

## TECHNICAL NOTE

### THERMALLY STIMULATED DEPOLARIZATION CURRENTS IN LiF + Be<sup>2+</sup>

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**Keywords:** Thermally, stimulated, current, lithium fluoride, beryllium.

**Abstract**—The reorientation of dipolar complexes in a LiF single crystal doped with Be<sup>2+</sup> has been studied by means of the thermally stimulated depolarization currents technique (T.S.D.C) in the temperature region 80–300 K.

Three main bands were observed. The low temperature band has an enthalpy smaller by a factor of two than the intermediate band. The enthalpy of the latter is comparable to that of the migration process of the free cation vacancy but smaller (i.e. by 40%) than the enthalpy of the high temperature band. The general behaviour is similar to that of the systems: KCl + Be<sup>2+</sup> and NaCl + Be<sup>2+</sup> studied two decades ago.

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#### 1. INTRODUCTION

When divalent cation impurities are added to an alkali halide crystal dipoles are formed which can reorientate themselves preferentially under the action of an external field. In order to study the reorientation parameters of these dipoles the most accurate experimental technique is the so-called ionic thermocurrents technique (I.T.C.) or thermally stimulated depolarization currents technique (T.S.D.C.) [1–3]. This technique consists basically of the following steps [4, 5]. For a time  $t$  an external field  $E_p$  is applied to the crystal at a temperature  $T_p$  so that the relaxation time  $\tau(T_p)$  of these dipoles is appreciably smaller than  $t$ . Under the continuous action of the electric field the specimen is cooled down at a temperature  $T_0$  so that the relaxation time  $\tau(T_0)$  reaches values of the order of some hours or more. The electric field is then switched off but the specimen remains polarized due to the high value of  $\tau(T_0)$ . The temperature is gradually increased at a constant rate

$$b \left( b \equiv \frac{dT}{dt} \right)$$

and the relaxation time  $\tau(T)$  becomes smaller according to the usual relation [5]:

$$\tau(T) = \tau_0 \exp\left(\frac{H^m}{kT}\right), \quad (1)$$

where  $H^m$  is the reorientation enthalpy of the dipoles,  $k$  is the Boltzmann constant and  $\tau_0$  the usual pre-exponential factor. During the increase of temperature the depolarization current  $i$  is recorded and study of the curve  $i$  vs  $T$  leads to the determination of  $\tau_0$  and  $H^m$ .

In cases where the ionic radius of the divalent impurity is appreciably smaller than the host cation the phenomenon attracts a strong theoretical interest [6]. Systems of this type which have been studied to date are [6] NaCl + Be<sup>2+</sup> and KCl + Be<sup>2+</sup>. It is the object of the present paper to report a preliminary experimental study of the system LiF + Be<sup>2+</sup> in which both the Debye and melting temperature of the host crystals are appreciably higher than the crystals mentioned above. Details concerning the kinetics of aggregating dipoles will be published very shortly.

#### 2. THEORY

Assuming a linear increase of temperature the following well-known expression for the T.S.D.C. current is valid:

$$i(T) = \frac{AP_0}{\tau_0} \exp\left(-\frac{H^m}{kT}\right) \times \exp\left\{- (b\tau_0)^{-1} \int_{T_0}^T \exp\left(-\frac{H^m}{kT'}\right) dT'\right\}, \quad (2)$$

where  $A$  is the surface area of the specimen, and  $P_0$  the initial polarization. The main features of function (2) are:

1. There is a maximum of the current at a temperature  $T_M$ , given by

$$T_M = \frac{bH^m\tau_0(T_M)^{1/2}}{k} \quad (3)$$

which is independent of  $T_p$  and  $E_p$ .

2. The low temperature tail is described by the simplified expression

$$\ln i(T) = \text{const.} - \frac{H^m}{kT} \quad (4)$$

from which we can calculate the parameter  $H^m$ . Once the value of  $T_M$  is known we can estimate  $\tau(T_M)$  from eqn (3) and then the factor  $\tau_0$  is determined from eqn (1).

3. The migration enthalpy  $H^m$  can be determined not only from eqn (4) but also by utilizing the whole curve  $i(T)$ . Thus we have the following relation:

$$\tau(T) = \frac{1}{bi(T)} \int_T^{T_\infty} i(T') dT'. \quad (5)$$

The quantity  $P_0$  is given by:

$$P_0 = \frac{n\mu^2}{3kT_p} E_p \quad (6)$$

where  $n$  is the concentration of dipoles and  $\mu$  the electric dipole moment.

Other details concerning the analysis of the data are given in Refs [5–10].

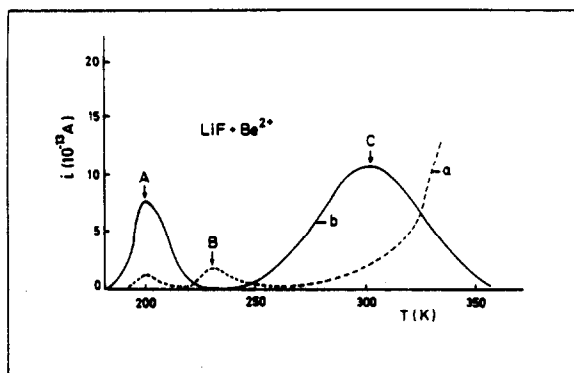


Fig. 1. I.T.C. spectrum from LiF doped with  $\text{Be}^{2+}$ . Curve (a) before annealing; curve (b) after annealing at 770 K for 4.5 h.

### 3. EXPERIMENTAL DETAILS

A vibrating reed electrometer (Carry 401) is used for measurement of the current, and the sample is placed between platinum electrodes in a vacuum of  $10^{-3}$  Torr. The temperature varies in the range between  $-196$  (liquid nitrogen) and  $80^\circ\text{C}$  and is measured with Chromel–Alumel thermocouple which is in contact with the upper surface of the sample. The samples were monocrystals of LiF doped with  $\text{BeF}_2^+$ , silver painted for better contact, and have the typical dimensions  $10 \times 10 \times 1 \text{ mm}^3$ .

A previous crystal was doped with  $5 \times 10^{-3}$  mole fraction of  $\text{BeF}_2$  in the melt. Chemical analysis of this first crystal showed it to contain 10 mole ppm at the top and less than 1 ppm at the bottom [10]. Hence we can estimate that the present crystal contains less than 50 mole ppm Be.

In each cycle the crystal was annealed at  $500^\circ\text{C}$  for 4.5 h and then quenched to room temperature ( $\sim 20^\circ\text{C}$ ).

A polarization field  $E_p = 8 \text{ KV/cm}$  was applied for 5–6 min at room temperature (about  $20^\circ\text{C}$ ) and the sample cooled down to  $-196^\circ\text{C}$ . After switching off the field the temperature was increased at a constant rate  $b = 0.1\text{--}0.2 \text{ K/sec}$  and the depolarization current recorded.

### 4. RESULTS AND DISCUSSION

The ITC spectrum of LiF +  $\text{Be}^{2+}$  before (curve a) and after (curve b) annealing at 770 K for 4.5 h is depicted in Fig. 1 for one of the samples. The spectrum consists of three bands: band A in the region of 199 K, band B in the region of 229 K and band C in the region of 307 K.

In Table 1 are given the values of the characteristic parameters calculated for the above bands according to eqns (5) and (1). In Table 2 we give the values calculated for NaCl +  $\text{Be}^{2+}$  and KCl +  $\text{Be}^{2+}$  [6] for the sake of comparison. By studying the behaviour of the bands after adequate thermal treatment we can state the following.

By applying eqn (5) for band A we find the Arrhenius plot  $\ln \tau$  vs  $1/T$  depicted in Fig. 2. Obviously this plot indicates the coexistence of two mechanisms, the parameters of which are given in Table 1. Due to the fact that band A is at a maximum immediately after the thermal treatment we attribute it to the (re)orientation of Impurity–Vacancy (I–V) dipoles, probably through  $nn \rightarrow nn$  and  $nn \rightarrow nnn$  vacancy jumps.

Band B is attributed to the aggregation of I–V dipoles because of its disappearance after the aforementioned thermal treatment. Band C may be attributed to a Suzuki phase because it exhibits all the characteristic properties described in Ref. [11]. This phase has also been identified by ionic

† These crystals were grown at the Crystal Growth Laboratory, University of Utah.

Table 1. Reorientation parameters of the system LiF +  $\text{Be}^{2+}$  obtained in the present work

Host Crystal	$T_M$ (K)	$H^m$ (eV)	$\tau_0$ (sec)	
LiF	Band A	$196$	$0.31 \pm 0.03$	$8.24 \times 10^{-7}$
	Band B	$203$	$0.56 \pm 0.03$	$2.46 \times 10^{-12}$
	Band C	$232$	$0.65 \pm 0.04$	$1.82 \times 10^{-12}$
	Band C	$315$	$0.93 \pm 0.10$	$5.4 \times 10^{-11}$

Table 2. Reorientation parameters of KCl +  $\text{Be}^{2+}$  and NaCl +  $\text{Be}^{2+}$  from Ref. [6]

Host Crystal	$T_M$ (K)	$H^m$ (eV)	$\tau_0$ (sec)	
KCl	Band A	40	?	?
	Band B	133	0.24	$10^{-8}$
	Band C	161	0.45	$5 \times 10^{-13}$
NaCl	Band A	50	?	?
	Band B	142	0.26	$5 \times 10^{-9}$
	Band C	170	0.50	$1.5 \times 10^{-13}$

conductivity measurements in LiF +  $\text{Mg}^{2+}$  [12]. The only Be-doped alkali halides for which the ITC spectrum has been studied are NaCl and KCl. In both cases the spectrum was characterized by three types of relaxations, a feature which is similar to the present case. The application of eqn (5) to the bands B and C leads to the parameters given in Table 1.

Concerning the concentration  $n$  of I–V dipoles the following should be noted; in spite of the fact that, as mentioned, band A is a complex one we can roughly assume that  $\mu = a\sqrt{2}e$ , where  $a$  denotes the shortest anion–cation

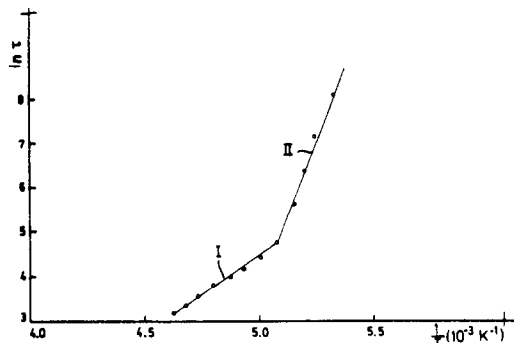


Fig. 2. The Arrhenius plot for band A as obtained from the application of eqn (5).

distance. By applying the usual formula [3]

$$P_0 = \int_0^{\tau} i(t) dt, \quad (7)$$

and estimating  $P_0 = 782 \times 10^{-13}$  A sec we find from eqn (6) that  $n \approx 50$  ppm. This value is consistent with the results of the chemical analysis mentioned above.

Concerning the parameters of the first mechanism of the low temperature band we see the following striking properties:

1. The migration enthalpy  $H^m$  is only 0.31 eV, which is less than half of the enthalpy of 0.7 eV corresponding to a free cation vacancy [13].

2. The factor  $\tau_0$  is unusually large, i.e. by comparing  $\tau_0^{-1}$  with the Debye frequency ( $\nu_D = 1.6 \times 10^{-13}$ /sec) [14] we see that the attempt frequency is roughly five orders of magnitude less.

Our experimental findings for the low temperature peak are similar to those observed by Bucci [6] for NaCl and KCl doped with  $\text{Be}^{2+}$ , or for LiD doped with  $\text{Mg}^{2+}$  [15]. In discussing these results one can suggest the explanation that the low values of  $H^m$  and  $\tau_0^{-1}$  are due to the fact that  $\text{Be}^{2+}$  occupies off-centre positions and, in the migration process, frequencies from the acoustical branch dominate [6].

Concerning the intermediate band one notices that the migration enthalpy 0.65 eV is a little less than that corresponding to a free cation vacancy (around 0.70 eV) but comparable to the enthalpy found in the case of  $\text{LiF} + \text{Mg}^{2+}$  [16].

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