

## A Comparative Study of the Conduction Mechanism in Potassium Halides

KALPANA SHAHI\* and PRAHLAD KUMAR†

*Department of Chemistry, J.D. Women's College, Patna-800 001, India*

The electrical conduction mechanisms, in direct current and alternating current fields, have been studied using KCl, KBr and KI as samples. Space charge limited conduction and the presence of traps play a major role in direct current measurement. The relaxation effect is predominant in these alkali halides in alternating current fields. Effects of orientational polarization is noted.

**Key Words: Potassium halides, D.C. and A.C. Conductance, Space charge limited conduction, Polarization.**

### INTRODUCTION

The electrical conduction mechanisms in solids depend on the chemical composition, structure of substances and various external factors such as temperature, humidity, frequency changes and electric field. Such studies reveal the polarization mechanism in compounds and give considerable evidence regarding the structure of the compounds under investigation. Structure property relations of chemical compounds provide immense possibilities for the development of new molecules, radicals and ions of unusual and interesting properties. The diversity in the range of properties open up possibilities of newer applications and is of fundamental importance to solid state chemistry.

The samples under study-potassium chloride, potassium bromide and potassium iodide in the solid state behave as dielectrics which offer a high resistance to the passage of electric current and therefore sharply differ in their basic electrical properties from metals, semiconductors or superconductors. All the alkali halides have a common rock salt type of crystal structure<sup>1</sup>. In their crystal, they have a cubic close packed (*i.e.*, face centered cubic) arrangement of ions and differ only in the position of the cations.

Some interesting crystalline solids in which polarization can take place leading to a dipole moment can broadly be divided into two classes (a) polar (dipole) dielectrics and (b) non-polar (neutral) dielectrics. In polar dielectrics, a finite and permanent polarization known as spontaneous polarization ( $P_s$ ) exists even in the absence of the applied electric field<sup>2-5</sup>. In the case of non-polar dielectrics there is no permanent

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†Department of Chemistry, Patna University, Patna-800 005, India.

or spontaneous polarization in the absence of an electric field. When solid carriers are trapped in the material, in course of their motion, they either become trapped in them or settle on the interfaces and cannot be freely discharged or replaced at the electrodes. In this way special charges and a macroscopic field directly results in the material.

In present studies, the results of investigations on the conduction mechanisms in D.C. as well as A.C. fields are reported.

### EXPERIMENTAL

Potassium halides (KCl, KBr and KI) were of analytical grade obtained from BDH, India. After recrystallization the samples were compressed into pellets using a hydraulic press.

**Direct current measurements:** The stabilized mains voltage was stepped up beyond 1000 volts with the help of a DC power unit fabricated in the laboratory. For further smoothing of the voltage a series of zener diodes were used. The output voltage was calibrated using a digital Phillips multimeter (Model PM 2525). The experimental material in the form of a pellet was placed between the electrodes of a specially designed sandwich, type cell. The temperature of the experiment was varied using electrically operated air oven.

**Alternating current measurement:** An AF signal generator (Type H, Model 1) manufactured by Advance Components, England was used for applying alternating field to the experimental material. This gave an output voltage from 0-20 V and the frequency ranged from 300 Hz to 50,000 Hz.

### RESULTS AND DISCUSSION

Pellets of potassium halides of different thickness (0.5 to 5.0 mm) were subjected to varying D.C. voltage (50-1000 V). currents through these samples were measured in the manner described earlier<sup>6</sup>. The effect of temperature on the current through the samples was also recorded.

Table-1 gives the values of current through two different samples of KCl (of thickness 1.43 and 2.38 mm). The voltage is varied from 50 to 1000 V. A graphical plot of  $\log I$  vs.  $\log V$  of the above results showed two regions of different slopes. Till about 600 V, *i.e.* between 50 to 600 V, the samples show ohmic behaviour, the graphical plots being linear. At higher voltage the current is non-ohmic. The slopes of the non-ohmic regions lie between 2.0 to 2.5.

$$i.e., I \propto V^{2 \text{ to } 2.5}$$

The voltage at which change from ohmic conduction to non-ohmic occurs is called the transition voltage ( $V_t$ )<sup>7</sup>. The transition voltage shifts to lower values with increase of temperature.

Table-2 gives the values of current at different temperatures through a sample of KCl at two constant voltages. A graphical plot of  $\log I$  vs.  $T^{-1}$  for the above

TABLE-1  
CURRENT VOLTAGE MEASUREMENTS FOR POTASSIUM CHLORIDE  
SAMPLES OF DIFFERENT THICKNESS

Voltage (V) in volts	Current (I) in micro amperes	
	Sample I (1.42 mm thick)	Sample II (2.38 mm thick)
50	0.795	0.476
100	1.386	0.931
150	2.400	1.291
200	3.049	1.830
250	3.981	2.321
300	5.101	2.526
350	6.227	2.877
400	7.100	3.366
450	7.223	3.945
500	9.438	4.221
550	11.825	4.747
600	13.910	5.712
650	16.524	6.231
700	20.086	7.524
750	23.098	8.731
800	27.541	9.292
850	30.887	11.639
900	35.059	13.074
950	39.719	14.879
1000	44.040	15.818

TABLE-2  
VARIATION OF CURRENT WITH TEMPERATURE FOR  
POTASSIUM CHLORIDE AT CONSTANT VOLTAGE

Temperature (K)	Current in micro ampere	
	200 V	800 V
373	0.135	1.319
383	0.174	1.387
393	0.298	1.751
403	0.340	2.159
413	0.404	2.478
423	0.581	3.277
433	0.590	4.275

Sample thickness = 2.38 mm

measurements showed linear curves with slopes nearly equal to -1.91 in the ohmic and -1.39 in the non-ohmic regions, respectively. Thus the activation energy has a higher value ( $36.56 \text{ JK}^{-1} \text{ mol}^{-1}$ ) in the ohmic region than in the non-ohmic region ( $26.61 \text{ JK}^{-1} \text{ mol}^{-1}$ ).

Potassium bromide in the form of pellets were subjected to similar investigations as for KCl sample. Table-3 gives values of current through different samples of KBr. A graphical plot of  $\log I$  vs.  $\log V$  shows ohmic conduction (linear curves) till about 650 V. At high voltages the rate of increase of current drops and the slope shows decrease in magnitude.

TABLE-3  
CURRENT VOLTAGE MEASUREMENTS FOR POTASSIUM BROMIDE  
SAMPLES OF DIFFERENT THICKNESS

Voltage (V) in volts	Current (I) in micro amperes	
	Sample I (1.17 mm)	Sample II (3.17 mm)
50	0.050	0.029
100	0.101	0.058
150	0.153	0.089
200	0.219	0.127
250	0.271	0.145
300	0.319	0.181
350	0.363	0.205
400	0.403	0.230
450	0.459	0.275
500	0.512	0.292
550	0.564	0.321
600	0.509	0.353
650	0.685	0.384
700	0.720	0.417
750	0.727	0.423
800	0.747	0.455
850	0.783	0.473
900	0.821	0.491
950	0.843	0.504
1000	0.879	0.525

At higher temperatures fall in the values of the slopes become less prominent and ultimately ohmic conduction occurs in the range of voltage chosen. Table-4 shows the values of current through KBr sample at different temperature.  $\log I$  vs.  $T^{-1}$  plots for the above measurements show linear curves with slopes equal to -3.10. The activation energy  $E_a$  for both regions is  $59.34 \text{ JK}^{-1} \text{ mol}^{-1}$ . Investigations similar to KCl and KBr were carried out for KI samples.

Table-5 shows the values of current through different sample thickness of KI pellets. A graphical plot of  $\log I$  vs.  $\log V$  show that the current through the samples are ohmic till about 800 volts. Beyond this voltage the slopes of the curve decrease to a value nearly equal to 0.70. Similar measurements at higher temperatures show that the nature of the curves remain the same with a slight shift in the transition voltage to higher values.

TABLE-4  
 VARIATION OF CURRENT WITH TEMPERATURE FOR  
 POTASSIUM BROMIDE AT CONSTANT VOLTAGE

Temperature (K)	Current in micro ampere (sample thickness - 3.17 mm)	
	200 V	800 V
373	0.122	1.422
383	0.271	1.896
393	0.352	2.657
403	0.536	3.839
413	0.974	7.438
423	1.302	9.123
433	2.281	16.701

TABLE-5  
 CURRENT VOLTAGE MEASUREMENTS FOR POTASSIUM IODIDE  
 OF DIFFERENT THICKNESS

Voltage (V) in volts	Current (I) in micro amperes	
	Sample I (1.17 mm)	Sample II (3.17 mm)
50	0.350	0.257
100	0.760	0.456
150	1.239	0.773
200	1.520	0.930
250	2.009	1.288
300	2.379	1.545
350	2.860	1.811
400	3.140	2.051
450	3.420	2.369
500	3.691	2.677
550	4.279	2.934
600	4.560	3.133
650	4.830	3.399
700	5.420	3.606
750	5.810	3.865
800	6.183	4.265
850	6.340	4.346
900	6.603	4.556
950	6.863	4.699
1000	7.115	4.878

A plot of  $\log I$  vs.  $T^{-1}$  for a KI sample at a definite voltage shows a linear behaviour activation energy calculated from the slope of the curve is found to be nearly equal to  $10.72 \text{ JK}^{-1} \text{ mol}^{-1}$ .

Electrical conduction in potassium chloride may be divided into two major parts:

(i) where ohm's law is obeyed,  $I \propto V$

(ii) where ohm's law is not obeyed,  $I \propto V^n$

where  $2 < n < 3$ . This region corresponds to the space charge limited conduction.

Rose<sup>8</sup> has treated conductance of insulators with traps distributed in their energy levels. For a given applied voltage the charge  $Q$  forced into the insulator is distributed in three major parts (a) free charge in the conduction band (b) trapped charge near the newly developed Fermi level and (c) trapped charge condensed in the states between the original Fermi level and the newly developed Fermi level. Since the condensed charge is likely to be close to the total charge, the new location of the Fermi level is given clearly by considering all the charge  $Q$  to be condensed. With this approximation the shift in Fermi level will be proportional to the space charge  $Q$  which is in turn proportional to the applied voltage  $V$ .

The free carrier density  $n_c$  is given by

$$n_c = N_c e^{-E_F/KT} e^{\Delta E/KT} \quad (1)$$

where  $N_c$  = number of states at the bottom of the conduction band.  $E_F$  = original distance of the Fermi level from the conduction band and  $\Delta E$  = shift in the position of the Fermi level owing to the charge  $Q$  forced into the insulator by the applied voltage  $V$ .

$$\Delta E = \frac{Q}{en_t a} \quad \text{or,} \quad \Delta E = \frac{VC}{en_t a} \quad (2)$$

where  $n_t$  = number of traps per  $\text{dm}^3$  per unit range in energy,  $e$  = electronic charge,  $a$  = distance of separation between the two plates,  $C$  = capacitance of the material between the plates.

From eqns. 1 and 2, the free carrier density is given by

$$\begin{aligned} n_c &= N_c e^{-E_F/KT} e^{VC/n_t a e KT} \\ &= n_\infty e^{\alpha V} \end{aligned} \quad (3)$$

where  $n_\infty$  = initial thermal equilibrium concentration of the free carriers and  $\alpha$  is used for  $C/n_t a e KT$ .

The density of the trapped carriers is nearly equal to the total density of the injected electrons.

*i.e.* density of trapped carrier is equal to

$$\frac{Q}{ae} = \frac{VC}{ae} \quad (4)$$

The fractional value of the free charge from eqns. 3 and 4 is equal to

$$Q = (en_\infty a / VC) e^{\alpha V} \quad (5)$$

$Q$  depends exponentially on the applied voltage  $V$ . The distribution of traps in energy causes the space charge limited current to increase exponentially with voltage, in the non-ohmic region. The exponential dependence is a consequence of the

assumption of a uniform distribution of traps. If the uniform distribution of traps is replaced by one that decreases with distance from the conduction band, the exponential is replaced by a high power function of the voltage.

The steepness of the trap distribution is approximated by a characteristic temperature  $T_C$  such that

$$n_t \propto e^{-E/KT_C} \quad (6)$$

where  $E$  = measured from the bottom of the conduction band. Small values of  $T_C$  lead to trap distribution varying rapidly with energy while large values of  $T_C$  approximate a slowly varying trap distribution. The voltage dependence of space charge limited current is

$$I \propto V^{(T_C/T+1)} \quad (\text{for } T_C > T)$$

which means that the current varies more rapidly with the applied voltage than in the case of the trap free or discrete levels with traps.

Electrical conduction in potassium bromide can be divided into two regions.

(i) Region I in which ohm's law is obeyed.

(ii) Region II in which ohm's law is not obeyed and the slope falls to a value less than one. In this region the slope is nearly equal to 0.7 indicating a fall in the rate of rise of conductivity. This is attributed to interaction between electrons and phonons. This interaction of electrons with phonons and the consequent distortion of the material around a trapped or free carrier, may lead to the following effects.

(a) A carrier which is trapped by a defect in a crystal will distort its surroundings. This distortion will lower the energy.

(b) For a carrier in the conduction band of a crystal, if the interaction energy between the carriers and the phonons is high in comparison with the band width, a small polaron may form. These polarons behave like a particle with enhanced mass at low temperature. At high temperatures it moves by thermal hopping.

The electron phonon coupling is dominant only over a limited temperatures range. From the current voltage characteristics of potassium bromide at different temperature it was seen that at room temperature all samples showed a fall in the rate of rise of current. At temperatures beyond 50 °C the current continues to increase with the applied voltage.

In case of potassium iodide (Table-5) the  $\log I$  vs.  $\log V$  plots show a linear behaviour except for a slight decrease in the value of the slopes at higher voltages in some samples. The magnitude of the current is however, greater in case of potassium iodide as compared to potassium bromide for similar field strengths.

A fresh approach to the theory and discription of non-molecular crystals has been developed by Sanderson. This theory regards all bonds in non-molecular crystal structure as being polar covalent. The atoms contain partial charges and from these partial charges, the relative contributions of the ionic and covalent bonding to the total bond energy may be estimated. Since all non-molecular crystals contain only partially charged atoms, the ionic model represents an extreme form of bonding

TABLE-6  
 VARIATION OF CURRENT WITH TEMPERATURE FOR A SAMPLE OF  
 POTASSIUM IODIDE AT A CONSTANT VOLTAGE (200 V)

Temperature (K)	Current in micro ampere (sample thickness - 3.40 mm)
373	0.469
383	0.470
393	0.460
403	0.530
413	0.593
423	0.683
433	0.723

and is not attained in practice. In KCl the charge on the atoms are calculated to be  $\pm 0.76$  instead of  $\pm 1.0$  for a purely ionic structure. Considering the above argument the covalent character in potassium bromide and iodide would be even more because the halide atoms show greater polarization with increase size. Thus potassium iodide in which the covalent character should be the greatest, shows the highest value of current (ohmic) and the lowest activation energy in this region. However, in a study of the kinetics of trapped electrons in alkali halide crystals under electron injection<sup>9</sup>, it was observed that KI needed a lower electric field than KCl for similar current and the current growth in KCl was sluggish as compared to KI. This was explained by the presence of shallower distribution of traps in KI as compared to KCl.

**(ii) Electrical conductance in potassium halides using alternating current:**

Samples of potassium chloride, bromide and iodide were prepared in the form of pellets of different thickness (0.35-2.25 mm). Current through these samples at different voltages and varying frequencies were recorded. Such measurements were repeated at different temperatures to study the effect of temperature on electrical conduction. Table-7 shows the variation in current through potassium chloride with varying frequencies at three different voltages of 1, 5 and 10 V. The current rises initially with an increase in frequency. However, saturation sets in at about 8 KHz and the current then begins to fall at higher frequencies before it becomes more or less constant. This phenomenon indicates the relaxation effect in such compounds. With increasing voltage too, the relaxation frequency remains the same. However, the current rises with increase in voltage and the curves where plot become sharper. Similar observations were made for potassium bromide and iodide sample. A graphical plot of current *versus* frequency for these samples showed that the peaks in the current values (*i.e.*, relaxation frequency) occurred at 6.5 KHz for potassium bromide and 3.5 KHz for potassium iodide (Table-8). Thus all the three potassium halides (KCl, KBr and KI) show a relaxation effect in the current with increasing frequency of the applied field. The electric dipoles present in these polar compounds keep rotating in order to keep themselves in line with the applied field. However,



TABLE-7  
CURRENT FREQUENCY MEASUREMENTS FOR  
POTASSIUM CHLORIDE AT DIFFERENT VOLTAGES

Frequency (KHz)	Current in micro amperes		
	1 Volt	5 Volt	10 Volt
0.5	2.071	2.118	2.287
1.0	2.190	2.301	2.574
2.0	2.192	2.467	3.052
3.0	2.195	2.538	3.325
4.0	2.210	2.617	3.477
5.0	2.220	2.670	3.560
6.0	2.230	2.696	3.640
7.0	2.240	2.722	3.740
8.0	2.248	2.730	3.780
9.0	2.250	2.749	3.778
10.0	2.246	2.776	3.775
15.0	2.240	2.777	3.751
20.0	2.230	2.748	3.505
25.0	2.160	2.742	3.245
30.0	2.147	2.630	3.044
35.0	2.145	2.595	2.913
40.0	2.130	2.523	2.749
45.0	2.129	2.487	2.646
50.0	2.120	2.433	2.562

Samples thickness 0.88 mm.

as the frequency of the field is increased a point is reached because of inertia the dipoles cannot keep up their orientation with the changing alternating field *i.e.* the alternation of the polarization lags behind the field. This stagnation and decrease in the current through the sample is due to relaxation. The frequency beyond which the polarization no longer follows the field is called relaxation frequency. In this frequency range orientational/polarization plays the most important role in potassium halides.

The larger the size of the anion or cation of the dipole the greater will be the inertia and hence lower the relaxation frequency. The relaxation frequencies for the three potassium halides are in the following order KCl (8 KHz) > KBr (6.5 KHz) > KI (3.3 KHz) (Table-8).

The variation of current through samples of potassium halides was also recorded at different temperature. Table-9 shows the values of current through samples of KCl, KBr and KI at different temperatures. The graphical plots of  $\log I$  vs.  $\log V$  for these samples show linear curves with slopes equal to -0.55, -0.087 and -0.13 for KCl, KBr and KI, respectively.

In alternating current fields the alkali halides exhibit effects due to orientational polarization. Relaxation occurs because of the inertia of the charges. Relaxation

TABLE-8  
CURRENT FREQUENCY MEASUREMENTS FOR  
KCL, KBr AND KI AT 5 VOLT

Frequency (KHz)	Current in micro amperes		
	KCl (0.88 mm)	KBr (1.86 mm)	KI (1.17 mm)
0.5	2.118	0.230	1.461
1.0	2.301	0.352	1.474
2.0	2.467	0.551	1.542
3.0	2.538	0.670	1.588
4.0	2.617	0.724	1.605
5.0	2.670	0.767	1.615
6.0	2.696	0.780	1.617
7.0	2.722	0.792	1.619
8.0	2.730	0.813	1.625
9.0	2.749	0.822	1.626
10.0	2.776	0.813	1.625
15.0	2.777	0.817	1.624
20.0	2.748	0.815	1.621
25.0	2.740	0.800	1.620
30.0	2.630	0.790	1.618
35.0	2.595	0.782	1.614
40.0	2.523	0.764	1.594
45.0	2.487	0.733	1.583
50.0	2.433	0.688	1.571

TABLE-9  
VARIATION OF CURRENT WITH TEMPERATURE FOR  
KCl, KBr AND KI AT 5 VOLT AND 10 KHz FREQUENCY

Temperature (K)	Current in micro amperes		
	KCl (3.40)	KBr (1.76)	KI (2.25)
373	0.469	0.579	1.898
383	0.470	0.584	1.956
393	0.480	0.596	2.040
403	0.530	0.607	2.070
413	0.593	0.609	2.087
423	0.683	0.619	2.102
433	0.723	0.622	2.124

rather than a peak is explained by the presence of restoring forces which act in the opposite direction. The relaxation frequencies decrease with the increasing anion size.

#### ACKNOWLEDGEMENT

One of the authors (KS) acknowledges with thanks research grants offered to her as JRF and SRF from CSIR, New Delhi, India.

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(Received: 22 October 2007;

Accepted: 13 September 2008)

AJC-6859

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