9. J. A. DEAN, "Long's Handbook of Chemistry" (McGraw-Hill, New York).
10. ZBIENIEWO and JASTRZEBSKI, "Nature and Properties of Materials" (John Wiley, New York, 1959).

Received 30 April
and accepted 10 June 1980

M. K. SURAPPA
P. K. ROHATGI
Regional Research Laboratory,
Council of Scientific and Industrial Research,
Trivandrum 695019,
India

F-band absorption and thermoluminescence in X-ray irradiated NaI single crystals

The properties of colour centres formed in alkali halides by ionizing irradiations have been studied [1, 2]. Such studies gave considerable insight into the electronic processes taking place in these solids. Though much work has been reported on KCl and NaCl, other crystals particularly NaI received very little attention. An absorption band with a peak of 588 nm is identified as being due to the F-centres [2]. Luminescence of free and self trapped excitons in NaI has been discussed by Luschik *et al.* [3]. It is our purpose to report in this paper results of our investigations on (i) the absorption bands produced in NaI single crystals by X-ray irradiation, (ii) the growth of the F-band with time of irradiation (i.e. X-ray dosage), (iii) thermal bleaching characteristics of the F-band and (iv) thermoluminescence of these X-ray irradiated NaI crystals. As NaI is highly hygroscopic, X-ray irradiation was carried out and all measurements were taken at an elevated temperature of 40° C (room temperature is about 25° C).

Some of the NaI single crystals used in the present work were supplied by Bhabha Atomic Research Centre, Bombay. Flame photometric

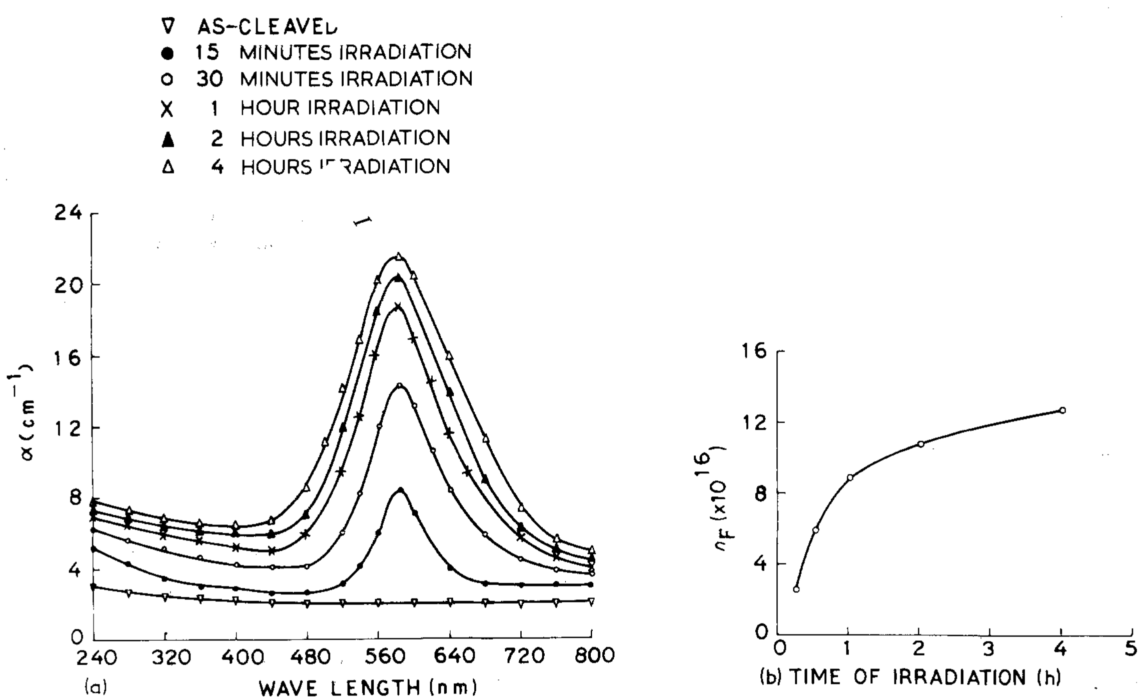

Figure 1 (a) Absorption coefficient (α) as a function of wavelength for NaI crystals for different X-ray irradiation times at 40° C. (b) Growth of F-band in X-ray irradiated NaI crystals.

0022–2461/81/020564–04$02.40/0

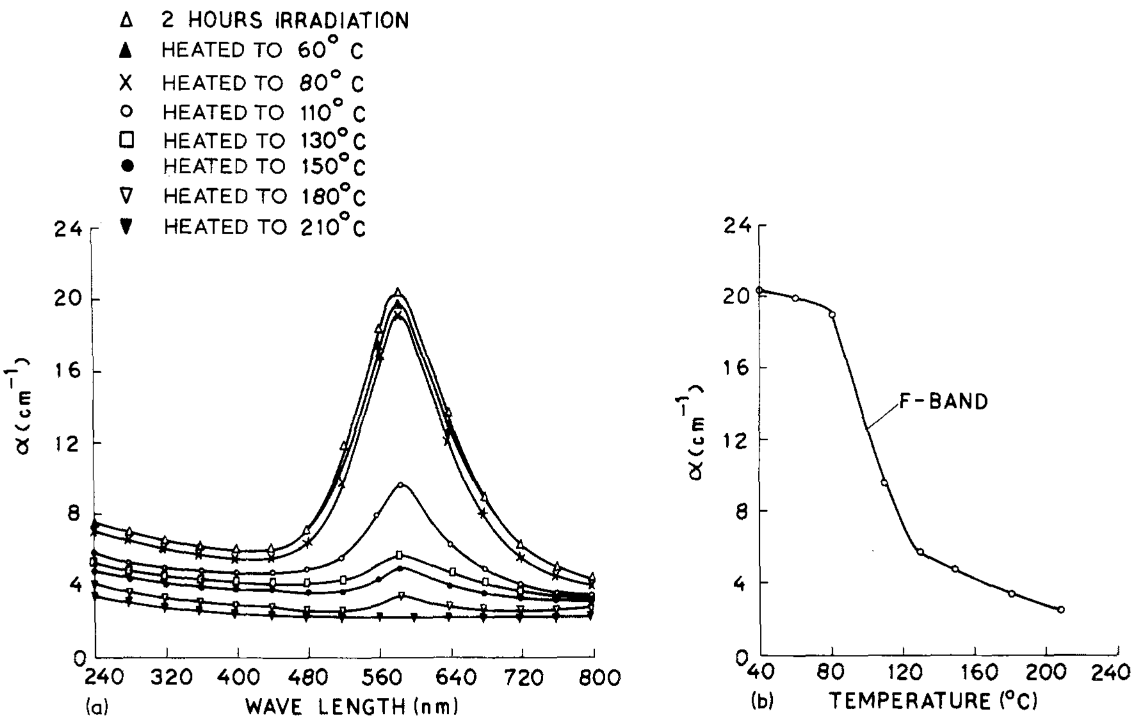

Figure 2 (a) Thermal bleaching characteristics of F-band in X-ray irradiated NaI crystals. (b) Thermal bleaching curve for F-centres in NaI crystals irradiated with X-rays.

measurements and chemical analysis showed that potassium is present up to 3 ppm; no other impurities could be detected. Samples having dimensions of about 1 cm × 1 cm × 0.1 cm were cut by the wet thread method (using glycerine as the liquid) from the boule and well polished. X-ray irradiation of the crystals was carried out at 40° C using 35 kV and 10 mA, from a Philips Norelco unit keeping the sample at a distance of 2 cm from the target of the tube. The samples were always irradiated on one side for half of the mentioned time and for the remaining half time on the other side.

Optical absorption measurements were taken on a Beckman DU spectrophotometer in the range 240 to 800 nm. The maximum error in α is 0.3 cm^{-1}. Thermoluminescence glow peaks were recorded with an Esterline–Angus recorder using a conventional set-up [4].

The variation of the optical absorption coefficient (α) with the wavelength of NaI crystals before and after X-ray irradiation is shown in Fig. 1. α has a low value ($\alpha \simeq 2.8\ cm^{-1}$) which is constant down to 450 nm below which it increases slightly with decreasing wavelength. X-ray irradiation produces the F-band at 586 nm, the absorption increasing with X-ray dosage; also the absorption in the low wavelength region slightly increases with the dosage. Using Smakula's equation [5] the F-centre concentration was calculated for a particular time of irradiation; the inset of Fig. 1 shows how the F-centre concentration in NaI crystals increases with time of X-ray irradiation (i.e. dosage). A rapid increase in F-centre concentration with time was noticed up to about 1 h but a slow increase was observed later.

The thermal bleaching characteristics of the F-band are presented in Fig. 2. (In these measurements, the sample was heated to the corresponding temperature, kept at that temperature for about 2 min and then slowly cooled to 40° C at which temperature the absorption measurements were made). It was found that when the coloured NaI was heated up to 80° C, there was practically no change in the F-centre concentration. Marked F-centre destruction takes place in the two temperature regions 80 to 130° C and 130 to 210° C; the crystal was found to attain its original condition after this heat treatment.

The thermoluminescence (TL) light output of

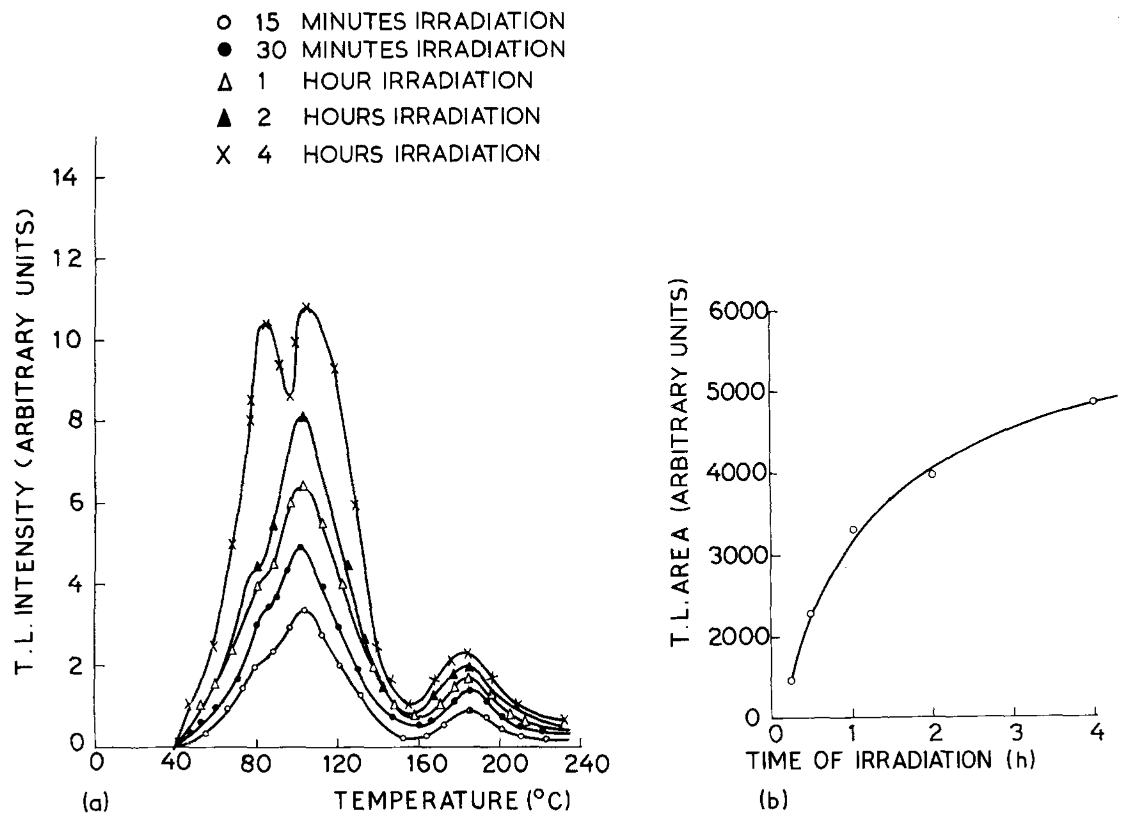

Figure 3 (a) Thermoluminescence curve for NaI crystals irradiated with X-rays for different times. (b) Growth of total TL light output of X-ray irradiated NaI for different irradiation times.

NaI crystals irradiated with X-rays for different times is given in Fig. 3. With 15 min irradiation, two TL peaks at temperatures 105 and 185° C are exhibited; the presence of a peak around 80° C can also be seen. Longer irradiation times do not affect the pattern of the TL curve except that TL light output in the peaks increases; the peak around 80° C seems to become prominent at very large irradiation times (for example 4 h). The inset of Fig. 3 shows how the total TL light output (area under TL curve) increases with time of irradiation (i.e. The X-ray dosage).

The value of absorption coefficient in the UV region of a solid (around 240 nm) is an indication of the concentration of crystal defects [6]. The comparatively low value of α ($\alpha \simeq 2.8\,\text{cm}^{-1}$, at 240 nm) shows the moderately high quality of the crystals used in the present investigations. The intrinsic defect concentration (e.g. vacancies etc.) is of the order of $10^{15}\,\text{cm}^{-1}$ [2]. The increase in α in the low wavelength region exhibited by NaI crystals irradiated with X-rays suggests production of hole-trapped centres (V-centres) in these crystals (with X-ray irradiation) which have absorption bands below 240 nm [2]. The increase of absorption in the low wavelength region may be connected with the long wavelength tail of such a V-centre absorption band. The F-band growth curve for NaI exhibits the usual two-stage colouration [7] (Fig. 1 inset). The initial fast stage colouration (that is up to about 1 h X-ray irradiation) is apparently due to the initially present negative ion vacancies forming F-centres, whereas the slow second-stage colouration (beyond 1 h) is connected with the generation of negative ion vacancies by X-ray irradiation and their subsequent conversion to F-centres.

X-ray irradiation of an alkali halide is known to produce both electron-trapped and hole-trapped centres in the crystals; thermoluminescence is a consequence of radiative recombination of these two types of centres [8]. The absorption bands due to the various hole-trapped centres in alkali halides usually lie in the far ultra-violet region; as such their absorption bands are not generally detected. In the present measurements it was found (Fig. 2 inset) that the F-band destruction takes place in two stages (i) in the temperature range 80 to 130° C and (ii) 130 to 210° C. Though it is not possible to understand the exact mechanisms giving rise to the two TL peaks at 105 and 185° C from the present measurements, it is tempting to point out the possibility that these TL peaks may be due to the recombination of F-centres with two different types of hole-trapped centres. In a similar way, we may ascribe the TL peak around 80° C as being due to colour centres (produced by X-ray irradiation) having an absorption band beyond the range of present measurements.

It may be mentioned here that data have been taken on samples obtained from the source mentioned as well as those commercially available (from Harshaw Chemical Company, USA); the data are reproducible to the accuracy mentioned. The points shown in the curves in the figures are average values from four different samples – two from each of the mentioned sources. Cutting and polishing of the samples did not bring about any appreciable change in either optical absorption or thermoluminescence.

Further work is now in progress on the quenching of NaI crystals near the melting point as well as on the dielectric properties before and after X-ray irradiation. This, it is felt, will give more insight into the fundamental processes taking place in this material. It is planned to communicate this work in the course of time.

Acknowledgements
The authors are grateful to Dr. R. Y. Deshpande, Head, Crystal Growing Section, BARC, India, for kindly making available to us some NaI single crystals. One of the authors (AKG) is grateful to UGC, Government of India, for the award of Teacher Fellowship.

References
1. F. SEITZ, *Rev. Mod. Phys.* **26** (1954) 7.
2. J. H. SCHULMAN and W. D. COMPTON, "Colour Centres in solids" (Pergamon Press, London, 1963) p. 29.
3. Ch. LUSCHIK, I. KUNSMANN and V. PBKHANOV, *J. Luminescence* **18/19** (1979) 11.
4. H. N. BOSE, *Proc. Phys. Soc.* **B68** (1955) 249.
5. A. SMAKULA, *Zeif. fur Physik* **59** (1930) 603.
6. A. SMAKULA, "Einkristalle" (Springer Verlag, Berlin, 1959).
7. M. D. AGRAWAL and K. V. RAO, *Phys. Stat. Sol. (a)* **6** (1971) 693.
8. K. V. RAO and J. SHARMA, *Physica* **28** (1962) 653.

Received 13 March
and accepted 5 June 1980

A. K. GUPTA
K. V. RAO
Department of Physics,
Indian Institute of Technology,
Kharagpur – 721302, India