

Dielectric and AC Conductivity of Potassium Perchlorate, KClO_4

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The AC conductivity $\sigma(\omega)$ and the complex dielectric permittivity $\varepsilon^*(\omega)$ were studied as function of temperature $300 \text{ K} < T < 600 \text{ K}$ and at some selected frequencies (1–20 kHz) for polycrystalline sample of KClO_4 . The differential thermal analysis (DTA) thermograph was also performed. The combined data support each other and indicate the existence of a structural phase transition at $\approx 575 \text{ K}$. Moreover, the temperature dependence of the ac conductivity behaves in accordance with Arrhenius relation, whereas the frequency dependent conductivity obeys the power law $\sigma(\omega) = A\omega^{s(T)}$. The behavior of s with temperature suggests that the hopping over the barrier model prevails. No evidence for the existence of a ferroelectric phase transition at the transition temperature.

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1. Introduction

Potassium perchlorate KClO_4 is an important member of monovalent or alkali metal of the general molecular formula MClO_4 where M stands for a monovalent metal ion ($\text{M} = \text{Cs}, \text{Rb}, \text{K}, \text{Na},$ and/or NH_4). On the other hand, the molecular formula of a related series, namely divalent metal perchlorates is $\text{D}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ where D is a divalent metal ion ($\text{D} = \text{Zn}, \text{Cu}, \text{Ca},$ etc.) and x is the number of water molecules, *i.e.*, $x = 0, 1, 2, \dots$. All these perchlorates are salts of perchloric acid which attract the attention of investigators owing to their interesting properties. For example, most of these compounds undergo structural phase transitions at high and low temperatures [1–8]. Furthermore the crystal structures of some members of these series were determined [9–11]. Among other things one may replace the above mentioned formula by MhO_4 and $\text{M}(\text{hO}_4)_2 \cdot x\text{H}_2\text{O}_4$, where h is a halogen atom ($\text{h} = \text{Cl}, \text{Br}, \text{I}, \dots$) the other symbol take their usual meanings. For perbromate compound the crystal structure of $\text{LiBrO}_4 \cdot 3\text{H}_2\text{O}$ [12] and $[\text{Ca}(\text{H}_2\text{O})_4](\text{BrO}_4)_2$ [13] were also investigated.

For the alkali metals perchlorate with $\text{M} = \text{Cs}, \text{Rb},$ and K , the modulus spectroscopy and dielectric dispersion were performed on single crystals prepared by the gel technique [2]. A high temperature phase transition was detected around $\approx 302^\circ\text{C}$ (575 K).

Literature survey indicated that there are no reported data on the type of conduction mechanism in the present compound. This initiated the motivation behind the

present work, where the electrical parameters are determined and presented according to the current style. This is considered as a continuation of our research program where the dielectrical properties are investigated as a function of both frequency and temperature [14] for some selected disordered solids. Furthermore, the confirmation of the structural phase transition in the compound is also one of our objectives.

The starting point is that, the complex dielectric permittivity $\varepsilon^*(\omega)$ can be resolved into, the real part $\varepsilon'(\omega)$ and the imaginary part $\varepsilon''(\omega)$ according to the equation:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \quad (1)$$

Furthermore, the total measured conductivity $\sigma_{\text{tot}}(\omega, T)$ for a wide class of dielectric materials (semiconductors, organic, inorganic, glass, etc.) shows dispersion behavior through its dependence on the frequency (ω) according to Jonsher relation [15]:

$$\sigma_{\text{tot}}(\omega, T) = \sigma(0, T) + \sigma_{\text{ac}}(\omega, T). \quad (2)$$

The frequency dependent part $\sigma_{\text{ac}}(\omega, T)$ follows the power law:

$$\sigma_{\text{ac}}(\omega, T) = A(T)\omega^{s(T)}. \quad (3)$$

The above equation is called the power law or universal dynamic response and is used to analyze the conductivity in all disordered solids [15–29]. In this equation $A(T)$ and $s(T)$ are characteristic parameters which are temperature dependent. Of particular interest, is the frequency exponent whose value lies in the range $0 < s < 1$. The exponent measures the degree of interaction of mobile ions with the environment [16]. $A(T)$ determines the polarizability [29]. For Debye type interaction $s \approx 1$ and for pure ionic crystal $s \approx 0$, *i.e.*, s decreases with the increase of interaction. The temperature dependence of

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s determines, to a large extent, the type of conduction mechanism.

2. Experiment

The samples used in the present work were supplied by BDH Laboratory Reagent, the British Drug Houses LTD., London and manufactured in England (99.9% purity). The polycrystalline powder was compressed under a suitable pressure to form discs (pellets) of about 1 cm diameter and 1–2 mm thickness, and good contact was obtained by painting both faces of sample with air-drying conducting silver paste. A sample holder with brass electrodes was especially designed to fit the present measurements. The sample holder was inserted into an electric furnace which is connected to a temperature controlled ac-variatic. The electrical parameters (R , C and Z) were measured using a digital RLC bridge Philips PM6304. Data were collected for at least three samples and the results were found to be quite consistent and reproducible. The measured values of R , C and Z at different temperature and frequency were converted into AC-conductivity σ_{ac} and relative permittivity ϵ' , using the area and the thickness measurements of the pellet by using a simple program where the bridge is interfaced with a computer. All measurements were carried out at thermal equilibrium. Calibration, using standard material is usually performed before any actual measurements. The experimental errors of both σ_{ac} and ϵ' are lower than $\pm 3\%$.

2.1. Electrical parameters

2.1.1. Dielectric permittivity

The temperature dependence of the real part ϵ' of the complex dielectric permittivity measured in the temperature range $300\text{ K} < T < 600\text{ K}$ and at different frequencies 1–20 kHz is shown in Fig. 1. As one can see, the value of ϵ' (for frequencies higher than 5 kHz) is nearly temperature independent up to $\approx 560\text{ K}$, beyond which, the value of ϵ' decreases to a minimum value at $T \approx 575\text{ K}$ then it starts to increase again with temperature. This behavior of ϵ' vs. T , suggests the existence of some sort of structural phase transition at this particular temperature.

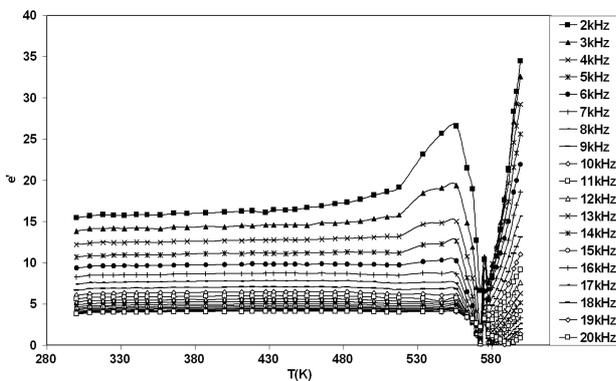


Fig. 1. Temperature and frequency dependence of the real part ϵ' of the dielectric permittivity.

The dependence of ϵ' on the frequency in the same temperature interval is shown in Fig. 2. For the purpose of clarity only selected temperatures are chosen. The general feature of the plot is that the dispersion increases with increasing temperature and decreasing frequency in accordance with the typical behavior of the dielectric.

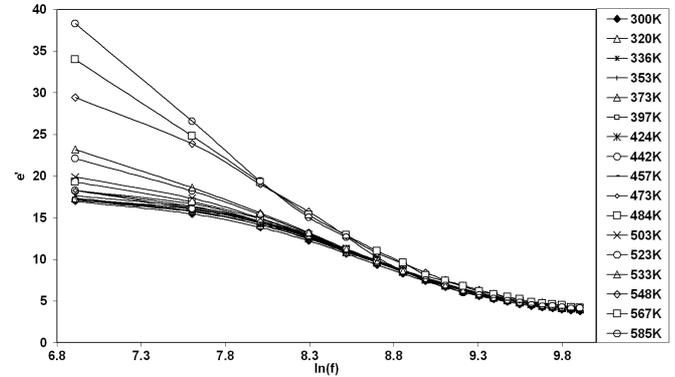


Fig. 2. Relation between ϵ' versus $\ln(f)$.

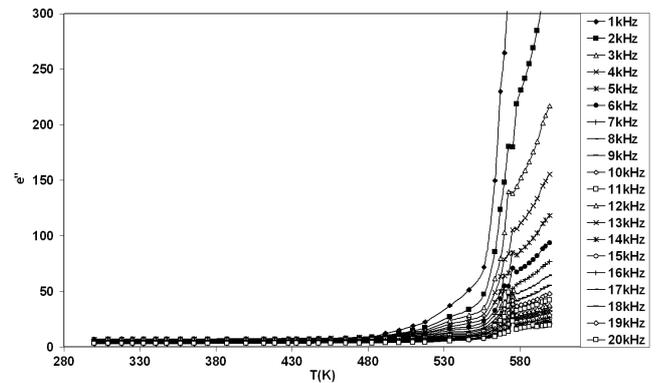


Fig. 3. Variation of the imaginary part ϵ'' of the dielectric permittivity as function of temperature measured at different frequencies.

Figure 3 shows the variation of the imaginary part ϵ'' with temperature measured in the same frequency range 1–20 kHz. The general feature of this plot is that, the value of ϵ'' is almost temperature independent and also frequency independent in the interval $300\text{ K} < T < 480\text{ K}$. However, as the temperature exceeds 500 K, the loss factor ϵ'' increases. Another point of interest is the existence of a kink at about $T \approx 575\text{ K}$, indicating also the possibility of phase transition and/or a change in the conduction mechanism.

2.1.2. Electrical conductivity $\sigma(\omega)$, temperature dependence

The AC conductivity data is usually presented in terms of an Arrhenius relation:

$$\sigma_{ac}(T) = \sigma(0) \exp(-E_g/kT), \quad (4)$$

where E_g is the activation energy of the process and the other terms take their usual meanings.

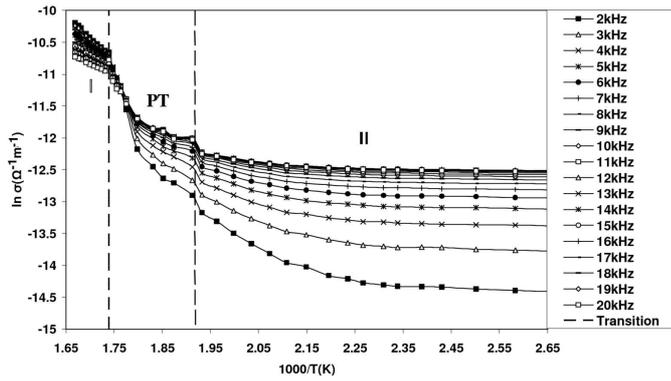


Fig. 4. Relation between $\ln(\sigma_T)$ versus $1000/T$ at different frequencies.

Figure 4 represents a relation between $\ln\sigma(T)$ and $1000/T$. One can identify two temperature regions designated by I and II, in addition to a limited-pretransition-region.

Region II ($300\text{ K} > T \geq 480\text{ K}$):

This region is characterized by a linear variation of $\ln(\sigma)$ and $1000/T$. Moreover, the value of $\ln(\sigma_{ac})$ (and hence σ_{ac}) is almost temperature independent, but frequency dependent. This behavior reflects an extrinsic conduction type. The values of E_g are nearly equal. The more acceptable value is $E_g = 0.05 \pm 0.01\text{ eV}$.

Pretransition region (PT) ($480\text{ K} > T \geq 575\text{ K}$):

In this region the change in the conductivity is very fast and becomes temperature and frequency dependent. The results show abrupt change in the slope of the curve compared with region II. In the vicinity and just before the transition, the conductivity becomes frequency independent. The data in this case are so limited and hence the value of E_g is not calculated here.

Region I ($575\text{ K} > T > 630\text{ K}$):

In this temperature range, the conductivity depends on both the frequency and the temperature. As one can see, for a given frequency, the value of $\ln(\sigma_{ac})$ increases with increasing temperature, and decreases with increasing frequency. The values of the activation energy decrease from 0.55 eV at 1 kHz to 0.3 eV at 20 kHz .

2.1.3. Electrical conductivity $\sigma(\omega)$, frequency dependence

Figure 5 shows, the double logarithmic plot, *i.e.*, $\ln(\sigma_{ac})$ vs. $\ln(\omega)$. The graph is characterized by a set of, approximately, straight lines of different slopes in accordance with the universal dynamic response (the power law, Eq. (3)). The slope of each line gives the value of the frequency exponent s at the corresponding temperature:

$$s = [\delta \ln(\sigma_{ac}) / \delta \ln(\omega)] \quad (5)$$

In Fig. 6, the temperature dependence of s is displayed. The general behavior of the plot is that s decreases slowly with increasing temperature and its value is less than unity. Figure 7 shows the variation of parameter $A(T)$ with temperature plotted as $\ln(A(T))$ versus T . The gen-

eral trend of the plot is that there is a gradual increase in the value of $\ln A(T)$ as the temperature increases.

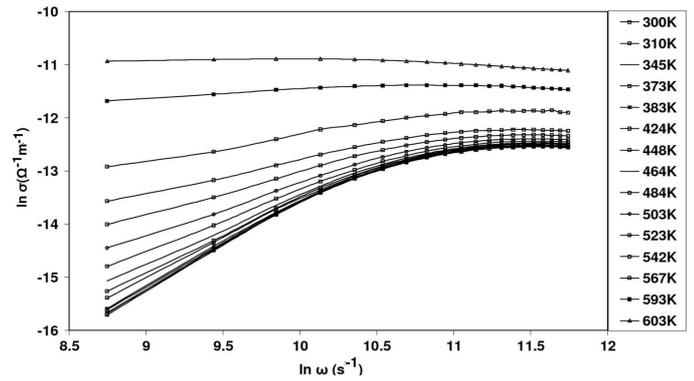


Fig. 5. Double logarithmic plot ($\ln(\sigma)$ vs. $\ln(\omega)$).

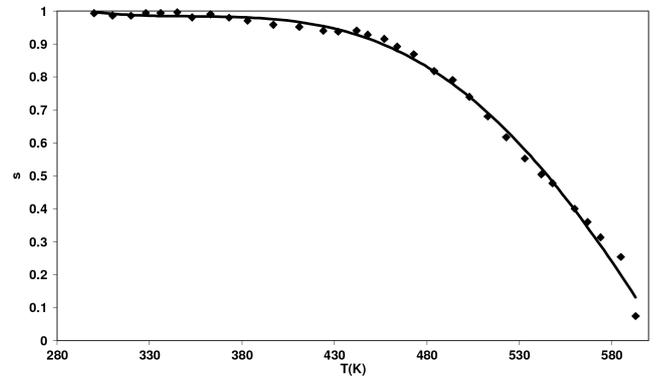


Fig. 6. Temperature dependence of frequency exponent s .

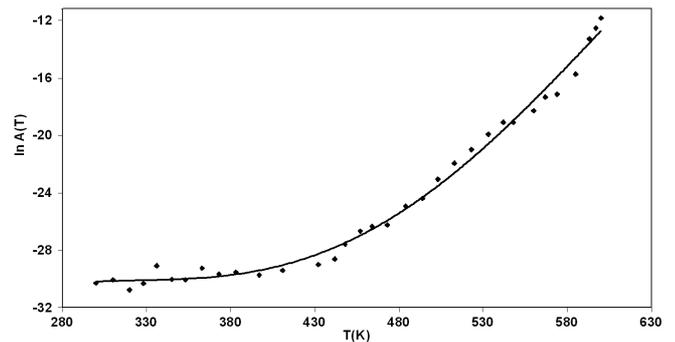


Fig. 7. The variation of $\ln(A(T))$ with the temperature T .

2.2. Thermal parameters

The differential thermal analysis (DTA) thermogram as performed by Shimadzu detector DTA-50 with a heating rate $5^\circ\text{C}/\text{min}$ in the temperature range $280\text{ K} < T <$

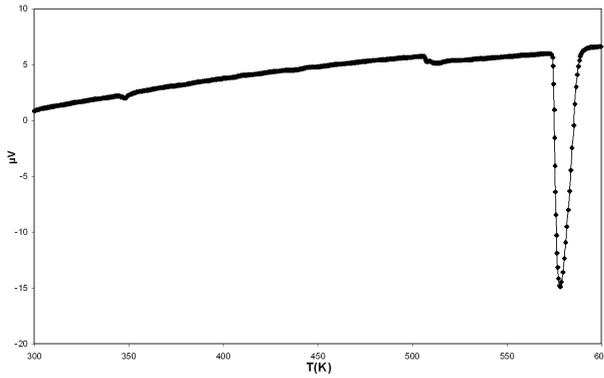
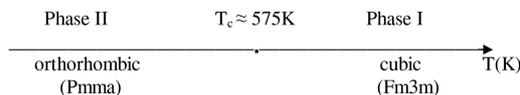


Fig. 8. The DTA thermogram.

670 K is shown in Fig. 8. The plot is characterized by a very sharp endothermic peak centered at $T \approx 578$ K. This behavior shows a clear structural phase transition at ≈ 575 K.

3. Discussion

The endothermic peak centered at $T \approx 578$ K in the DTA thermogram, Fig. 8, is considered as an indication of the existence of a structural phase transition at this temperature, specially where there is no practically any loss in the weight of the sample at that temperature as given in reference [1]. Therefore, the anomalies found in the measured electrical parameters, around $T \approx 580$ K, are a reflection of the structural phase transition and not due to the change in the conduction mechanism. This transition is of the order — disorder type, *i.e.*, it is due to the disorder of the ClO_4 group. Further details are given elsewhere [2]. This is in good agreement with previous work [1, 2]. The higher values of ε' and/or ε'' in the transition temperature region may suggest the existence of Ferro electricity. For this reason, a usual circuit for testing such possibility was used. However, the test was found to be negative. Thus, the possibility of a ferroelectric phase transition has been excluded in the present work since there is no evidence for the formation of hysteresis loops over the investigated temperature range. Thus the higher values of ε' and ε'' is therefore due to the surface polarization effect [2] rather than Ferro electricity. One can summarize the phase transition as follows:



Regarding the conduction mechanism, it is known that, there are three distinct processes [26] that have been proposed; namely, quantum mechanical tunneling (QMT) through the barrier, classical hopping over the barrier (CBH) and small polaron tunneling (SPT). The expression for AC conductivity due to (QMT) is given by [27]:

$$\sigma(\omega) = (\eta/3)e^2kT(N(E_f)T)^2\alpha^{-5}\omega[\ln(v_{ph}/\omega)]^4 \quad (6)$$

where $N(E_f)$ is the density of states at Fermi level, v_{ph} is the phonon frequency in the order of 10^{13} sec^{-1} and α is the decay of the localized states wave function ($\alpha \approx 1 \text{ \AA}$) [16]. The expression that describes the behavior of s , in the QMT model is given by:

$$s = 1 - \{4/\ln(v_{ph}/\omega)\} \quad (7)$$

whereas, for classical hopping:

$$s = 1 - 6kT/\{E_o - kT \ln(v_{ph}/\omega)\} \\ = 1 - 6kT/\{E_o - kT \ln(1/\omega\tau)\}. \quad (8)$$

and for small polaron [16]

$$s = 1 - 4/[\ln(1/\omega\tau) - W_H/kT] \quad (9)$$

The symbols take their usual meanings. k is Boltzmann's constant, T — absolute temperature, E_o — optical energy gap, ω — angular frequency, v_{ph} and τ ($\tau = 1/v_{ph}$) are the phonon frequency and the relaxation time respectively, and W_H is the activation energy involved on the electron transfer process between a pair.

From Eqs. (6) and (7) for QMT model, it is clear that the value of s is temperature independent whereas, for hopping model, Eq. (8), the value of s decreases with increasing temperature and less dependent on the frequency, and finally, Eq. (9) predict that s increases as T increases.

Figure 6 indicates that the value of s decreases with increasing temperature. This means that, in the investigated temperature region, the data confirm the hopping model (CBH).

Figure 7 shows an increasing of $A(T)$ as the temperature increases which means the polarizability increases as temperature increases.

4. Conclusions

The present work represents the first report on AC conductivity and permittivity on the polycrystalline sample of $KClO_4$. The data confirm the existence of a structural phase transition at $T \approx 575$ K. Moreover, the absence of ferroelectric hysteresis loops gives strong evidence that the structural transition is not associated with a ferroelectric phase change. Another important point of interest is the use of the power law in the analysis of our data where the conduction mechanism is found to occur via the hopping over the barrier model (CBH).

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