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KINETIC BEHAVIOUR OF F-CENTRES UNDER THERMAL STRESS

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The migration of colour clouds after the electron injection in pure and doped KCl and KBr alkali halides under thermal and field stresses is studied with an anode contact of spherical geometry. The diffusion coefficient of the colour clouds has been obtained using a derived analytical expression and the experimental data, and the activation energy of the colour centre was estimated. The dissociation energy values under thermal and field stresses for doped crystals are deduced through the mobility transport equation. The results indicate the effect of doping in an otherwise pure counterpart of the same crystals.

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1. *Introduction*

The elegant and fundamental research of coloured specimens of normally colourless materials has excited the curiosity of scientists for more than a century. The colouration phenomenon is of general importance for the understanding of electronic processes in solids. The major concepts in the field of colour centres stem from research on the alkali-halide crystals, and these materials are still the predominant subjects of study in the realm of colour centre research.

The mechanism of formation of colour centres [1, 2] and their annihilation or transformation into other centres have been extensively studied, but the kinetic behaviour of pure and doped materials of even alkali halides and their phosphors have not yielded definite results for their use as promising materials for practical purposes.

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For a long time, we are in the game to understand the basic properties of traps under stress related kinetics in these crystals [3]. Electrical transport in solids is so very important in device manufacturing industries therefore the need to be more specifically understood particularly in the cases of photo-electronic processes. We are presently interested in solving the carrier current injection under space charge electrical conduction process only.

The current work deals with the extension of the same work on mixed crystals of KCl:KBr in different proportions and special stress has been given to study the signature of these trapped centres along with the effect of doping concentration if any during decay of colouration under thermal stress.

2. Experimental

Powdered material through which the single crystals to be drawn was heat treated at an elevated temperature (below the melting point) in a quartz ampoule for several hours under the argon atmosphere in order to eliminate the occluded materials. Pure KCl and KBr single crystals and different mole % of mixed crystals were then grown in the laboratory by the Czochralski-Kyropolous method, using a microprocessor-controlled furnace under argon atmosphere and servo-controlled rotation pulling arrangements. Crucible rotation rate $\sim 5-8$ r.p.m. and pulling rate of seed fixed at 120 μm min^{-1}.

Crystals cleaved along the $\langle 100 \rangle$ direction of appropriate dimensions were taken from the central portion of the grown single crystal and one face of it was symmetrically rounded and etched by water polishing process, ensuring the radius of curvature of the crystal to be in congruence with the patterned platinum anode. A sample was placed between a heterogeneous contact of spherical platinum anode and a sharp pointed brass cathode [3 – 8], housed in an electrical furnace for carrying electron injection. The injection experiment was carried out at different temperatures (795 K to 945 K) by the application of constant field (710 Vcm^{-1}), and stopped well before the commencement of the third zone [9]. The decay of colour centres augmented by reversing the electric field and the process was continued until the crystal regained its original transparency. The pristine time was checked. By shining the specimen with appropriate F-light using reflection grating monochromator (ORIEL, USA) the reduction of colour centre or the emergence of transparency of crystals were studied. The transmitted light through a crystal was recorded by a photo-multiplier detector system. Simultaneous recording of the injection and photocurrent was done during the growth and decay processes with the help of a Bausch and Lomb series 5000 strip-chart two-pen recorder.

3. Results and discussion

The growth of electrolytic colouration may be assumed to be a diffusion process where electrons from pointed cathode are diffused radially within the bulk of alkali halide crystals whose outer periphery is a spherical one and mechanically pressed by spherical platinum anode of the same radius. In order to obtain a uniform electric field inside the crystal, the pointed cathode is placed at the centre of the sphere. In earlier work [10], we developed an analytical expression for current flow following Poisson's equation in spherical polar co-ordinates by considering single-carrier injection from the curved contacting electrode. The analytical expression for the diffusion coefficient (D) is derived in the following, considering the additional current caused by the diffusion of colour centres by applying the concept of the well-known diffusion process.

The electrical conductivity (σ) of the crystal at any point is given by

$$\sigma = Ne\mu \,,$$

where N is the instantaneous density of stoichiometric excess of alkali ions associated with the density of colour centres at the point concerned (obviously $N = f(r)$), e is the electronic charge and μ is the mobility.

The radial electric field (E) at any point for a current I passing through the specimen of uniform width d is

$$E = -\frac{I}{(Ne\mu)\,\pi}\,\frac{1}{rd} \,.$$

The negative sign is indicative of the field directed towards the cathode.

In time, the colour cloud will spread out from the cathode. The continuity equation for density of colour centres at any point, in analogy to the charge carriers in semiconductors, may be written as

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N}{\partial r^2} - N\mu\frac{\partial E}{\partial r} - \mu E\frac{\partial N}{\partial r} \,. \tag{1}$$

Now,

$$\frac{\partial E}{\partial r} = -\frac{\partial}{\partial r}\left(\frac{I}{e\mu\pi drN}\right) = \frac{I}{e\mu\pi dNr^2} + \frac{I}{e\mu\pi drN^2}\frac{\partial N}{\partial r}.$$

Therefore,

$$-N\mu\frac{\partial E}{\partial r} = -\frac{I}{e\pi dr^2} - \frac{I}{e\pi dNr}\frac{\partial N}{\partial r}$$

and

$$-\mu E\frac{\partial N}{\partial r} = -\mu\left(-\frac{I}{Ne\mu\pi rd}\right)\frac{\partial N}{\partial r} = \frac{I}{Ne\pi rd}\left(\frac{\partial N}{\partial r}\right) \,.$$

Then Eq. (1) takes the form

$$\frac{\partial N}{\partial t} = D\frac{\partial^2 N}{\partial r^2} - \frac{I}{e\pi dr^2} = \frac{\partial^2}{\partial r^2}\left[DN + \frac{I}{e\pi d}\ln r\right] .$$

At $t = 0$ (i.e., at the time of application of the field), $I = 0$ and $N = 0$.

The solution of the above equation yields

$$D + \frac{I}{\pi de}\frac{\ln r}{N} = \frac{A}{N\sqrt{t}}\exp\left(-\frac{r^2}{4Dt}\right).$$

Corresponding to $r = r_1$, r_2 and r_3, the above equation takes the forms

$$D + \frac{I}{\pi de}\frac{\ln r_1}{N_1} = \frac{A}{N_1\sqrt{t}}\exp\left(-\frac{r_1^2}{4Dt}\right), \tag{2}$$

$$D + \frac{I}{\pi de}\frac{\ln r_2}{N_2} = \frac{A}{N_2\sqrt{t}}\exp\left(-\frac{r_2^2}{4Dt}\right), \tag{3}$$

$$D + \frac{I}{\pi de}\frac{\ln r_3}{N_3} = \frac{A}{N_3\sqrt{t}}\exp\left(-\frac{r_3^2}{4Dt}\right). \tag{4}$$

Simplifying equations (2), (3) and (4), we get

$$\frac{IE_1}{\pi de} = \frac{A}{\sqrt{t}}\left[A_1 + \frac{B_1}{4Dt}\right], \tag{5}$$

where

$$E_1 = \frac{\ln r_1}{N_1} - \frac{\ln r_2}{N_2}, \qquad A_1 = \frac{1}{N_1} - \frac{1}{N_1} \qquad \text{and} \qquad B_1 = \frac{r_2^2}{N_2} - \frac{r_1^2}{N_1}$$

and

$$\frac{IF_1}{\pi de} = \frac{A}{\sqrt{t}}\left[C_1 + \frac{D_1}{4Dt}\right], \tag{6}$$

where

$$F_1 = \frac{\ln r_2}{N_2} - \frac{\ln r_3}{N_3}, \qquad C_1 = \frac{1}{N_2} - \frac{1}{N_3} \qquad \text{and} \qquad D_1 = \frac{r_3^2}{N_3} - \frac{r_2^2}{N_2}.$$

Dividing (5) by (6), we get

$$D = \frac{1}{4t}\,\frac{B_1F_1 - D_1E_1}{C_1E_1 - A_1F_1}. \tag{7}$$

After further simplification, Eq. (7) gives

$$D = \frac{1}{4t}\,\frac{N_1\ln(r_2/r_3) + N_2\ln(r_3/r_1) + N_3\ln(r_1/r_2)}{N_1\big(r_3^2\ln r_2 - r_2^2\ln r_3\big) + N_2\big(r_1^2\ln r_3 - r_3^2\ln r_1\big) + N_3\big(r_2^2\ln r_1 - r_1^2\ln r_2\big)}.$$

In the actual experiment, the process of colouration performed at different temperatures was restricted within the second zone [6] and quenched to room temperature. In its steady state, the variation of optical density along three different r-values was measured by shining F-light from the Oriel monochromator on the specimen mounted upon a vernier movement. Using the above equation, values of the diffusion coefficient have been calculated for different temperatures. Typical data for KCl specimen is shown in Table 1.

TABLE 1. Diffusion coefficient (D) for different temperatures (T).

Temperature (T) (K)	Diffusion coefficient (D) (cm^2s^{-1})	$1/T$ (K^{-1})	$\ln(D)$
870	0.01762	0.00115	-4.03872
845	0.01222	0.00118	-4.40468
820	0.00951	0.00122	-4.65499
795	0.0066	0.00126	-5.02069

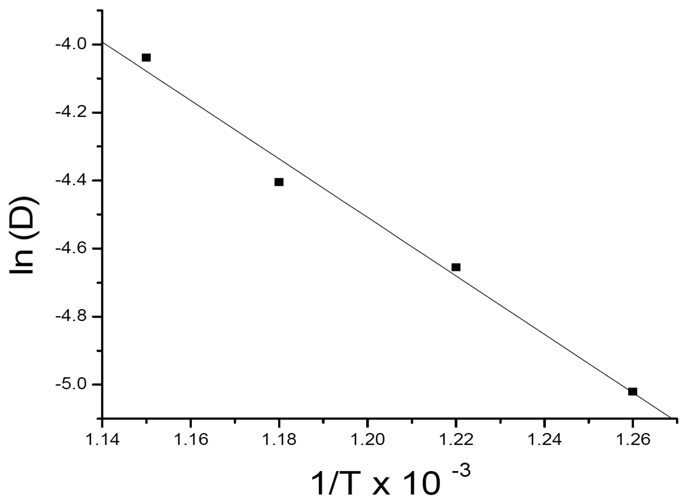


Fig. 1. Plot of $\ln(D)$ *against* $1/T \times 10^{-3}$.

Using the relation $D = D_0 \exp(-W/(kT))$, the activation energy (W) for the movement of colour centres during growth is calculated from the slope in $\ln D$ vs. $1/T$ plot (Fig. 1), yielding $W = 0.7$ eV for KCl, which is lower than the value of 0.9 eV for the self diffusion of K-ions [11].

It is expected that there must be a similarity between the mechanisms of diffusion of F-centres and the alkali ions (K-ions in the present case). The lower value obtained from the present experiment may be due to the lowering of the potential barrier under the applied electrical field.

To pursue the effect of nature of stresses on trapped centres, an experiment was performed where only thermal stress was applied on electrolytically-coloured crystals (both pure and doped). Only the case of 10-mole% KCl:KBr has been studied as an example. Immediately after colouration, shining lights with different wavelength regions scanned the crystal (Fig. 2). It clearly shows from the F-peak intensity that from 60 °C to 550 °C the optical density (OD) value remains more or less the same, indicating practically no loss of colour centres. However, at 600 °C, OD abruptly declined thereby bleaching almost all colour centres. Thus above a certain optimum temperature, thermal bleaching becomes prominent.

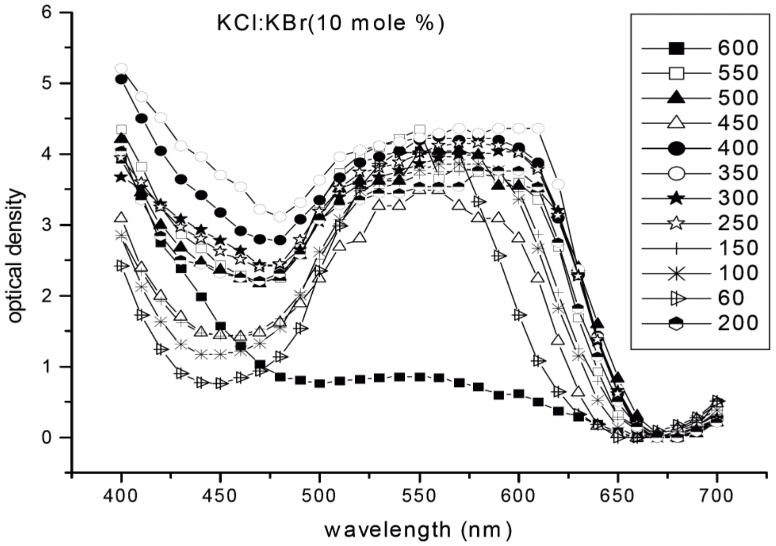


Fig 2. Plot of optical density against wavelength for KCl:KBr (10 mole%) *at different temperatures.*

Incorporating field stress along with the thermal one, the bleaching of colour centres becomes faster. When the polarity of the electrodes is reversed, there is no creation of high electron density near the cathode, instead the F-centres will have the affinity to rush towards the pointed electrode. Figure 3 shows the change of optical density during decay of colour centres [12].

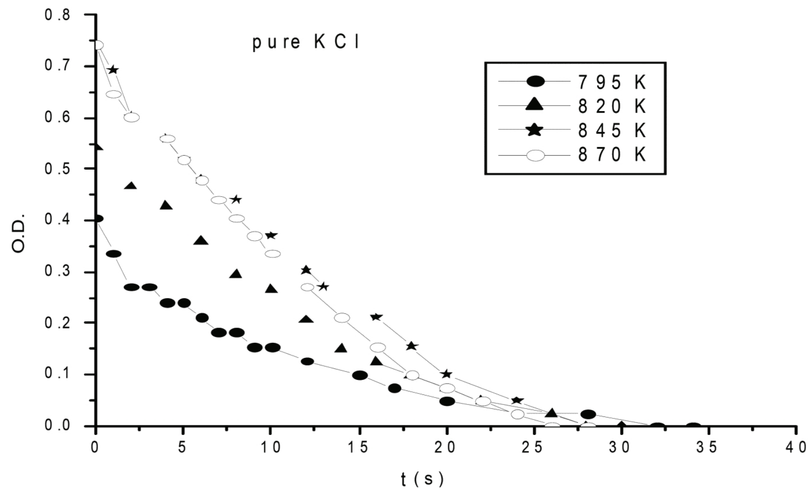
The time of bleaching (t) was determined and mobility (μ) has been calculated from the following equation [13]

$$\mu = \frac{L}{tE} \,,$$

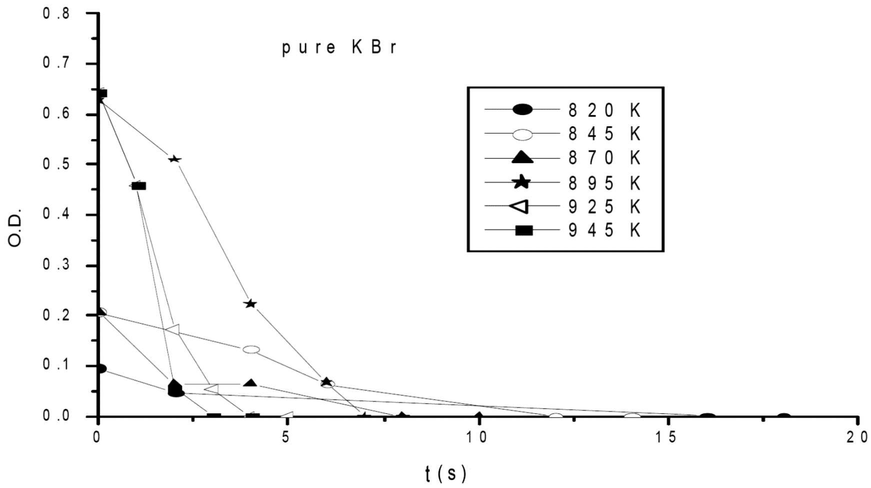
where L is the effective length of the crystal and V is the applied field in Vcm^{-1}. The dependence of transition time on temperature [$t = f(T)$] leads to the relation

$$\mu = \mu_0 \exp\left(-\frac{W_F}{kT}\right) \,,$$

where, W_F is the activation energy of bleaching, k is the Boltzmann constant and T is the temperature in the absolute scale.



(a)



(b)

Fig. 3: Plot of optical density (OD) during decay process at different temperature for a) pure KCl *b) pure* KBr.

If we plot $\ln(\mu)$ versus $1/T$, (Fig. 4), straight lines are obtained, and their slope yields the activation energy for bleaching or migration of F-centres by injected electrons.

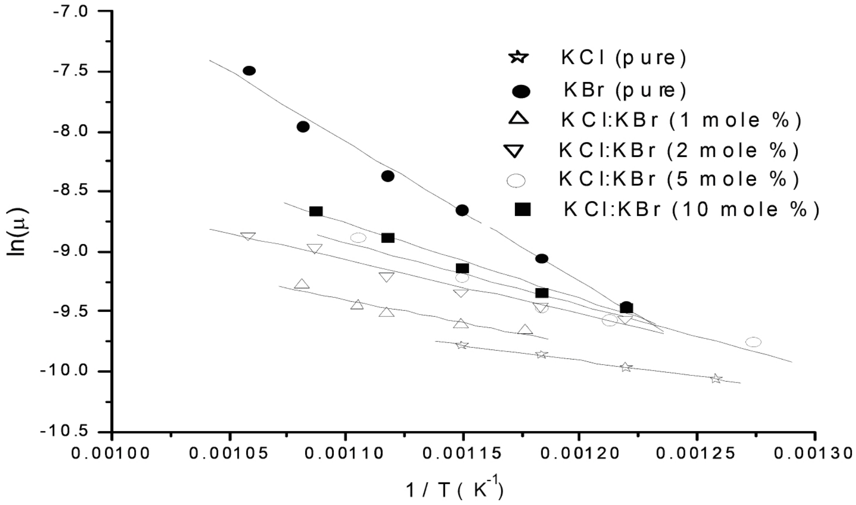


Fig. 4. Plot of $\ln(\mu)$ *versus* $1/T$ *in* K^{-1}.

Again, we know,

$$W_F = E_F - \frac{W}{2},$$

where E_F is the energy required to dissociate the F-centre thermally and W is the energy required to form a Schottky defect. From the experimentally determined values of W_F, we can have estimate E_F (Table 2).

TABLE 2. Activation Energy (W_F) for mobility of different specimens.

Specimen	Activation energy (W_F) (eV)	Dissociation energy E_F (eV)
KCl (pure)*	0.224	1.224
KBr (pure)*	1.007	2.007
KCl:KBr (1 mole%)	0.329	1.329
KCl:KBr (2 mole%)	0.386	1.386
KCl:KBr (5 mole%)	0.446	1.446
KCl: KBr (10 mole%)	0.542	1.542

*See reference [12].

From Table 2, it is clear that the thermal dissociation energy values increase with the doping percentage. The incorporation of impurities leads to localized levels in the forbidden band [14]. The bleaching process involves electronic excitations. These excitations are smooth in the case of a pure specimen, but become complicated as the interaction associated between these states and the conduction band. This mechanism must have a bearing on activation energy.

4. *Conclusion*

The diffusion coefficient of colour centres has been obtained using contacting heterogeneous spherical electrodes and by the application of thermal and field stresses in pure and doped alkali halide single crystals. The effect of doping of KBr in stressed KCl matrix is analysed by estimating the dissociation energy.

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KINETIČKA SVOJSTVA F-CENTARA POD UTJECAJEM TOPLINE

Proučavamo premještanje oblaka boje nakon ubacivanja elektrona u čiste i punjene kristale alkalnih halida KCl i KBr, pod djelovanjem topline i električnog polja, uz primjenu kuglaste elektrode. Pomoću izvedene analitičke relacije i mjernih podataka odredili smo koeficijent difuzije oblaka boje i ocijenili aktivacijsku energiju centara boje. Primjenom jednadžbe pokretljivosti izveli smo vrijednosti disocijacijske energije pod toplinskim i električnim naprezanjem za punjene kristale. Podaci pokazuju učinak punjenja u odnosu na čiste kristale.