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Properties of colour centres in CaF_2 single crystals subjected to high electric fields and X-ray irradiation

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Optical absorption in the region 200 to 680 nm, and thermoluminescence, have been studied for CaF_2 single crystals subjected to high d.c. fields (up to 70 kV cm^{-1}) and later irradiated with X-rays for 2 h. Similar data were also taken when the crystals were X-ray-irradiated under high d.c. or a.c. fields. Under both conditions, absorption bands with peaks at 375 and 580 nm were obtained. Partial thermal bleaching measurements carried out on the optical absorption of CaF_2 crystals subjected to a 50 kV cm^{-1} d.c. field and later irradiated with X-rays indicate no correlation between the destruction of the colour centres (responsible for the absorption bands) and the thermoluminescence exhibited by these samples. It is noticed that the influence of high d.c. or a.c. field on the colour centre concentration is different depending on whether the CaF_2 crystals are first subjected to the field and later X-ray irradiated, or are X-ray irradiated under the fields.

1. Introduction

The colour centre phenomenon in alkalihalide crystals irradiated with ionizing radiation (X-rays) gives valuable information regarding the defect processes occurring in these crystals [1–3]. Similar studies carried out on the optical absorption and thermoluminescence of alkaline earth fluorides – particularly CaF_2 – also gives useful data [4–7]. It has been reported that the F-band is not formed in CaF_2 at room temperature when irradiated with X-rays [6]. This has been explained as being due to the existence of negative ion vacancies as Frenkel pairs (an interstitial negative ion associated with the vacancy it has created [4, 5]). It has been shown that such Frenkel pairs in CaF_2 can be dissociated at room temperature with doping of oxygen, manganese etc.; recently it has also been shown that this dissociation could be brought out by quenching the alkaline earth fluoride crystals from near their melting temperatures or by subjecting the crystals to high electric fields (a.c. or d.c.) [8, 9]. Under these conditions, the F-centres are found to be formed at room temperature with the irradiation of CaF_2 crystals by X-rays [9, 10].

It has been noticed during the present investigation that the influence of high a.c. and d.c. fields on colour centre concentration is different depending on whether the CaF_2 samples are first subjected to the field and later X-ray irradiated, or the samples are X-ray irradiated under the fields. Here we present the relevant data and try to explain this difference in the influence of the a.c. and d.c. fields on the colour centre concentration and thermoluminescent light output.

2. Experimental procedure

The CaF_2 single crystals used in the present investigations were a gift from Professor A. Smakula. The samples were cleaved from large boules, then ground and optically polished. The final dimensions of the samples were about $1 \times 1 \times 0.1$ cm^3.

Flame photometric and chemical analysis of these samples showed impurity concentrations of less than 2 p.p.m. The impurities sought included strontium, barium, manganese, cadmium, sodium and potassium. The details of application of the d.c. or a.c. field have been reported earlier [8]. Thin aluminium foil, placed on the large area faces of the samples during the field applications, served as electrodes. The electrodes were later removed during X-ray irradiation and other measurements. X-ray irradiation was done using a Norelco Unit run at 35 kV, 10 mA for 2 h – half the time on either side of the crystal, keeping the samples at a distance of 2 cm from the window.

The optical absorption measurements were taken using a Beckmann 26 spectrophotometer (Systronics Co., India) in the wavelength range 200 to 680 nm at room temperature (~30 °C). The accuracy in the measurement of absorption coefficient (α C m^{-1}) is 0.05. The thermoluminescence (TL) light output was recorded with an Esterline–Angus recorder using a conventional TL set-up [11].

3. Results

Fig. 1 presents the optical absorption characteristics of CaF_2 crystals before and after subjecting them to

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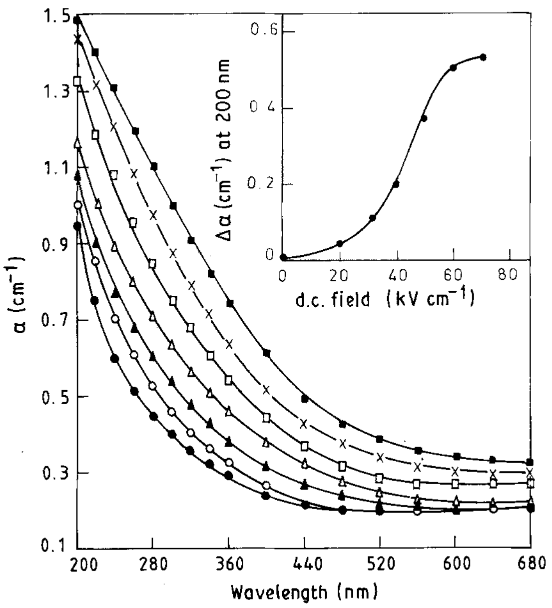

Figure 1 Optical absorption coefficient α (cm^{-1}) at 30 °C as a function of wavelength for CaF_2 crystals subjected to different d.c. fields. ●, As-cleaved; ○, 20; ▲, 30; △, 40; □, 50; ×, 60; ■, 70 kV cm^{-1}.

high d.c. fields. The optical absorption coefficient has a low value ($\alpha \approx 1.0$ C m^{-1}) at 200 nm and decreases with wavelength. The field-treated samples show larger absorption in the low wavelength region; the inset to Fig. 1 shows that the absorption at 200 nm increases with the field slowly up to about 20 kV cm^{-1}, but considerably faster later upto 55 kV cm^{-1}, beyond which the absorption seems to reach a saturation value.

The absorption characteristics of these field-treated samples after being irradiated with X-rays for 2 h are shown in Fig. 2. Two absorption bands with peaks at 375 and 580 nm are observed, the absorption in these bands increasing with the field (inset, Fig. 2). This inset also represents data on CaF_2 crystals subjected to different a.c. fields and later irradiated with X-rays [8].

The variation of the optical absorption coefficient with wavelength for as-cleaved (or quenched) CaF_2 crystals, X-ray irradiated under a d.c. or a.c. field of 10 kV cm^{-1}, is presented in Fig. 3. We find more absorption in the 375 and 580 nm bands in the quenched crystals; interestingly we also notice that the absorption in the bands is more in samples which are irradiated under d.c. fields compared to those irradiated under similar a.c. fields.

Partial thermal bleaching characteristics of optical absorption in CaF_2 crystals d.c.-field-treated at 50 kV cm^{-1}, and later X-ray irradiated for 2 h, are given in Fig. 4. The data indicate that the absorption in the two bands at 375 and 580 nm decreases with bleaching temperature (inset, Fig. 4).

The bands practically disappear when the samples are heated to around 300 °C. It may be mentioned here that the sample is heated to the mentioned temperature, kept there for 3 min and then slowly cooled to room temperature where the measurements are taken.

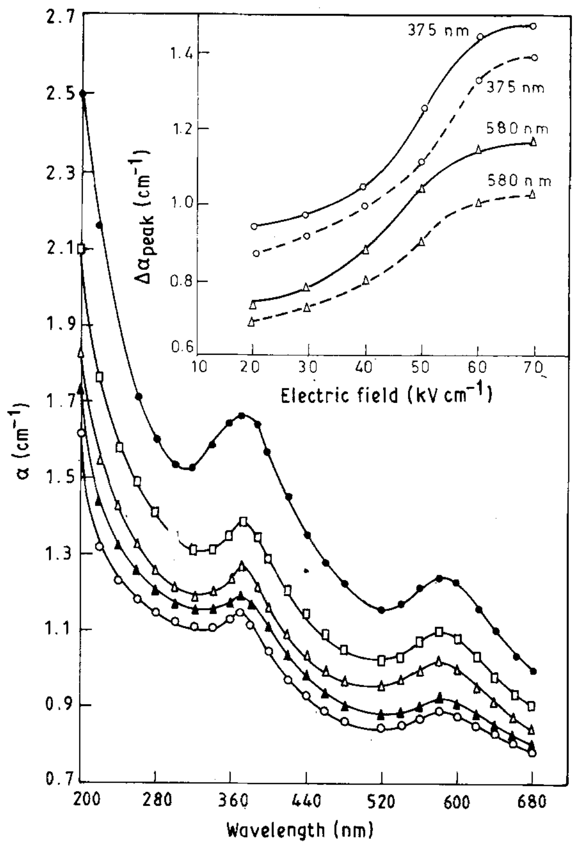

Figure 2 Optical absorption coefficient α (cm^{-1}) as a function of wavelength for CaF_2 crystals subjected to different d.c. fields and later irradiated with X-rays. ○, 20; ▲, 30; △, 40; □, 50; ●, 70 kV cm^{-1}. (——) a.c.; (- - -) d.c. field.

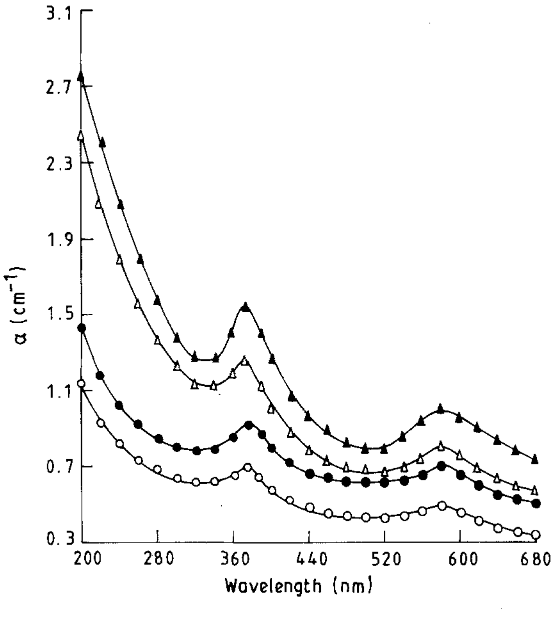

Figure 3 Variation of optical absorption coefficient α (cm^{-1}) at 30 °C as a function of wavelength for (○) as-cleaved or (△) quenched CaF_2 crystals X-ray irradiated under an a.c. or d.c. field of 10 kV cm^{-1}. Open symbols, a.c.; closed symbols, d.c.

The thermoluminescence curves for CaF_2 crystals which are (i) subjected to an electric field of 50 kV cm^{-1} (d.c. or a.c.) and later X-ray irradiated; and (ii) X-ray irradiated under an electric field (d.c. or a.c.) of 10 kV cm^{-1}, are shown in Fig. 5. The samples under condition (i) exhibit a larger TL light output,

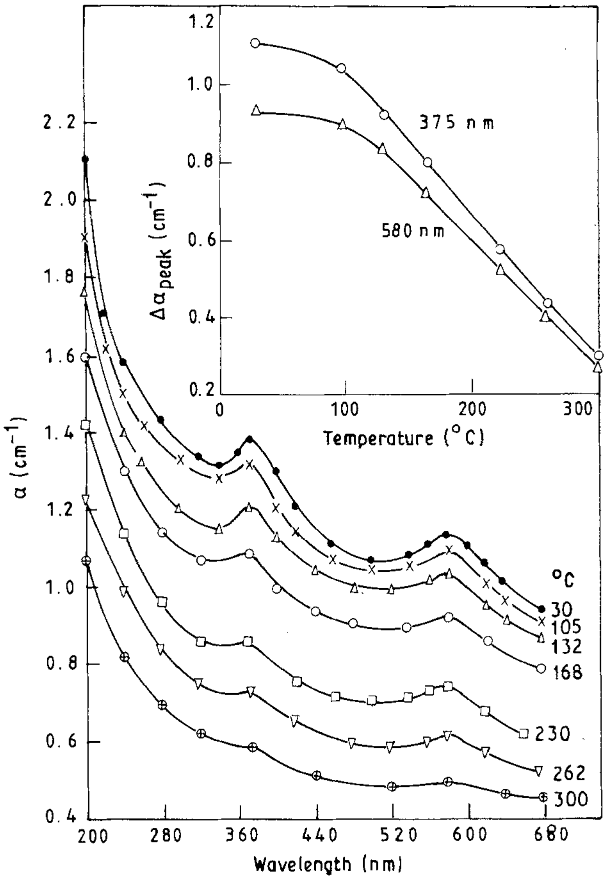

Figure 4 Partial thermal bleaching characteristics of optical absorption in as-cleaved CaF_2 crystals d.c. field-treated at 50 kV cm^{-1} and later X-ray irradiated for 2 h. Inset: thermal bleaching curves for 375 and 580 nm bands. ●, 30; ×, 105; △, 132; ○, 168; □, 230; ▽, 262; ⊕, 300 °C.

those subjected to a.c. fields exhibiting more output. Interestingly, under condition (ii) the samples X-ray irradiated under the d.c. field exhibit larger TL light output compared to the a.c. samples.

4. Discussion

The level of optical absorption in a crystal, particularly in the low wavelength region (around 200 nm), is considered as a measure of the crystal's defect concentration [12]. The law value of the absorption coefficient ($\alpha \sim 1\ \mathrm{C\,m^{-1}}$) is an indication of the concentration of such defects being small in these CaF_2 samples (about $10^{15}\ \mathrm{cc^{-1}}$ [13]). When CaF_2 crystals are subjected to high electric fields (d.c. or a.c.), there seems to be considerable interaction of the field with the crystal lattice – particularly at major defect regions like dislocations – increasing the concentration of lattice defects, hence the absorption at 200 nm as observed in the present measurements. The earlier reported work [14, 15] indicates that the d.c. field interaction produces a smaller concentration of defects compared to the a.c. field of the same value. The present results also indicate that the field–crystal interaction is appreciable beyond 20 kV cm^{-1} but saturates after about 55 kV cm^{-1}.

The absorption bands at 375 and 580 nm observed in the d.c. field-treated samples which are later-X-ray irradiated, are the F- and β-bands (due to colloidal centres), respectively [8]. The formation of F-band at room temperature in these crystals suggests that the field–crystal lattice interaction leads to dissociation of

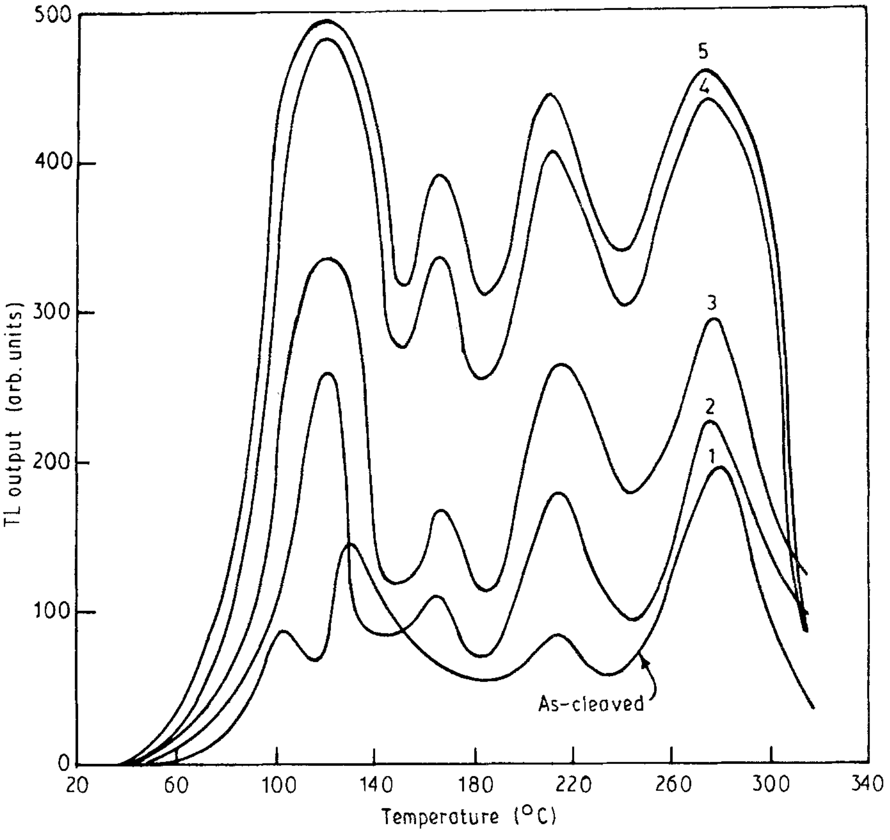

Figure 5 Thermoluminescence of CaF_2 crystals X-ray irradiated at 30 °C under different conditions. 1, as-cleaved; 2, ac 10 kV cm^{-1}; 3, dc 10 kV cm^{-1}; 4, dc 50 kV cm^{-1}; 5, ac 50 kV cm^{-1}.

the anion Frenkel pairs, leading to free negative ion vacancies which trap electrons (produced during irradiation) being converted into F-centres. It is also likely that some of these electrons can be caught up at Ca^{2+} of the lattice converting them into Ca^0 resulting in the colloidal calcium band (β-band) at 580 nm [8, 9]. These conclusions seem to be supported by the fact that the growth of defect concentration is similar to the growth characteristics of the F- and β-bands (at 375 and 560 nm, respectively). The results on quenched crystals can be understood in a similar way. As expected, quenching produces a larger concentration of colour centres.

It is interesting to observe that the absorption in the F- and β-bands is greater in CaF_2 crystals which are X-ray irradiated under d.c. fields (compared to those irradiated under the same a.c. fields). This result is opposite to the above-mentioned finding in the crystals which were subjected to the field and later X-ray irradiated. When the crystals are subjected to an a.c. field for a sufficiently long time, there is an 'electrical fatigue effect', [14, 16], similar to mechanical fatigue in metals [17]. The d.c. field simply stretches the crystal lattice, including the dislocation regions. Our results indicate that the fatigue effect leads to a larger concentration of vacancies.

When the CaF_2 crystals are X-ray irradiated under a.c. fields, they exhibit weak phosphorescence: this phosphorescence was not observed in CaF_2 crystals which were X-ray irradiated under d.c. fields. Apparently, this phosphorescence may be connected with the destruction of some of the F- and colloidal centres at room temperature, as these are produced by X-ray irradiation under the a.c. field. This may be the reason why the concentration of these two types of centres is smaller in the crystals irradiated under a.c. fields.

Although the TL light output in these crystals may be a consequence of the destruction of F- and the colloid centres [6, 7], the gradual decrease of absorption in these bands with the temperature of bleaching indicates no correlation between the TL output and the colour centres destroyed. The larger the concentration of the colour centres, the larger the TL light output exhibited by the CaF_2 crystals when they are subjected to the field (a.c. or d.c.) and later X-ray irradiated or irradiated under the field.

Acknowledgements

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