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Optical absorption of BaF_2 crystals irradiated with γ-rays

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This paper describes some ways of producing F-centres at room temperature in BaF_2 single crystals, and contains an attempt at understanding the phenomena involved therein.

1. Introduction

Colour centres in alkaline earth fluorides have been well studied, yielding valuable information regarding defect-controlled processes in them [1–3]. Several investigators have suggested models for colour centres responsible for various absorption bands observed in these crystals under different conditions [4–8]. Hartog [9] observed that BaF_2 single crystals additively coloured at 550° C and quenched very rapidly afterwards showed several absorption bands; according to him, the F-band (two electrons trapped at a negative-ion vacancy) in BaF_2 is situated at 606 nm and the M-band, which is an aggregate of two F-centres, at 720 nm.

Gorlich *et al.* [10] and others [11] pointed out that BaF_2 crystals exhibit different coloration spectra depending on whether they are coloured at room temperature or at a lower temperature. In fact they found that the F-band in BaF_2 was not formed at room temperature with X-ray irradiation. We notice from the literature that a systematic study of the optical absorption bands of variously coloured BaF_2 crystals is lacking. It is the aim of this paper to describe some ways of producing F-centres at room temperature in BaF_2 crystals, and to study the growth of absorption bands produced in these crystals under various conditions. Also experiments have been carried out on partial thermal bleaching of colour centres in these samples.

2. Experimental methods

All the BaF_2 single crystals used in the present investigations were a gift from Professor A. Smakula. The crystal preparation apparently did not produce any damage or distortion in the crystal lattice, as is evidenced from the very low value for optical absorption coefficient at 200 nm ($\alpha \sim 1.0\,\mathrm{cm^{-1}}$) [12]. The samples are cleaved from large boules, then ground and optically polished. The final dimensions of the samples are about 1 cm × 1 cm × 0.1 cm.

Flame photometric and chemical analysis of these samples showed impurity concentration less than 2 p.p.m. Some of the impurities looked for were calcium, strontium, manganese, iron, magnesium, cadmium, sodium and potassium. X-ray irradiation was done usign a Norelco unit run at 35 kV, 10 mA for the time mentioned — half the time on either side of the crystal. The details of X-ray irradiation under high a.c. field were reported earlier [13].

γ-ray irradiation was carried out with a Co^{60} source of strength 10^3 curie giving a dose of $80\,\mathrm{krad\,h^{-1}}$.

The optical absorption measurements on the coloured crystals were taken on Beckman 26 spectrophotometer in the wavelength region 200 to 800 nm at room temperature ($\sim 30°$ C). The accuracy in measurement of absorption coefficient, α ($\mathrm{cm^{-1}}$), is 0.05.

3. Results

Fig. 1 presents the data on the optical absorption of BaF_2 single crystals under different conditions. (The absorption data on the quenched crystal γ-ray irradiated for 150 h are not presented because the absorption is much larger, and also the resolution of the absorption bands is very much adversely affected.) Except for a slight increase in the absorption, even prolonged X-ray irradiation (for 8 h) of these crystals at room temperature does not produce any absorption bands. But when the irradiation is carried out under a large a.c. field ($14.6\,\mathrm{kV\,cm^{-1}}$), weak absorption bands are found to be produced with peak positions at 260, 500, 611 and 720 nm. If BaF_2 crystals are γ-ray irradiated for very long times, we notice that weak bands at 538, 611 and 720 nm are developed. However, in crystals quenched and γ-ray irradiated only for 24 h we notice formation of pronounced absorption bands at 440, 500, 538, 611 and 720 nm. As mentioned earlier, the absorption bands to 611 and 720 nm are respectively due to F- and M-centres; the bands at 500 and 538 nm may be connected with F-centres formed at perturbed regions of the crystal [14].

The absorption characteristics of BaF_2 γ-ray irradiated for different times, given in Fig. 2, indicate that up to an irradiation time of 72 h only the absorption band at 720 nm is formed, whereas the bands at 538 and 611 nm are developed at still larger times of irradiation. It is also observed that the absorption in 720 nm and in the other bands increases with time of γ-ray irradiation; the inset of this figure shows the growth pattern of these bands with γ-ray dose. The quenched and γ-ray irradiated BaF_2 exhibits significantly large absorption in the bands (Fig. 3).

Partial thermal bleaching characteristics of the absorption bands in BaF_2 crystals irradiated with

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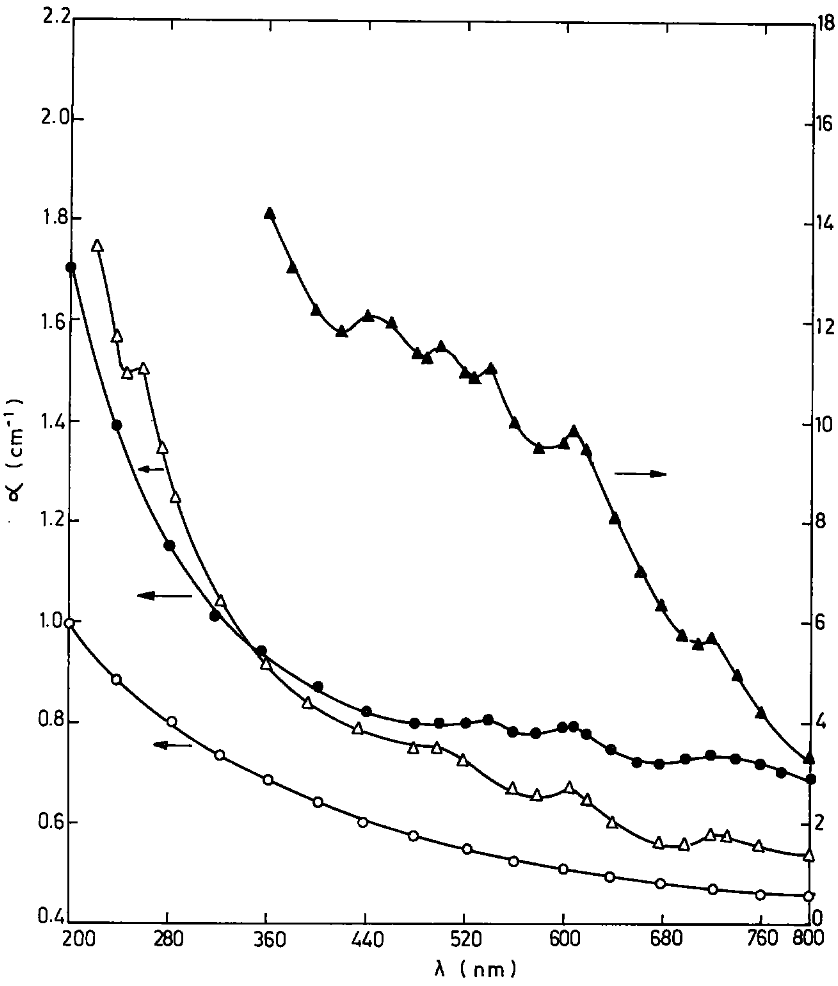

Figure 1 Optical absorption α ($\mathrm{cm^{-1}}$) at room temperature (~30° C) as a function of wavelength for BaF_2 crystals under different conditions. (○) As-cleaved; (△) X-ray irradiated for 4 h under a.c. field of $14.6\,\mathrm{kV\,cm^{-1}}$; (●) γ-ray irradiated for 150 h; (▲) quenched and γ-ray irradiated for 24 h.

γ-rays for 150 h are shown in Fig. 4; the inset of this figure shows how the absorption at the peak of the bands at 611 and 720 nm varies with temperature of bleaching. Similar data for crystal quenched and γ-rays irradiated for 24 h are presented in Fig. 5. It can be seen that the absorption in the bands gradually decreases with the temperature of bleaching in γ-ray irradiated (for 150 h) BaF_2; this is also true of the absorption bands in BaF_2 X-ray irradiated under a.c. field (data not presented). However, in quenched and γ-ray irradiated BaF_2, the absorption in all the bands gradually decreases up to about 100° C, followed by a rapid fall up to 140° C beyond which the decrease is again gradual.

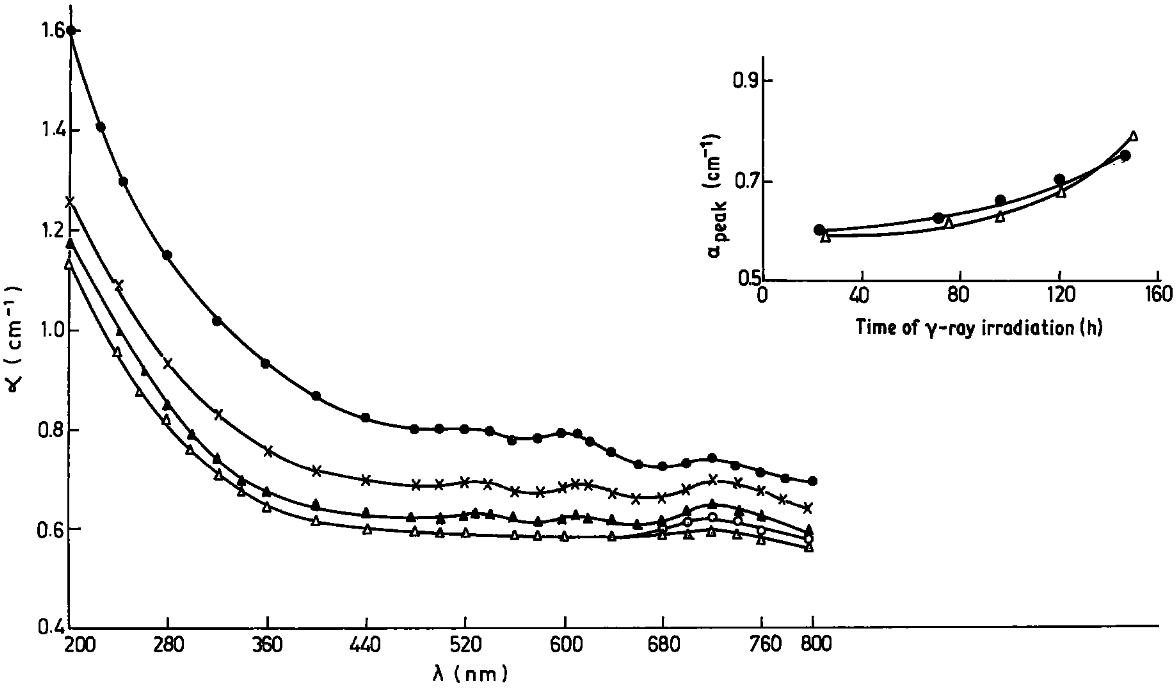

Figure 2 Optical absorption α ($\mathrm{cm^{-1}}$) as a function of wavelength for BaF_2 crystals irradiated with γ-rays at 30° C for different times. (△) 24 h, (○) 72 h, (▲) 96 h, (x) 120 h, (●) 150 h. Inset: growth of F- and M-bands. (△) 611 nm, (●) 720 nm.

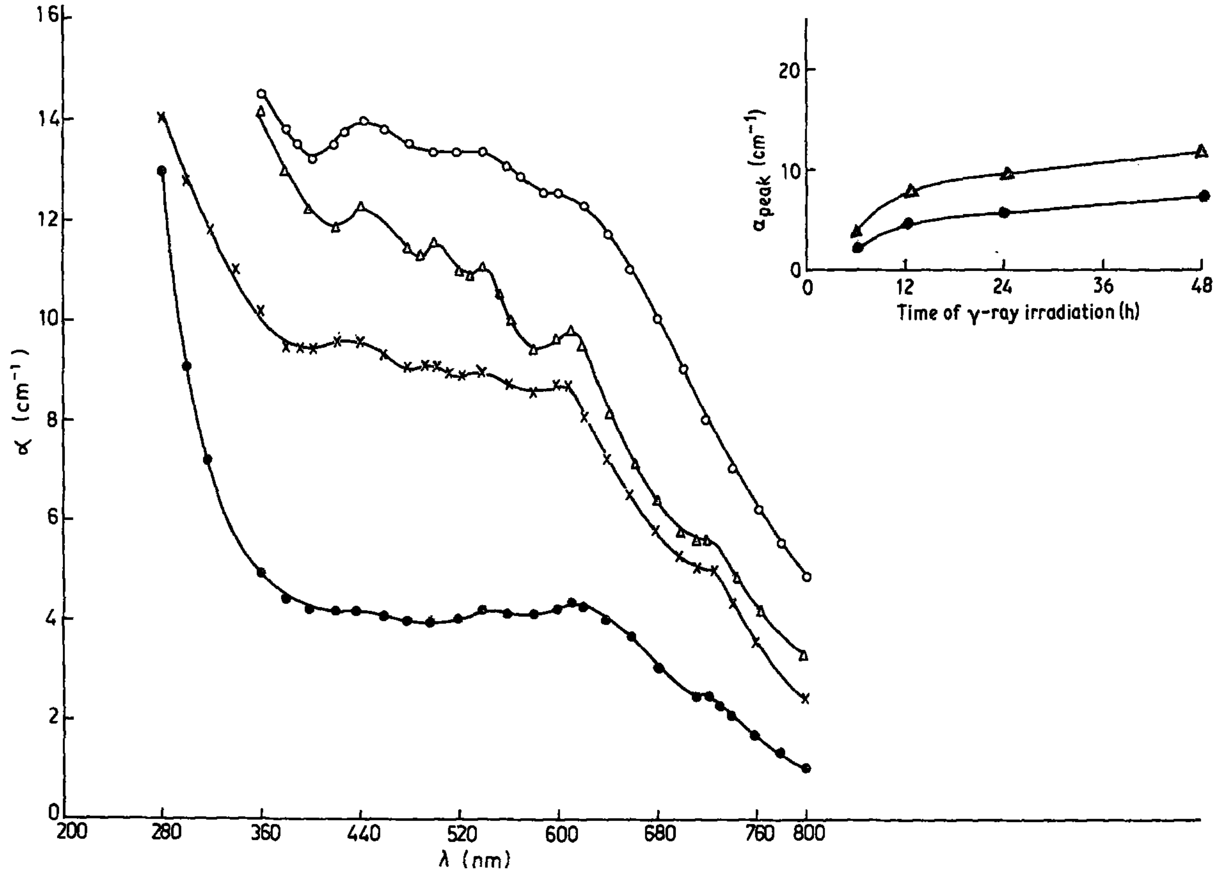

Figure 3 Variation of optical absorption α (cm^{-1}) with wavelength for quenched BaF_2 crystals (γ-ray irradiated at 30° C for different times). (●) 6 h, (x) 12 h, (△) 24 h, (○) 48 h. Inset: growth of F- and M-bands. (△) 611 nm, (●) 720 nm.

4. Discussion

BaF_2 contains Frenkel pairs (an interstitial anion which is associated with the anion vacancy that it created) [15, 16]. Even at room temperature, a certain small fraction of the anion Frenkel defects are dissociated. When BaF_2 crystals are subjected to a high a.c. field, this field may interact with the crystal lattice – particularly at major defect regions like dislocations – and will increase the fraction of the dissociated defects. The negative-ion vacancies thus formed will be

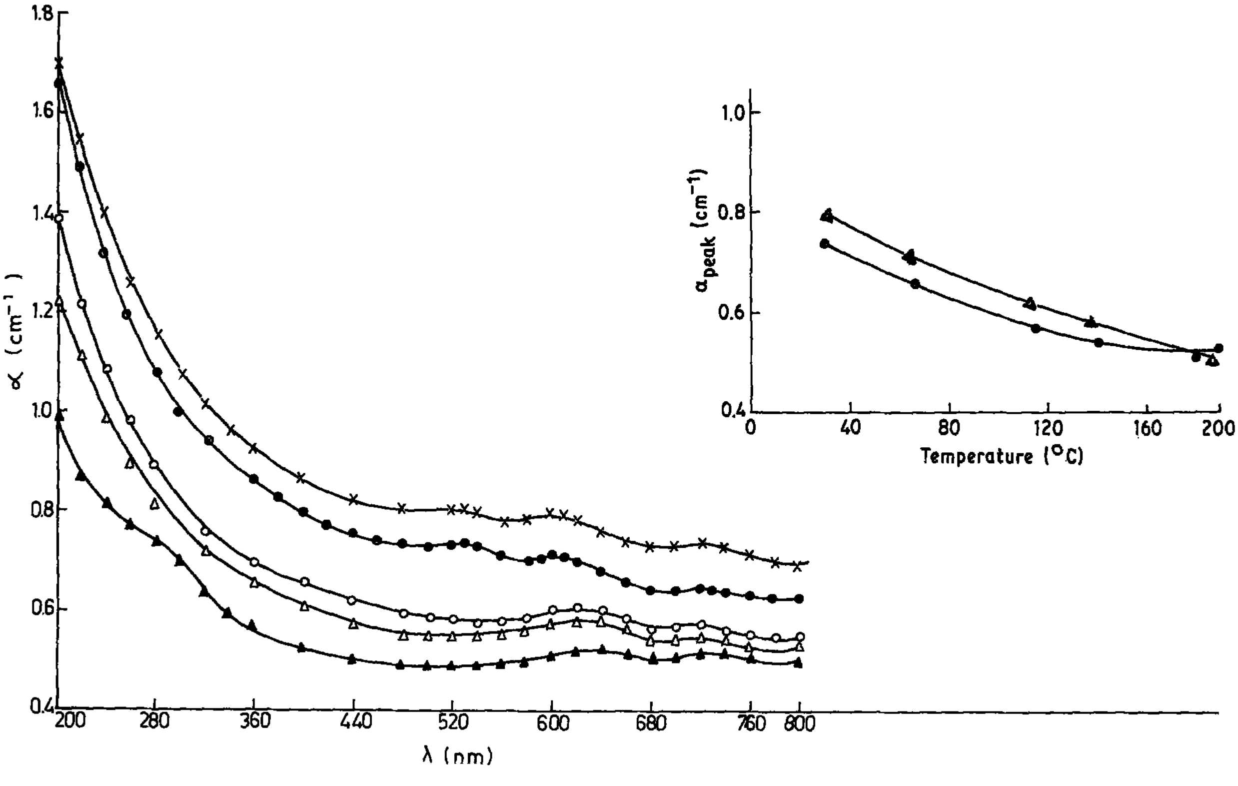

Figure 4 Thermal bleaching characteristics of absorption bands in γ-ray irradiated (for 150 h) BaF_2 crystals. (x) 30° C, (●) 65° C, (○) 115° C, (△) 140° C, (▲) 190° C. Inset: thermal bleaching curves for (△) F-band and (●) M-band.

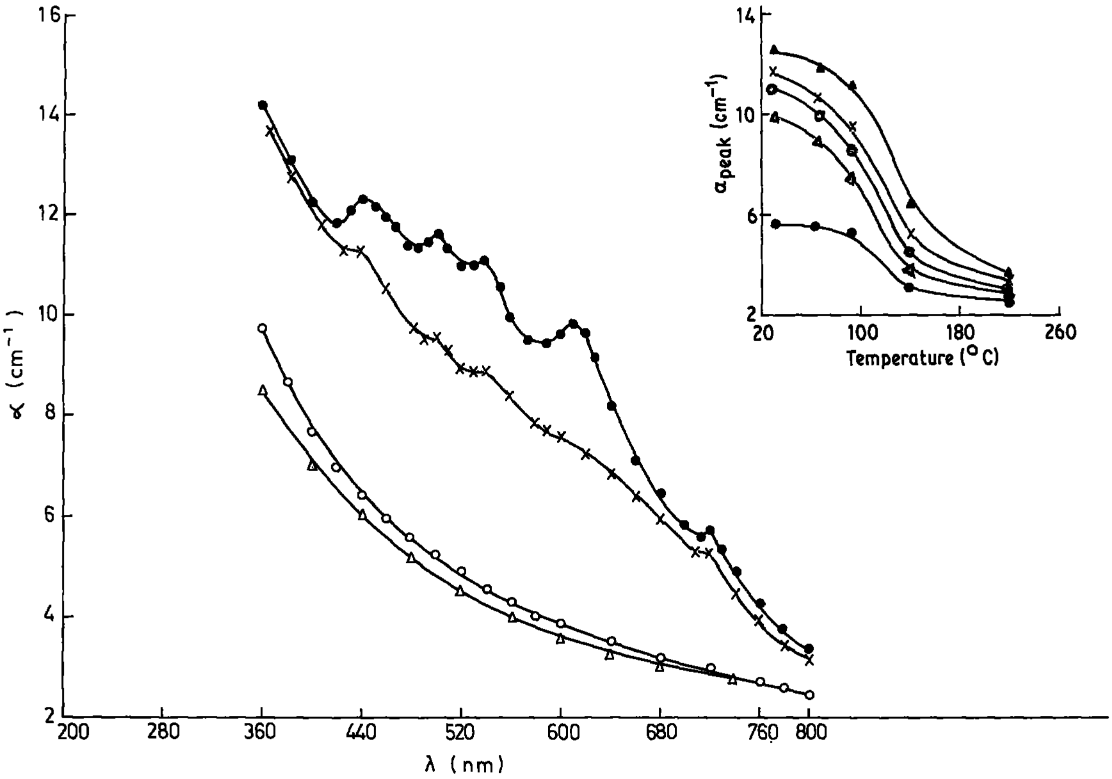

Figure 5 Thermal bleaching characteristics of absorption bands in quenched and γ-ray irradiated (for 24 h) BaF_2 crystals. (●) 30° C, (x) 95° C, (○) 140° C, (△) 230° C. Inset: thermal bleaching curves for various absorption bands. (▲) 440 nm, (x) 500 nm, (○) 538 nm, (△) 611 nm, (●) 720 nm.

converted into F-centres, trapping the electrons produced during X-ray irradiation. The increase in the dissociated anion Frenkel pairs may also occur due to high energetic γ-ray irradiation which also produces free electrons, the end result being formation of F-centres under this irradiation also.

If the BaF_2 crystals are quenched (prior to γ-ray irradiation) there will be an appreciable concentration of dislocations produced in it and also a "freezing-in" of the point defects appropriate to the higher temperature; this is expected to lead to some lattice distortion, which is a condition of the crystal conducive to the breaking up of the anion Frenkel pairs leading to a larger concentration of the dissociated defects (compared to that at room temperature). Under these conditions if the BaF_2 crystal is γ-ray irradiated, the concentration of F-centres is expected to be enhanced. In other words, this analysis shows some of the possible ways of producing F-centres at room temperature in BaF_2; the results of the present work support these conclusions. It is interesting to see that the M-band only is formed (but not the F-band) at room temperature when BaF_2 is irradiated at room temperature with γ-rays up to about 72 h; this is apparently due to the formation of F-centres but their immediate coagulation to M-centres [9].

Our data also show that the absorption in the various bands increases with γ-rays dosage instead of exhibiting saturation behaviour, as normally observed in alkali halide crystals. This may again be due to considerable lattice distortion occurring in the BaF_2 crystal (due to the large concentration of defects produced for such γ-ray doses) which makes the condition of the crystal suitable for easy production of more defects on further γ-ray irradiation. For the same dosage, as expected, the quenched and γ-ray irradiated BaF_2 crystals show larger absorption in all the bands compared to γ-ray irradiated samples.

It is interesting to find that the partial thermal bleaching characteristics of the colour centres in BaF_2 crystals γ-ray irradiated before and after quenching are different. The absorption in the quenched samples is ten times larger, even for a smaller time of γ-ray irradiation. The lattice distortion in the quenched samples is larger. Under these conditions and at a moderately high temperature of 100° C, it is likely that the process of destruction of the colour centres may be different, e.g. by tunnelling, leading to a rapid fall in their concentration as observed in quenched and γ-ray irradiated BaF_2 beyond 100° C.

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