CHAPTER IV

THE INFLUENCE OF ADMIXTURES OF ALKALIHALIDES AND OTHER METALLIC IONS ON ELECTRICAL BREAKDOWN STRENGTH
4.1 Introduction

It is well known that in intrinsic semiconductors of group IV elements (e.g., germanium) N type semiconductivity can be introduced by adding a group V element (e.g., arsenic) as a donor, or alternatively P type semiconductivity by a group III element (e.g., gallium) as an acceptor. In hetro polar substances the effect of foreign ions of a valency different from the ions of the host lattice can be threefold. The way in which foreign ions are accommodated is determined by a number of factors, such as, concentration of foreign ions, the position of energy levels associated with the various lattice imperfections, the width of the forbidden zone, the tendency of base lattice to form lattice imperfections and the atmosphere in equilibrium with the compound. One way of maintaining charge neutrality is by forming vacancies. Thus when one Cd ion replaces two Na ions, one cation position is left vacant.

\[
\begin{align*}
\text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- \\
\text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- \\
\text{Na}^+ & \quad \text{Cl}^- & \quad \text{Cd}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- \\
\text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- \\
\text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- \\
\text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+ & \quad \text{Cl}^- & \quad \text{Na}^+
\end{align*}
\]

**Fig.** Substitution of two Na ions in sodium chloride by one Cd ion.
This way of maintaining charge neutrality may be described by:

$$ + \text{NaCl} + \text{CdCl}_2 \rightarrow \text{Na}_{1-2\xi} + \text{Cd}^{2+} + \text{V}_{\text{cat}} \text{Cl} $$

where $\xi$ is the fraction of cation position occupied by cadmium ions. The effect of cation vacancies caused by the addition of cadmium chloride on the ionic conductivity of sodium chloride is shown in the above figure.

The substitutional divalent admixtures dominate the situation in the high temperature region, since they determine the magnitude and the temperature dependence of the electrical conductivity which, in turn, determines the thermal breakdown strength. To determine the effect of substitutional admixtures of other alkalis or halides, breakdown strength of a series of mixed KCl - RbCl crystals were measured by Von Hippel (1934). Measurements on mixed KCl - KBr yielded similar results.

The effect of metallic impurity ions that are chemically less similar than another alkali has been investigated by Von Hippel and Lee (1941) who added AgCl to NaCl, Cooper et al. (1960) who added PbCl$_2$ to KCl and CdCl$_2$ to NaCl, and also by Hanscomb (1970) who added SrCl$_2$ to KCl and MnCl$_2$ to NaCl.

4.2 Experimental procedure and sample preparation

The experimental procedure and sample preparation have been described in Chapter II.
4.3 Details of measurements

(1) Firstly the percentage combination of KCl and RbCl which gives the maximum electrical breakdown strength was determined. To achieve this, various samples with continuously increasing percentage of RbCl in KCl were studied. Similar studies of breakdown strength were also made for KCl–KBr poly crystals. The results are shown in Fig. 4.1.

(2) After determining the percentage composition to get optimum electric breakdown strength, the effect of temperature was investigated. Fig. 4.2 shows the breakdown strength of RbCl as a function of temperature with mixture of KCl.

(3) The effect of other metallic admixtures of foreign ions was determined for NaCl and KCl poly crystals in the following way:

(i) The breakdown strength of NaCl polycrystals as a function of temperature with various admixtures of AgCl was determined.

(ii) The breakdown strength of pure NaCl was compared with NaCl–PbCl₂, NaCl–CdCl₂ and NaCl–MnCl₂ polycrystals.

(iii) The above experiments, viz., (i) and (ii) were repeated with KCl polycrystals.
Fig. 4.1 - Breakdown strength of mixed polycrystals of KCl-RbCl and KCl-KBr at 20°C.
Fig. 4.2 - Breakdown strength of polycrystalline RbCl, KCl and their mixture as a function of temperature.
Fig. 4.3 - Breakdown strength of polycrystalline NaCl as a function of temperature with various admixtures of AgCl.
Fig. 4.4 - Breakdown strength of polycrystalline NaCl as a function of temperature with admixtures of (i) PbCl₂, (ii) CdCl₂ & (iii) MnCl₂.
Fig. 4.5 - Breakdown strength of polycrystalline KCl as a function of temperature with various admixtures of AgCl.
Fig. 4.6—Breakdown strength of polycrystalline KCl as a function of temperature with admixtures of (i) PbCl₂, (ii) CdCl₂ & (iii) MnCl₂.
4.4 Results

From Figs. 4.1 to 4.6 the following inferences can be drawn :-

(1) Breakdown strength of alkali halides (polycrystal) is influenced by substitutional admixtures of other alkali halides as well as metallic foreign ions. It is seen that the admixtures of other alkali halides influence the breakdown strength in a poor way as compared to the other metallic ions that are chemically different, i.e. 25% RbCl and 75% KCl admixture increases the breakdown strength by 20% of that for pure KCl, while 10% AgCl admixture increases the breakdown strength by 50% at room temperature (Fig. 4.3).

(2) It is also seen that the admixture of foreign ions greatly raises the breakdown strength in the low temperature region (below critical temperature $T_C$). Above the critical temperature the strength decreases sharply.

(3) The admixture of foreign ions also reduces the critical temperature but increases the electric breakdown strength as compared to that of the parent substance.

(4) Figs. 4.4 to 4.6 show that :-

(i) The addition of CdCl$_2$ to NaCl or KCl causes an increase in breakdown strength at all temperatures as compared to that for the pure material.
(ii) The addition of PbCl₂ shows an uniform decrease in breakdown strength.

(iii) The addition of MnCl₂ causes maximum increase in breakdown strength as compared to the other admixtures studied earlier.

4.5 Discussion

As already mentioned (page 8), only the conduction and valence bands are important in pure, strain free crystals at low temperatures. However, the admixtures of foreign ions may provide some isolated energy levels called the electron traps in the forbidden band. The number of such levels in this band depends upon the degree of imperfections of the polycrystals and on foreign ions. Since the process involves merely the replacement of one atom by another having the same valency but different atomic number, the disorder is increased till the replacement is complete.

The imperfection energy levels or defects in the structure will influence the electric breakdown strength by scattering in the same way as the increase of electrical resistance. Because of the increasing number of scattering collision of electrons with defect-sites, the relaxation time is reduced and the loss of electron energy is increased; hence the electric breakdown strength is increased, as is observed in the present studies. In Fig. 4.1 the electric breakdown strength goes on increasing with
the disorder caused by the increasing percentage of the other substance till an optimum value is reached, beyond which the value of electric breakdown strength decreases to the characteristic value corresponding to the second substance. This state corresponds to the complete replacement of the lattice, which may mean a condition of order is again reached. The two extremes (0% and 100%) of the curves correspond to the order, while the 75% KCl and 25% RbCl corresponds to the maximum disorder.

The above situation may also be considered as follows. As explained by Equ. (1.10), the gain of energy A is proportional to $F^2$ (F is the electric breakdown strength). The relaxation time $\tau$ depends on scattering by thermal oscillation. By analogy with theory of the resistance of metals an additional scattering due to foreign atoms can be obtained by replacing $\tau^{-1}$ by $\tau_0^{-1} + \tau_C^{-1}$, where $\tau_C$ is the relaxation time caused by the foreign atoms. Since the chance of meeting a foreign atom is proportional to their density $\tau_C$ will be inversely proportional to the concentration C. From Equ.(1.11) in a pure crystal, the loss of energy $B \propto \frac{1}{\tau_C}$; while the gain of energy $A \propto F^2 \tau_C$. Equ.(1.10)

Accordingly for the pure substance:

$$F^2 \propto (\tau_C \tau)^{-1}$$

and for the admixture

$$F_C^2 \propto (\tau_C \tau)^{-1} + (\tau \tau_C)^{-1}$$
From the above analysis it may be concluded that electric strength is not much affected by small amounts of impurity or foreign atom present in the mixture, since relaxation time is very little affected by the small amounts of the foreign atoms.

At low temperature high electric field is necessary to cause breakdown, because there are a few free electrons available to initiate the avalanches (Ref. page 73). With rise in temperature the electric strength would increase due to the scattering from the lattice defects or imperfections, resulting in the loss of energy of electrons which have gained energy from the applied field. It may also be possible that the free electrons for breakdown, may be trapped during their journey inside the lattice. The electric breakdown would continue to rise till a critical temperature is reached, when interactions between free and trapped electrons become more important than electron-lattice collisions.

Above a critical temperature $T_c$, the electric strength would decrease with increase of temperature. This is because the number of electrons both in the conduction band and trapping sites increases with rise in temperature, resulting in a good supply of excited electrons to take part in the conduction process. A low electric field is then required to initiate the breakdown. With the rise in the number of such excited electrons, the electric breakdown strength decreases rapidly (Fig. 4.5).
An increase in the number of defects in the polycrystal structure would increase the number of imperfection levels and hence reduce the critical temperature. This can be qualitatively explained as follows. If the imperfection energy levels were grouped around a level \( V \) electron volts above the ground level of trapped electrons, from which electrons could be excited, then it might qualitatively be said that \( T_c \) would be associated with the condition that \( \frac{n e^{-V}}{k T_c} \) should give a high enough density of excited electrons responsible for breakdown (\( n \) is the number of electrons in the ground state). Higher percentage of admixture causes larger disorder as explained earlier. Thus more imperfect the structure, the lower will be \( V \) and hence \( T_c \) is also lowered resulting in the increment in the breakdown strength. The maximum in breakdown strength \( V_s \) vs. temperature curve is found at about 50\(^\circ\)C for pure NaCl polycrystal and 60\(^\circ\)C for pure KCl polycrystal, shifts to about 30\(^\circ\)C by doping with 5\% AgCl foreign admixture. This shift in the maximum (\( T_c \)) could be associated with a transition such that at temperatures above the maximum the number of electrons in imperfection levels and conduction band increases rapidly.

Hanscomb (1970) found that the addition of PbCl\(_2\) led to an uniform decrease in breakdown strength and this could be interpreted as being due to a decrease in hole mobility. Similarly the influence of MnCl\(_2\) admixture on breakdown strength of NaCl and KCl
polycrystals, corresponding to the maxima of the curve may be ascribed to the largest hole mobility for the samples (vide infra, page 75).
REFERENCES


