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TEMPORAL BEHAVIOUR OF TRAPPED CENTRES IN KCl:KBr CRYSTALS DURING SECOND ZONE COLOURATION

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Electron injection was carried out in single crystals of KCl doped with KBr under constant temperature for different fields. The injection current and optical density were measured as functions of time. The process was stopped arbitrarily. An analytical theory has been worked out and the growth coefficient (κ) has been found to behave in an anomalous way in describing the detrapping process.

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1. Introduction

Carrier transport through insulating solids is a complex phenomenon. Many years of research on various insulating solids have not fully resolved the behaviour of their transport properties [1]. The basic idea is that an insulator can carry a current only if electrons are raised into a band of energy levels which are normally empty. Some processes, like light absorption and heating, can agitate electrons to flow from a metal electrode into the conduction band of an insulator on application of an electric field. The electron injection into a heavily doped region of such materials may take place through quantum-mechanical tunnelling. Takai et al. [2] observed that the surface states at the interface between a metal and an insulator may assist the carrier injection. Once the carrier injecting contact can provide a reservoir of carriers, the behaviour of injected carriers, and hence the current, are controlled by the properties of the material in which they are flowing. Carrier-injecting contact is not perfect through the insulator because of the large forbidden gap, and also the intrinsic resistivity of the material is usually much larger than

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the contact resistance. The natural imperfections present in a crystal subsequently create traps inside it and interact with the injected carriers.

In the present work, the carrier (electron) injection through a non-rectifying contact [3,4] on KBr-doped KCl single crystals was studied, and the growth parameters related to trapping centres have been estimated. The effect of the characteristic field on the transport behaviour and detrapping is discussed.

2. Experimental

Single crystals of KCl:KBr (1 and 2 mole% KBr) were cleaved from a crystal block grown by the Kyropoulos method in our laboratory, using a microprocessor-controlled furnace and servo-controlled rotation-pulling arrangement. A specimen of 1 mole% crystal was placed between a heterogeneous pair of contacts [5 − 10], a flat platinum anode and a sharply pointed brass cathode. The system was housed in an electrical furnace for electron injection. The measurements were carried out at constant temperatures of 790, 810, 835 and 860 K, and the applied fields were 700, 800, 900, 1000, 1100 and 1200 V/cm. The same measurements were repeated with the other specimen with 2 mole% of KBr. The injection process [1, 10, 11] was carried out for a period of time and stopped abruptly within the space charge limited current (SCLC) region. The anode and cathode contacts were not disturbed from the initial setting at the beginning of injection for the entire period of operation, for any set of temperature-voltage combinations. The in-situ measurements were carried out after decolouring the injected carriers for each combination by reversing the polarity. The pristine time was not disturbed in any way. The optical density ($Y = \log_{10} I_0/I_{\mathrm{C}}$) as a measure of optical absorption is obtained from the ratio of intensities of uncoloured (I_0) and coloured (I_{C}) specimen at a given temperature, by shining it with appropriate F-light (564.2 nm) using the reflection-grating monochromator (Model 77250, ORIEL, USA). The mounted specimen surface inside the furnace was collinear with the light source, monochromator on one side and photomultiplier on the other side in the dark. The light intensity transmitted through the crystal was measured by a photomultiplier tube. The injection current and the photocurrent were simultaneously recorded using a two-pen plotter (Bausch & Lomb, Series 5000).

3. Results and discussion

At a very high temperature, $\gtrsim$ 1000 K (near the melting point of the crystal, 1045 K), the crystal behaves like a semiconductor. The metal electrode to semiconductor contact in the absence of an applied field must be considered in order to analyse the space-charge-limited (SCL) current injection into the crystal [6, 8, 11]. When the semiconductor and metal are brought into contact, impurity centres in the layer of the semiconductor in the vicinity of the contact immediately lose electrons to the metal. A positive space charge is generated in the surface layer of the semiconductor, together with an induced negative charge on the metal surface, causing a force on electrons in the direction from the metal towards the semiconductor. According to Mott [12], the electron states in the viciniy of the contact

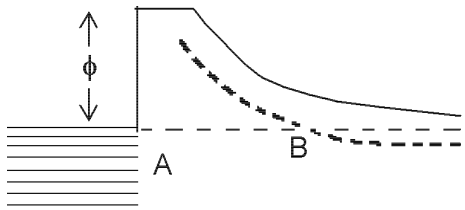

Fig. 1. Energy-level diagram for a contact of a metal and a semiconductor. Tha dashed line indicates the position of impurity levels. ϕ is the work function and AB represents the spread of the potential barrier.

may be considered in the following way (see Fig. 1). The density of electrons at a position x on the axis perpendicular to the surface is given by

$$n(x) = n_0 \exp(-V/kT)\,,$$

where n_0 is the number of electrons in the conduction band at a large distance from the contact, $V(x)$ is the potential energy gained by an electron in the semiconductor in bringing it from a large distance in the semiconductor to the point x, while the density of the positive charges, i.e. vacant impurity levels, is

$$n'(x) = n_0 \exp(-V/kT)\,.$$

For small V, the Laplace equation yields the solution

$$V(x) = const \times \exp(-2x/x_0)\,,$$

where $x_0 = kT/(2\pi n_0 e^2)^{1/2}$, k is the Boltzmann constant and T is the absolute temperature. The equation was verified using the cuprous-oxide data. In the present case, the situation is slightly different. A strong field is required to detrap an electron from the vacant site under space-charge limited (SCL) electron injection. In order to analyse the data in the second zone, the growth-coefficient κ is defined. Characteristics of the zones (I, II and II) are described in Ref. [3].

3.1. Analytical approach

In single crystals, the trapping energy levels are generally discrete, in contrast to those in amorphous and polycrystalline materials. Material specimens have "active" boundaries at metallic contacts. In the present experiments, the cathode was a pointed one, having a diverging boundary with a strongest field near the tip of the anode. The trap distribution [13 − 15] is different near such a boundary than in their bound counterpart.

In the present analysis, we shall confine the considerations only to the steady D.C. one-dimensional current flow on the basis of the following assumptions:

(i) the occurence of injection under Ohmic contact is perfect;

(ii) energy-band models can be used to study the characteristics of the injected electron carriers;

(iii) free-electron density follows the Maxwell-Boltzmann (MB) statistics, while the density of trapped electrons follows the Fermi-Dirac (FD) statistics;

(iv) free-electron mobility is independent of the electric field and is not affected by the presence of traps.

For insulators, the thermal-equilibrium concentration of free electrons [11] is given by

$$n_0 = N_{\rm c} \exp\Big((F_0 - E_{\rm c})/kT\Big) , \tag{1}$$

where $N_{\rm c}$ is the effective density of states in the conduction band, $E_{\rm c}$ is the energy at the bottom edge of the conduction band and F_0 is the Fermi energy at thermal equilibrium. From the assumption (iii), the concentration of filled electron traps follows the FD statistics,

$$n_{\rm t0} = N_{\rm t} \left(1 + \frac{1}{g} \exp\left(\frac{E_{\rm t} - F_0}{kT}\right)\right)^{-1} = N_{\rm t} \left(1 + \frac{1}{g}\,\frac{N}{n_0}\right)^{-1} , \tag{2}$$

where $N = N_{\rm c} \exp\big(E_{\rm t} - E_{\rm c})/kT\big)$, $N_{\rm t}$ is the concentration of traps, g the degeneracy factor (or statistical weight) for the traps and $E_{\rm t}$ the energy level of the traps. Thermal equilibrium is maintained by the capture of electrons into the traps and their re-emission into the conduction band.

Due to the steady-state injection, disruptions in the equilibrium initiate the colour-centre formation, thereby modifying the energy levels. The free-electron equation will now be governed by the spatially distributed one

$$n = n(x) = N_{\rm c} \exp\left(\frac{F(x) - E_{\rm c}(x)}{kT}\right) . \tag{3}$$

The corresponding trapped-electron concentrations for j-th set of trap (n_{tj}) will follow the equation

$$n_{tj}(x) = N_{{\rm t}j} \left(1 + \frac{1}{g_j} \exp\left(\frac{E_{{\rm t}j} - F(x)}{kT}\right)\right)^{-1} = N_{{\rm t}j} \left(1 + \frac{1}{g_j}\,\frac{N_j}{n(x)}\right)^{-1} , \tag{4}$$

where

$$N_j = N_{\rm c} \exp\left(\frac{E_{{\rm t}j} - E_{\rm c}}{kT}\right)$$

Here the position of the virtual cathode refers to $x = 0$, and the collection of electrons, i.e., the position of anode, is at $x = L$. In SCL flow, the Poisson's equation takes the form

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{e}{\epsilon}\left[(n - n_0) + \sum (n_{tj} - n_{tj0})\right]. \tag{5}$$

The present experimental condition is valid even for the pointed cathode. As the cathode is an infinite reservoir of electrons, and also the applied voltage is much larger than kT/e, the drift current density plays dominant role over the diffusion current. So we can write

$$J = J_{\mathrm{drift}} = e\mu nE. \tag{6}$$

Relations (3), (4), (5) and (6) are the basic equations.

From Eqs. (4) and (6), we have

$$n = n_0\,\frac{E_J}{E}, \quad n_{tj} = N_{\mathrm{t}j}\left(1 + \frac{E}{E_{J,j}}\right)^{-1}, \quad E_J = \frac{J}{e\mu n_0}, \quad E_{J,j} = \frac{g_j\,J}{e\mu N_j}, \tag{7}$$

where the subscript J is used to emphasize the linear dependence on current density (CD),

$$J_{\mathrm{CD}} = \frac{E_J e\mu N}{g}\ \text{(omitting } j\text{)} = \frac{E_J\,e\mu\,N_{\mathrm{c}}}{g}\ \exp\left(\frac{E_{\mathrm{t}} - E_{\mathrm{c}}}{kT}\right). \tag{8}$$

Analysis of the experimental data shows that J is a function of time, following the equation of the type

$$J = p\ t^q. \tag{9}$$

From Eqs. (8) and (9), we have

$$pt^q = \frac{E_J\,e\mu\,N_{\mathrm{c}}}{g}\ \exp\left(\frac{E_{\mathrm{t}} - E_{\mathrm{c}}}{kT}\right), \qquad Kt^q = \exp\left(\frac{E_{\mathrm{t}} - E_{\mathrm{c}}}{kT}\right),$$

where

$$K = \frac{pg}{E_J\,e\mu\,N_{\mathrm{c}}},$$

Therefore,

$$(E_{\mathrm{t}} - E_{\mathrm{c}}) = K' + K''\ \ln t, \tag{10}$$

where $K' = kT\ \ln(k)$ and $K'' = kTq$.

Due to the propagation of the trapping cloud in the crystal, the conditions within it change rapidly with time, hence the term $(E_{\mathrm{t}} - E_{\mathrm{c}})$ may change. We modify the term $(E_{\mathrm{t}} - E_{\mathrm{c}})$ in tune with the relation (10), justifying as to why the current density is a function of time, even though the external stresses, like the electric field and temperature remain fixed.

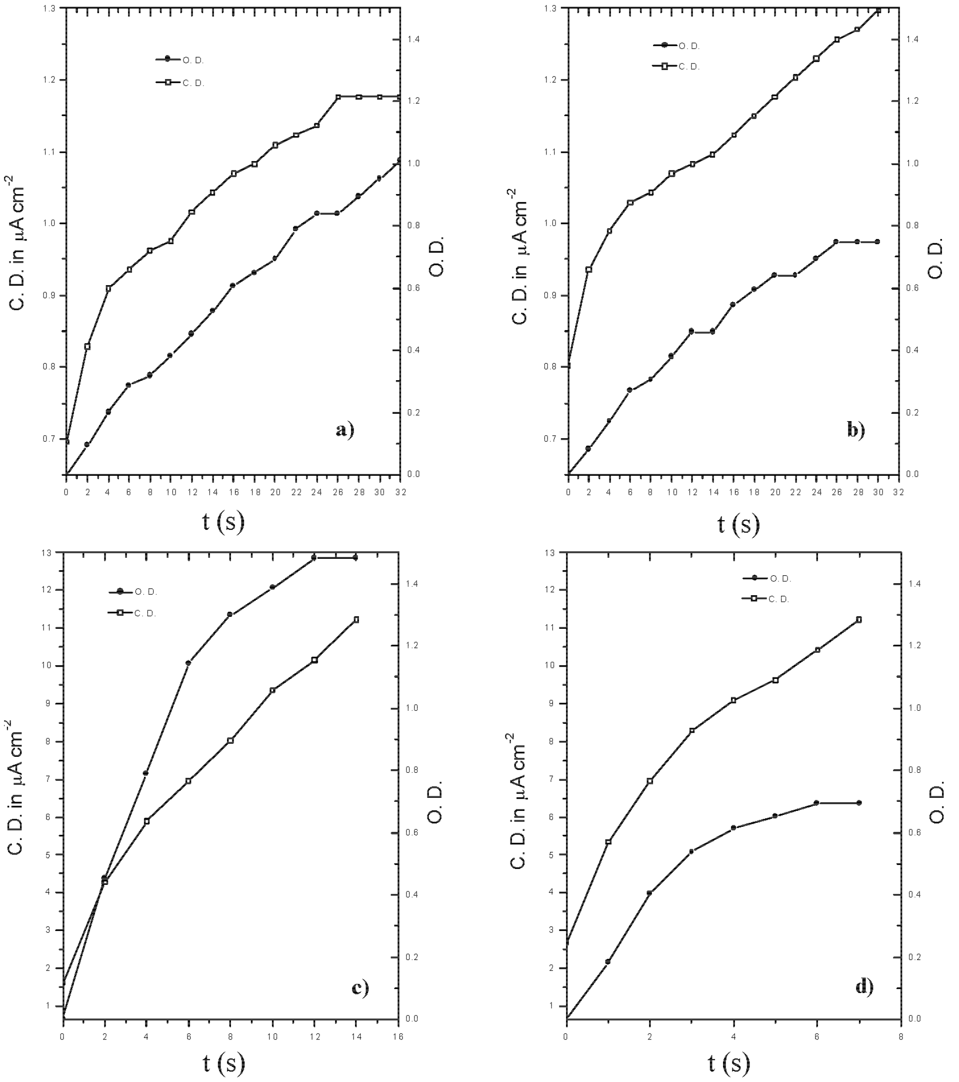

Fig. 2. Injection current density (CD) and optical density (OD) versus time during colouration of KCl:KBr *(1 mole%) under electric field of 800* V/cm *at constant temperatures of a) 790* K*, b) 810* K*, c) 835* K *and d) 860* K.

Some of the temporal growth patterns, both for the injection current and the optical density (OD) are shown in Figs. 2 and 3. From the best fit, it is evident that OD follows the time dependence given by the equation

$$Y = a\,t^{b} + c\,, \tag{11}$$

where a, b and c are constants.

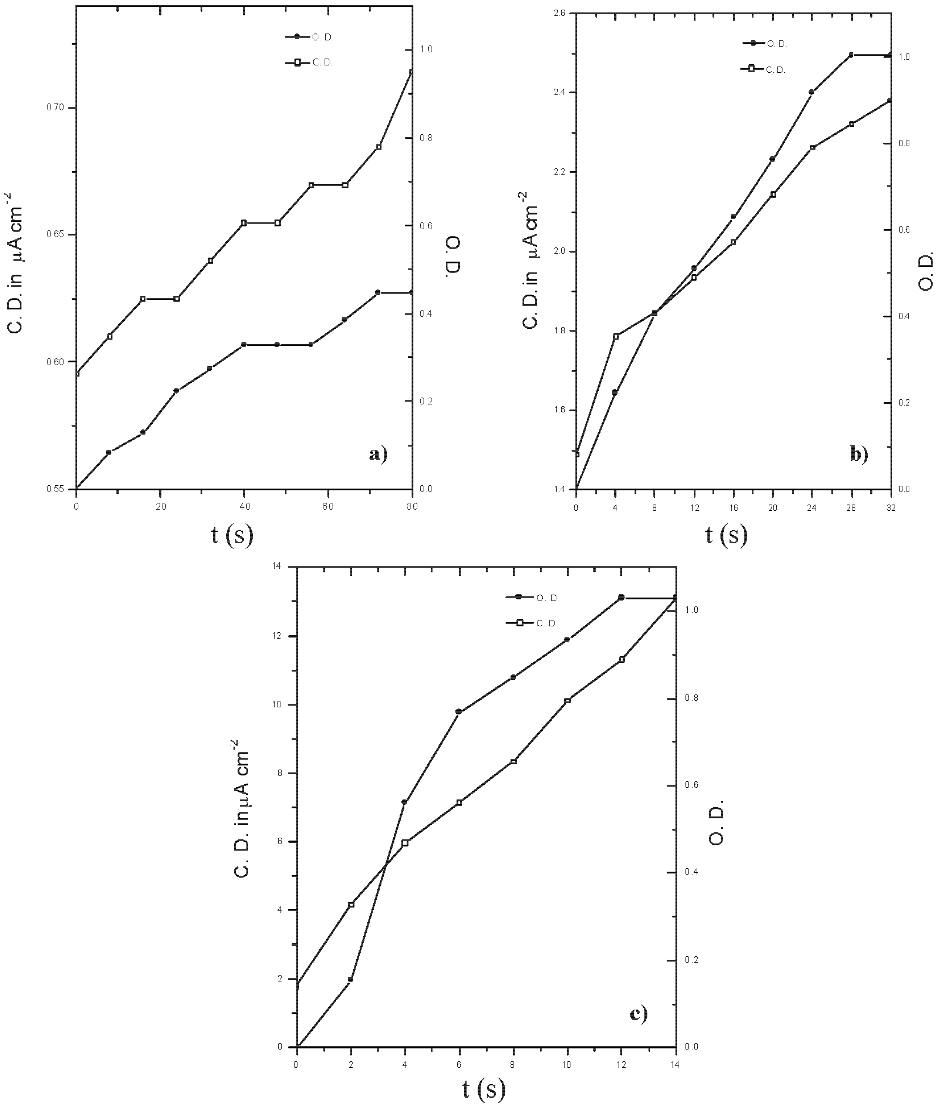

Fig. 3. Injection current density (CD) and optical density (OD) versus time during colouration of KCl:KBr *(1 mole%) under electric field of 800* V/cm *at constant temperatures of a) 790* K*, b) 810* K*, c) 835* K *and d) 860* K.

The number of F-centres grown per unit volume is given by $F = N' Y(\mathrm{OD})$ and the rate of growth by

$$\frac{\mathrm{d}F}{\mathrm{d}t} = N' \frac{\mathrm{d}Y}{\mathrm{d}t} = N' a\, b\, t^{b-1}\,, \tag{12}$$

where $N' = 2.3036 \times 0.87 \times 10^{17}\left(n_r/(n_r+2)^2\right)W_{1/2}/f$, which follows from the Smakula-Dexter's equation [16], n_r is the refractive index of the material, $W_{1/2}$ is the full width at half maximum (FWHM) and f is the oscillator strength.

The growth coefficient, κ, may be defined as the rate of F-centre formation per area and unit unit energy,

$$\kappa = \frac{\text{Rate of F–centre formation per unit area}}{\text{Rate of flow of electrons per unit area} \times V} = \frac{N'\,a\,b\,t^{b-1}\,L}{N\,J(t)\,V} = \frac{N'\,a\,b\,t^{b-1}}{N\,J(t)\,E} \tag{13}$$

where V is the potential difference between the two electrodes, L the inter-electrode distance, $J(t)$ the current density as a function of time, $N = 6.25 \times 10^{18}$ the number of electrons per one ampere of current flow and $E = V/L$ is the applied electric field. E is taken approximately equal to V/L because of the large length of the crystal, which was chosen for that purpose.

TABLE 1. Transit times (t_T (in seconds) and the corresponding growth coefficients (κ_0) of KCl:KBr *crystals for different injection fields and temperatures.*

(a) KCl:KBr, 1 mole%

	Electric field (V/cm)											
T	700		800		900		1000		1100		1200	
(K)	κ_0	t_t	κ_0	t_t	κ_0	t_t	κ_0	t_t	κ_0	t_t	κ_0	t_t
790	0.0482	27.9	0.0513	32.04	0.0377	26.3	0.0302	24.1	0.0247	30.06	–	–
810	0.0461	26.2	0.0405	29.9	0.0256	24.1	0.0156	24.1	0.0153	21.08	0.0131	24.1
835	0.0425	15.9	0.0164	13.9	0.0085	17.8	0.0116	20.06	0.0161	20.06	0.0111	29.9
860	0.0177	10.01	0.0172	7.09	0.0183	7.4	0.0116	7.99	0.0084	7.18	–	–

(b) KCl:KBr, 2 mole%

	Electric field (V/cm)											
T	700		800		900		1000		1100		1200	
(K)	κ_0	t_t	κ_0	t_t	κ_0	t_t	κ_0	t_t	κ_0	t_t	κ_0	t_t
810	0.0169	80.8	0.014	93	0.0216	106.5	0.0104	105	0.0097	107.3	0.0056	81.7
835	0.0298	38	0.0214	41	0.0156	39	0.0109	31.6	0.0056	27.8	0.0032	27
860	0.0077	33.1	0.0146	16	0.02	10.8	0.032	6.9	–	–	–	–

From Eq. (13), the values of κ have been calculated. The plots of κ vs. t (time are shown in Figs. 4 and 5. The curves $\kappa(t)$ clearly follow the exponential form,

$$\kappa = \kappa_0 + M\,\exp(-\lambda\,t)\,, \tag{14}$$

where λ is a factor that governs the rate of change of κ.

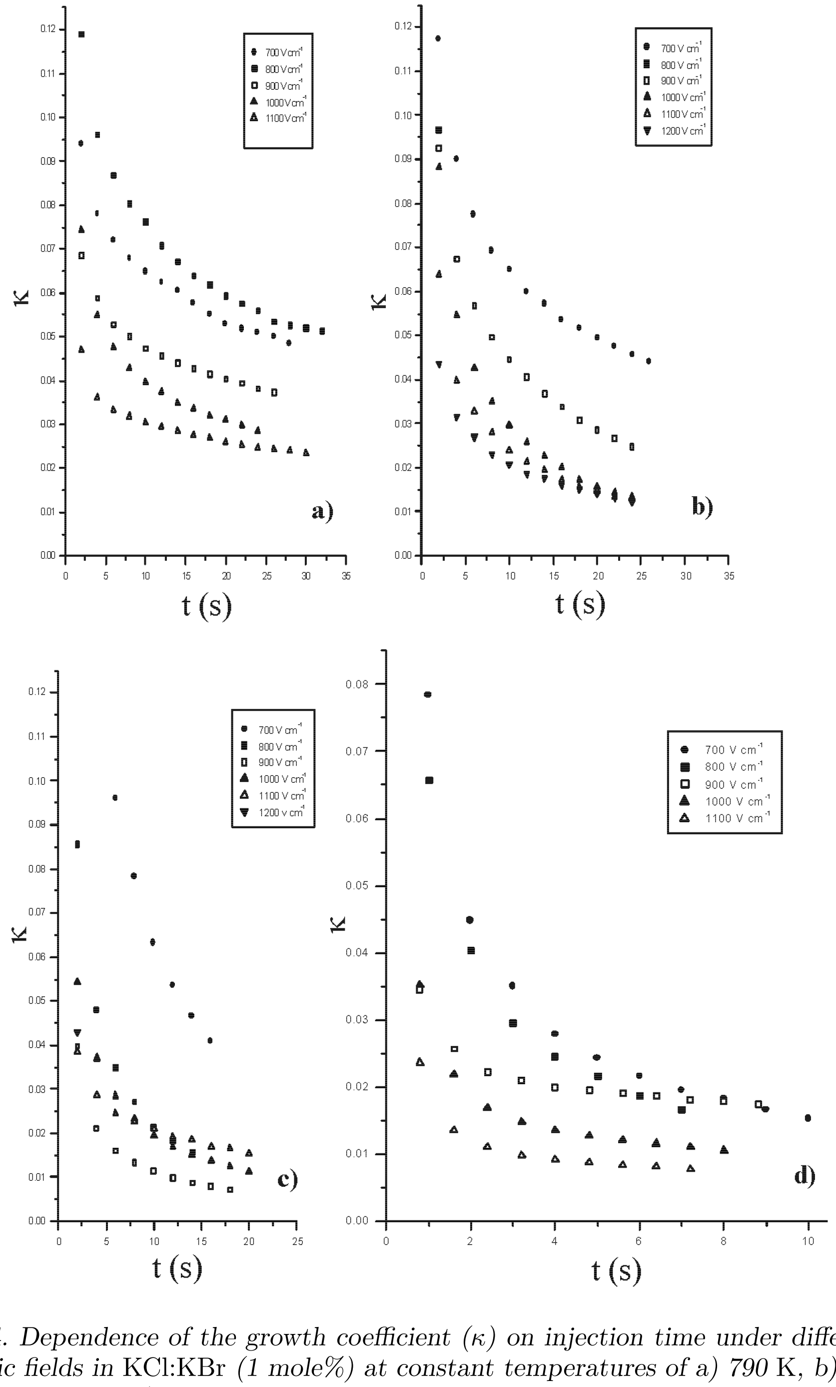

Fig. 4. Dependence of the growth coefficient (κ) on injection time under different electric fields in KCl:KBr *(1 mole%) at constant temperatures of a) 790* K, *b) 810* K, *c) 835* K *and d) 860* K.

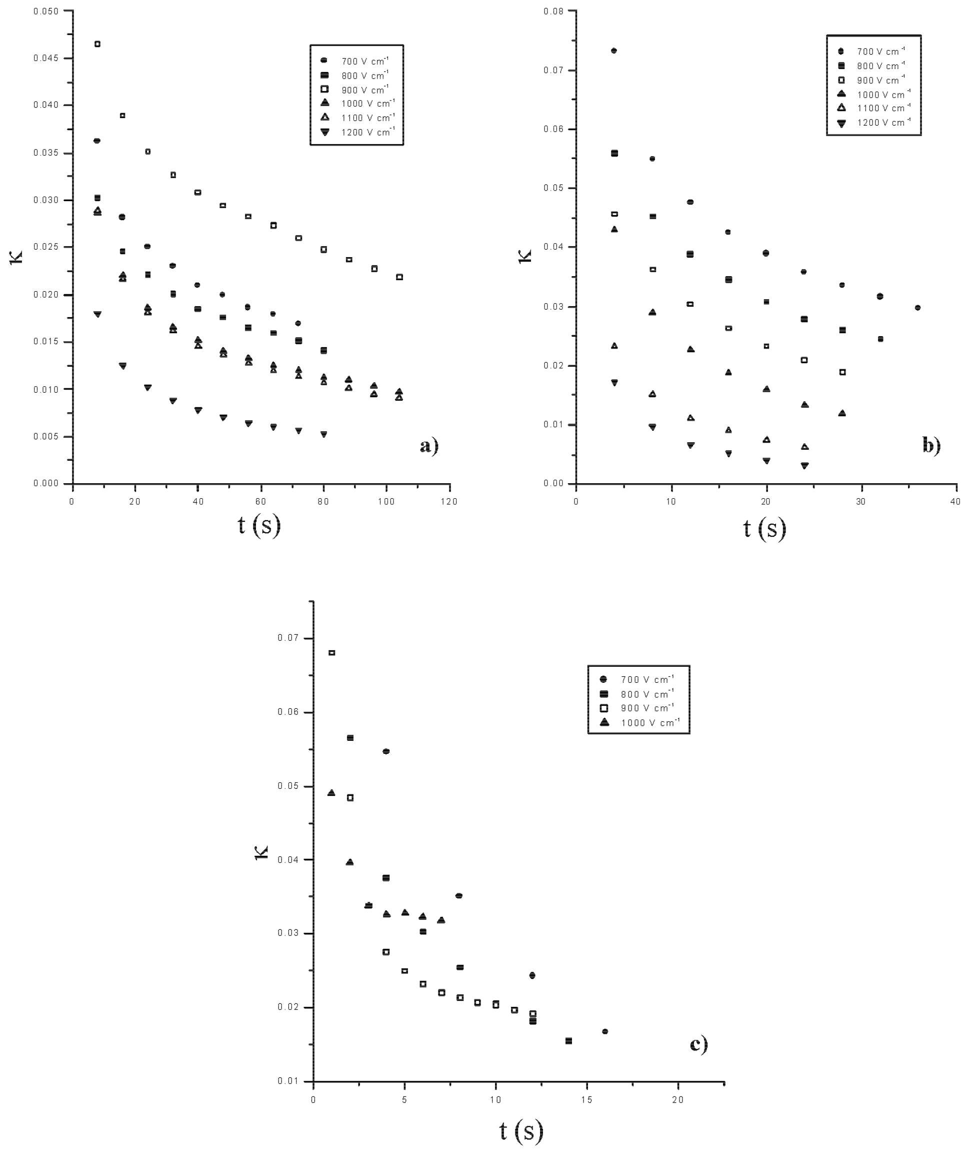

Fig. 5. Dependence of the growth coefficient (κ) on injection time under different electric fields in KCl:KBr *(2 mole%) at constant temperatures of a) 810* K*, b) 835* K *and c) 860* K*.*

The growth coefficient, κ, decreases exponentially from an initial value to a constant value, κ_0. The characteristic time of the transition, the transit time $t_{\mathrm{T}} =$

$1/\lambda$, indicates the beginning of the III zone. The values of the transit times derived from the κ vs. t curves for various fields and temperatures are given in Table 1. It is observed that the transit times attain larger values on lowering the field, indicating a threshold field below which the III zone cannot be reached.

According to the present knowledge, the curves of κ vs. time are expected to show a monotonouos shift to lower values of κ as the applied field increases. However, Figs. 4 and 5 show that there are some anomalies in the positions of the κ–t curves for some constant applied fields. The anomalies are clearly seen in Fig. 4a (in KCl:KBr 1 mole%, at 790 K, the data for 700 V/cm are below the data for 800 V/cm), and in Fig. 5a (in KCl:KBr 2 mole%, at 810 K, the data for 700 and 800 V/cm are below the data for 900 V/cm). This is contrary to the normal behaviour in insulating solids containing traps [17]. The anomaly in the ordering of the κ–t curves indicates that the detrapping shows a threshold voltage. Such a break of the sequence of κ–t curves may be explained by the Poole-Frenkel detrapping model [4]. We can only qualitatively compare the nature of the observed anomalies with the Poole-Frenkel detrapping model for the neutral F-centres when they loose their effective charges. More work is in progress with other doped alkali halides with the aim to observe further anomalous effects of trapping centres.

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VREMENSKA OVISNOST PUNJENJA KLOPKI U KRISTALIMA KCl:KBr ZA VRIJEME BOJENJA DRUGE ZONE

Izvodili smo ubacivanje elektrona u monokristale KCl punjene s KBr na stalnoj temperaturi i za niz električnih polja. Mjerili smo struju ubacivanja i optičku propusnost kao funkcije vremena. Ubacivanje smo prekidali. Razvili smo analitičke izraze za analize i našli da je koeficijent rasta (κ), koji opisuje izlazak elektrona iz klopki, anomalan.