

ROLE OF SPACE CHARGE ON F CENTRE FORMATION IN KCl CRYSTAL DURING ELECTRON INJECTION

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Single crystal of KCl has been coloured by electron injection method under various temperatures and voltages. Growth of colouration is due to space charge limited injection current and is effective in zone II. Efficiency value has been determined and is found to be time dependent in zone II region. The diffusion coefficient in zone III is estimated.

1. Introduction

Atomic imperfections in a crystal sometimes trap excess electrons or holes and localize them. Colour centre such as F centre is one such localized trapping centre. It is believed¹⁾ that at an elevated temperature alkali halide crystals contain a large number of unassociated positive and negative ion vacancies. If an electric field is applied to an alkali halide crystal pressed mechanically between two electrodes (pointed cathode and flat anode) and heated at an elevated temperature, F centre originates from the pointed tip of the cathode and moves towards the anode²⁾. The positive ion vacancies are attracted to the plate and some get destroyed with an outflow of negative charge. On the other hand an equal number of negative vacancies does not drift out at the pointed electrode; instead some electrons are injected into the conduction band.

Paramo and Sanchez³⁾ pointed out that there are several difficulties for the injection of electrons. Alkali halides are ionic and not electronic conductors; before being injected, electrons need a good ohmic contact. According to their suggestion, during initial stage electrolysis in the bulk of the crystal occurs by the influence of the applied field as a result of which both alkali metal and halide ions are produced. Metal ion has an affinity towards the pointed cathode and becomes neutralized by interchanging one electron with the pointed tip, thereby producing metal atom. If the elimination rate is slower than the production rate, metal atom will accumulate around the cathode forming a new cathode. As soon as the contact is formed electron injection starts. Electrons on its way within the crystal will be trapped in the anion vacancies and F centres are produced. F centres being electrically neutral become free from the influence of the applied electric field. However some of the F centres are thermally dissociated into free electrons and vacant anion sites and migrate towards opposite directions with each other. Electrons will drift into originally uncoloured region, trapped by the new anion vacancies present and these create new F centres. Repetition of such a process will help F centres to migrate from pointed cathode towards the plate. The creation and diffusion of F centre will substantially contribute to the instantaneous current.

It is known^{4, 5)} that the growth of current during electrolytic colouration exhibits four distinct zones. In zone I the current is due to ionic transport and due to electrolysis of the crystal an ohmic contact is produced. Injection of electrons from the fresh ohmic contact marks the beginning of zone II; current and colouration does occur. The zone II colouration continues until the colouration approaches the anode and the entire crystal gets densely coloured when the injection current remains almost constant, known as the steady state situation (zone III).

In the present paper some results on the growth of injection current at various stages of colouration in KCl crystal under different temperatures are reported.

2. Experimental procedure and results

A KCl crystal (8 mm \times 5 mm \times 5 mm) was cleaved from a single crystal block (obtained from Department of Atomic Energy Commission, Government of India). An electric furnace fitted with a flat platinum anode and pointed brass cathode holds the crystal. The temperature of the furnace was controlled within $\pm 2^\circ\text{C}$. The injection procedure was performed under constant temperature and voltage. The injection current and F absorption (shining F light on the central part of the crystal) were simultaneously recorded by a Bausch and Lomb series 50000 strip chart recorder with pen speed 12.5 cm \cdot min⁻¹. The injection procedure was stopped within zone III, when, the current was found to be almost constant. The original transparency of the crystal was established and the same specimen was successively coloured under altered conditions of temperatures and voltages. The injection current and optical density against time have been plotted for KCl crystal at various temperatures and voltages, as shown in Fig. 1. The optical density growth curves in Zone II follow an equation of the type $y = a t^b$ where y and t stand for optical density and time, respectively, a and b are arbitrary constants.

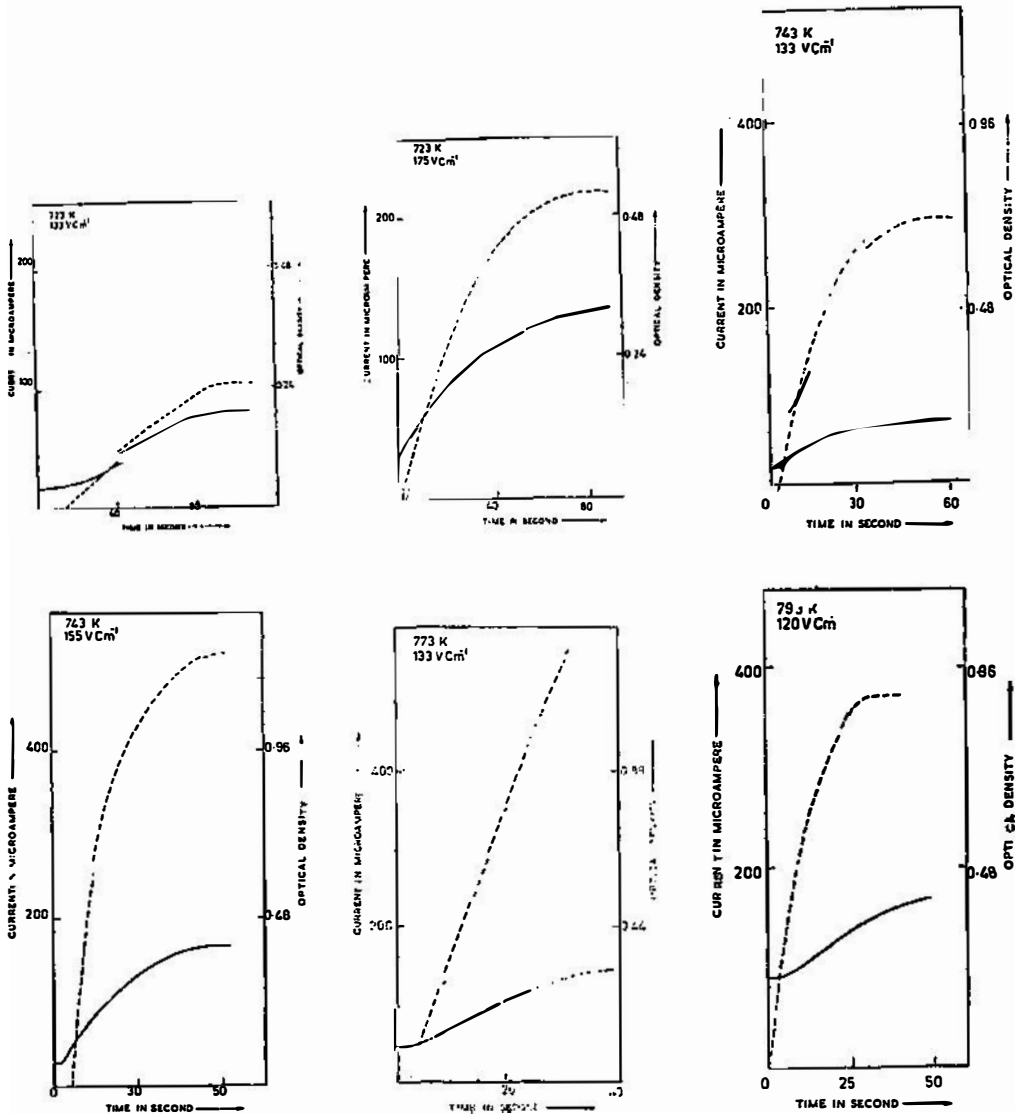


Fig. 1. Injection current (continuous line) and optical density (dashed line) against time during colouration at various temperatures and voltages for KCl crystal.

The efficiency (η) of F centre formation at any instant of time in zone II is calculated in the following way

$$\eta = \frac{\text{Rate of flow of electrons per unit area of the crystal}}{\text{Rate of } F \text{ centre production per unit area of the crystal}} \times \text{Applied electric field.}$$

Now, the number of electrons (N_e) per unit area participating in the formation of colour centres is given by

$$N_e = \frac{N}{a} \int_0^t i(t) dt.$$

Here, zero time corresponds to the start of electron injection; $i(t)$ at any instant of time in Zone II is obtained after subtracting the ionic current (which does not contribute to the colour centre formation) from the measured current, a is the cross sectional area of the crystal and N equals 6.25×10^{18} .

Again,

$$\frac{dN_e}{dt} = \frac{N}{a} i(t).$$

The number of colour centres (N_F) per unit area is estimated, using Smakula-Dexter equation¹⁾

$$N_F = 2.3026 N' a t^b$$

where, the constants a and b can be computed from the optical density (y) vs. time (t) graph, N' depends upon the refractive index of the specimen, oscillator strength and half width ($W_{1/2}$) of the F band. The half width is calculated from the equation⁶⁾

$$W_{1/2} = A [\text{Coth}(h\nu_0/2kT)]^{1/2}.$$

Therefore,

$$\eta = \frac{dN_e/dt}{dN_F/dt} \left(\frac{V}{L} \right) = N'' i(t) t^{1-b} \quad (1)$$

where,

$$N'' = 0.4343 (N/N') \frac{1}{a ab} (V/L).$$

L is the interelectrode distance. Knowing the value of N'' , η can be evaluated for each value of injection current and corresponding time. The results are shown in Fig. 2.

3. Discussion

It is clear from Fig. 1 that during Zone I, current is practically constant and colouration does not occur. When the colour centres begin to form, current increases rapidly. In order to rationalize the temperature, applied injection field and the time dependence for the colour centre formation, let us analyse the graphs for the specimen. At temperatures 743 K, as the injection field is changed from 133 V cm^{-1} to 155 V cm^{-1} the slope of the injection current increases appreciably leading to the colour centre formation at a faster rate. Considering the results of 723 K at 133 V cm^{-1} and 743 K at 133 V cm^{-1} , due to the change of temperature optical density has been increased nearly about four times. To have the results in the same

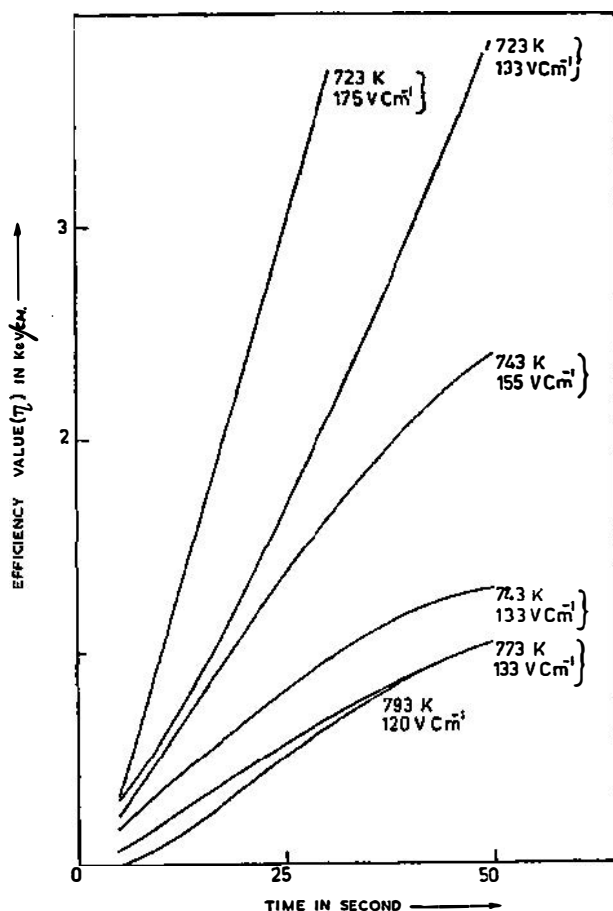


Fig. 2. Efficiency of F centre formation (in zone II) against time at various temperatures and voltages for KCl crystal.

time scale we have to apply higher field at lower temperature. Thus the evolution of electrical current through alkali halide crystal during electrolytic colouration is a function of temperature.

In some earlier works^{3,5)} it has been pointed out that the current in Zone II is space charge limited and is due to the thermionic emission of electrons from the potassium cathode formed on electrolysis. The shape of the curves of current vs. time and the behaviour of current with voltage and temperature indicate that the second zone current is characterised by the space charge limited current. On an application of electric field at high temperature copious amount of space charge help colour centres to spread rapidly within the bulk of the crystal. Augmentation of current in the initial part of Zone II signifies colour centres to grow at a rapid rate. But the current in Zone III is nearly steady and the influence of space charge in this zone slows down considerably, resulting in decrease in the rate of F centre production.

The space charge limited injection current has a definite bearing with the efficiency of F centre formation. The efficiency (η) increases with the increase of time (Fig. 2) in the space charge zone (Zone II). For a field of 133 V cm^{-1} and at temperature 723 K the η values for KCl are

$$\eta_{\text{KCl}} = 0.33 \text{ KeV/cm at } t = 5\text{s}; \quad \eta_{\text{KCl}} = 2.74 \text{ KeV/cm at } t = 40 \text{ s.}$$

During the early part of the second zone, colour centres in the particular section of the crystal are produced rapidly but as the current approaches the steady state situation, the rate of formation of colour centre lags very much behind the rate of electron conduction, i. e. when $\frac{dN_e}{dt}$ is constant, $\frac{dN_F}{dt}$ becomes very small. It implies immediately that there is no further production of F centres, while most of the electrons instead of being trapped, go to the conduction band.

Thus the presence of space charge favours the formation of F centre and when the colour cloud reaches the anode the process becomes less efficient for further production of F centres.

In the case of the crystal, efficiency (η) value (Fig. 2) is found to decrease with the increase of temperature of injection. It leads us to believe that there must be a lower limit of temperature, below which one cannot inject electrons to form colour centres in any way presumably because sufficient number of vacancies are produced at high temperatures to initiate the process of colouration. The process of colouration analysed here is entirely different from other modes of colouration and we will not attempt to compare the present efficiency value with those found by means of other methods. It is evident from the present experiment that in Zone III colouration is not affected by the space charge and near the anode (which is a flat plate) the distribution of colour centres is uniform and we can discard the spatial inhomogeneity in field arising due to the use of pointed cathode.

Following Lampert and Mark⁷⁾ and also with the help of Nernst-Einstein relation ($\mu = \frac{eD}{kT}$), F centre diffusion coefficient (D_F) can be written in terms of the injection current density (\mathcal{J} e s in $\text{A} \cdot \text{cm}^{-2}$) in Zone III as

$$D_F = \frac{8}{9} \mathcal{J} e s \left(\frac{kT}{e \epsilon} \right) \frac{L^3}{V^2}$$

where, kT is expressed in eV; e and ϵ are the electron charge and the static dielectric constant of the material, respectively. The D_F values at various temperatures are calculated and are shown in Table 1.

The diffusion coefficients of F centres (D_F) in additively coloured KCl single crystal have been measured as a function of F centre concentration and temperature by Kuczynski and Byun⁸⁾. The degree of correspondence between the present value of D_F with their results is quite reasonable although the modes of colouration in two cases are not identical. The activation energy (U) associated with the diffusion process is estimated from the conventional plot of logarithm of diffusion coefficient as a function of temperature (not shown). The value U for KCl is 0.5 eV . Activation energy for anion vacancy diffusion obtained by Schneider⁹⁾ is 0.6 eV for KCl crystal. It may be suggested that F centre diffusion is a thermally activated process.

TABLE 1

| Injection temperature K | $\frac{D_F}{10^{-10} \text{ cm}^2 \text{ s}^{-1}}$ |
|----------------------------|--|
| 723 | 1.38 |
| 743 | 2.03 |
| 773 | 2.35 |
| 793 | 2.74 |

F centre diffusion coefficient (D_F) values in zone III for KCl crystal at different injection temperatures.

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ULOGA PROSTORNOG NABOJA U STVARANJU F CENTARA U KRISTALIMA KCl ZA VRIJEME ELEKTRONSKOG UPUCAVANJA

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Monokristali KCl bojani su metodom elektronskog upucavanja na raznim temperaturama i naponima. Rast bojanja posljedica je struje ograničene prostornim nabojem i efektivan je u zoni II. Određena je vrijednost efikasnosti i nađeno je da vremenski ovisi u zoni II. Također je procijenjen i koeficijent difuzije u zoni III.