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Dielectric properties of LiF single crystals X-ray irradiated under d.c. fields

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The dielectric constant (K), loss (tan δ) and a.c. conductivity (σ) of LiF single crystals subjected to X-ray irradiation in the presence of d.c. fields up to 16 kV cm^{-1} are measured in the frequency range 10^2 to 10^5 Hz and in the temperature range 30 to 400° C. The space charge and dipolar effects observed from this study are discussed in the light of optical absorption data.

1. Introduction

A study of dielectric properties like dielectric constant, loss and conductivity of solids as a function of frequency and temperature over wide ranges helps us in understanding a number of defect processes in them [1–3]. Also such studies carried out after subjecting the materials to mechanical cyclic stress and large a.c. or d.c. fields *in situ* with X-ray irradiation help in a better understanding of their insulating properties. Additionally such treatments are found to produce lattice defects which influence the physical properties of the materials. Work along these lines was carried out on a number of solids, for example NaCl and KCl, giving valuable information [4, 5].

Recently we have reported the results of our study on the dielectric properties of LiF single crystals as a function of frequency and temperature over moderately wide ranges [6], LiF was earlier considered as a good material for thermoluminescence dosimetry [7]; its optical absorption and thermoluminescence were well studied [8–10]. It may be noted here that though a.c. field treatment of some alkali halides prior to X-ray irradiation yielded considerable insight into the electronic processes, particularly in the formation of defects in these crystals [4], a similar treatment with d.c. fields has shown little effect [11, 12]. However, when the X-ray irradiation was carried out simultaneously with the d.c. field, interesting changes in the optical properties of these samples were observed [11–13]. The study along these lines on the optical properties of LiF single crystals has been very interesting [14]. In order to find out in more detail the nature of the structural defects created by the action of X-rays under d.c. fields in LiF, it is important to have data on its dielectric constant, loss and a.c. conductivity. Moreover, investigation on the dielectric properties of the coloured alkali halides is of interest in itself. It is therefore the aim of this paper to report the results of our measurements on the dielectric constant (K), loss (tan δ), and hence the a.c. conductivity (σ) of LiF single crystals: (i) in the frequency range 10^2 to 10^5 Hz and (ii) in the temperature range 30 to 400° C when these crystals are X-ray irradiated for 1 h under different d.c. fields varying from 0 to 16 kV cm^{-1}. As far as we know, no basic research has been devoted to such studies on LiF single crystals.

2. Experimental methods

The LiF single crystals used in the present measurements were obtained from Harshaw Chemical Company, USA. The samples were cleaved from the same chunk, then ground and polished. Final dimensions of the samples were about 1 cm × 1 cm × 0.1 cm. A thin coating of silver paint was applied (to the large-area faces) on either side of the samples to serve as electrodes. Thin aluminium foils were used for the d.c. field application. The d.c. source was a stabilized power supply variable between 0 and 2.5 kV. The samples were irradiated from a Norelco X-ray unit operated at 35 kV, 10 mA.

The dielectric measurements were made on a GR 716 C capacitance bridge (General Radio Company, Cambridge, USA). The accuracy of the measurements in dielectric constant (K) was 2% and that in loss about 3%. When d.c. fields higher than 16 kV cm^{-1} were applied to the LiF crystals during X-ray irradiation at room temperature a considerable electrolytic current appeared to pass through the sample which prevented measurements beyond this field.

3. Results

The dielectric constant at 30° C of LiF crystals (8.3, which is frequency-independent) remained unaffected by X-ray irradiation under d.c. field. However, the dielectric loss was found to increase considerably (Fig. 1).

Fig. 2 shows the dielectric constant (K) as a function of temperature at different frequencies for LiF crystals after they were subjected to a d.c. field of 15.8 kV cm^{-1} (with no X-ray irradiation) for 1 h; K is slightly increased at high temperatures and at low frequencies only. However, these graphs for X-ray irradiated samples remain practically the same as for as-grown LiF crystals. Under these conditions tan δ against temperature graphs exhibited similar behaviour.

When the irradiation is carried out with X-rays for

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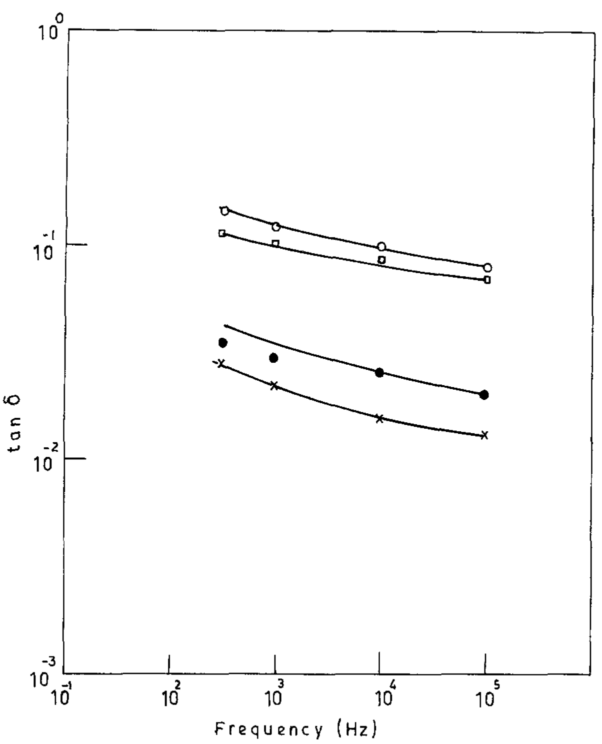

Figure 1 Variation of dielectric loss (tan δ) with frequency at 30° C for LiF crystals X-ray irradiated under different d.c. fields: (x) 2.2, (●) 6.4, (□) 10.4, (○) 15.8 kV cm^{-1}.

1 h in the presence of different d.c. fields (0 to 16 kV cm^{-1}), K for LiF exhibits a considerable increase at high temperatures, particularly at low frequencies. The behaviour of K for LiF for a field of 10.4 kV cm^{-1} is presented in Fig. 3.

Fig. 4 shows that the rate of increase of K at 10^3 Hz with temperature for LiF crystals X-ray irradiated for 1 h under d.c. fields is larger at higher fields. However, these samples exhibit a low rate of increase of K with temperature at higher frequencies.

Curves of tan δ against temperature of X-ray irradiated LiF crystals under a d.c. field of 15.8 kV cm^{-1} at different frequencies (Fig. 5) have distinct maxima in the high-temperature region. With increasing temperature the frequency maximum becomes shifted towards high temperatures, which indicates the presence of dipoles in these samples [15]. Similar behaviour is also observed for other fields (2.2 to 15.8 kV cm^{-1}) for these samples, though the tan δ values are different.

Using the relation $f = f_0\, e^{-E/KT}$ [15] for the relaxation frequency f, at a temperature T, where f_0 is a constant factor and K is the Boltzmann constant, the dipole activation energy (E) equal to the height of the potential barrier affecting the dipole's two equilibrium positions is calculated for different d.c. fields and presented in Table I along with other pertinent data. Data for tan δ are given in Table II.

The a.c. conductivity (σ) is calculated at different temperatures using the equation $\sigma = K\omega \tan \delta K_0$ (where K_0 is the vacuum dielectric constant and ω is the frequency [16] at different frequencies, and the plots of log σ against $1/T$ are shown in Fig. 6 for X-ray irradiated LiF crystals in the presence of a d.c. field of 6.4 kV cm^{-1}. For these plots in the frequency-independent region, the activation energy is calculated to be 0.74 eV. The activation energy is found to decrease with d.c. field (Table I).

4. Discussion

When LiF crystals are subjected to a d.c. field it may be possible that vacancies are generated at the defect regions due to the interaction between the field and dislocations that are present in the sample. Earlier measurements [12, 13] on KCl and NaCl crystals show that this interaction leads to the generation of both negative and positive ion vacancies. X-ray irradiation converts these vacancies along with initially present vacancies in the LiF crystal into corresponding colour centres which lead to prominent space charge and dipolar effects [17, 18].

It is well known that electronic, ionic, dipolar and space-charge polarizations contribute to the dielectronic constant. Among these, the space-charge polarization depends on the purity and perfection of the crystals and its influence is noticeable in the low frequency region. Recollecting our data, the considerable

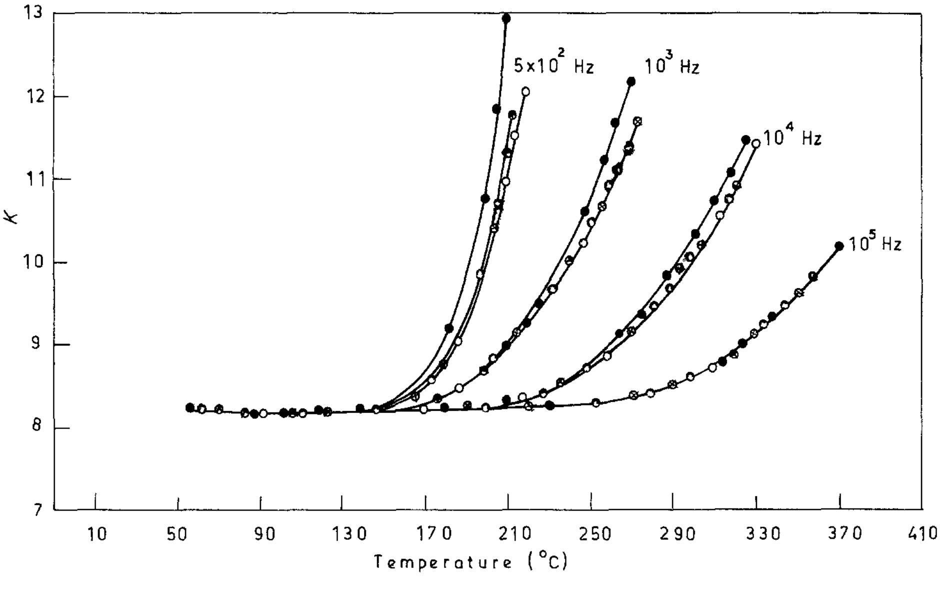

Figure 2 Variation of dielectric constant (K) of LiF single crystals with temperature under different conditions and at different frequencies. (○) As-grown, (⊗) X-ray irradiated for 1 h, (●) subjected to 15.8 kV cm^{-1} d.c. field for 1 h.

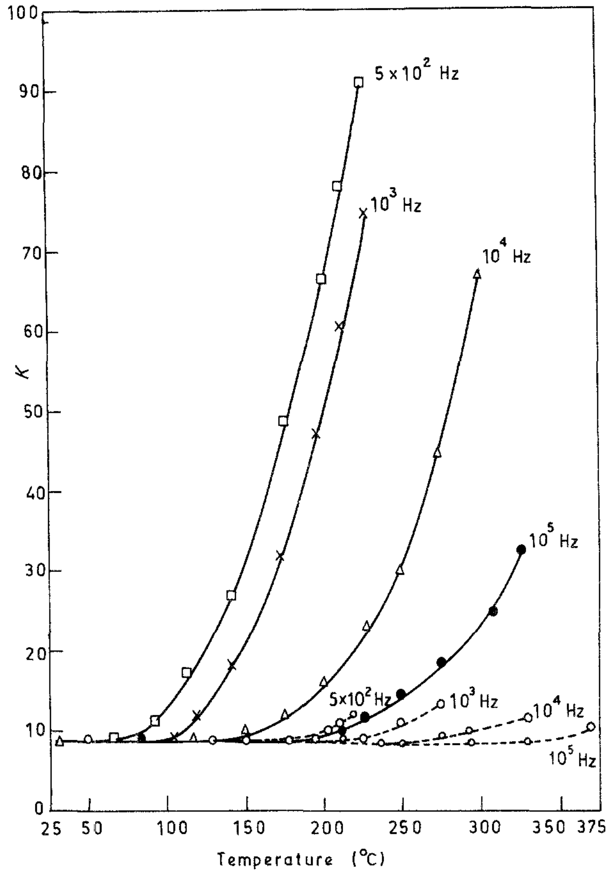

Figure 3 Variation of dielectric constant (K) of LiF crystals with temperature: (---) X-ray irradiated for 1 h without field, (——) X-ray irradiated for 1 h under a d.c. field of 10.4 kV cm^{-1}.

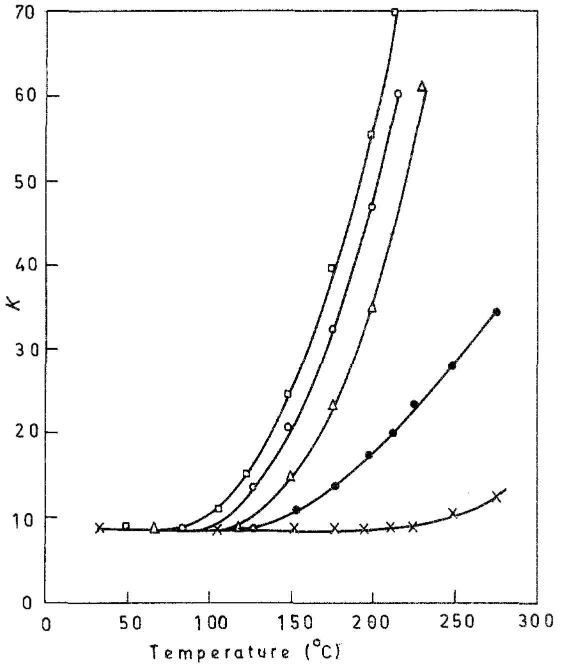

Figure 4 Variation of dielectric constant (K) with temperature at 10^3 Hz for LiF single crystals X-ray irradiated under different d.c. fields: (x) zero, (●) 2.2, (△) 6.4, (○) 10.4, (□) 15.8 kV cm^{-1}.

increase in dielectric loss at room temperature ($\approx 30°$ C) particularly at low frequencies exhibited by LiF crystals X-ray irradiated under d.c. fields may be ascribed to the lattice defects produced which contribute to the space-charge polarization. However, the maximum value of tan δ measured at 10^2 Hz in LiF X-ray irradiated under d.c. field of 15.8 kV cm^{-1} is only 1.5×10^{-1}, which is still small enough not to affect the dielectric constant at that frequency.

Generally, increasing the temperature of the crystal decreases the electronic part of the dielectric constant by about 3% for a temperature change of about 400° C [19]. Similarly it appears that the changes in the ionic polarization are not large. Even the presence of dipoles, according to Debye's theory, should also not influence the K values significantly when the tan δ values of the samples are comparatively small. However, in the present measurements of K against temperature on these samples (Figs 2 and 3) we notice a large increase of K with temperature; such a behaviour can only be attributed to space-charge polarization due to crystal defects [20, 21].

It is interesting to see that K against temperature graphs at different frequencies for LiF crystals before and after X-ray irradiation are practically the same (Fig. 2). However, we have observed larger changes in

TABLE 1 Data on the dielectric constant of LiF crystals

d.c. field under which X-ray irradiation done (kV cm^{-1})	K (room temperature)		Variation of K with temperature under the corresponding d.c. field			Activation energy (E) for conductivity in the frequency independent region (eV)
	10^3 Hz	10^5 Hz	Temperature (° C)	10^3 Hz	10^5 Hz	
0	8.3	8.3	100	8.3	8.3	0.93
			200	8.8	8.3	
			300	–	8.6	
2.2	8.3	8.3	100	8.5	8.3	0.89
			200	17.5	8.3	
			300	–	9.0	
6.4	8.3	8.3	100	8.7	8.3	0.74
			200	33.5	8.3	
			300	–	11.5	
10.4	8.3	8.3	100	9.0	8.3	0.69
			200	47	8.4	
			300	–	12.5	
15.8	8.3	8.3	100	11	8.3	0.64
			200	55	8.5	
			300	–	14.0	

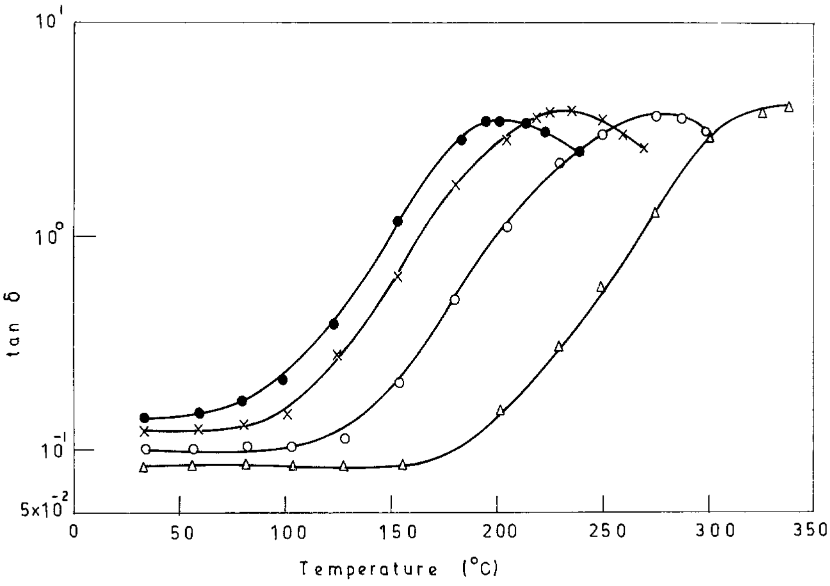

Figure 5 Dielectric loss (tan δ) as a function of temperature at different frequencies for LiF crystals X-ray irradiated for 1 h under a d.c. field of 15.8 kV cm^{-1} (●) 5×10^2 Hz, (x) 10^3 Hz, (○) 10^4 Hz, (△) 10^5 Hz.

K for these samples when the d.c. field is applied along with the X-ray irradiation (Fig. 3). This indicates that field treatment combined with X-ray irradiation produces a larger concentration of defects compared to X-ray irradiation in the absence of a d.c. field. We also find that when these crystals are irradiated under d.c. fields, the rate of increase of K with temperature is more pronounced, particularly at low frequencies, e.g. 10^3 Hz as the d.c. field increases (Fig. 4); this may be due to an increase in the concentration of defects (such as vacancies and colour centres) with d.c. field, which in turn enhances the space charge polarization [22].

Fig. 7 shows ΔK, the difference in the dielectric constant at a particular temperature (225° C) and a frequency of 10^3 Hz between K values for LiF crystals before and after X-ray irradiation for 1 h under a particular field, as a function of the applied d.c. field. We observe that K increases linearly up to a field of about 10 kV cm^{-1}, beyond which it exhibits saturation effects.

It is not possible to identify uniquely the dipoles responsible for the relaxation effects exhibited by X-ray irradiated LiF crystals under d.c. fields. However, it was shown earlier [8] that for LiF crystals irradiated with X-rays for prolonged times (6 h) an appreciable concentration of F-aggregate centres with absorption bands at 310 and 380 nm was found which exhibited dipolar relaxation effects in the same temperature range; these dipolar relaxation effects were ascribed to the F-aggregate centres. Such centres are observed with a considerably larger concentration in the present samples. Hence the observed relaxation effects may be ascribed to F-aggregate centres. As the concentration of these centres in X-ray irradiated LiF seems small, these effects are not pronounced.

Our present results also indicate that the activation energy of dipoles decreases with field (Table II); this is possibly because of the larger lattice distortion due to a larger concentration of defects produced under high d.c. field treatments [23].

Our analysis on the conductivity of as-grown LiF

TABLE II Data on dielectric loss of LiF crystals

d.c. field under which X-ray irradiation done (kV cm^{-1})	Dielectric loss (tan δ) at room temperature		Variation of tan δ with temperature under the corresponding d.c. field			Activation energy for dipoles (eV)
	10^3 Hz	10^5 Hz	Temperature (° C)	10^3 Hz	10^5 Hz	
0	Not detectable ($< 10^{-4}$)		100	1.3×10^{-3}	–	–
			200	4.5×10^{-2}	1.2×10^{-3}	
			300	–	1.1×10^{-2}	
2.2	2.2×10^{-2}	1.3×10^{-2}	100	2.7×10^{-2}	1.3×10^{-2}	0.27
			200	1.1	3.0×10^{-2}	
			300	–	5.0×10^{-1}	
6.4	3.0×10^{-2}	2.0×10^{-2}	100	3.0×10^{-2}	2.0×10^{-2}	0.25
			200	1.5	7×10^{-2}	
			300	–	1.5	
10.4	1.0×10^{-1}	8.0×10^{-2}	100	1.0×10^{-1}	8.0×10^{-2}	0.21
			200	2.0	1.1×10^{-1}	
			300	–	2.0	
15.8	1.3×10^{-1}	8.2×10^{-2}	100	1.3×10^{-1}	8.2×10^{-2}	0.20
			200	2.8	4.0×10^{-1}	
			300	–	3.0	

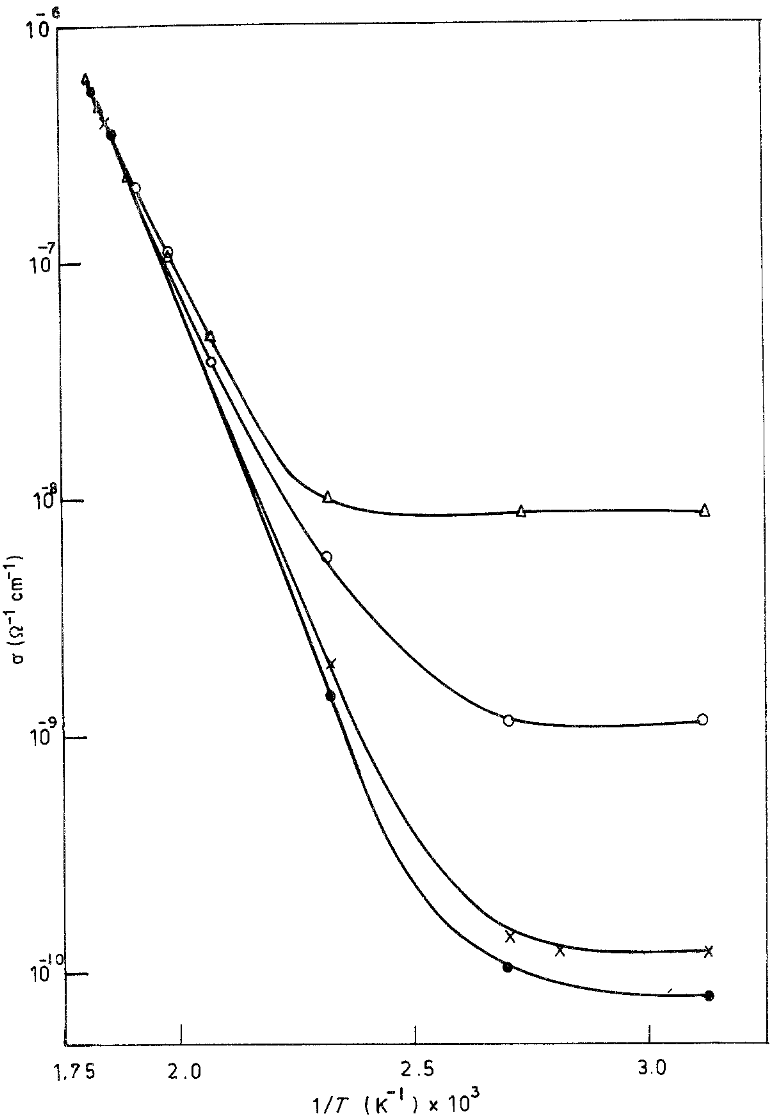

Figure 6 Conductivity (σ) against $1/T$ at different frequencies for LiF crystals X-ray irradiated for 1 h under a d.c. field of 6.4 kV cm^{-1}. (●) 5 × 10^2 Hz, (x) 10^3 Hz, (○) 10^4 Hz, (△) 10^5 Hz.

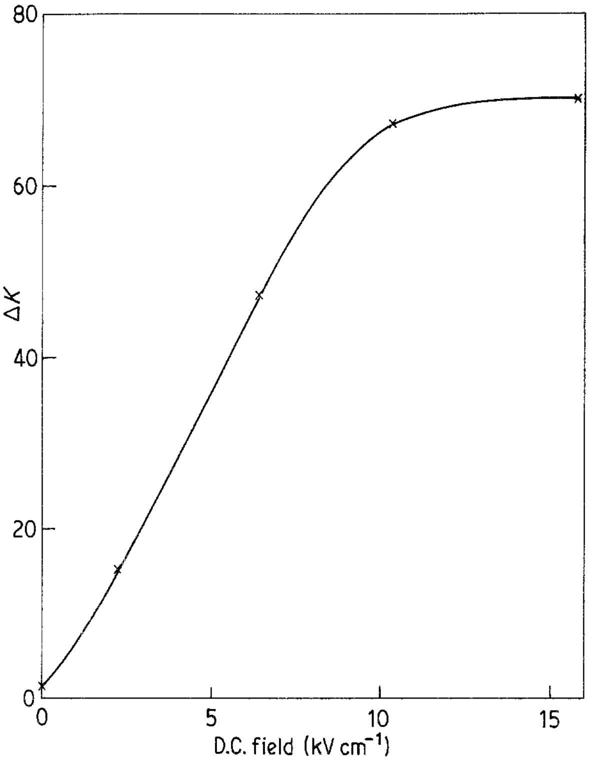

Figure 7 Change in dielectric constant (ΔK) at temperature 225° C and frequency 10^3 Hz for LiF crystals before and after X-ray irradiation under different d.c. fields.

single crystals at high temperatures [6] indicated that the conduction is connected with cationic vacancies. The observed decrease in the activation energy for conduction in the frequency-independent region in the present samples may be due to the presence of a large concentration of such cationic vacancies in them [22, 23].

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