CHAPTER III

AC AND DC BREAKDOWN STRENGTH OF SOME ALKALIHALIDES
3.1 Introduction

When a high electrical field is applied to a solid dielectric, work is done on the current carriers which in turn transfer some of their energy to the lattice, thus raising its temperature. It is also possible that the number of free electrons will increase due to the application of the field which will enhance the energy transfer to the lattice. Dielectric breakdown occurs when the lattice temperature 'T' reaches some critical value 'T'' at which there is a permanent change in the lattice. The different theories of dielectric breakdown (mentioned in the 1st Chapter) arise because of the different conditions which can govern the energy transfer from the field to the lattice via the current carriers. The theories show that if the applied field is less than or equal to a certain critical field, a steady state will arise with a stationary current flowing in the direction of the applied field and with a stationary distribution of the average lattice temperature which is everywhere less than 'T''. For field in excess of the critical field a non-stationary state will occur with a current which increases continuously as a function of time. This will cause the lattice temperature at some points to increase to 'T''. This leads to breakdown. Thus any field in excess of the critical field will lead to breakdown.
Measurements on the DC breakdown strength of various alkalihalides at room temperature were reported by Von Hippel (1935 a ), and Vorob'ev (1956). Present studies suggest a simple relationship for DC breakdown strength in terms of properties of alkalihalides and hence the average breakdown strength of 16 alkalihalides at room temperature have been calculated. A good agreement between the observed and calculated breakdown strength has been reported ( Table 3.1 ). Further the studies have been extended with AC and DC fields and for various extraneous media. Thickness and temperature dependence of breakdown strengths for NaCl, KCl and RbCl crystals were also measured.

3.2 Experimental procedure and sample preparation

The experimental procedures and sample preparations have been described in Chapter II.

3.3 Details of measurements

(1) Effect of extraneous medium: AC and DC breakdown strengths of alkalihalides (having thickness 0.05 mm to 0.10 mm ) were measured under the following ambient media:

(1) Air at atmospheric pressure and room temperature,
Fig. 3.0 - A plot of F and inter-ionic distance for Li-halides (using data ref. 3)
Fig. 3.1
Experimental values of breakdown strength versus atomic number in some alkali halides for semi-conducting liquid (12% sol. of acetone in xylene) as an ambient medium at room temperature.
Experimental values of breakdown strength versus atomic number in some alkali halides for transformer oil as an ambient medium at room temperature.
Experimental values of breakdown strength versus atomic number in some alkali halides for air as an ambient medium at room temperature.
(ii) Transformer oil.

(iii) Semiconducting liquid (12% solution of acetone in Xylene).

(2) The effect of thickness on breakdown strength: The variation of the breakdown voltage with thickness for NaCl, KCl and RbCl samples was measured in the range 0.05 to 0.25 mm at room temperature using the above mentioned media.

(3) Effect of temperature: The temperature range used in the present study is 0° to 250°C. The temperature is maintained constant with the help of a thermostat. The medium used for these studies is transformer oil.

3.4 Results

(1) The breakdown field strength of some alkali halides are compared in Figs. 3.1 to 3.6 for three different ambient media and from these curves following conclusions may be drawn:

(i) The magnitude of electric strength for DC and AC (50 Hz frequency) voltage is practically the same if AC peak value and DC value of voltages are taken into consideration.
Fig. 3.7 - Breakdown voltage versus thickness of NaCl.
Fig. 3.8 - Breakdown voltage versus thickness of KCl.
Fig. 3.9—Breakdown voltage versus thickness of RbCl.
(ii) The breakdown field is highest for the fluoride compounds of all the alkali-metals, followed by a decreasing value, as one goes from chloride to iodide compounds.

(iii) The breakdown strength is highest for Li compounds (alkalihalides) followed by Na, K and Rb in the gradually decreasing order.

(iv) The fall of breakdown strength for all the elements is observed to be very fast from fluoride to chloride, whereas the rate of all becomes less in going to bromide and iodide alkalihalides.

(v) The breakdown strength for all the samples is found to be lowest for air and highest for semiconducting ambient medium whereas for transformer oil the value is intermediate between the two values mentioned above. Approximately the value in air is found to be one half of that in semiconducting medium.

(2) Figs. 3.7, 3.8 and 3.9 indicate that the breakdown voltage varies very greatly for the samples of same thickness with the nature of the surrounding medium, being highest for semiconducting medium. The apparent electric strengths
Fig. 3.10 - The reciprocal of the mean breakdown field strength of NaCl as a function of the logarithm of the inter-electrode distance.
Fig. 3.11 - The reciprocal of the mean breakdown field strength of KCl as a function of the logarithm of the inter-electrode distance.
Fig. 3-12 - The reciprocal of the mean breakdown field \( \frac{1}{F} \) for RbCl as a function of the logarithm of the inter-electrode distance.
Fig. 3.13 – Breakdown field strength and calculated critical field strength over a range of temperature from 0° to 250°C for NaCl sample.
Fig. 3.14 - Breakdown field strength and calculated critical field strength over a range of temperature from 0° to 250°C for KCl sample.
Fig. 3.15 - Breakdown field strength and calculated critical field strength over a range of temperature from 0°C to 250°C for RbCl sample.
of the materials are not independent of thickness, but the applied voltage \( V \) at the breakdown is a linear function of thickness \( d \), thus \( V = a + bd \).

where \( a, b \) are arbitrary constants.

While \( b = 1.0 \) for semiconducting medium.

\[ b = 0.75 \] for transformer oil medium.

\[ b = 0.60 \] for air medium.

(3) The values of ionization parameters are shown in Table 3.2, calculated from Figs. 3.10, 3.11 and 3.12.

(4) The critical field strength for the Fröhlich high energy criterion Eqn. (1.19), Von Hippel-Callen low energy criterion Eqn. (1.22), and the Fröhlich-Paranjape collective criterion Eqn. (1.25) are plotted as function of temperature for NaCl in Fig. 3.13, for KCl in Fig. 3.14 and for RbCl in Fig. 3.15. The values of the relevant crystal constants were obtained from the standard data.\(^4\) The theoretical values as shown in the figures differ from those obtained experimentally which are indicated by vertical lines showing the range of variation of the observations.
### Table 3.1

**DC Breakdown Strength**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Experimental Breakdown strength F = 10^5 V/cm</th>
<th>Deviation from calculated values F = 10^6 V/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>3.05</td>
<td>+ 0.002</td>
</tr>
<tr>
<td>LiCl</td>
<td>2.03</td>
<td>+ 0.112</td>
</tr>
<tr>
<td>LiBr</td>
<td>1.76</td>
<td>- 0.120</td>
</tr>
<tr>
<td>LiI</td>
<td>1.42</td>
<td>+ 0.074</td>
</tr>
<tr>
<td>NaF</td>
<td>2.42</td>
<td>+ 0.048</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.53</td>
<td>- 0.022</td>
</tr>
<tr>
<td>NaBr</td>
<td>1.30</td>
<td>- 0.020</td>
</tr>
<tr>
<td>NaI</td>
<td>1.03</td>
<td>- 0.030</td>
</tr>
<tr>
<td>KF</td>
<td>1.80</td>
<td>+ 0.031</td>
</tr>
<tr>
<td>KCl</td>
<td>1.08</td>
<td>- 0.042</td>
</tr>
<tr>
<td>KBr</td>
<td>0.90</td>
<td>- 0.054</td>
</tr>
<tr>
<td>KI</td>
<td>0.77</td>
<td>+ 0.015</td>
</tr>
<tr>
<td>RbF</td>
<td>1.50</td>
<td>- 0.023</td>
</tr>
<tr>
<td>RbCl</td>
<td>0.95</td>
<td>- 0.027</td>
</tr>
<tr>
<td>RbBr</td>
<td>0.80</td>
<td>- 0.017</td>
</tr>
<tr>
<td>RbI</td>
<td>0.57</td>
<td>- 0.067</td>
</tr>
</tbody>
</table>
Table 3.2

$\lambda_{ni}$ and $H$ ionization parameters

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\lambda_{ni}$ (cm$^{-1}$)</th>
<th>$H$ (MV cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>$1.45 \times 10^5$</td>
<td>$5.15 \times 10^6$</td>
</tr>
<tr>
<td>KCl</td>
<td>$0.70 \times 10^5$</td>
<td>$3.00 \times 10^5$</td>
</tr>
<tr>
<td>RbCl</td>
<td>$0.30 \times 10^5$</td>
<td>$2.40 \times 10^6$</td>
</tr>
</tbody>
</table>

3.5 Discussion

(1) Effect of extraneous medium: Von Hippel has suggested a mechanism for the effect of extraneous ionization which appears to explain the most of the observed facts. The electric field between the electrodes will be strongest at points near the two electrode surfaces. As the applied voltage increases, the breakdown field strength of the medium is reached at some points, setting up brush discharges. The electrons so liberated move very much more rapidly than the positive
ions, with the result that around the anode surface a positive space charge is established. If this is uniformly distributed, it virtually increases the size of the anode and thus tends to reduce the field strength below the breakdown value for the medium. At the cathode on the other hand, the positive space charge left by the fast moving electrons, causes an increase of potential gradient and the brush discharge persists for a time, until eventually the electrons liberated from the cathode, produce a negative charge on the surface of the sample which is sufficient to stop the discharge. Thus a uniformly distributed brush discharge will not produce spurious results. Normally the brush discharges, especially at high voltage, are not uniform, but spread from the electrodes in tree formation and the branches virtually form additional electrodes. Thus instead of two symmetrically arranged electrodes, there becomes effectively an unsymmetrical arrangement consisting of the original anode, and a group of points connected to the original cathode as cathode.

Thus electrodes in air are unsuitable for breakdown strength measurement if the electric strength of material is much more above $0.1 \times 10^6$ V/cm. For transformer oil, although electric field strength and permittivity are much greater, it is doubtful whether the electrodes in oil are suitable for electric strength greater than that of the order of $0.5 \times 10^6$ V/cm. The 12½ solution of acetone in xylene mixture offers a wide range of measurement of field strength.
In Von Hippel's view the beneficial effect of semiconducting medium is due to the fact that the conductivity tends to prevent the strong local variation of field strength, minimizing the branched discharge. In the present study it was used as an immersion medium which provides linear breakdown potential variation with thickness, similar to chlorinated diphenyl with nitrobenzene which has been used by Thomas, and Hackett and Thomas up to 300°C. Alcohol in xylene has been used by Inge and Walther, and aniline by Grunewald, but it is also doubtful whether electric strength much more above $2 \times 10^5$ V/cm can be measured by this means. Moreover this type of the ambient medium suffers from the disadvantages of the chemical activity, limited temperature range, and high viscosity leading to air bubbles which may discharge locally.

The highest breakdown strength for fluoride compounds of alkali metals may be explained on the basis of inter-ionic distance for all these polar molecules. The data shows that the inter-ionic distance $'a'$ is lowest for fluorides increasing to higher value as one goes to iodide compounds. Franz empirical relation, $F = K \frac{26}{a^3}$ explains the present observations very well. The inter-ionic distance also increases with the atomic number $Z$ of the alkali group metals and hence the breakdown strength would decrease from Li halides to Rb halides. A plot of $F$ and inter-ionic distance $'a'$ gives a curve shown in Fig. 3.0. It is seen that the rate of fall of field with $'a'$ is very fast
indicating a cube power dependence. The volume of the unit cell is expressed as \( a^3 \) and as such the breakdown strength varies inversely as the volume of the unit cell of the substances.

Vorob'ev\(^2\) empirical relation connecting the breakdown strength and cohesive energy also supports the present observations. Since these are polar compounds, the inter-ionic forces are of electrostatic nature (Coulombian) i.e. a force of attraction existing between the two ions. The corresponding potential energy of the lattice may also be called cohesive energy. As the inter-ionic distance increases, the attractive force gets weaker and therefore the associated cohesive energy is reduced. This is true for all the alkalihalides, as it is clear from the Tables.\(^3\) The cohesive energy is the highest for Li halides, decreasing to Rb halides.

The experimental results indicate that the breakdown strength, in DC and AC (50 Hz frequency) voltage are of the same order of magnitude, if AC peak values of voltages are taken into account. However AC voltage favours a more non-uniform discharge because of undesirable ionization effects occurring near the electrodes more readily with alternating than with direct voltage. The surface charges as explained on page 67 which tend to reduce the potential gradients are reformed every half cycle with change of sign. Thus extraneous ionization effect becomes more pronounced.
However as shown in Chapter VI, a very short impulse voltage of duration of the order of a microsecond tends to give higher breakdown values because the voltage rise time is insufficient for the establishment of a strong subsidiary discharges (which tend to lower the breakdown strength) and with negligible Joule heating effect.

(2) Effect of thickness on breakdown strength: The thickness dependence of breakdown strength for all the samples as shown in Figs. 3.10 to 3.12, indicates a relationship (Equ. (1.37)), showing that the breakdown strength varies with inverse half power thickness. Vorob'ev and Murashko\textsuperscript{10}(1953) observed the thickness dependence breakdown strength in NaCl for thin specimen (5 - 20 \textmu m) at room temperature. Schissler\textsuperscript{11}(1950) investigated the breakdown strength of KBr with 1 \textmu s impulse at -150°C, 20°C and 100°C over a considerable range of thickness. All these observations for alkalihalides point out unambiguously to an increase of breakdown strength with decreasing thickness.

It may be pointed out here that the earlier measurements by Calderwood and Cooper\textsuperscript{12} showed that the breakdown field of Potassium chloride and Sodium chloride at various temperatures was independent of the specimen thickness over the range 2\times10^{-2} to 7\times10^{-2} cm.
However in the present investigation, the breakdown field increases by more than 50 percent as thickness is decreased from $2.5 \times 10^{-2}$ to $5 \times 10^{-3}$ cm for NaCl, KCl and RbCl at room temperature. If the breakdown field is determined by avalanche multiplication it should increase as the thickness is decreased. The experimental results are consistent with the theory of avalanche breakdown (page 54) for these alkali halides. It may be mentioned that Austen and Whitehead (1940) had observed that the breakdown field for thin flakes of mica increased as the thickness was decreased from about $8 \times 10^{-4}$ to $2 \times 10^{-3}$ cm.

The above observations point out that the results may be explained on the basis of forty generation theory involving avalanches which have been explained on page 55. However, these Figs. 3.10 to 3.12 show that the fit with the straight line corresponding to forty generation theory is not very good. This may be attributed to the fact that besides avalanche formation, space charges are also effective due to poor ionic mobility. Observations fit very well with the Equ. (1.43) based on space-charge enhanced cathode emission theory. In all cases, the reciprocal of the breakdown field strength shows an approximate linear variation with the logarithm of thickness. Using the experimental data, Equ. (1.31) yields the values for
the ionization parameters shown in Table 3.2. The calculated values are not entirely satisfactory, since the ionization rate for the materials at the highest field strength, for which experimental results are given in Figs. 3.10 to 3.12 correspond to a good deal more expenditure of energy than is available from the applied field. Vorob'ev and Pikalova (1959) have estimated the collision-ionization rate for NaCl. Over a limited range of field strength, they find a linear dependence on the field rather than the strongly varying dependence of Eq. (1.30). However, their experimental results agree within about 30 per cent with those calculated from Eq. (1.30).

(3) **Effect of temperature** : The present study is not connected in any way with the Joule heating effect of the pre-breakdown current. The instability develops very rapidly but is not of thermal origin. For sufficiently high temperature the breakdown of alkalihalides is undoubtedly thermal, although the low temperature limit of the thermal breakdown is difficult to determine. The intermediate temperature range 0°C to 250°C is taken to be the safe upper limit of pure electrical breakdown.

The critical field strengths for the Frohlich high energy criterion Eq. (1.19), the Von Hippel-Callen low energy criterion Eq. (1.22) and the Frohlich-Paranjape collective criterion Eq. (1.25) are plotted as function of temperature for NaCl, KCl and RbCl in Figs. 3.13, 3.14 and 3.15 respectively. The numerical breakdown value have been calculated by using
appropriate crystal constants. The DC breakdown field strengths at different temperatures obtained experimentally for NaCl, KCl and RbCl are shown in the above figures. The experimental points on the curves represent mean values for several samples measured at each temperature. The calculated values from the curves differ from the experimental values. However, they all lie within the limits of the critical field curves $[A]$ and $[C]$. It is observed that the breakdown field rises with increasing temperature, reaching to the maximum value at a critical temperature and then decreases linearly. The critical temperatures for alkali halides are $313^\circ\text{K}$ for NaCl, $333^\circ\text{K}$ for KCl and $358^\circ\text{K}$ for RbCl. Near the critical temperature region there is tolerably good agreement between the experimental data and curve $[A]$ whereas for the rest of the temperature range, the curve $[B]$ may represent the average values. The curve $[C]$ lies well below the experimental results, as would be expected, since Frohlich high energy criterion gives a lower value for the critical breakdown field which can give rise to electron multiplication.

Theory of pure electrical breakdown predicts that a decrease in the breakdown field, as the lattice temperature rises, is due to numerous electron traps present in solids. As the temperature increases, the number of electrons trapped also increases and hence the number of free electrons available for avalanche formation will be diminished. The breakdown field
has to be increased to compensate the decrease in free electrons. At a higher temperature (above critical temperature $T_c$), the collision of the trapped electrons with the lattice becomes more so that these electrons may get released and thus a kind of electron gas in the solid is formed. These will facilitate the breakdown mechanism and hence the breakdown strength beyond $T_c$ decreases rapidly.

Calderwood and Cooper$^{12}$ had suggested that in order to explain their results, traps at above 0.1 eV below the conduction band should be present. Such an explanation, however, implies that these traps are only present at temperature above the critical temperature.

Although a sharp decrease of breakdown strengths have been observed by Austen and Whitehead,$^{13}$ their subsequent measurements indicated that they were associated with secondary effects due to the electrodes and heating of the samples. The whole subject of breakdown at these high temperatures is still somewhat obscure. There are doubts that breakdown observed at these temperatures is not really pure electrical but is influenced by heating effect (vide supra, page 164).

Hanscomb$^{15}(197_.)$ has explained the rise of breakdown strength with temperature (positive temperature characteristic) by considering the reduction of electron mobility with increase
of temperature. If the possibility of breakdown due to space-charge caused by positive holes is considered, then the temperature dependence of hole mobility would also play a role in determining the temperature dependence of the breakdown strength. It is clear that increased hole mobility causes increase in breakdown strength, because the applied field is then more effective in preventing the accumulation of space charge. The decrease in breakdown strength on addition of foreign elements may also be explained on this hypothesis if the impurity reduces the effective hole mobility (Chapter IV, page 85).
REFERENCES


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7 Inge and Walther. (1934), E.J.M. 52, 243.

8 Grunewald. (1923), Arch. fur 41. 12, 79; E.T.Z. 1924, 1084.


