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Dielectric properties of quenched and laser-excited or field-treated LiF single crystals irradiated with X-rays

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Frequency and temperature dependences of dielectric constant, K, and loss, $\tan\delta$, and hence a.c. conductivity, σ, have been studied for LiF single crystals under a combination of treatments such as quenching, laser excitation, a.c. field treatment and X-ray irradiation. The measurements were made in the frequency range 10^2–10^7 Hz and in the temperature range 30–400 °C. The dielectric constant, K, of LiF at 30 °C was found to be 8.4 and to be independent of frequency, while the dielectric loss, $\tan\delta$, was below 10^{-3} at 10^2 Hz. The results indicate that the different treatments on LiF single crystals increase the room-temperature and also high-temperature K and $\tan\delta$ values appreciably in the low-frequency region. $\log\sigma$ versus $1/T$ plots at frequency 10^2 Hz give the activation energy for conduction in the intrinsic region as 0.97 eV for as-cleaved LiF; this value was found to decrease in variously treated LiF samples. The different treatments on LiF help to increase the concentration of charged lattice defects which, in turn, increases the K and $\tan\delta$ values.

1. Introduction

LiF has industrial applications in thermoluminescence (TL) dosimetry and as a radiation detector [1]. As such, the optical properties, e.g. optical absorption and thermoluminescence, of LiF crystals under different conditions have been investigated [2–6]. A considerable amount of work on the dielectric properties of LiF crystals has been reported by many authors [7–9]. If LiF single crystals are subjected to different treatments, such as quenching, laser excitation, high-field treatment, X-ray irradiation, it is felt that interesting results on dielectric properties may be obtained. This paper reports detailed measurements on dielectric constant, K, and loss, $\tan\delta$, of LiF crystals under different conditions over a moderately wide frequency (10^2–10^7 Hz) and temperature (30–400 °C) range.

2. Experimental procedure

The LiF single crystals in the present work were either laboratory grown or obtained as gifts from the Crystal Physics Laboratory, Massachusetts Institute of Technology, USA. Some samples commercially obtained from Harshaw Chemical Company, OH, USA, were also used for checking reproducibility of the results. Samples were cleaved from large boules, ground and polished, the final dimensions of the samples being $1.5 \times 1.5 \times 0.1$ cm^3. Silver paint was applied for electrodes on either side of the samples.

The dielectric measurements were taken on a GR 716 capacitance bridge in the frequency range 10^2–10^5 Hz [10] and a Marconi Circuit Magnification Meter Type TF 329G in the range 10^6–10^7 Hz using a resonance curve principle [11]. The accuracy of measurement in K was 2% and loss ($\tan\delta$) was about 5%. Laser excitation was done using a He–Ne laser of 2 mW power and emitting at 632.8 nm wavelength by keeping the samples at a distance of about 30 cm from the laser source. The details of a.c. field treatment were reported elsewhere [12]. The samples were subjected to the a.c. field for 45 min. Samples were irradiated at 30 °C for 1 h (half the time on either side of the sample) with X-rays from a Norelco unit running at 35 kV and 10 mA, keeping them at a distance of 2 cm from the window.

3. Results

The frequency dependence of dielectric constant, K, and loss, $\tan\delta$, of LiF crystals under different conditions is given in Fig. 1. The K value of LiF at 30 °C is 8.4 and independent of frequency; the dielectric loss, $\tan\delta$, is below 10^{-3} at 10^2 Hz. Quenching affects the values of K and $\tan\delta$ at low frequencies, but laser excitation or subjecting the crystals to an a.c. field of 50 kV cm^{-1} for 45 min has practically no effect on these values. Quenching and later subjecting the crystals to X-ray irradiation or exciting the quenched crystals with laser light and subsequently irradiating them with X-rays, was found to increase K and $\tan\delta$ appreciably at low frequencies. The maximum change in K was about 15% in quenched LiF crystals excited with laser light for 30 min and subsequently irradiated with X-rays; $\tan\delta$ at 10^2 Hz increases by about two decades. Similar behaviour is shown by the quenched crystals subjected to an a.c. field of 50 kV cm^{-1} followed by X-ray irradiation. However, the largest change (about 30%) in K is observed in quenched LiF

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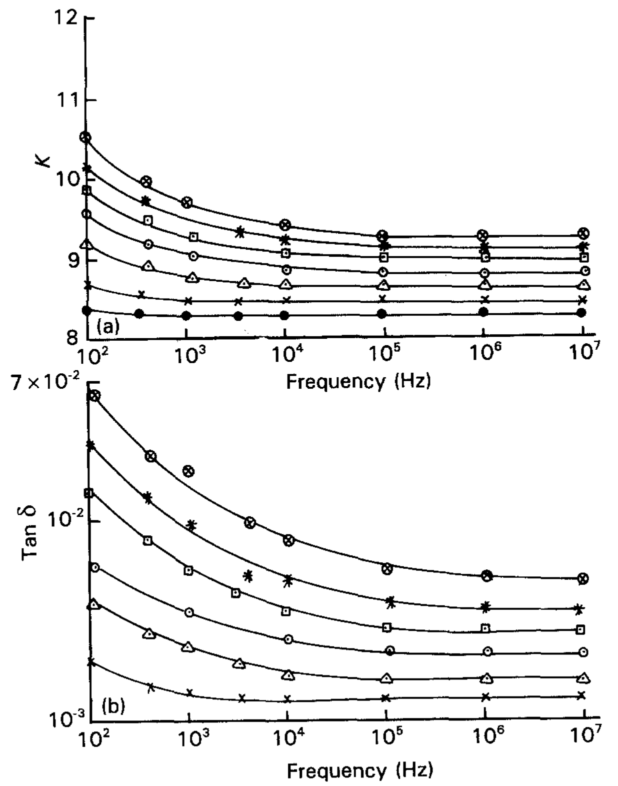

Figure 1 Variation of (a) dielectric constant, K, and (b) loss, $\tan\delta$, at 30 °C as a function of frequency for LiF single crystals under conditions 1–7 as given in Table I. (●) 1, (×) 2, (△) 3, (□) 4, (⊗) 5, (⊙) 6, (∗) 7.

crystals and subjected to an a.c. field of $50\ \mathrm{kV\,cm^{-1}}$, later X-ray irradiated and again subjected to the same a.c. field; under these conditions, $\tan\delta$ of the crystals increased to 7×10^{-2} at 10^2 Hz.

Figs 2 and 3 show the variation of K and $\tan\delta$ with temperature at two different frequencies (10^2 and 10^5 Hz) for LiF crystals under different conditions. The dielectric constant, K, increases with temperature in two stages: (i) a slow increase up to about 150 °C, and (ii) a fast rise at higher temperatures, K being considerably frequency dependent having larger values at lower frequencies. It is observed that the rate of increase of K with temperature (i.e. $\mathrm{d}K/\mathrm{d}T$) in the high-temperature region is larger when LiF crystals are quenched or subjected to various treatments; in addition the $\mathrm{d}K/\mathrm{d}T$ value in the high-temperature region under the same conditions of the sample is larger at 10^2 Hz compared to that at 10^5 Hz. $\mathrm{d}K/\mathrm{d}T$ is largest for quenched LiF crystals subjected to $50\ \mathrm{kV\,cm^{-1}}$ a.c. field, X-ray irradiated and subsequently again subjected to the same a.c. field ($50\ \mathrm{kV\,cm^{-1}}$). Similar behaviour is observed for the dielectric loss ($\tan\delta$) of the crystal.

Using the relation for conductivity $\sigma = \omega K K_0 \tan\delta$, where $\omega = 2\pi f$ (f being the frequency of measurement and K_0 the vacuum dielectric constant) and plotting $\log\sigma$ versus $1/T$ at frequency 10^2 Hz (Fig. 4), the activation energy for conduction in the intrinsic region (275–375 °C) for LiF crystals under different conditions, has been calculated and is given in Table I along with some other pertinent data of the work. The value of activation energy in the intrinsic conductivity region for as-cleaved LiF crystals is 0.97 eV and this decreases with different types of treatment. Activation energies for LiF which are quenched, a.c.-field treated at $50\ \mathrm{kV\,cm^{-1}}$ (or laser excited for 30 min), X-ray irradiated and subsequently again subjected to $50\ \mathrm{kV\,cm^{-1}}$ (or laser excited for 30 min) being the lowest 0.64 eV (or 0.68 eV).

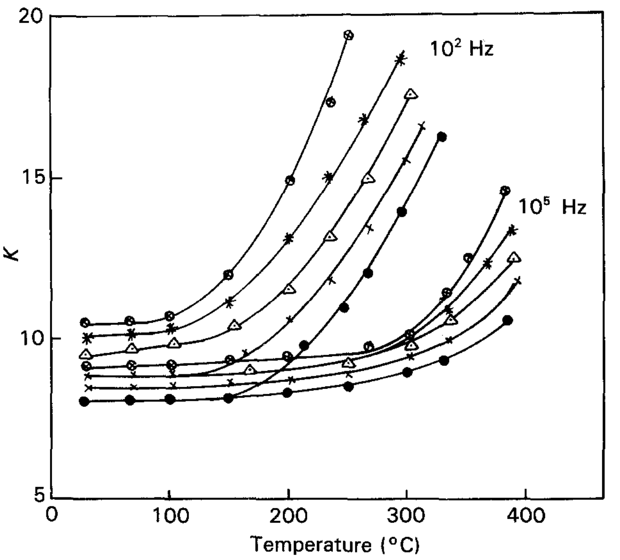

Figure 2 Variation of dielectric constant, K, with temperature for LiF crystals at frequencies of 10^2 and 10^5 Hz conditions 1–3, 5 and 7. See Fig. 1.

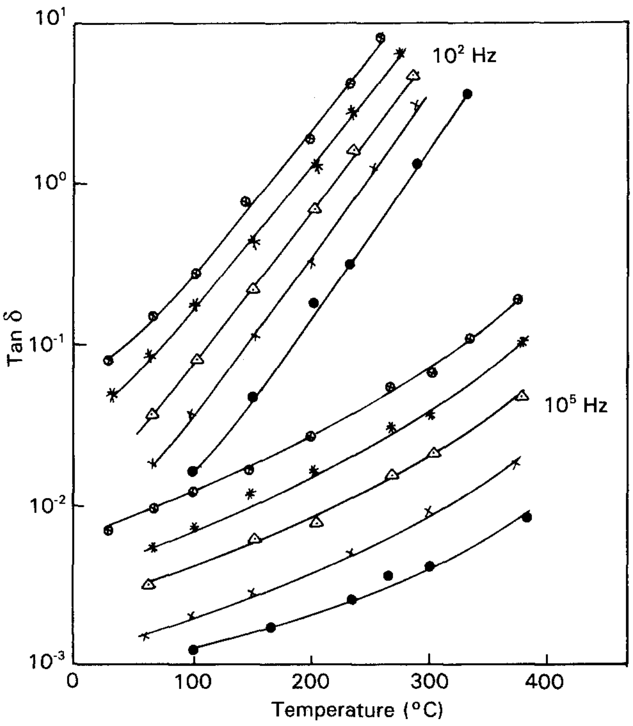

Figure 3 Variation of dielectric loss, $\tan\delta$, with temperature for LiF crystals at frequencies of 10^2 and 10^5 Hz under conditions 1–3, 5 and 7. See Fig. 1.

4. Discussion

The dielectric constant of a solid is known to consist of contributions from electronic, ionic, dipolar and space charge polarizations, each dominating in a particular

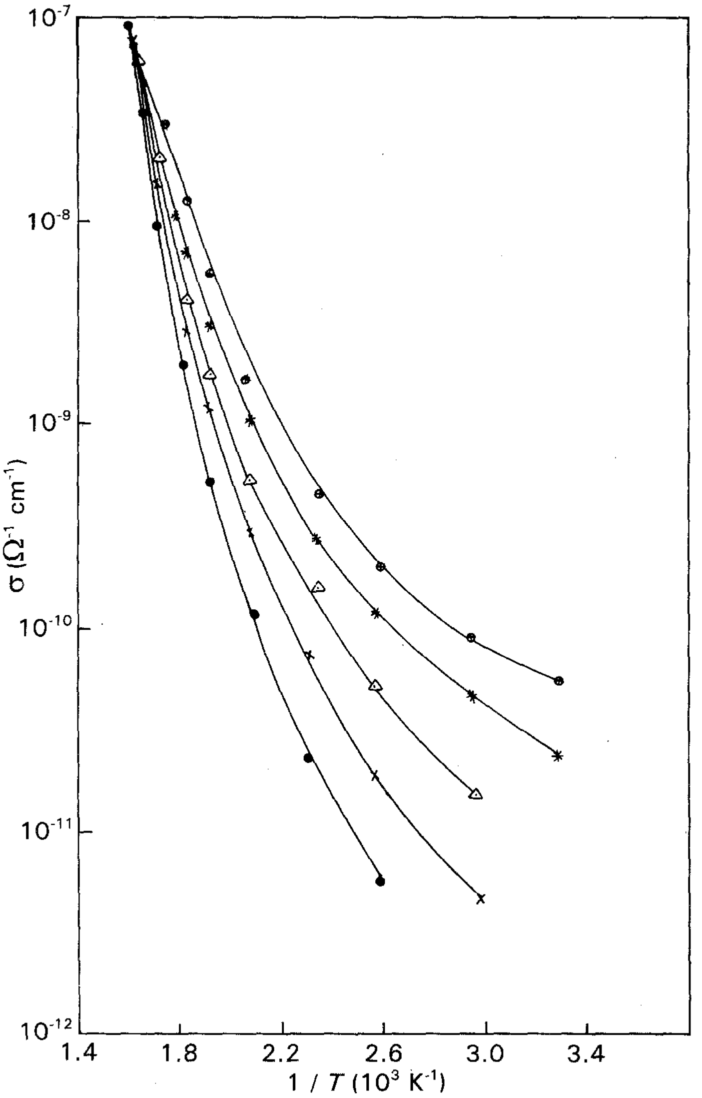

Figure 4 Conductivity versus $1/T$ plots for LiF single crystals at frequency 10^2 Hz under conditions 1–3, 5 and 7. See Fig. 1.

frequency range. It is well established that the space charge polarization is very predominant at lower frequencies. This polarization is known to arise from charged defects or impurities present and also due to the creation and distribution of dipoles either within the bulk or at the surface of the crystal. The dipolar orientational effect can sometimes be seen in some materials up to 10^{10} Hz. The ionic and electronic polarizations always exist below 10^{13} Hz.

Referring to our data, the frequency-independent value of K of as-cleaved LiF at room temperature (~ 30 °C) shows that it consists of only electronic and ionic polarizations. The dielectric loss, $\tan\delta$, is lower than 10^{-3} at 10^2 Hz; this indicates that the LiF crystals used in the present investigation are of high quality. It is known that the result of quenching an alkali halide crystal such as LiF from a high temperature is the production of defects such as vacancies [1]. In addition, the excitation of laser light on LiF crystals produces defects such as vacancies and even dislocations, through the mechanism of generation of thermal spikes in these crystals [13]. When LiF is subjected to a high a.c. field, defects such as vacancies and their clusters may be formed, due to the interaction between the field and major defect regions, like dislocations [14]. X-ray irradiation of LiF produces holes and electrons; additionally it may break up any cluster of vacancies [1]. Thus considering the mechanism of all the treatments, the increase in K and $\tan\delta$ at low frequencies (and at 30 °C) observed in LiF crystals subjected to various treatments such as quenching, laser excitation, electric field treatment, X-ray irradiation or a combination of them, may be attributed to space-charge polarization due to the charged lattice defects produced by these treatments. Taking the percentage changes in K and $\tan\delta$ to be related to the concentration of defects, our results indicate that the concentration of the defects attains significantly larger values in the samples which are quenched, a.c.-field treated at 50 kV cm^{-1} (or laser excited for 30 min), X-ray irradiated and finally again subjected to an a.c. field of 50 kV cm^{-1} (or laser excited for 30 min).

The two-stage increase in K with temperature appears to be common for this type of material; the first stage up to 150 °C (which is slightly frequency-dependent) is apparently connected mainly to ionic polarization, whereas the second stage at higher temperature, where the increase in K is quite large and highly frequency dependent, is due to space-charge polarization. This conclusion seems to be supported by the fact that the dielectric loss at these high temperatures is

TABLE I Some pertinent data on dielectric properties of LiF single crystals

Sample condition	Temp (°C)	K		Tan δ		Activation energy (eV)
		10^2 Hz	10^5 Hz	10^2 Hz	10^5 Hz	
1. As-cleaved	30	8.4	8.35	–	–	0.97
	150	8.55	8.5	6.7×10^{-2}	1.6×10^{-3}	
	250	11.0	8.65	4.8×10^{-1}	2.4×10^{-3}	
2. Quenched	30	8.65	8.5	2.3×10^{-3}	1.5×10^{-3}	0.86
	150	9.35	8.65	9×10^{-2}	2.5×10^{-3}	
	250	12.5	8.9	1.1	3.8×10^{-3}	
3. Quenched + X-ray (1 h)	30	9.15	8.6	4.5×10^{-3}	2.1×10^{-3}	0.79
	150	10.3	8.8	2×10^{-1}	5×10^{-3}	
	250	13.7	9.3	1.25	1.2×10^{-2}	
4. Quenched + laser (30 min) + X-ray (1 h)	30	9.56	8.8	6.1×10^{-3}	2.8×10^{-3}	0.74
	150	10.4	9.0	7.5×10^{-1}	6.7×10^{-3}	
	250	13.9	9.3	2.5	1.5×10^{-2}	
5. Quenched + a.c. field 50 kV cm^{-1} + X-ray (1 h)	30	9.8	9.1	1.5×10^{-2}	3.5×10^{-3}	0.71
	150	10.5	9.4	3.3×10^{-1}	8×10^{-3}	
	250	14.7	9.6	5.1	1.8×10^{-2}	
6. Quenched + laser (30 min) + X-ray (1 h) + laser (30 min)	30	10.15	9.1	3.1×10^{-2}	4.5×10^{-3}	0.68
	150	11.2	9.3	3.3×10^{-1}	1.2×10^{-2}	
	250	15.8	9.6	4.2	2.8×10^{-2}	
7. Quenched + a.c. field 50 kV cm^{-1} + X-ray (1 h) + a.c. field 50 kV cm^{-1}	30	10.5	9.3	6.8×10^{-2}	5.5×10^{-3}	0.64
	150	11.9	9.4	8.7×10^{-1}	2.2×10^{-2}	
	250	19.3	9.7	8.5	6.7×10^{-2}	

large [15]. Taking dK/dT (the rate of variation of K with temperature) at 10^2 Hz and in the high-temperature region as a measure of the concentration of lattice defects, our results show that this concentration increases with the combination of treatments undergone by the crystal.

The conductivity plots exhibit the usual extrinsic (frequency-dependent) region and the intrinsic (frequency-independent) region. It is known that the extrinsic conductivity region is associated with defects and the small concentration of impurities present in the samples. The decrease in the activation energy in the intrinsic conductivity region in variously treated LiF samples may be connected with the larger charge carrier concentration in them; as expected, the lowest values for activation energy are observed for quenched LiF crystals which are laser excited (or a.c. field treated), X-ray irradiated and finally excited with laser light (or subjected to an a.c. field).

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