

Dielectric losses and ionic conductivity of LiF:Ba²⁺

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Ba²⁺-doped LiF crystals were studied using the "dielectric loss" and "ionic conductivity" methods. By the first method we have indicated the existence of two relaxation mechanisms. The first mechanism is attributed to reorientation of ion-vacancy dipoles by means of nearest-neighbor to nearest-neighbor jumps. The estimated activation enthalpy h_m and the preexponential factor τ_0 are 0.43 eV and 3.30×10^{-9} sec, respectively. The second mechanism is attributed to nearest-neighbor to next-nearest-neighbor jumps. The enthalpy parameters are $h_m = 0.34$ eV and $\tau_0 = 2.75 \times 10^{-8}$ sec. By the ionic conductivity method the migration enthalpy of free vacancies is estimated to be $h_m = 0.67$ eV.

I. INTRODUCTION

Cation vacancies are formed when divalent metal impurities are introduced in LiF substituting Li⁺ ions. The divalent impurity and the cation vacancy are mutually attracted forming several kinds of dipoles. These dipoles are nearest-neighbor (NN) type when the vacancy is the nearest neighbor to the divalent impurity and next-nearest-neighbor (NNN) type when the vacancy is the next-nearest neighbor to the impurity.

In a recent paper¹ we have studied Ba²⁺-doped LiF crystals using the thermally stimulated depolarization currents (TSDC) or ionic thermocurrents method and the depolarization current (DC) method at a constant temperature.

In the present paper we study the same system by using the dielectric loss and the ionic conductivity methods. By the first method we evaluate the migration enthalpy h_m and the preexponential factor τ_0 involved in the classical Arrhenius relation $\tau = \tau_0 \exp(h_m/kT)$. By the second technique we can only measure the migration enthalpy of the free vacancies.

II. EXPERIMENTAL DETAILS

In the experimental setup a Boonton-Electronics Bridge (model 75c) was used operating between 5 and 500 kHz. The sample, between platinum electrodes, was put inside a quartz tube. The system was placed in an oven connected to a temperature controller. Our measurements were taken in the temperature of 650–750 K.

Our samples were LiF single crystals having Ba²⁺ as an added impurity with a nominal concentration of 10⁴ ppm. They were provided by the Crystal Growth Laboratory, University of Utah. According to the certification of this laboratory, there are no other impurities having a concentration more than 10 ppm. The samples were cut and prepared with the following dimensions: area $S = 64$ mm², thickness $d = 1.85$ mm. Good contact between the electrodes and the samples was achieved by painting the parallel surfaces of the crystal with a layer of graphite.²

III. EXPERIMENTAL METHODS AND RESULTS

A. The dielectric loss method

The dielectric constant of a crystal is usually written in a complex form $\epsilon = \epsilon_1 + j\epsilon_2$, where ϵ_1 and ϵ_2 are the real and imaginary parts, respectively. The imaginary part ϵ_2 is determined by the dielectric losses of the crystal and is written as $\epsilon_2 = \epsilon_2' + \epsilon_2''$. The first term corresponds to the so-called DC conductivity (e.g., motion of "free" vacancies); the second term corresponds to the reorientation of dipoles (e.g., motion of "bound" vacancies).

At a certain temperature T , ϵ_2'' as a function of the circular frequency ω ($\omega = 2\pi f$) has a maximum at $\omega_m = 1/\tau$, where τ is the relaxation time of the dipoles at this temperature.

From the Debye equations we find $\epsilon_2 = \sigma_{DC}/(\epsilon_0\omega)$ where σ_{DC} is the DC conductivity and ϵ_0 the permittivity of free space. At low enough frequencies, relative to ω_m , $\epsilon_2'' = 0$ and $\epsilon_2 = \epsilon_2'$. Then $\epsilon_2' = \sigma_{DC}/(\epsilon_0\omega)$ which implies

$$\log_{10}\epsilon_2' + \log_{10}\omega = \log_{10}(\sigma_{DC}/\epsilon_0). \quad (1)$$

For low frequencies, $\sigma_{AC} = \sigma_{DC}$ since only the free vacancies contribute to the conductivity. In this case $\log_{10}\epsilon_2$ as a function of $\log_{10}\omega$ is linear with slope equal to -1 [Eq. (1)]. For higher frequencies, the above curve deviates from the straight line. The reason is the dipole contribution to the conductivity. The net contribution of the dipoles to the conductivity can be found by subtracting the straight line from the above experimental curve. The resulting curve is described by the Debye equations and has a maximum at $f_m = \omega_m/(2\pi)$ which corresponds to the relaxation frequency of the dipoles. For various temperatures T , we take the corresponding ω_m . The Arrhenius relation gives

$$\ln\omega_m = -\ln(\tau_0) - h_m/(kT).$$

The plot of $\ln\omega_m$ as a function of $1/T$ is a straight line from which h_m and τ_0 can be obtained.

Curve *a* in Fig. 1 shows the imaginary part ϵ_2 of the

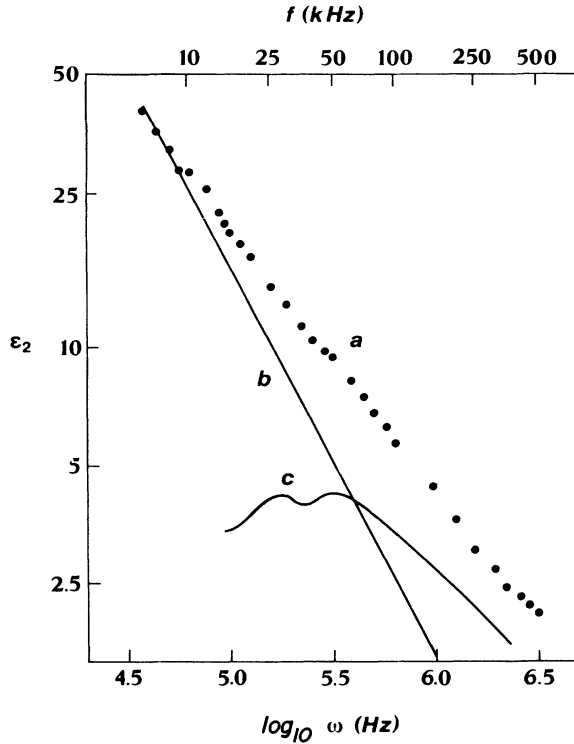


FIG. 1. Curve *a* is the plot of imaginary part ϵ_2 of the dielectric constant vs $\log_{10}\omega$ at $T=728$ K. Curve *b* represents the contribution of the vacancies to ϵ_2 . Curve *c* is found by the subtraction of curve *b* from *a*. This curve represents the contribution of the dipoles.

dielectric constant versus frequency at $T=728$ K in the frequency range of 6–500 kHz. The slope of the straight line *b* is equal to -1 thus indicating that *b* is solely due to the DC conductivity. The two peaks appearing in curve *c* indicate that there are two kinds of dipolar relaxation. Figure 2 shows the $\ln\omega_m$ versus $1/T$ plot. From the two straight lines we can easily find the relaxation parameters τ_0 and h_m of the two mechanisms, which are cited in Table I. Table I also has the relaxation parameters of LiF: Ba²⁺ crystals obtained by the TSDC and DC techniques which are comparable to our values. We can assume that the two relaxation mechanisms are due to NN→NN and NN→NNN jumps of the bound cation vacancy.¹ Because of the high temperatures of this experiment there are no clusters in the crystal.

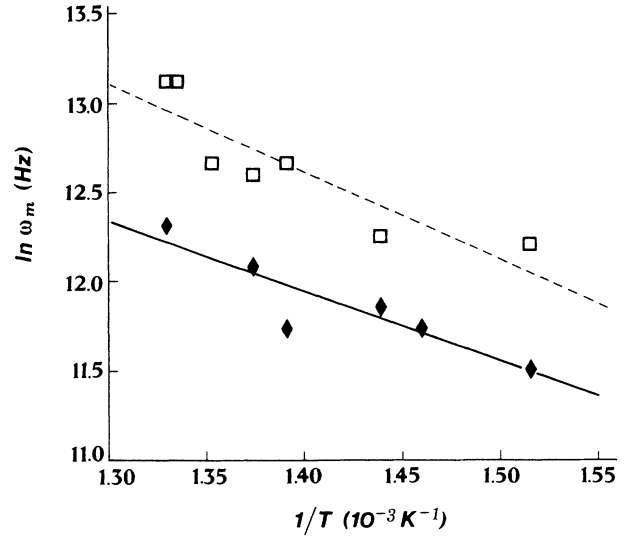


FIG. 2. Arrhenius plot.

B. The ionic conductivity method

Thermodynamic reasons and/or added impurities create vacancies in an ionic crystal. The conductivity of the crystal is due to the above vacancies.

The ionic conductivity can be written⁴ as

$$\sigma = ne^2\lambda\nu a^2(kT)^{-1} \exp[-g_m/(kT)], \quad (2)$$

where n is the density of charge carries, e is their charge, k is Boltzmann's constant, T is the absolute temperature, λ is a geometrical factor of order unity, ν is the attempt frequency of the ion to hop over the barrier g_m , and a is the jump distance.

In the dissociation region the amount of vacancies due to thermodynamical reasons is negligible. The dominant defects are free cation vacancies which preserve the whole electroneutrality as Ba²⁺ ions are incorporated into the lattice of LiF.

Substitution of the relation $g_m = h_m - Ts_m$ into (2) yields

$$\ln\sigma T = \ln(ne^2\lambda\nu a^2 k^{-1}) + s_m/k - h_m/(kT).$$

The plot of $\ln\sigma T$ versus $1/T$ in the dissociation region is a straight line with slope $-h_m/k$.

Our measurements were carried out at several fre-

TABLE I. Energy parameters of the migration of the bound cation vacancies in LiF:Ba²⁺.

Technique	Type of dipoles	NN→NN		NN→NNN		Clusters		Ref.
		h_m (eV)	τ_0 (s)	h_m (eV)	τ_0 (s)	h_m (eV)	τ_0 (s)	
Dielectric loss		0.43±0.09	3.30×10 ⁻⁹	0.34±0.08	2.75×10 ⁻⁸			Present work
TSDC		0.50	1.78×10 ⁻¹¹	0.24	6.59×10 ⁻⁵	0.81	4.93×10 ⁻²⁰	1
						0.80	1.28×10 ⁻¹⁹	1
DC ^a		0.45	9.69×10 ⁻¹⁰	0.23	1.31×10 ⁻⁴	0.79	1.05×10 ⁻¹⁶	1

^a Depolarization current at constant temperature.

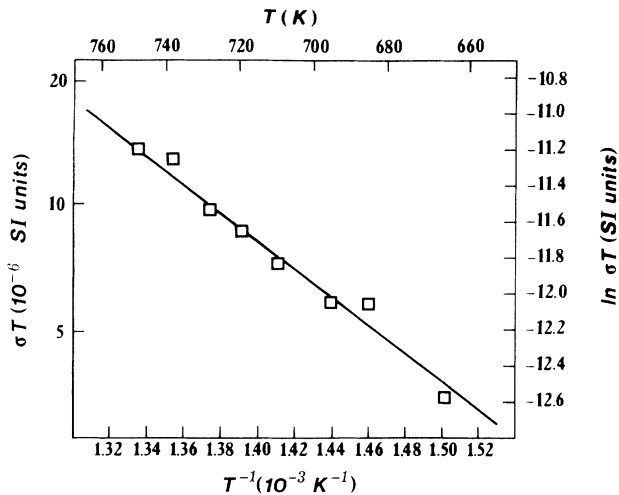


FIG. 3. The temperature dependence of the conductivity in the extrinsic region.

quencies (6, 8, 12 kHz) giving comparable results. Figure 3 shows our experimental data taken at a frequency of 6 kHz in the temperature range between 660 and 760 K, which corresponds to the dissociation region. The above temperature range was known from previous experiments on LiF:Be^{2+} .³ We attribute the conductivity σ to the free vacancies only, since the frequency of 6 kHz is very

low so the bound vacancies do not contribute to the conductivity. It is also known that the migration enthalpy h_m of free vacancies does not depend on the kind of divalent impurities. The calculated value from the slope of $\ln \sigma T$ versus $1/T$ plot is $h_m = (0.67 \pm 0.04)$ eV which is close to the values 0.65,⁵ 0.70,^{6,7} 0.66,⁸ and 0.68,^{1,9} obtained by other investigators.

IV. CONCLUSION

The dielectric loss method indicates that there are two kinds of relaxation mechanisms. We can attribute the first one (see Table I) to a $\text{NN} \rightarrow \text{NN}$ jump, because the energy parameters are in agreement with the Cussó and Jaque model¹⁰ for the reorientation of ion-vacancy dipoles via NN jumps ($\text{NN} \rightarrow \text{NN}$). Also, we can attribute the second relaxation mechanism (see Table I) to a $\text{NN} \rightarrow \text{NNN}$ jump because the energy parameters are in agreement with those suggested by Refs. 1, 3, and 11. The above results are in agreement with the corresponding values obtained by the TSDC and DC techniques.¹

The deviation which appears in the order of magnitude of τ_0 is due to the accuracy of the techniques. The TSDC method is the most sensitive one.

The calculated value $h_m = (0.67 \pm 0.04)$ eV from the ionic conductivity measurements is due to the free cation vacancies, while that in the Table I corresponds to the bound vacancies.

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