Dipole Centres in Rare-Earth-Doped CaF₂ *

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The reorientation of dipole centres in CaF_2:RE^{3+} (RE: Gd, Tb, Lu) is investigated by the method of ionic thermo-current (ITC). ITC peaks below 200 K are caused by re-orientation of RE^{3+}-F^{-}-complexes and related dipole centres, whereas peaks above 200 K seem to be of other origin. Both types of ITC peaks cannot be discriminated by polarization field strength dependence.

Measurements of ionic thermocurrent were carried out as follows. The crystal was provided with silver electrodes by vapourization. An external electric field E_p ($5 \cdot 10^3 \, \text{Vcm}^{-1}$) was applied to the crystal at a polarization temperature T_p of 300 K. Then the crystal was cooled to a lower temperature T_0 (4.2 K) in the external electric field within 5 minutes. At this temperature the electric field was removed and the crystal was heated at a constant heating rate q ($20 \, \text{Kmin}^{-1}$). During the heating period ITC was measured with an electrometer (Keithley, 610 C) in short circuit and plotted against temperature by an XY-recorder (Yokogawa, 3078). This technique delivers a representation, which is similar to usual glow curves.

Depending on the investigated sample and the temperature range we must consider two different processes, which are responsible for ITC phenomena:

1. Dipole centres are orientated in the external electric field. At low temperature dipole relaxation is hindered even after the external field is turned off. When heating the sample different types of dipole centres relax at characteristic temperatures. This re-orientation current is measured as ITC. In this case theory delivers for electric current density [1]:

$$i(T) \sim E_p \cdot \exp(-E/kT) \qquad (1)$$
$$\cdot \exp\left\{ -\frac{1}{q \, \tau_0} \int_{T_0}^{T} exp(-E/kT) \, dT \right\},$$

E_p electric field strength; E reorientation energy; k Boltzmann's constant; q heating rate; τ_0 relaxation time.

This means $i(T)$ is given by a relation, which is equivalent to first order thermoluminescence kinetics.

2. Free charge carriers are separated by the external electric field until resulting space charges and

diffusion potentials stop further motion of the charge carriers. This charge distribution is frozen in at low temperatures even after the electric field is removed. Warming the crystal charge carriers become mobile and this motion is measured at ITC. In this case electric current density is given by [2]:

$$i(T) \sim E_p \exp(-E/kT) \qquad (2)$$
$$\cdot \exp\left\{ -\frac{\sigma_0}{q \, \varepsilon \, \varepsilon_0} \int_{T_0}^{T} \exp(-E/kT) \, dT \right\},$$

E activation energy; σ_0 conductivity; ε dielectric constant; ε_0 electric field constant.

This representation (2) is equivalent to (1) and it is obvious that in both cases $i(T)$ is proportional to the polarization field strength E_p. That means both processes unfortunately cannot be discriminated by ITC methods.

We measured ionic thermocurrents of gadolinium, terbium and lutetium doped CaF_2 single crystals. Characteristic results are given in Figure 1. This representation illustrates that the glow curves of different dopants have nearly the same shape. Mainly the peak at about 140 K appears in all samples. This peak is already reported by other authors [3—5] and it is ascribed to the reorientation of tetragonal
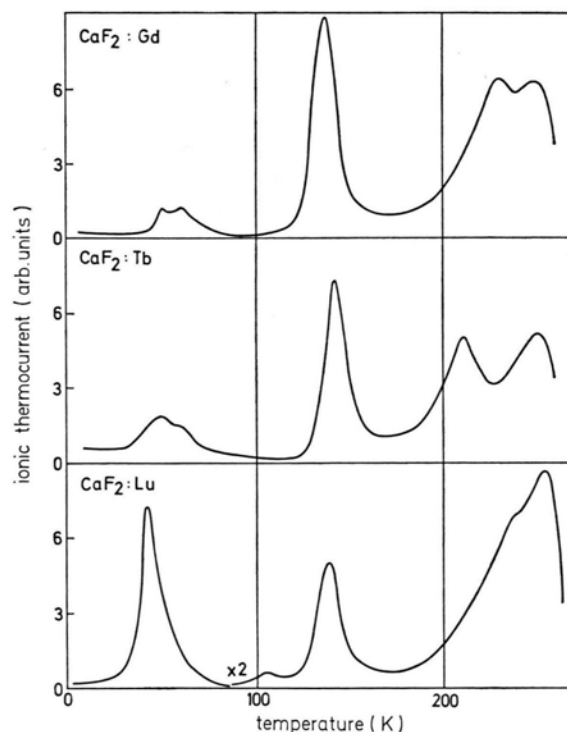
Fig. 1. Ionic thermocurrent (ITC) glow curves of CaF_2:RE (RE = Gd, Tb, Lu) after electric polarization ($E_p = 5 \cdot 10^3 \, \text{V cm}^{-1}$; $q = 20 \, \text{Kmin}^{-1}$).
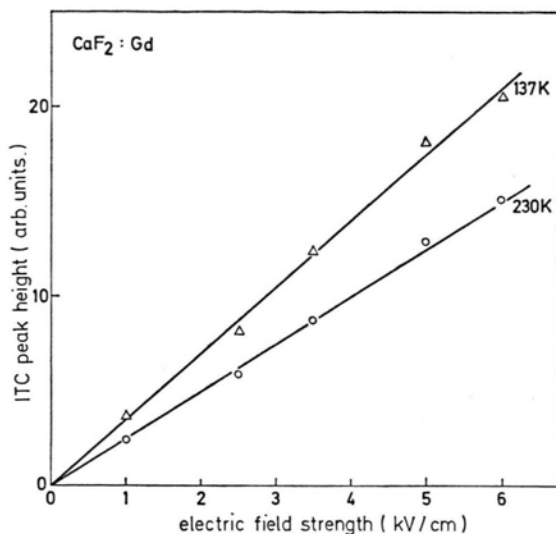
Fig. 2. ITC peak height in CaF$_2$:Gd as function of polarization field strength.
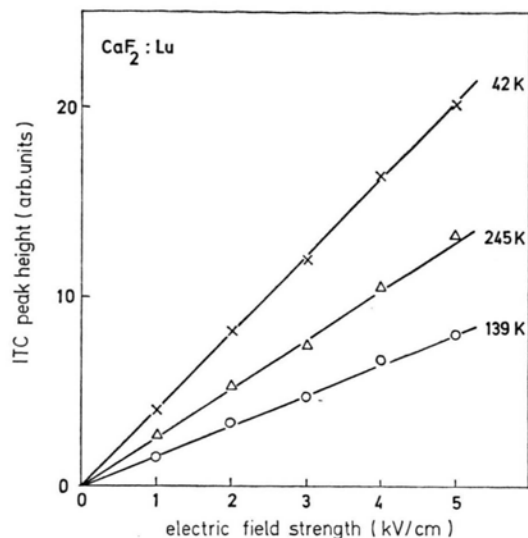

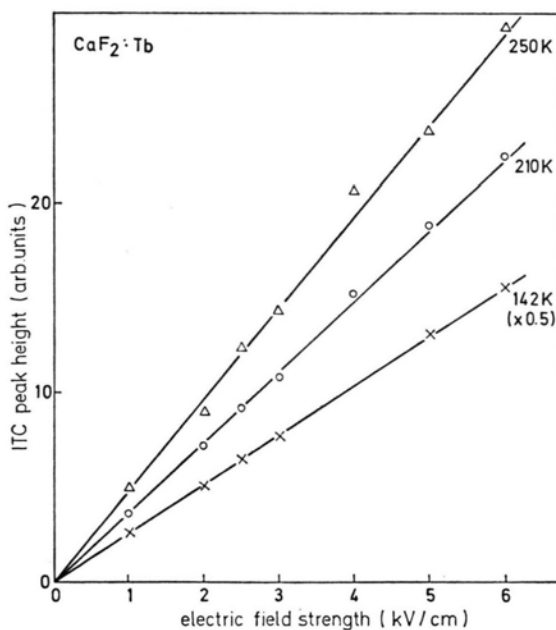Fig. 4. ITC peak height in CaF$_2$:Lu as function of polarization field strength.

Fig. 3. ITC peak height in CaF$_2$:Tb as function of polarization field strength.

RE^{3+} − F$^-$-complexes. The complex consists of a trivalent rare earth ion and a neighbouring F$^-$-ion. This imagination is also supported by EPR- and ENDOR-investigations [6]. The peaks below 100 K also seem to be of dipolar origin [3, 4], whereas peaks above 200 K are supposed to be caused by free charge carriers. Correlation of ITC-glow curves with thermoluminescence and absorption investigations is not possible [7].

Beside ITC glow curves we investigated the dependence of ITC peak height on the polarization field strength. The results of the main peaks are shown for different dopants in Figures 2 to 4. ITC peak height is obviously proportional to the polarization field up to $6 \cdot 10^3$ V cm^{-1} independent of dopant and special peak. This result is in good agreement with theoretical considerations. Because of the above cited reason, however, it gives no hint, of which origin the peaks are.

Finally we had a look at the influence of polarization time and -temperature on ITC glow curves. Measurements demonstrated that neither polarization duration nor polarization temperature has any influence on ionic thermocurrent.

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