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IONIC TRANSPORT IN ALKALI HALIDES WITH DOPING-INDUCED DEFECTS AND COLOUR CENTRE MIGRATION BY THERMAL BLEACHING

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Measurements of ionic conductivity in pure alkali halides and in alkali halides with doping-induced defects were made to determine the activation energies and mobility of F-centres. The activation energies in NaCl:Cd^{+2} were found large in comparison with NaCl with other divalent impurities. The mobilities of F-centre migration on bleaching of injected electrons were measured and the activation energies of bleaching W_F have been found. The results for space-charge-limited conduction of F-centres are explained with the determined values of activation energies W and W_F.

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1. *Introduction*

The effects of point defects on bulk properties of broad-band insulators is used to study the properties of dopant materials. The ionic transport [1] in pure alkali halide crystals and in alkali halide crystals with doping-induced defects (solid electrolites) at elevated temperatures is used to estimate defect concentrations, enthalpies, activation energies and other physical parameters. It is generally considered [2] that Schottky defects are present in most alkali halides with concentrations far larger than the Frenkel defects. The effect of Schottky vacancies can provide a clear picture about their structure and defect concentrations.

Another noteworthy point is that the impurities provide localized energy levels within the forbidden band. These states allow the injection of free carriers either into the conduction or in the valence band [3]. The space charge thus induced causes the movement of colour centres from cathode to anode by simultaneous trapping and detrapping of free carriers in the vacancies. This constitutes the space-charge limited (SCL) current. The SCL current is thus a bulk phenomenon [4,5] and can provide information about the defects.

Study of the electrical properties of ionic crystals by electron injection revealed a transient response of the current which is characteristic of four zones [6]. The electron transport is responsible for the conduction in zone II and zone III, while the first-zone current is due to ionic conductivity [7]. For a given electric field, first-zone current does not change with time. However, due to the nonlinearity and inhomogeneity of the contact [8], ionic current is initially constant until the deposition of ions of alkali metal causes the formation of the secondary cathode which acts as a reservoir of free carriers. Hence, the electron injection gets a boosting. The formation of such a contact is the prerequisite for the flow of SCL current through the crystal and it is a precursor for the growth of the colour centres.

Electrons on their way through the crystal get trapped in anion vacancies and form colour centres. The colouring of a specimen can be varied by incorporating impurities of different vacancies which may act as traps or may have a deteriorating effect on F centre formation.

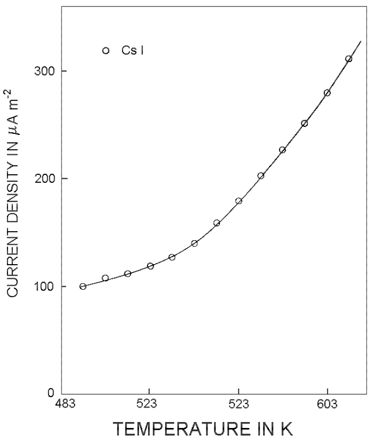
Previous theoretical and experimental analyses of different zones in doped alkali halides [3,4,9–15] have not explored all effects and there are also very few investigations of the ionic conductivity zone [7,16,17]. In the present work, attempt is made to find relation between ionic and electron-injection zones and to investigate the effects of dopants, like divalent materials, on the kinetics of detrapping carriers during bleaching.

2. *Experimental*

Pure CsI and NaCl (E-mark powder 99.99%) and impurity-doped NaCl:Ba^{2+} (0.006M%), NaCl:Mg^{2+} (0.001M%) and NaCl:Cd^{2+} (0.001M%) single crystals were grown in the laboratory by the Czochralski-Kyropoulos method, using a microprocessor controlled furnace and servo-controlled rotation cum-pulling accessories. NaCl crystals were cleaved along the <100> direction, while the CsI crystals were mechanically cut and polished in an arbitrary direction. Each specimen thus produced was placed between a pointed brass cathode and a platinum anode, and housed in an electrical furnace. The injection experiments were carried out in two phases. First, the injection was studied as a function of temperature and with a fixed field, and the process was stopped before the appearance of the second zone. In the second phase, the injection was performed on the same specimen in a stronger field of 1000 V/cm (fixed) at various temperatures and the process was stopped well before the appearance of the third zone. Then the field direction was quickly reversed [18], while maintaining the temperature constant. The measurements were continued until the current decayed to its original ionic value. During both phases, the increase and decay of the current (ionic and electronic) were recorded with a Bausch and Lomb series 5000 strip-chart recorder.

3. Results and discussion

Figures 1 and 2 show the ionic transport of different crystals represented by the current density J as a function of temperature. The ionic zone shows approximately exponential changes with temperature in the high-temperature region. Comparing the current-density curves of CsI (Fig. 1) and NaCl (Fig. 2) crystals, it is observed that J rises sharply at a somewhat lower temperature in CsI.



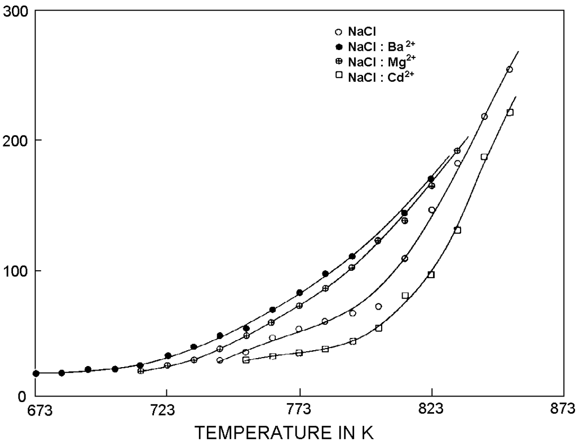


Fig. 1. Dependence of the current density on temperature for a constant injection field of 550 V/cm *in a pure* CsI *crystal.*

Fig. 2 (right). Dependence of the current density on temperature for a constant injection field of 550 V/cm *in a pure* NaCl *crystal and in doped* NaCl:Ba, NaCl:Mg *and* NaCl:Cd *crystals.*

The crystals NaCl:Ba^{2+} and NaCl:Mg^{2+} augment the electronic zones at lower temperatures in comparison with pure NaCl, while NaCl:Cd^{2+} behaves abnormally. In order to restrict the onset of the electronic zone in Ba^{2+}- and Mg^{2+}-doped crystals of NaCl, the temperature was raised up to 873 K. The ionic current density can be approximately expressed by [16]

$$J = A \exp(-W/(kT)) \,, \tag{1}$$

where $A = e\mu E n_e$, e is the electronic charge, E is the applied electric field, μ and n_e are, respectively, the carrier mobility and density of states in the conduction band and W is the activation energy of ionic conduction.

The validity of Eq. (1) has been tested by the plots of $\ln J$ vs. $10^3/T$. The slope of the straight lines thus obtained yield the activation energies of the different specimens (see Table 1). The results in the table indicate that $W_{\rm NaCl} > W_{\rm CsI}$. It has previously been established that the SCL zone is the consequence of the first-zone current [7]. Hence, lower activation energy of ionic conduction in CsI suggests that SCL conduction is more pronounced in CsI than in NaCl. A similar situation is observed in the cases of NaCl:Ba^{2+} and NaCl:Mg^{2+}. It can be accounted for by

Table 1. Ionic-conductivity activation energies of pure Cs *and* NaCl *crystals and of doped* NaCl:Ba, NaCl:Mg *and* NaCl:Cd *crystals for fixed injection fields of* 550 V/cm.

Crystal	Activation energy in eV	
	From graph	By method of averages
Pure CsI	0.43	0.41
Pure NaCl	1.23	1.36
Doped NaCl:Ba^{2+}	0.84	0.81
Doped NaCl:Mg^{2+}	0.89	0.87
Doped NaCl:Cd^{2+}	1.73	1.71

considering the defect production due to the charge compensation [15]. The electric neutrality requires the creation of vacancies in the cation side due to the incorporation of the divalent atoms. Hence, the vacancy concentration is proportionally increased with the doping. This process augments the movement of the vacancies and the ionic conduction is enhanced, thereby lowering the W values. Effect of the lowering is the increase of the SCL current which is basically electronic current due to the trapping and detrapping of injection electrons. This may be seen in Figs. 3 which show the data on the growth and decay of the current density during the trapping and detrapping processes.

A deviation is seen in the case of NaCl doped with Cd^{2+} which shows a rather different behaviour. In NaCl:Cd^{2+}, activation energy rises sharply to 1.7 eV, even more that in pure NaCl (1.2 eV). A peculiar behaviour of Cd^{2+} is also seen in the growth and decay currents in pure NaCl and NaCl doped with divalent impurities.

Previous work on alkali halides [19] has shown that the growth rate of F-band in NaCl with the $CdCl_2$ (0.1M%) substitution is considerably lowered when compared with the $CaCl_2$ (0.5M%) substitution. Both Ca^{2+} and Cd^{2+} create a large number of negative ion vacancies. Still higher growth rate of F-centres occurs only in Ca^{2+} doped crystals. An indirect explanation may be obtained from the nuclear magnetic relaxation data on NaCl doped with Cd^{2+}, Ca^{2+} and Mg^{2+} [20]. It has been infered that almost all vacancies exist in isolated states or no complex is formed except in the case of Cd^{2+} doping in which case the vacancies cluster round the Cd^{2+} ions forming complexes. That is based on the assumption that the quadrupole interaction energy for the forming of isolated vacancies is much larger than what is needed to form the complexes with Cd^{2+} ions [21]. The association energy for the forming of the complex between the vacancy and Cd^{2+} was found to be 0.4 eV, while for Ca^{2+} it was found to be almost zero (0.08 eV) [22]. The net result of the clustering of vacancies around the Cd^{2+} ions is that the conductivity is suppressed in spite of the increase of vacancy concentration. The experimental observation of the change of current with time at a particular temperature (833 K) in a field of

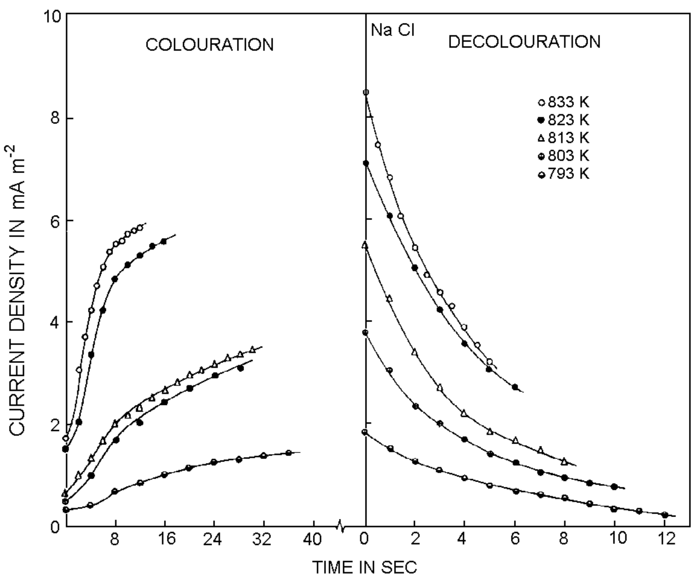


Fig. 3a. Dependence of the space-charge-limited current density on injection time for both colouration and decolouration at different temperatures in a pure NaCl *crystal.*

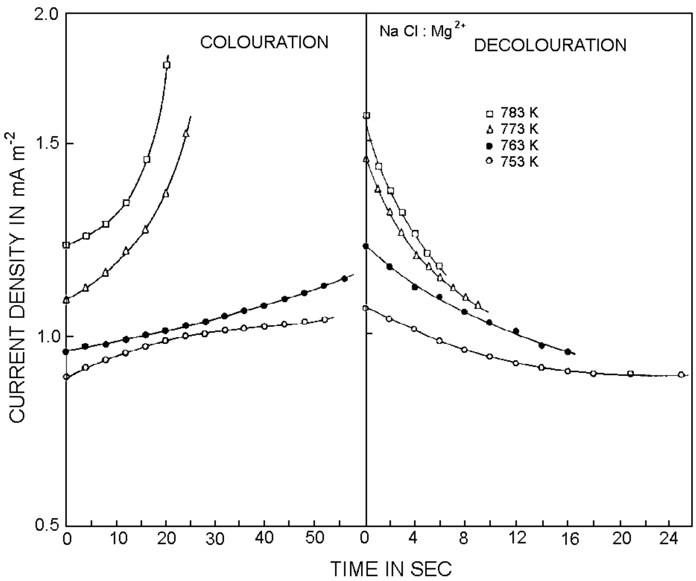


Fig. 3b. Dependence of the space-charge-limited current density on injection time for both colouration and decolouration at different temperatures in doped NaCl:Ba *crystal.*

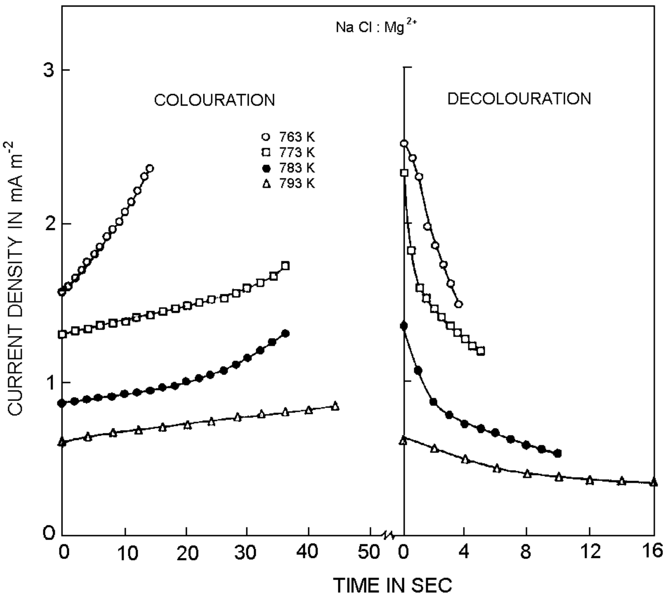


Fig. 3c. Dependence of the space-charge-limited current density on injection time for both colouration and decolouration at different temperatures in doped NaCl:Mg *crystal.*

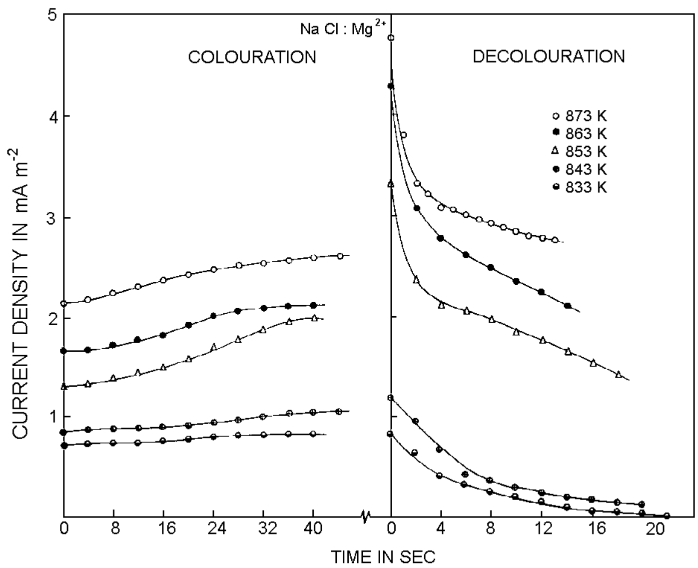


Fig. 3d. Dependence of the space-charge-limited current density on injection time for both colouration and decolouration at different temperatures in doped NaCl:Cd *crystal.*

1000 v/cm causes not only a sluggish growth rate but the decay of the current is also poor. The anomalous positive R_H value of the Hall coefficient [23] for cadmium, which significantly deviates from the nature of the carriers responsible for the transport phenomenon, may be the reason for such a complex formation.

Because of these effects, the electron current in the second zone with Cd^{2+} in NaCl is reduced. From the experimental data, the mobility of F-centre migration during the bleaching has been derived using the equation

$$\mu_F = \frac{L}{Et}\,, \tag{2}$$

where L is the length of the crystal from cathode to the anode, t the time of bleaching and E the applied field. The F-centre mobility is temperature dependent, and considering the temperature dependence to be of the Arrhenius type, mobility of F-centre migration can be expressed as [7,18]

$$\mu_F = \mu_0 \exp\left(-\frac{W_F}{kT}\right)\,. \tag{3}$$

Here, μ_0 is the constant related to an ideal insulator, W_F the activation energy of F-centre migration during the bleaching and k and T are the Boltzmann constant and temperature, respectively. Table 2 gives the experimental results on the mobility

Table 2. Mobilities (μ_F) and activation energies of F-centre bleaching in a pure NaCl *crystal and in doped* NaCl:Ba, NaCl:Mg *and* NaCl:Cd *crystals for fixed injection fields of* 1000 V/cm.

Sample (M%)	Temp. (K)	F-centre mobility (10^4 cm^2/(V s))	Activ. energy (eV)
Pure NaCl	793	0.167	1.33
	803	0.200	
	813	0.250	
	823	0.333	
	833	0.400	
NaCl:Mg^{2+} (0.001)	763	0.179	2.46
	773	0.286	
	783	0.520	
	793	0.817	
NaCl:Ba^{2+} (0.006)	773	0.200	2.49
	783	0.313	
	793	0.555	
NaCl:Cd^{2+} (0.001)	833	0.141	0.86
	843	0.155	
	853	0.172	
	863	0.221	
	873	0.238	

which is in the range 10^{-4} to 10^{-3}, in agreement with the results obtained by other methods.

The plots of $\ln \mu_F$ vs. $1/T$ provide straight lines for all samples, verifying thus Eq. (3). The activation energies W_F have been evaluated from the slopes of the straight lines. The results are in a fair agreement with those obtained from other measurements [7,24–28].

It is clearly seen that the specimens with better SCL conduction posses large value of W_F. However, the specimen of NaCl:Cd^{2+} has a very low value of the activation energy for F-centre bleaching. Overall results can be justified by considering that higher activation energy of F-centre bleaching means that the samples are more prone to F-centre formation. That means, bleaching of F-centres requires more energy in those samples which have a steep rising current curve, implying high concentration of F-centres in them within the second zone. So, this sample requires a higher activation energy for F-centre bleaching.

Comparing Tables 1 and 2, it is clear that the obtained results of the two types of activation energy (ionization and bleaching) are justified. The lesser the energy of the ionization process, the larger is the activation energy in bleaching, and the converse is also true.

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GIBANJE IONA U ALKALNIM HALIDIMA S PRIMJESNIM DEFEKTIMA I SELJENJE CENTARA BOJE TOPLINSKIM BIJELJENJEM

Načinili smo mjerenja ionske vodljivosti u čistim alkalnim halidima i u alkalnim halidima s primjesnim defektima radi određivanja aktivacijskih energija i pokretljivosti F-centara. U NaCl:Cd^{+2} našli smo velike vrijednosti aktivacijske energije u odnosu na NaCl s drugim divalentnim nečistoćama. Mjerili smo pokretljivost F-centara pri bijeljenju i odredili aktivacijske energije bijeljenja W_F. Ishodi mjerenja za vodljivost F-centara ograničenu prostornim nabojem objašnjavaju se vrijednostima određenih aktivacijskih energija W i W_F.