Perkin – Elmer DSC.

To clarify the dynamic properties of the high temperature phase transition of KIO$_3$ crystals, the temperature dependence of low frequency (soft) optical modes was measured by Raman scattering [24]. More recently, detailed polarized Raman study were performed on KIO$_3$ single crystals over 78.5-553K [26]. The improper character of ferroelectricity of the compound was suggested by Ahart et al. [24], supported by Liu et al. [26] and confirmed by Abdel-Kader et al. [20].

From the accurate measurements of some mentioned properties as a function of temperature[15, 17, 19,20, 22-25], it has been reported that, the KIO$_3$ undergoes a ferroelectric phase transition around 486K and several phase transitions as summarized in Table 1. The Table shows also the symmetry of some phases of KIO$_3$

Regarding the crystal structure, it is known that the structure of phase III using the single crystal x-ray diffraction technique, was determined by Crane [14] who also summarized the results of studies on KIO$_3$ until 1971 [14]. Furthermore, based on x-ray powder diffraction data, Hamid [27] suggested the space group of phase I as R3m which has not been confirmed later. He also suggested the symmetry of phase II and determined the structure of Phase I from intensities taken by photographic method. It is known that, single crystals x-ray diffraction technique, has been faced with the some problems due to the existence of ferroelectric and/or ferroelastic domains [27].

Again single crystal technique has been used by Kalinin et al [28] and has been faced with the same problems namely the tendency towards twinning and polymorphism [28].
To overcome all these problems, recently Kasatani et al. [29] determined, the crystal structure of phase I at 530K using high energy X-ray technique and the MEM/Rietveld analysis. On the other hand, the high resolution neutron powder diffraction has been employed for determination of the crystal structure of phase I at 523K [30], and also phase III at 300K [31a], at 100K and 10K [31b].

We have found that it is of interest to measure the ac conductivity and dielectric permittivity in the low temperature range 95K < T < 280K on polycrystalline samples. This technique is absent in literature for the title compound. Another reason for the use of this technique in the present work is the dependence of the physico-chemical properties of this compound on the method of its recrystallization. For example, different NQR $^{127}$I spectra were found for crystals grown from water solution with or without HIO$_3$ [32]. Moreover, for crystallization of KIO$_3$ from an aqueous solution containing HIO$_3$ and KIO$_3$ with a ratio of HIO$_3$/KIO$_3$ greater than 7.4%, crystals of KIO$_3$ and KH(IO$_3$)$_2$ are formed [23].

According to the best of our knowledge, no data on "electrical transport mechanism" in the investigated low temperature region was reported. Also the motivation behind the present work, is to compare our data with that of the very similar compound namely NH$_4$IO$_3$ [33].

In order to discuss the different models for conduction mechanism, the starting point is that, the total measured ac conductivity $\sigma_{ac(total)}$ at a given angular frequency ($\omega$), can be separated into dc and ac components namely:

$$\sigma_{ac(total)} = \sigma_{dc} + \sigma_{(ac)}$$

(1)

The ac component $\sigma_{(ac)}$ is a function of both frequency ($\omega$) and temperature (T) and may be written as $\sigma_{(ac)}(\omega,T)$ whereas the dc component is a function of temperature only. According of Jonscher [34]

$$\sigma_{(ac)}(\omega,T) = A(T)\omega^{s(T)}$$

(2)

This is the well known power law [34-42] and has been so widely observed for highly disordered materials and hence it has come to be known as a universal dynamic response.

The pre-factor A (T) is a constant and represents the degree of polarizability [37] and the frequency exponent $s$ ($0 < s < 1$) describes the interaction (mainly of an electrostatic type) between the mobile ions with lattice around them or in more details, and according to the many body interaction model [34,37], the interaction between all dipoles participating in the polarization process is characterized by the parameter s. A unit value of s implies a pure Debye type interaction. The value of s decreases with the increase of interaction [37,40]. The thermal behavior of the ac conductivity follows Arrhenius relation in most cases.

$$\sigma T= \sigma_0 \exp(-E/kT)$$

(3)

where E is the activation energy for the process, k is the Boltzmann’s constant and $\sigma_0$ is constant.

Furthermore, it is known that the complex dielectric permittivity $\varepsilon^*(\omega)$ can be divided into the real part $\varepsilon'(\omega)$ and the imaginary part $\varepsilon''(\omega)$ according to the equation:

$$\varepsilon^*(\omega)=\varepsilon'(\omega)-j\varepsilon''(\omega)$$

(4)

($\varepsilon'$ and $\varepsilon''$ are frequency-dependent and represent the charging and loss currents respectively) [43].
2. Experimental procedures

2.1. Sample preparation. The material used in the present work was manufactured by the BDH Chemical Company Ltd. For electrical and/or ferroelectric measurements, a suitable amount of the fine polycrystalline powder of the compound, sufficient to prepare 5–6 pellets was further grained under 2μm (micronized). The aim of this technique is to remove the effect of grain size and also to minimize the effect of porosity.

A microanalytical balance, type Sartorius, was used to achieve the equality of masses between all samples before compressing, (the mass of each sample was ≈ 0.6 gm). These samples were pressed under the same pressure (of about 2*10^8 N/m²) so we have practically identical pellets of thickness ≈ 2mm and of diameter ≈ 1cm.

Good electrical contact was attained by painting the opposite faces of each pellet with air drying conducting silver paste. Before any measurements, the samples were inserted into a dessicator over night to remove any humidity. A sample holder with brass electrodes was specially designed to fit the present measurements.

2.2. Characterization techniques. To demonstrate and to check the presence of ferroelectricity at different temperatures, the circuit shown in ‘figure 1a’, was designed and manufactured in the Science Technical Center, Cairo University to fit the present measurement. The digital storage oscilloscope type Instek GDS-820S, provided with a computerized camera as connected in the designated circuit shown was used to record ferroelectric hysteresis loops at different temperatures. Calibration, using triglycine sulphate (TGS), was carried out just before any actual run.

A computerized LCR bridge type Philips PM6304 was used to determine the ac conductivity and the dielectric permittivity at some selected frequencies. The bridge measures precisely the values of R, C, Z, Q… However, in the present work the values of R and C are converted into conductivity and permittivity using the dimensions of the pellet and a simple program, since the bridge is interfaced to computer. The dc conductivity was measured by using an electrometer, type Keithly 614. Data were collected on at least three virgin samples and the results were found to be quite consistent and reproducible. All measurements were performed during heating run. The heating rate was 0.5K/min and the experimental error of temperature is better than +1%. All measurements were performed at the thermal equilibrium. Calibration was done on a standard sample before any actual measurements.

![Figure 1a. The designated circuit for detecting ferroelectric hysteresis loops.](image-url)
3. Results

3.1. Ferroelectricity. The ferroelectric hysteresis loops (D-E loops) at some selected temperatures in the range 95K < T < 280K have been displayed and recorded on the monitor of the digital oscilloscope. Two of these loops are shown in 'figure 1b', together with D-E loops recorded at high temperature up to 490K where the compound is in the paraelectric phase. It seems likely that, the saturation in the D-E loops is not complete. This problem will be discussed later on (in the discussion section). The existence of this type of D-E loops is an indication that the compound behaves as an improper ferroelectric material.

![Figure 1b. The D-E hysteresis loops for KIO₃. (Arb. Scale)](image)

3.2. Dielectric Permittivity. The temperature dependence (95K<T<280K) of the real part ε' of the dielectric permittivity determined at some selected frequencies (0.7 kHz-20 kHz) is shown in ‘figure 2’.

![Figure 2. Temperature dependence of the real part (ε’) of the dielectric permittivity measured at different frequencies for KIO₃.](image)
In general, the value of \( \varepsilon' \) depends on both the frequency (f) and temperature (T). For a given frequency, each curve is characterized by the existence of two anomalies: a pronounced peak in the vicinity of \( T_3 \approx 258\text{K} \) and a small peak (anomaly) at \( T_4 \approx 110\text{K} \). Between the two transition regions, the value of \( \varepsilon' \) is almost temperature independent. It is known that, the compound undergoes a ferroelectric phase transition of an improper character (I-II) at \( T_1 \sim (486\pm1)\text{K} \), a change in the conduction mechanism at \( (428\pm2)\text{K} \) and a structural phase transition (II-III) at \( T_2 \sim 345\text{K} \).

The variation of \( \varepsilon'' \), the imaginary part of the dielectric permittivity, as a function of temperature, \( 95\text{K}<T<280\text{K} \) is shown in figure 3a'. The frequency range (1kHz-10kHz) has been only considered for the purposes of clarity. Apparently, the general trend of this plot is similar to that of \( \varepsilon'-T \) graph, ‘figure 2’, except that the value of \( \varepsilon'' \) at a given frequency and temperature is much reduced as compared with the corresponding value of \( \varepsilon' \), ‘figure 2’.

‘Figure 3b’ shows the frequency dependence of the imaginary \( \varepsilon'' \) plotted as \( \varepsilon'' \) vs ln(f) at some selected temperatures. The plot indicates that the dispersion increases with increasing temperature and decreasing frequency which is in agreement with the typical behavior of the dielectric materials.

The variation of the (dielectric loss), \( \tan\delta = \varepsilon'/\varepsilon'' \) as a function of temperature (95K<\( T<280\text{K} \)) measured at some selected frequencies is shown in ‘figure 4’. The general trend of the plot indicates also the existence of two phase transitions at the above mentioned temperatures and are reflected as two peaks.
### 3.3. Electrical conductivity.

Obviously the conductivity depends on both, the temperature and the frequency.

#### 3.3.1 Temperature dependence.

The ac conductivity $\sigma(\omega)$ as function of temperature, $95K<T<280K$ and frequency $0.7kHz - 20 kHz$, plotted as $\ln(\sigma T)$ versus $1/T$ is shown in ‘figure 5’. The behavior of $\sigma$ seems to be in accordance of Arrhenius relation. For a given frequency, and as the temperature
increases from about 95K, the first broad peak is observed at 258K. The other phase transition is found at \( \approx 110K \). Between the two transition regions the behavior of \( \sigma \) obeys Arrhenius relation.

3.3.2 Frequency dependence. The variation of \( \ln(\sigma) \) versus \( \frac{1}{T} \) at different frequencies is shown in ‘figure 6’.

![Figure 5. Variation of (ln(\sigma) T versus 1/T) at different frequencies for KIO3.](image1)

![Figure 6. Double logarithmic plot: (ln(\sigma) versus ln(o)) for KIO3.](image2)
The plot is consists of a series of straight lines of different slopes. The slope of each line gives the value of s, where \( s = \left( \frac{\partial \ln \sigma}{\partial \ln \omega} \right)_{\sigma=\text{const}} \) at that temperature.

The temperature dependence of s is shown in ‘figure 7’. Apparently, s is practically temperature independent except for around the phase transition regions.

‘Figure 8’ shows the variation of the pre-exponential factor (A) with temperature, plotted as \( \ln A \) vs T. The behavior of the plot indicates also the existence of two phase transitions at the same mentioned temperatures (258K and 110K) which are reflected in the graph shown as “inverted peaks”
4. Discussion.

The values of the transition temperatures $T_3$ (III-IV) = 258K and $T_4$ (IV-V) = 110K of the present work was found to be consistent with those found by previous workers (Table 1a and Table 1b). For example, from his previous investigation of the ferroelectricity in KIO$_3$ single crystal, Salje [17] observed two phase transitions in the low-temperature region at ≈ -15°C (258K) and at ≈ -163°C (110K).

Furthermore, Ivanov et al [15] studied the temperature dependence of the optical axes angle $2\nu$, the birefringence in the z-cut $\delta n_{(z)}$, and the spontaneous polarization axes $P_{sf}$ in a wide temperature range and they observed that at $T = -15^\circ C$ (258K) all three curves [(2$\nu$ ($T$), $\delta n_{(z)}$($T$) and $P_{sf}$ ($T$)] exhibit only breaks and thus they suggested that this transition is to be of a second order. Moreover, although Ivanov et al [15] did not investigate the phase transition (IV-V) in detail, yet they observed a regular quantitative change of the domain pattern which confirms the existence of a transition with a lowering of point symmetry. Moreover, they demonstrated the existence of ferroelectricity in the compound at the liquid nitrogen temperature -195°C (78K) by observing the D-E hysteresis loops which was found to be clear at that temperature and thus they concluded that phase V behaves as a ferroelectric which is in a good agreement with the present work and also with the work of Herlach [12], where the crystal remains ferroelectric below 485K [12]. In somewhat recent work Maeda et al. [19] demonstrated the existence of low temperature phase transitions at $T_3$ = -15°C (258K) and $T_4$ = -160°C (113K). A similar behavior has been observed for NH$_4$IO$_3$ where the compound undergoes a ferroelectric phase transition at ≈ 368K and behaves as a ferroelectric material below 368K down to liquid nitrogen temperature [33].

Among other things, although some investigators have been reported on the low-temperature phase transitions in KIO$_3$, through the study of the temperature dependence of some parameters, yet, the only crystal structure of the low temperature is that determined by Lucas [31b]. The data do not show significant change, on the atomic level, relative to that of the room temperature, i.e. no strong evidence for low temperature structural phase transitions. As we mentioned above, the temperature dependence of some properties show detectable change at ≈ 258K and at ≈ 110K. This inconsistence is not a major problem, since the structural phase transitions that involve only minor changes in atomic positions are not easy to detect [44a]. Potassium chlorate KClO$_3$ represents an example of a crystal with a reported phase transition with very small structural change where the atomic arrangement and coordination above and below the phase transition are identical [44a]. The same conclusion was also given by Brooker et al [44b]. From Raman studies of the phase transition in KClO$_3$, they observed that the difference in the vibrational spectra of the two phases was very small and hence the transition (at 545K) involved only minor rearrangement of the ClO$_3$ ion. Similar saturation may exist for the KIO$_3$ since the two compounds (KIO$_3$ and KClO$_3$) are members of halate series of the general molecular formula MXO$_3$ where (X=Cl, Br and I).

From the crystal structure point of view [29, 30, 31], the I and O atoms exist in the crystals as IO$_3$ molecules rather than the IO$_6$ complex. In other words unlike the typical perovskite structure of ABO$_3$ ferroelectrics where six O atoms form O$_6$ octahedron surrounding, a B atom each I atom in KIO$_3$ has three nearest O atoms forming an IO$_3$ molecule [26].

At this stage, it is necessary to mention that although there is a good agreement between different authors that the compound undergoes two phase transitions in the temperature interval 95K < T < 280K, yet there is a discrepancy concerning the nature and/or the exact mechanism of these transitions. Some authors consider these transitions to be associated with the orientational glass transitions [19]. Other authors [44b] proposed that these transitions might be associated with the structural changes of domain which is generally independent on atomic arrangements.
The present work tries to construct a bridge or link between different visions. The motion and/or the change of the structure of ferroelectric domains with temperature was first suggested by Byrom and Lucas [30]. On the other hand, and in a similar way to the role of ClO$_3^-$ as the main cause of the structural phase transition in the KClO$_3$ compound, one cannot neglect the effect of the reorientational motion of the IO$_3^-$; since, as we mentioned above, the spatial correlation between IO$_3^-$ decreases with increasing temperature [29]. Thus the thermal energy at each transition temperature may be enough to cause the change of the structure of ferroelectric domains and at the same time initiate (stimulate) the orientational motion of the IO$_3^-$ and hence a very slight rearrangement of the molecule with a very minor change in the atomic position in a way similar to that observed in the KClO$_3$ [44a,b].

It is of interest to mention here that even for the structural phase transition of the KIO$_3$ that have been observed at $\sim$ 487 K which is associated with the ferroelectric phase transition, the two X-ray diffraction patterns above and below the mentioned transition temperature are very similar [30]. In our vision, the exact mechanism of the low temperature phase transition is a future problem and requires the use of the high energy X-ray (synchrotron) powder (and not single) technique which is beyond the scope of the present work.

For the problems of unsaturated D-E hysteresis loops, it is known that the compound behaves as an "improper ferroelectric material" [20, 24-26] and not as (usual) ferroelectrics. The characteristic features of the improper ferroelectric are [45-46]:

i) a very slight change of dielectric constant near $T_c$

ii) a low spontaneous polarization

Logically the spontaneous polarization is not the order parameter and not proportional to it as in the case of proper ferroelectrics. The factor ii) is responsible for the unsaturation in the D-E hysteresis loops. The case of KIO$_3$ is very similar to the improper ferroelectric NH$_4$IO$_3$ where the D-E hysteresis loops in the ferroelectric phase are also unsaturated [33, 47].

Regarding the charge transport mechanism in different phases, it is known that the three main processes that contribute significantly to the ac conductivity [36, 48-49] are the quantum mechanical tunneling QMT, the correlated barrier hopping (CBH), and the small polaron tunneling (SPT).

For QMT model, the value of $s$ is given by

$$s = 1 - \frac{4}{\ln \left( \frac{\nu_0}{\omega \tau} \right)} = 1 - \frac{4}{\ln \left( \frac{\nu_0}{\omega \tau} \right)}$$  \hspace{1cm} (5)

whereas for (CBH) model, we have

$$s = 1 - \frac{\frac{6kT}{E_0 - \ln \left( \frac{\nu_0}{\omega} \right)}}{\ln \left( \frac{\nu_0}{\omega \tau} \right)} = 1 - \frac{\frac{6kT}{E_0 - \ln \left( \frac{\nu_0}{\omega \tau} \right)}}{\ln \left( \frac{\nu_0}{\omega \tau} \right)}$$  \hspace{1cm} (6)

and finally for the (SPT),

$$s = 1 - \frac{4}{\ln \left( \frac{1}{\omega \tau_p} \right) - \frac{w_H}{kT}}$$  \hspace{1cm} (7)

The symbols in equations (5), (6) and (7) take their conventional meanings where $k$ is Boltzmann's constant, $E_0$ is the optical energy band, $\nu_0$ is the frequency of the phonon, $\tau_p$ is the relaxation time of the polaron (of the order of $10^{-13}$ s) and $w_H$ is the activation energy involved in the electron transfer process between a pair of states. Moreover, the value of $s$ in equation (5) is temperature independent, whereas in equation (6) $s$ decreases with increasing the temperature and is less dependent on the frequency. For SPT, equation (7) predicts that, $s$ increases as $T$ increases.
Referring to ‘figure 7’, where s is plotted as a function of temperature, it is clear that the value of s is practically temperature independent i.e. in accordance with equation (5). Thus, the QMT model is the most likely one in this range of temperature. Moreover, if we put $\nu_{ph} \sim 10^{-13}$ sec.$^{-1}$ and $\omega \sim 10^4$ rad/sec.) [36] into equation (5), then the value of $s \sim 0.76$, which is in a good agreement with our experimental value, ‘figure 7’.

Furthermore, for QMT model, the value of $\sigma(\omega)$ as given by Auston and Mott [50] and Efros [51] is

$$
\sigma(\omega) = \frac{\eta}{3} e^2 kT[N(E_f)(T)]^2 \alpha^{-5} \omega^4 \left[ \ln(\frac{\nu_{ph}}{\omega}) \right]^4
$$

(8)

Where: $e$ is the charge of electron,
$T$ is the absolute temperature,
$N(E_f)$ is the density of energy states near the Fermi level,
$\alpha$ is the electron wave function decay constant 1 Å [33],
$\nu_{ph}$ is the phonon frequency, and $\eta$ is a constant.

Equation (8) predicted that, there is a linear relation between $\omega$ and $\frac{\sigma(\omega)}{\ln(\frac{\nu_{ph}}{\omega})}$ such a relation is presented in ‘figure 9’, which again confirm equation (8) where a series of almost straight lines of different slopes are observed. Thus the QMT model is the best one that describes the conduction mechanism in the investigated temperature region.
5. Conclusion. The present data indicate that in the investigated low temperature region $95\text{K} < T < 280\text{K}$, the compound remains ferroelectric (of an improper character) where the ferroelectric hysteresis loops, of quite insufficient saturation, are observed clearly over the mentioned temperature intervals. This is also the case for the similar compound NH$_4$IO$_3$ where it undergoes a ferroelectric phase transition of an improper character at $\approx 368\text{K}$ and remains ferroelectric down to liquid nitrogen temperature. For the compound KIO$_3$, the behavior of the temperature dependences for all electrical parameters confirm and support each other and indicate clearly that compound undergoes two structural phase transitions at $T_3 \approx 258\text{K}$ and at $T_4 \approx 110\text{K}$ over the mentioned temperature range. It is known that the iodine and oxygen atoms in the present compound exist as IO$_3$ rather than as IO$_6$ complex and the spatial correlation between IO$_3$ becomes weak with increasing temperature. The thermal energy (kT) at the transition temperature is enough to cause the rearrangement of IO$_3$ molecules in a way similar to the case of KClO$_3$. The thermal energy also causes an observable change in the structure of ferroelectric domain.

Regarding the electrical conduction, in the investigated low temperature region, the QMT model seems to be the main mechanism for the charge transport. This is to be expected, since this model usually exists in the low temperature range. The low and high phase transitions as well as the change in conduction mechanism at $(428\pm2)\text{K}$ are shown in the following scheme. The values of the transition temperatures are taken from ref. [20] and the present work except for transition at $T = 33\text{K}$ is taken from ref. [19].

![Scheme showing phase transitions and conduction mechanism](image)

| VI | V | IV | III | Change in conduction mechanism | I |
|----|---|----|-----|---------------------------------|---|
| 33 | 110| 258| 345 | 428±2                           | 486±1 |

| T$_5$ | T$_4$ | T$_3$ | T$_2$ | Ferroelectric phase II Monoclinic ($P\text{m}, z = 2$) | Paraelectric phase I rhombohedral ($R\text{3}m, z = 1$) |
|-------|-------|-------|-------|---------------------------------------------------|---------------------------------------------------|
| Ferroelectric | Room temperature phase III Triclinic ($P\overline{1}, z = 4$) | | | |

TK
Table 1a. Summary of Phase Transitions in KIO₃

| Phase Transition | Symmetry | Transition Temperature (TK) | Technique or property | Reference |
|------------------|----------|-----------------------------|----------------------|-----------|
| I-II             | I (R₃m, Z=1) | 485K | Raman Spectroscopy | [24] |
|                  |          |                | Elastic and piezoelectric | [19] |
|                  |          |                | Detewenning and domain removing procedure | [22] |
|                  | I (R₃, Z=1) | (486±1)K | Ferroelectricity and optical properties. | [15] |
|                  |          | 487K | Ac conductivity | [20] |
|                  |          |                | Thermal properties | [25] |
| II-III           | II Monoclinic (Cm, Z=8) | 345K | Raman Spectroscopy | [24] |
|                  |          |                | Ac conductivity | [20] |
|                  |          |                | Thermal properties | [25] |
|                  |          |                | Ferroelectricity and optical properties. | [15] |
|                  | Monoclinic (Pm, Z=4) | 345.5K | Elastic and piezoelectric | [19] |
|                  |          | 345.6K | Elastic properties | [23] |
|                  |          | 343K | Detewenning and domain removing procedure | [22] |
| III-IV           | III Triclinic (P1, Z=4) | 258K | Ac conductivity | Present work |
|                  |          |                | Raman Spectroscopy | [17] |
|                  |          |                | Elastic and piezoelectric | [19] |
| IV-V             | IV Triclinic (P1, Z=4) | 110K | Ac conductivity | Present work |
|                  |          |                | Raman Spectroscopy | [17] |
|                  |          | 113K | Elastic and piezoelectric | [19] |
| V-VI             | VI Triclinic (P1, Z=4) | 33K | Elastic and piezoelectric | [19] |
Table 1b: Summary of the crystal structure at some selected temperatures for the compound KIO3

| Temperature | Crystal Data         | Technique                          | Reference |
|-------------|----------------------|------------------------------------|-----------|
| 530K        | Rhombohedral, R3m, Z = 1 | High energy X-ray powder diffraction MEM/Reitveld analysis | [29]      |
| 523K        | Rhombohedral, R3, Z = 1   | Neutron powder diffraction technique (Rietveld method) | [30]      |
| (Room Temperature) | Triclinic symmetry | Single crystal X-ray diffraction | [28]      |
| 523K        | Triclinic, P1, Z = 4 | Neutron powder diffraction technique (Rietveld method) | [31a]     |
| 300K        | Triclinic, P1, Z = 4 | Neutron powder diffraction technique (Rietveld method) | [31b]     |
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