IONIC THERMOCURRENTS MEASUREMENTS ON LiH:Ca^{2+} AND LiD:Mg^{2+} CRYSTALS

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Summary

In this paper the ionic thermocurrent (ITC) in the LiH:Ca^{2+} and LiD:Mg^{2+} systems is studied. After selecting proper conditions of polarization and heating rate of the samples, two independent bands were observed in the ITC spectrum of the mentioned systems. The low-temperature band is attributed to relaxation mechanisms of the nn dipoles, while the higher-temperature band is attributed to dipole mechanisms related to relaxation of the oxygen anion with a bound anion vacancy.

Introduction

A widely used method for investigating the properties of dipolar complexes in dielectric media is to monitor the current arising from the relaxation of previously polarized dipoles during a linear increase in sample temperature. The technique was first introduced by Bucci and Fieschi [1, 2] and was given the name of ionic thermocurrents (ITC), although when applied to non-ionic compounds the more general name of thermally stimulated depolarization (or discharge) currents (TSDC) is more often used [3]. In the TSDC method the specimen is polarized at a given temperature by the application of an external electric field and is then cooled to a lower temperature, at which point the sample is short-circuited through a sensitive electrometer. The specimen is then heated at a controlled, linear rate and the relaxation of the dipoles is followed by monitoring the current arising from their thermally stimulated depolarization, i.e. their transition from an ordered to a random orientation.

ITC measurements in the LiH:Ca^{2+} and LiD:Mg^{2+} systems have been made

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in the past [4]. Since there was a suspicion that the ITC spectrum is complex, a new course of measurements was tried out on exactly the same samples. A characteristic feature of the ITC measurements in the above systems is that the pre-exponential factors of the classical Arrhenius relationship depart greatly from the expected values.

Not less interesting are the dielectric loss measurements (DLM) that have been applied to $LiD:Mg^{2+}$ [5], the d.c. conductivity measurements in LiH and LiD crystals [6], the dielectric constant and conductivity measurements in LiD [7], and finally, the ITC measurements in $LiH:Mg^{2+}$ [8]. The experimental results of the above mentioned works may be compared with the results of the present work.

Experimental

Beginning with the ITC measurements on the $LiH:Ca^{2+}$ we initially applied an electric field at temperatures T_p ranging between 250 and 270 K, while the heating rate b of the samples from liquid nitrogen temperature to room temperature was approximately 0.1 K/s. Under such conditions we observed two strongly overlapping bands in the ITC spectrum (Fig. 1). After lowering the temperature T_p and increasing the heating rate, the separation between the two bands became more and more evident.

For the measurement of ionic thermocurrents we used the following samples:

(i) LiH single crystal with divalent Ca^{2+} impurities. The crystal had been grown at Lawrence Radiation Laboratory of the University of California. Our
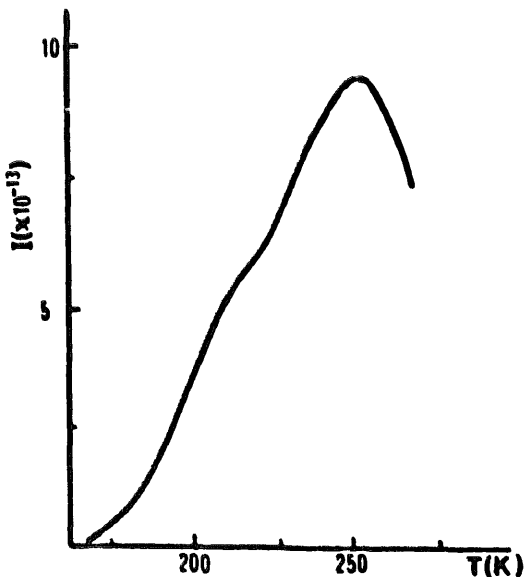

Fig. 1. ITC spectrum of $LiH:Ca^{2+}$. The sample has been polarized at $T_p = 258$ K and heated at a rate $b = 0.11$ K/s.

sample had an impurity concentration of 30 ppm. It was 1.9 mm thick with a cross-sectional area of 75 mm^2.

(ii) Polycrystalline LiD with divalent Mg^{2+} impurity at a concentration of approximately 10 ppm. The sample used was 3.1 mm thick and it had a cross-sectional area of 95 mm^2.

The sample crystals were mounted in a cryostat under a vacuum of 10^{-5} Torr between platinum electrodes and the depolarization currents were measured with a Cary 401 vibrating reed electrometer.

In the $LiH{:}Ca^{2+}$ sample, after a thermal treatment at 700 K for 7 h, the optimum separation of the two bands was encountered when an electric field of 70 kV/cm was applied for 9 min at a temperature $T_p{=}212$ K while the heating rate was 0.24 K/s.

The ITC spectrum obtained is depicted in Fig. 2; it evidently consists of two bands with maxima at temperatures T_M of 224 K and 253 K. A computer fitting was made according to the relationship:

$$J = \sum_{i=1}^{2} J_i = \sum_{i=1}^{2} \frac{P_{0i}}{\tau_{0i}} \exp\left[-\frac{h_m}{kT} - (b\tau_{0i})^{-1} \int_{T_0}^{T} \exp\left(-\frac{h_m}{kT'} \right) dT' \right] \tag{1}$$

where J is the depolarization current density, P_{0i} is the initial polarization, b is the heating rate and T_0 denotes the temperature from which the tail of the ITC spectrum starts. In deriving eqn. (1) the following Arrhenius relationship was assumed:

$$\tau = \tau_0 \exp\left(\frac{h_m}{kT} \right) \tag{2}$$

where τ denotes the relaxation time for the dipole reorientation process, h_m
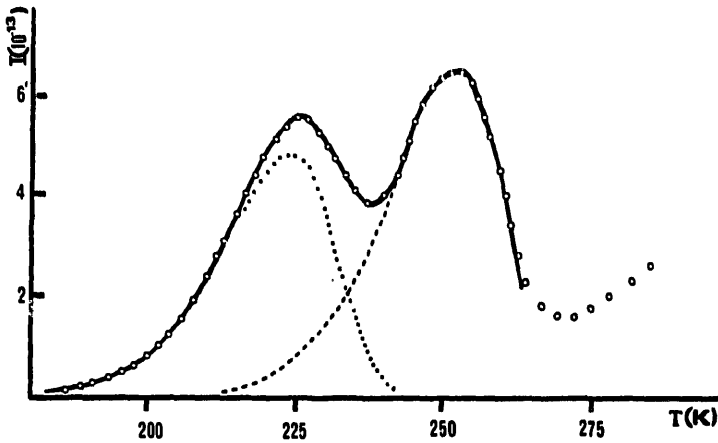

Fig. 2. ITC spectrum of $LiH{:}Ca^{2+}$. The open circles (○) denote experimental values. The dotted line (····) and the dashed line (----) depict the contributions of the two mechanisms (obtained from a computer fitting). The solid curve (———) is the sum of the dashed and dotted curves.

the migration enthalpy for the bound cation vacancy motion and τ_0 the usual pre-exponential factor.

In Table 1 the experimental results of the spectrum analysis (values of migration enthalpy h_m and pre-exponential factor) have been listed for both bands.

The ITC measurements in LiD:Mg^{2+} gave two bands hardly overlapping, as can be seen in Fig. 3, with maxima at temperatures T_M of 200 K and 245 K. The spectrum was obtained after quenching at 600 K for 7 h under an applied electric field of 15 kV/cm for 8 min at a temperature $T_p = 230$ K and a heating rate of 0.19 K/s.

In Table 2, the experimental results of the analysis of the spectrum (values of migration enthalpy h_m and pre-exponential factor) for both bands are given.

TABLE 1

Values of migration enthalpy h_m and pre-exponential factor τ_0 for both bands in LiH:Ca^{2+}

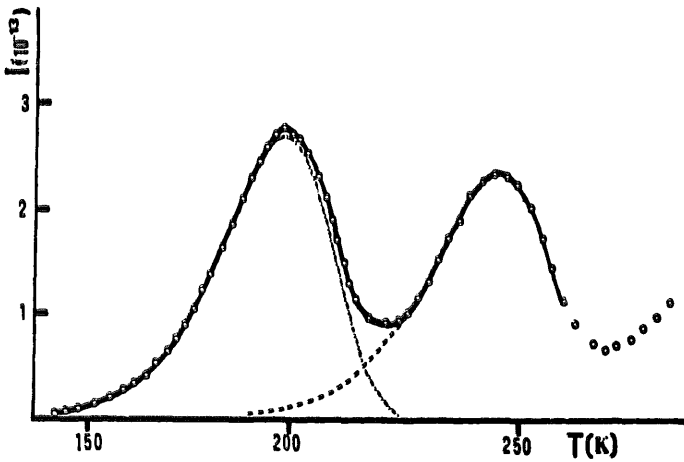|	T_M (K)	h_m (eV)	τ_0 ($\times 10^{-9}$ s)
1st band	224	0.42±0.01	70 ±3
2nd band	253	0.71±0.02	1.0±0.5

Fig. 3. ITC spectrum of LiD:Mg^{2+}. The open circles (O) denote experimental values. The axial line (-·-·-) and the dashed line (----) depict the contributions of the two mechanisms (obtained from a computer fitting). The solid curve (——) is the sum of the dashed and axial curves.

TABLE 2

Values of migration enthalpy h_m and pre-exponential factor τ_0 for both bands in LiD:Mg^{2+}

	T_M (K)	h_m (eV)	τ_0 ($\times 10^{-9}$ s)
1st band	200	0.38±0.01	13 ±6
2nd band	245	0.50±0.02	1.0±0.5

We should also mention a fact observed in LiD samples. Probably due to their polycrystalline structure, they could not withstand polarization fields in excess of 20 kV/cm and, thus they broke down with a spark in the first few seconds after applying the polarization field. On the other hand, the LiH single crystals did not experience such effects even under polarization fields of 150 kV/cm.

Conclusions

The experimental results mentioned above clearly verify the existence of two bands in the ITC spectrum of the LiH:Ca^{2+} system which had not been observed in the ITC spectrum of an earlier work [4].

Also, two bands are observed in the ITC spectrum of LiD:Mg^{2+} which, as far as the low-temperature band is concerned, is in good agreement with the respective band observed in an earlier work [4]. The second band in the ITC spectrum appears at exactly the same temperatures as the second band in the LiH:Ca^{2+} system.

Both bands in the respective systems are due to dipole reorientations because measurements taken with fields of 30–70 kV/cm on LiH:Ca^{2+} and 5–15 kV/cm on LiD:Mg^{2+} showed that the areas of the bands increase linearly with the polarization field [9].

As far as the low-temperature bands in LiH:Ca^{2+} and in LiD:Mg^{2+} are concerned, they can be attributed to the deorientation mechanism of the complex dipoles (divalent impurity-bound cation vacancy). This hypothesis is reinforced by the fact that the migration enthalpies h_m are comparable with values from other measurements (Table 3). The difference of approximately 0.1 eV observed between the migration enthalpies of the free cation vacancies (d.c. conductivity technique) and those of the bound vacancies (ITC technique) is to be expected [10]. The slightly smaller value of h_m in LiH:Mg^{2+} is justified

TABLE 3

Comparison of migration enthalpies

System	h_m (eV)	Measurement technique	Reference
LiH:Ca^{2+}	0.42	ITC	present work
	0.53	d.c. conductivity	[6]
LiH:Mg^{2+}	0.38	ITC	[8]
LiD:Mg^{2+}	0.38	ITC	present work
	0.52	d.c. conductivity	[6]

[11] because the ionic radius of Mg^{2+} (0.65 Å) is smaller than that of Ca^{2+} (0.94 Å).

The existence of a second band in the ITC spectra of $LiH{:}Ca^{2+}$ and $LiD{:}Mg^{2+}$, according to Dreyfus' suggestion [12, 13], cannot be attributed to nnn dipole relaxations because Li^+ and Mg^{2+} have slightly different ionic radii while the ionic radius of Ca^{2+} is considerably larger than that of Li^+.

Since in LiD relaxations have been observed [14] of dipoles consisting of a divalent O^{2-} anion and a bound anion vacancy, we accept this hypothesis in order to explain the existence of a second dipole relaxation mechanism in $LiH{:}Ca^{2+}$ as well as in $LiD{:}Mg^{2+}$. This hypothesis is also reinforced by the fact that the LiH and LiD crystals are strongly attacked by atmospheric oxygen.

Finally, another important fact arising from the experimental results of ITC measurements in $LiH{:}Ca^{2+}$ and $LiD{:}Mg^{2+}$ is that the pre-exponential factor τ_0 of the classical Arrhenius relation takes large values for both systems (see Tables 1 and 2). Taking into account that the transverse optical phonon frequencies (ν_{TO}, $k{\rightarrow}0$) are 1.83×10^{13} Hz and 1.33×10^{13} Hz for the LiH and LiD crystals respectively [15], then the reciprocals of the pre-exponential factors (τ_0^{-1}) are 4 to 5 orders of magnitude lower than 10^{13}. Of course, the experimental results refer to temperatures corresponding to regions of about $\Theta_D/3$ to $\Theta_D/4$ of the mother crystals LiH ($\Theta_D = 851$ K) and LiD ($\Theta_D = 638$ K) [16].

Finally, we can support the suggestion that in the regions $\Theta_D/3$ to $\Theta_D/4$ the Arrhenius relation is not valid in its classical form (eqn. 2), something which has been discussed in Ref. [17].

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