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Thermally stimulated depolarization current studies in sodium- and barium-doped potassium yttrium fluoride

Md. Shareefuddin, M. Narasimha Chary *

Department of Physics, Osmania University, Hyderabad 500 007, India

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Abstract

The results of thermally stimulated depolarization current (TSDC) and electrical conductivity studies of potassium yttrium fluoride (KYF_4) compound doped with sodium and barium are presented. The TSDCs were measured as a function of the polarizing temperature and polarizing field strengths at a constant heating rate of 0.09 K s^{-1}. The conductivity studies were carried out in the temperature range 370–835 K with different dopant concentrations. The variation of the conductivity with the doping concentration was found to be non-linear. The relaxation parameters and the activation energies were evaluated. The origin of the TSDC peak in KYF_4:Na was attributed to space charge polarization. However, in the case of KYF_4:Ba, in addition to space charge polarization, there is also a small contribution from the dipolar mechanism.

Keywords: Thermally stimulated depolarization current; Electrical conductivity; Potassium yttrium fluoride

1. Introduction

The increasing interest in the investigation of the properties in conducting ionic fluorine compounds is mainly because of their practical importance. Several types of fluoride are known to be good F^- ion conductors and a number of applications have been proposed, including solid electrolyte batteries [1–4].

Studying the thermally stimulated depolarization current (TSDC) is a very effective and sensitive method for investigating various phenomena, such as relaxation, the precipitation process of impurity–vacancy (I-V) complexes, and space charge effects associated with ions, electrons and holes in ionic and other materials [5–11]. Electrical conductivity measurements at different temperatures provide information on the state of point defects in ionic solids. The addition of impurities to the crystal influences the conductivity.

In this paper, an attempt has been made to understand the charge storage mechanism in potassium yttrium fluoride (KYF_4) compound doped with mono (Na^+) and divalent (Ba^{2+}) impurities, using the TSDC technique. Electrical conductivity measurements with variation of the doping concentration have also been carried out.

2. Experimental

The KYF_4 compound was synthesized in our laboratory by the solid state reaction method [12]. The samples were synthesized under an inert atmosphere. To prepare the KYF_4 compound, a saturated solution of potassium fluoride was added to a saturated solution of yttrium chloride. A white precipitate of KYF_4 was obtained. This was digested by being placed in a hot water bath for a few hours, washed several times with distilled water to remove the soluble KCl and KF completely, and then dried in an oven at 373 K. To this compound was added 0.5 mol.% Na (in the form of NaF), and this was then placed in a platinum crucible and heated in an electrically heated furnace at 900 K for about 2 h. The temperature was then lowered to 673 K. The polycrystalline material thus obtained was annealed at 673 K for about 6 h and then brought to room temperature. The procedure was repeated to obtain the compound KYF_4 containing Ba (in the form of BaF_2).

For the TSDC measurements, cylindrical pellets of KYF_4:Na and KYF_4:Ba were cold pressed at 500 kg cm^{-2}, and annealed at 873 K for 2 days to remove strains. The sample was spring loaded between two electrodes in a cell placed in an electrically heated furnace. The temperature was measured with a chromel–alumel thermocouple. To ensure good contact

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* Corresponding author.

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between the samples and the electrodes, the samples were coated with colloidal graphite paint. The TSDC measurements were made in the usual way, by polarizing the sample at a temperature T_p for a certain polling time t_p with a polarizing field E_p, and then quenching the sample to a lower temperature. The sample was then heated with a constant heating rate (β) and the depolarization current was measured with a Keithley electrometer. Conductivity measurements were carried out by applying a d.c. potential of 1.5 V and the current was measured using the Keithley electrometer at different temperatures.

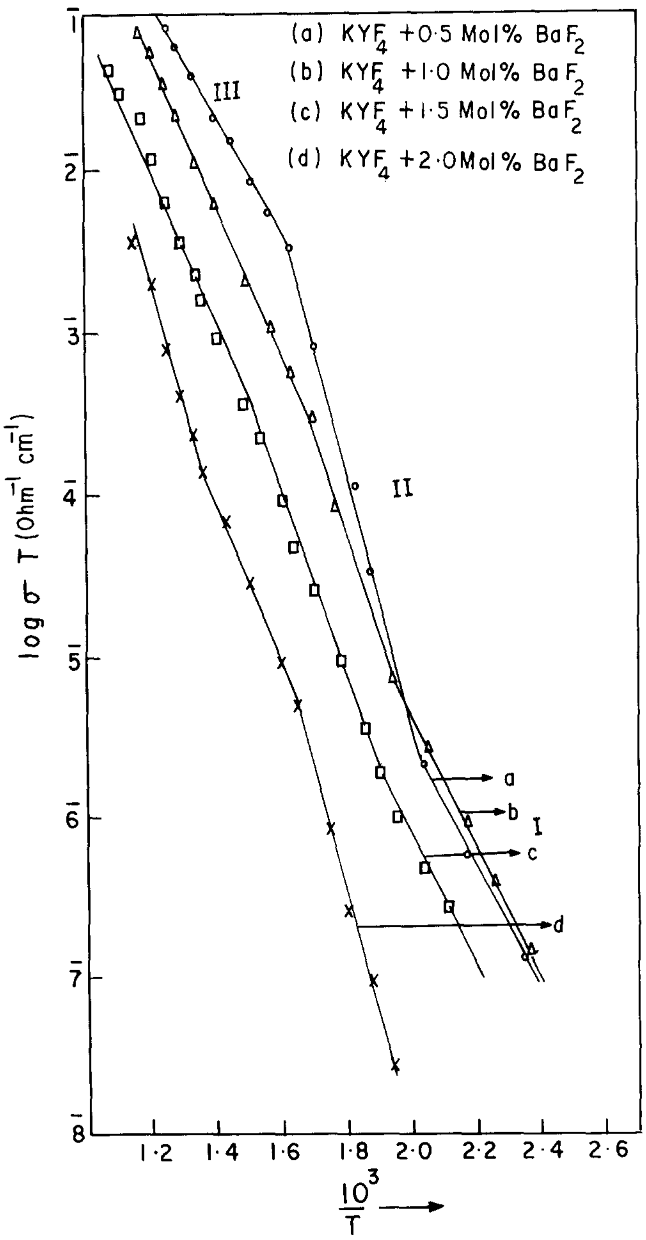

Fig. 1. Variation of log σT vs. $10^3/T$ for KYF_4 doped with different concentrations of Ba.

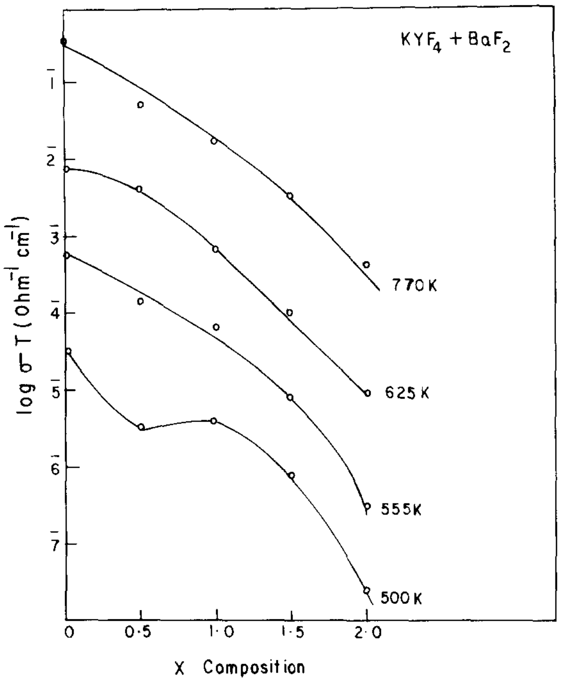

Fig. 2. Conductivity isotherms of KYF_4:Ba as a function of Ba concentration at different temperatures.

3. Theory

The relaxation time τ of the dipoles at the measurement temperature is given by

$$\tau=\tau_0 \exp\left(\frac{U}{kT}\right) \tag{1}$$

where τ_0 is a constant, U is the activation energy, k is Boltzmann's constant and T is the absolute temperature. An expression for the glow peak [5,13] during the heating of the sample at a constant rate $\beta=\mathrm{d}T/\mathrm{d}t$ is given by

$$i(T)=\frac{i_0}{\tau_0}\exp\left(\frac{-U}{kT}\right)-\frac{1}{\beta\tau_0}\int_{\tau_0}^{T}\exp\left(\frac{-U}{kT}\right)\mathrm{d}T \tag{2}$$

Differentiating Eq. (2), one obtains the temperature T_m at which the maximum current occurs ($\mathrm{d}i/\mathrm{d}t=0$), i.e.

$$\tau_0=\frac{kT_m^{\,2}}{\beta U\exp(U/kT_m)} \tag{3}$$

The low temperature tail of Eq. (2) can be written as

$$\log i(T)=\text{constant}-\frac{U}{kT} \tag{4}$$

From Eq. (4), U can be determined from the plot of $\log i(T)$ vs. $1/T$, and τ_0 can be calculated from Eq. (3). By making use of Eq. (1), τ can be calculated at T_m and at 300 K.

Table 1
Activation energies of KYF_4+0.5 mol.% NaF and KYF_4+0.5 mol.% BaF_2 samples

	Region I (eV)	Region II (eV)	Region III (eV)	Region IV (eV)
KYF_4+0.5 mol.% NaF	0.74	1.23	1.74	0.30
KYF_4+1.0 mol.% NaF	0.76	1.25	2.68	0.55
KYF_4+1.5 mol.% NaF	0.35	0.93	1.98	0.47
KYF_4+2.0 mol.% NaF	0.14	0.81	2.47	0.58
KYF_4+0.5 mol.% BaF_2	0.71	1.56	0.79	
KYF_4+1.0 mol.% BaF_2	0.89	1.16	0.79	
KYF_4+1.5 mol.% BaF_2	0.91	1.08	0.80	
KYF_4+2.0 mol.% BaF_2	1.52	0.91	1.50	

4. Results

The d.c. conductivity of KYF_4 doped with different concentrations of Na and Ba was studied in the temperature range 370–835 K. Fig. 1 shows the conductivity plot of KYF_4:Ba, while Fig. 2 presents the conductivity isotherms as a function of the Ba concentration. The variation of the conductivity with the doping concentration was found to be non-linear. The activation energies are given in Table 1.

Figs. 3 and 4 present the TSDC spectra of KYF_4 doped with 0.5 mol.% of Na and Ba, respectively, at a polarizing temperature of 303 K, using different polarizing field strengths at a constant heating rate of 0.09 K s^{-1}. A single TSDC peak of KYF_4:Na was observed, the magnitude of which was found to increase with increasing polarizing field strength E_p. There was also a shift of the peak towards a higher temperature on increasing the polarizing field. In the case of KYF_4:Ba, the TSDC spectra exhibited two peaks with varying magnitudes. The lower temperature peak was not well resolved, while the high temperature peak was well resolved. The peak current I_m increased with increasing E_p. The high temperature peak was found to shift towards a higher temperature with increasing E_p.

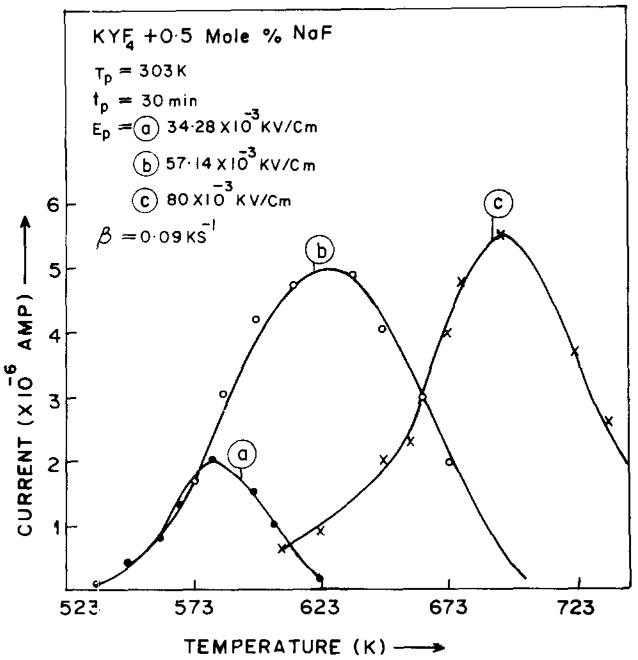

Fig. 3. TSDC spectra of KYF_4+0.5 mol.% NaF polarized for 30 min at 303 K using different field strengths.

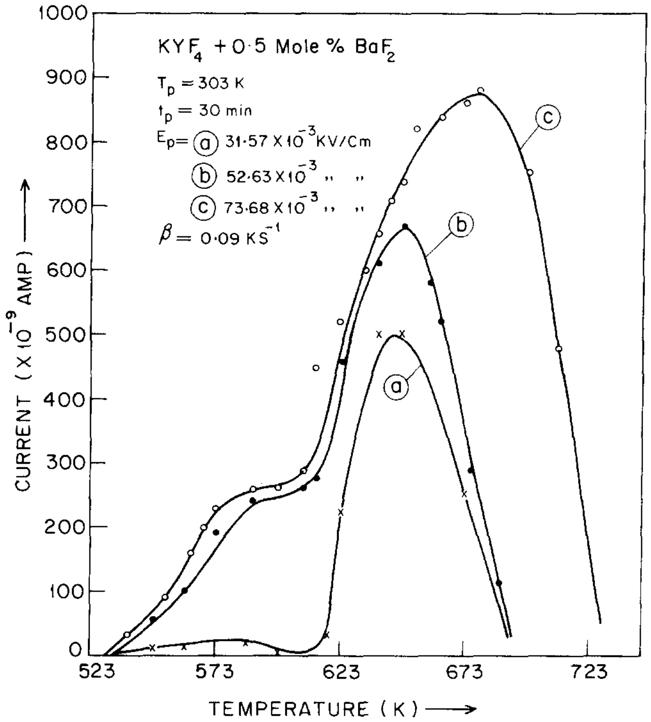

Fig. 4. TSDC spectra of KYF_4+0.5 mol.% BaF_2 polarized for 30 min at 303 K, using different field strengths.

The TSDC spectra of KYF_4:Na and KYF_4:Ba at a constant polarizing field strength and at different polarizing temperatures are given in Figs. 5 and 6 respectively. A single peak was observed in the case of KYF_4:Na, while two peaks were observed for KYF_4:Ba. The high temperature peak was found to shift towards a higher temperature. In both cases, the magnitude of the peak current was found to increase with increasing T_p.

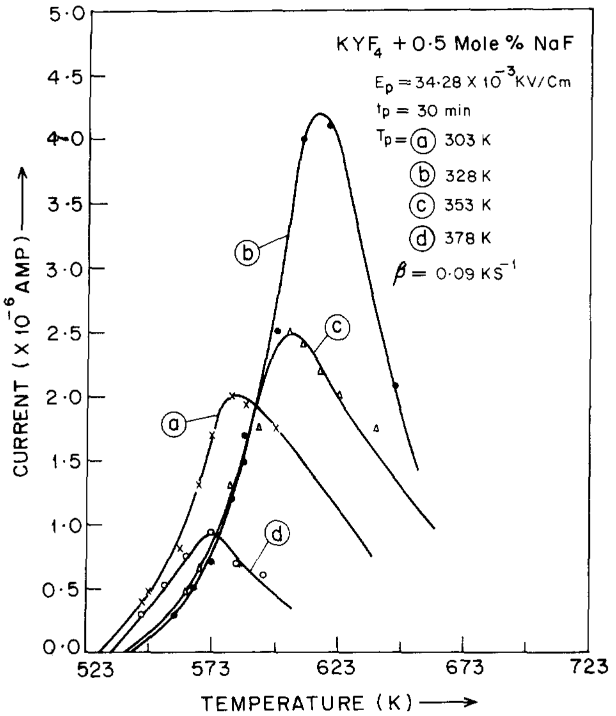

Fig. 5. TSDC spectra of $KYF_4+0.5$ mol.% NaF polarized for 30 min at different temperatures using a field strength of 34.28×10^{-3} KV cm^{-1}.

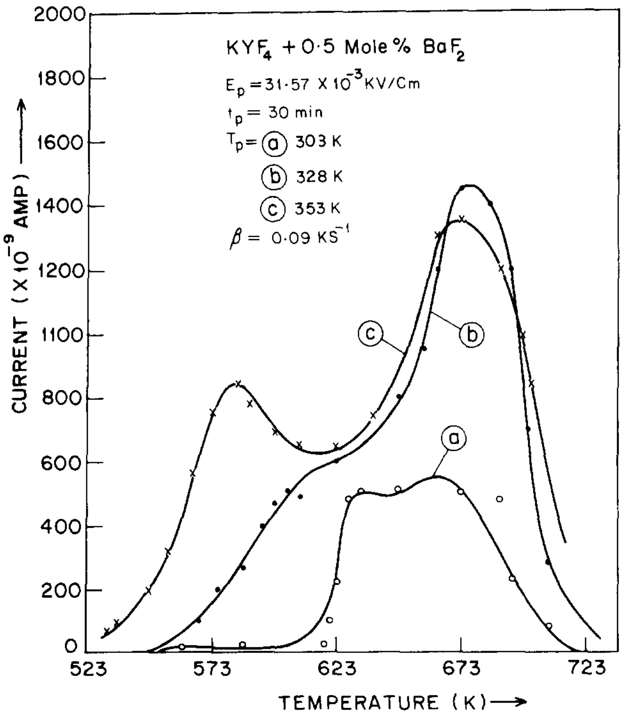

Fig. 6. TSDC spectra of $KYF_4+0.5$ mol.% BaF_2 polarized for 30 min at different temperatures using a field strength of 31.57×10^{-3} KV cm^{-1}.

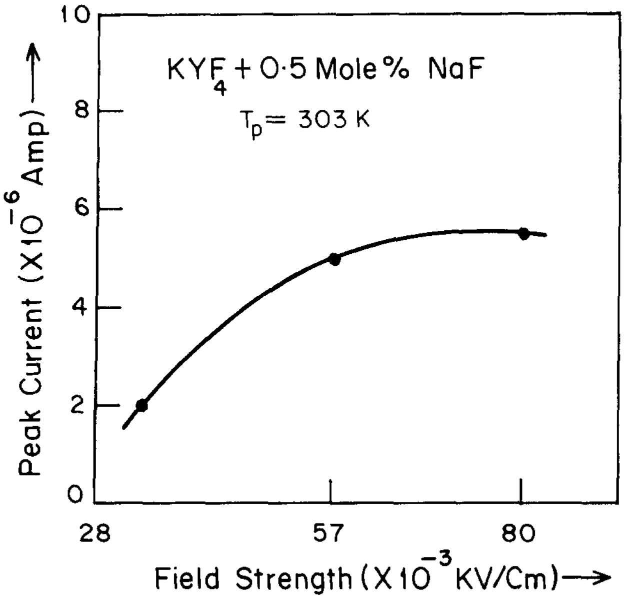

Fig. 7. Variation of the peak current of TSDC spectra as a function of polarizing field strength at 303 K for $KYF_4+0.5$ mol.% NaF.

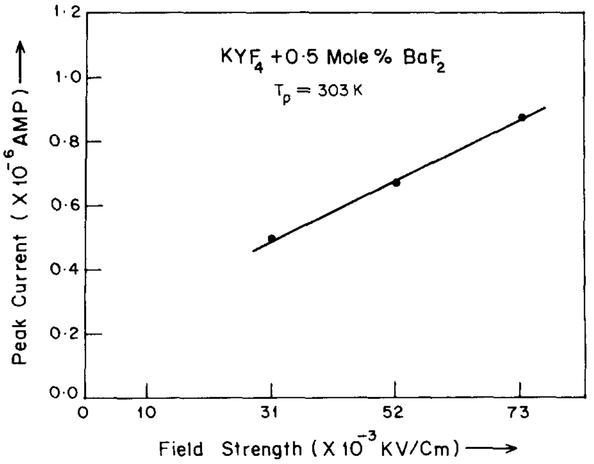

Fig. 8. Variation of peak current of TSDC spectra as a function of polarizing field strength at 303 K for $KYF_4+0.5$ mol.% BaF_2.

Figs. 7 and 8 show the variation of the peak current as a function of the polarizing field strength, polarized at 303 K, while Figs. 9 and 10 show the amount of charge Q released as a function of the polarizing field strength polarized at 303 K for KYF_4:Na and KYF_4:Ba respectively. Non-linear variations of the peak current and charge released were observed in the KYF_4:Na sample, while a linear behaviour was observed in the case of KYF_4:Ba. The activation energies also were evaluated [5] by plotting log $i(T)$ vs. $10^3/T$ (Fig. 11).

The characteristic relaxation times τ_m (relaxation time corresponding to peak temperature), τ_0 (relaxation time corresponding to infinite temperature) and τ_{300} (relaxation corresponding to 300 K) associated with the discharge processes were also calculated, and are presented in Tables 2 and 3, along with the values of the peak currents, peak temperatures and activation energies for KYF_4:Na and KYF_4:Ba compounds respectively.

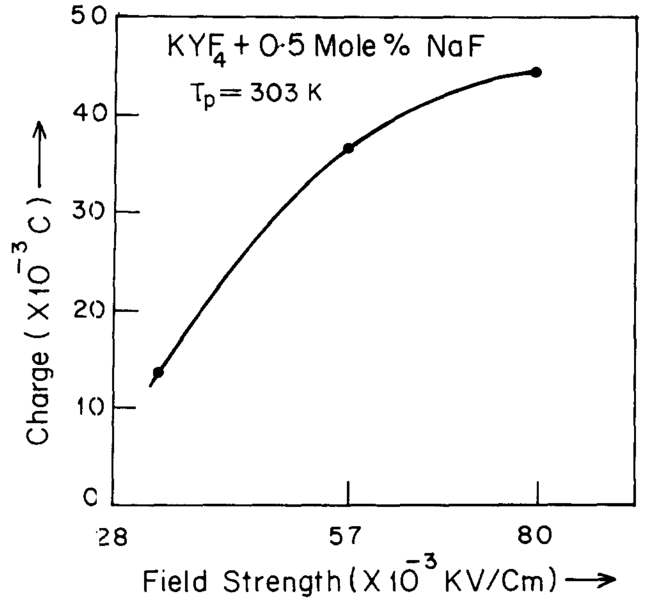

Fig. 9. Amount of charge released as a function of polarizing field strength at 303 K for KYF$_4$+0.5 mol.% NaF.

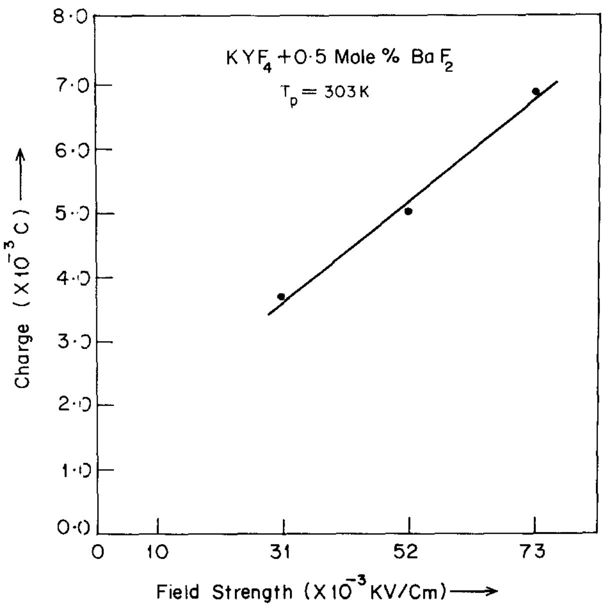

Fig. 10. Amount of charge released as a function of polarizing field strength at 303 K for KYF$_4$+0.5 mol.% BaF$_2$.

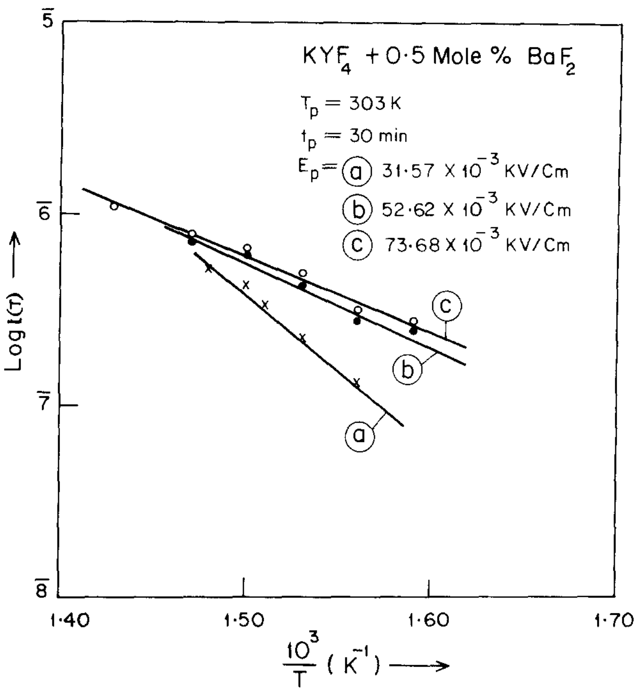

Fig. 11. Variation of log $i(T)$ vs. $10^3/T$ for KYF$_4$+0.5 mol.% BaF$_2$.

5. Discussion

TSDC spectra may originate because of different mechanisms, such as (1) dipolar orientation, (2) displacement of ions by a macroscopic distance with trapping, (3) ionic space charge resulting from the slow discharge rate of ions at their counter-electrodes, or (4) hopping of charge carriers from one localized state to another [14]. It was observed that [15] the shape of the TSDC spectra may be the same in all cases.

One of the arguments advocated [14] for distinguishing between dipolar and space charge polarization is based on the field dependence of the TSDC properties, such as the peak current, peak temperature and charge released. The linear dependences of the charge released and the peak current on the polarizing field strength are characteristics of dipolar origin, whereas, in the case of space charge polarization, the peak current and charge released will exhibit non-linear variation with the polarizing field strength. For a dipolar peak, the peak temperature will be independent of the polarizing field strength and polarizing temperatures, whereas the peak current depends on the polarizing fields and temperatures for space charge polarization [14].

In the present investigation, the TSDC spectra of KYF$_4$:Na exhibited a single peak. Also, there was a shift of the peak temperature towards higher temperatures with increasing polarizing field strengths. The peak current and charge released exhibited non-linear variation with the field strength. These observations favour the space charge origin for the TSDC spectra. The observation of a single peak may be a result of the fact that the dipolar contribution is very small and it is being masked by the space charge polarization. The shift in peak temperature is indicative of a distribution in relaxation times.

In the case of KYF$_4$:Ba, the peak current and charge released exhibited linear variation with the applied field strength, favouring a dipolar origin. However, the shift of the peak temperature indicates that the contributions result from space charge effects. Hence, both mechanisms may be operating to result in the above phenomena.

Table 2
TSDC parameters of $KYF_4 + 0.5$ mol.% NaF

Polarizing temperature T_p (K)	Polarizing field strength E_p ($\times 10^{-3}$ KV cm^{-1})	Peak temperature T_m (K)	Peak current (μA)	Total charge released (nC)	Relaxation parameters			Activation energy (eV)
					τ_m (s)	τ_0 (s)	τ_{300} (s)	
303	34.2	580	2.0	14.0	76.00	98.6×10^{-12}	145.7×10^{12}	1.44
303	57.1	625	5.0	37.0	277.80	1165.2×10^{-12}	8076×10^{12}	1.48
303	80.0	690	5.5	44.0	460.44	491.52×10^{-8}	36×10^{12}	1.12

Table 3
TSDC parameters of $KYF_4 + 0.5$ mol.% BaF_2

Polarizing temperature T_p (K)	Polarizing field strength E_p ($\times 10^{-3}$ KV cm^{-1})	Peak temperature T_m (K)	Peak current (μA)	Total charge released (nC)	Relaxation parameters			Activation energy (eV)
					τ_m (s)	τ_0 (s)	τ_{300} (s)	
303	31.5	643	0.51	3.7	270.9	279.5×10^{-12}	21.6×10^{16}	1.60
303	52.6	650	0.67	5.0	527.5	3.318×10^{-4}	3.43×10^{10}	0.83
303	73.6	680	0.87	6.8	594.5	10.65×10^{-4}	3.88×10^{10}	0.80

It was also observed that using different electrode materials had no effect on the TSDC spectra, so favouring heterogeneous origin, i.e. the space charge may result from the release of charge carriers from the traps within the samples.

Similar results were obtained in sodium yttrium fluoride ($NaYF_4$) compound [16], in which higher peak temperatures were observed.

In general, three TSDC peaks will be observed [17] in fluoride samples. The low temperature peaks result from dipole reorientation. However, the third TSDC peak, which is observed at high temperature (above room temperature), has often been associated with the space charge relaxation of free interstitial F^- ions and vacancies in fluoride-type compounds [18–21].

From these observations, it may be concluded that the origin of TSDC spectra in KYF_4:Na samples is from space charge polarization, whereas it is mainly from space charge effects in KYF_4:Ba compounds, with a small contribution from the dipolar mechanism.

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