Thermochimica Acta, 35 (1980) 349—358

EFFECT OF THERMAL TREATMENT ON THE THERMOLUMINESCENCE OF YELLOW AND COLOURLESS FLUORITES FROM AMBA DONGAR, GUJARAT (INDIA)

V.K. JAIN

Health Physics Division, Bhabha Atomic Research Centre, Bombay-400085 (India)

S. MITRA

Department of Geological Sciences, Jadavpur University, Calcutta-700032 (India)

(Received 18 June 1979)

ABSTRACT

The results of thermoluminescence (TL) investigations on yellow and colourless fluorite from Amba Dongar in Gujarat (India) are reported. The TL of both samples is found to be significant and peaks in the region of 250°C are not the dominant ones, unlike the TL of other fluorites. The peaks at temperatures below 150°C are the most prominent, and those above 200°C are only one-tenth as large. The effect of heating at temperatures of 700, 500, 400 and 300°C on the TL sensitivity and on the glow curves of these samples has been studied. The 700°C-annealed sample was irradiated with high dosages of gamma-rays and further annealed at 500, 400 and 300°C so that sensitization effects could be observed. Maximum sensitization was observed for the peak around 250°C for the sample annealed at 400°C. These results are discussed with respect to data from optical spectral studies at temperatures of 303 and 77 K and also after heating and annealing at various temperatures up to 700°C.

INTRODUCTION

Natural fluorites occur in various colours and their optical and thermal properties have been extensively studied by a large number of workers. Because of their characteristic thermoluminescence response they have been found to be very useful in dosimetric applications [1,2]. Schayes et al. [1] studied in detail the TL of many samples and found a particular specimen (colour and source not stated) to be most sensitive. Sunta [2] also observed the TL of several samples and found the light-green variety to be the most sensitive. The TL properties of a green variety were investigated by Watanabe and Okuno [3] and that of a violet sample by da Cruz et al. [4].

A common feature of the glow curves of these samples is the predominance of a peak occurring at temperatures around 250°C. The peaks occurring at lower temperatures are smaller than this peak and those at higher temperatures smaller still. Another general feature of the TL response of these samples is that the TL sensitivity is reduced on heating at temperatures greater than 450°C [1]. Natural fluorite is understood to be insensitive to lower-temperature heat treatment, unlike LiF [5]. However, the TL properties of all varieties of natural fluorites may not be the same, and it may also be instructive to compare the TL of different coloured samples from the same location. In this paper we report the thermoluminescence glow curves of yellow and colourless fluorite occurring in brecciated zones of a totally exploded volcanic crater, hosting carbonatite in Deccan trap lavas, around Amba Dongar village in Gujrat, India, and also the effect of thermal treatment on these samples.

EXPERIMENTAL

Clean crystals of yellow and colourless fluorites collected from the carbonatite environment of Amba Dongar (21° 59′ : 74° 4′) in Gujarat, India were used in this study. Large, good crystals were hand-separated and pulverised and sieved to about 200 mesh for thermal treatment. The powdered sample was kept in a silica (or alumina) boat and put in the furnace for controlled heat treatment. After the desired annealing time the boat was withdrawn onto a block of aluminium, thus quenching the powder to room temperature in a few minutes ($\simeq 3$ min). For irradiation the powder was wrapped in small paper packets, enclosed in a polythene vial, and exposed to gamma rays in a ^{60}Co cell. The TL glow curves were recorded at a linear heating rate of 30° C min^{-1} with an EMI 9514 S photomultiplier detector. Further experimental details have been described elsewhere [6].

RESULTS

Glow curves in virgin samples

Natural thermoluminescence (NTL) and that after gamma irradiation are shown in Figs. 1 and 2 for yellow fluorite (YF) and colourless fluorite (CF), respectively. The NTL of CF is only one-tenth that of YF. There is a broad peak in both cases occurring a little before 350° C in CF and at 360° C in YF. In YF the NTL glow is without any structure but in CF a clear shoulder at 270° C can be observed. In fact, under N_2 flow, this shoulder is accentuated and the other peak appears at about 360° C only without significant overall reduction in TL. This shows a very small proportion of tribo-luminescence in NTL, which it is not possible to eliminate satisfactorily [7]. This, however, may interfere only at very low dose measurements, as, for example, in personnel dosimetry. No further consideration was, therefore, given to it in the investigations presented here. On irradiation it is seen that the NTL is not saturated in either case, as both an increase in TL and also a shift in temperature are seen. In both samples, six gamma-ray induced peaks are indicated, but their temperatures and prominence differ. The YF has peaks at 85(I), 95(I′), 130(II), 240(III), 300(IV) and 350° C(V). Peak I is the most sensitive, followed by others in the order of their appearance. However, peak I saturates at about 10^6 R and shows a slight fall thereafter whereas peak II

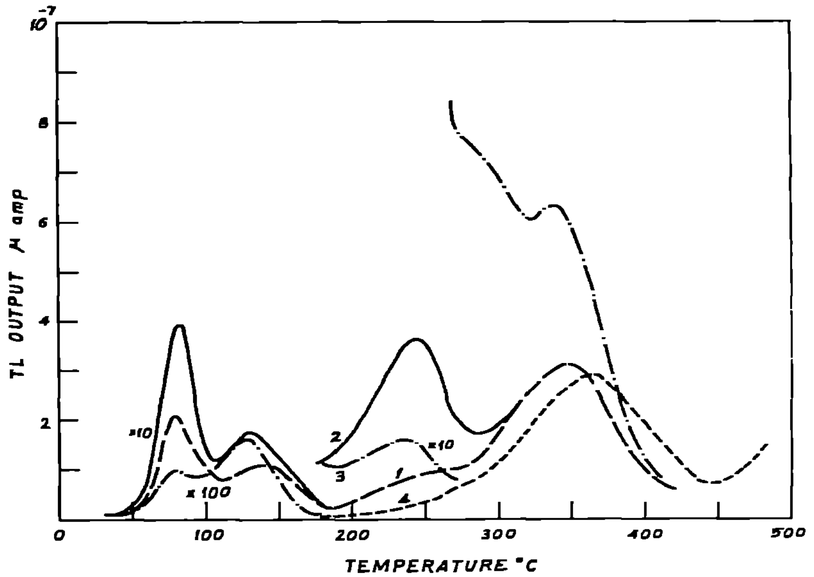

Fig. 1. TL glow curves of natural fluorite (yellow): (1) 7.7 x 10^3 R; (2) 9.2 x 10^4 R; (3) 2.3 x 10^6 R; and (4) NTL.

continues to grow, overtakes peak I and saturates at about 10^7 R (Figs. 6a and b). Peak I′ is indicated as a shoulder only at very high doses, and, because of the indistinguishable presence of this intermediate peak, the temperature of peaks I′ and II does not remain constant. In CF the gamma-ray induced peaks occur at 75(I′), 90(I′), 135(II), 230(III), 300(IV) and 340°C(V). The response of different peaks for this sample generally follows the same pattern as in YF. However, in CF the group of peaks I—II are more sensitive than in YF, and peak III is more sensitive in YF than in CF, with double the TL output at saturation.

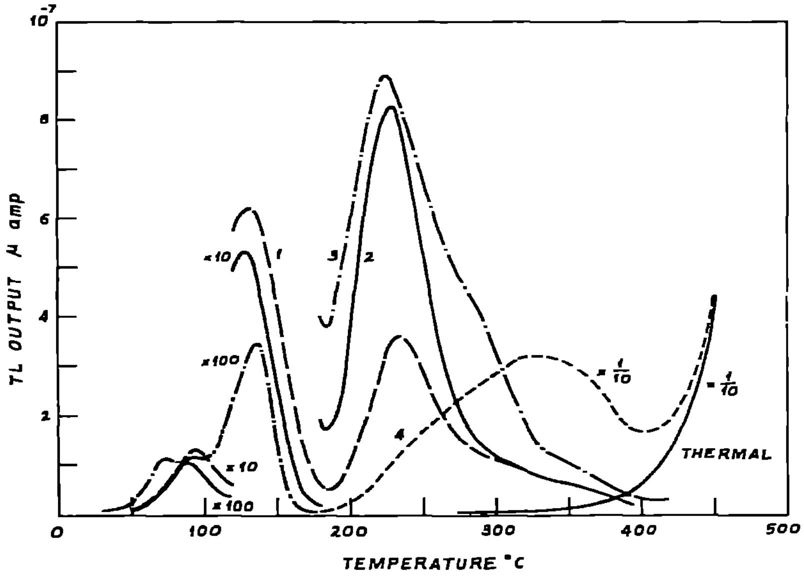

Fig. 2. TL glow curves of natural fluorite (colourless): (1) 7 x 10^3 R; (2) 5 x 10^4 R; (3) 4.1 x 10^6 R; and (4) NTL.

Glow curves in annealed samples

The powders were annealed at 300, 400, 500 and 700°C for 1 h to observe the effects upon TL response both of residual NTL, if any, and also of the annealing process itself. The results for 700°C-1 h treatment presented in Fig. 3 (curve 4) for CF and Fig. 5 (curve 5) for YF show a large decrease in sensitivity for CF and practically no change for YF. The general pattern of the glow curve otherwise remains the same. The latter finding is contrary to the results of most other workers [1,3,4]. This may be due to the different varieties (colour and origin) of fluorites used. One important difference between the fluorites used here and those reported by other workers is that in YF and CF peaks I and II are the most prominent, rather than peak III as is the case with the others. In fact, in both samples the glow curve consists of three regions: (i) 50—175°C, (ii) 175—275°C, (iii) 275—400°C. Each region has more than one peak and with increasing dose the peak positions shift to lower temperatures. The sensitivity of the first region is ten times, and that of the third one-tenth, of the sensitivity of the second region. Also the peak at 340/350°C remains indistinct in CF but is quite clear, though small, in YF. However, for CF the decrease in TL is more for 300°C than for 500°C and is least for the 400°C anneal for the first group of peaks (it is, of course, a maximum for 700°C). Peak III, on the other hand, increases with annealing temperature in the order 300, 500 and 400°C. For peak III, not only the TL sensitivity but also the TL output at saturation increases, being at a maximum for the 400°C anneal. Peak I′, occurring at about 125°C, is barely discernible for 7 × 10^3 R (Fig. 3), while peak II at 155°C is quite prominent. For 5 × 10^4 R peak II is barely seen while peaks I and I′ become distinct (Fig. 4). Annealing YF at 300 and 500°C has a slight sensitizing effect, and 400°C annealing causes more sensitization, in particular of peak

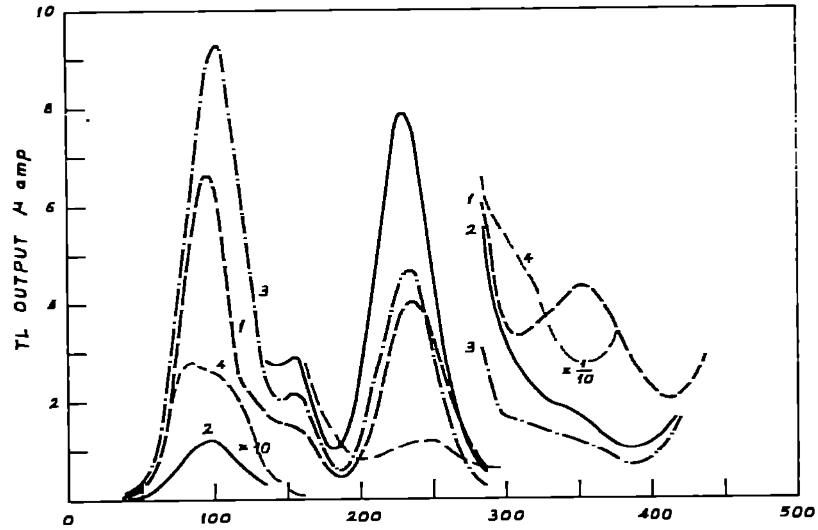

Fig. 3. TL glow curves of fluorite (colourless) annealed for 1 h at (1) 300°C; (2) 400°C; (3) 500°C; and (4) 700°C, exposure 7 × 10^3 R.

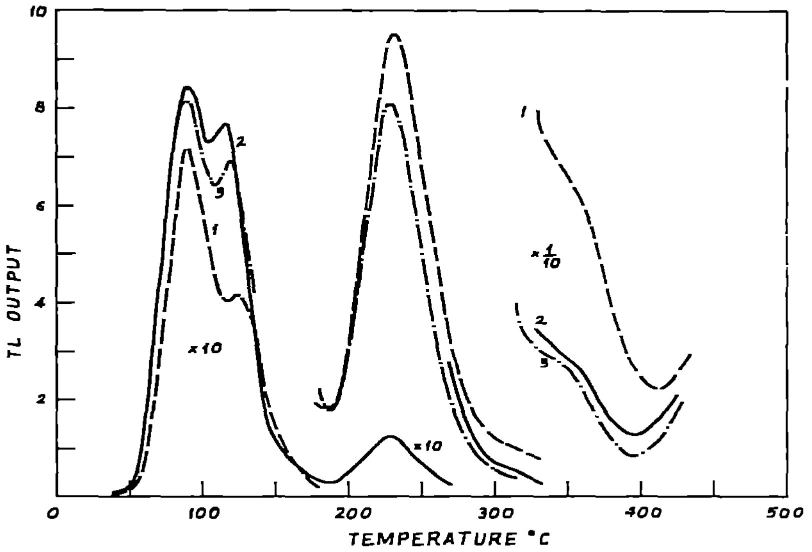

Fig. 4. TL glow curves of natural fluorite (colourless) annealed for 1 h at (1) 300°C; (2) 400°C; and (3) 500°C, exposure 5 × 10^4 R.

III. But the increase is much less compared with that in CF. Maximization of sensitivity in YF takes place under different conditions as we shall see in the next section.

In view of the fact that the NTL in these samples is not saturated, the samples were further exposed to high doses and then annealed, but this did not lead to any different results.

Glow curves in annealed irradiated annealed fluorite

In the last section, we have seen that 400°C annealing maximizes the response of peak III (used in dosimetry) in natural CF. A similar, but small, change in the response of peak III occurs in natural YF (see Fig. 5, curves 1 and 2). But natural YF, which has been put through a sensitization procedure (700°C-1 h annealing followed by saturation exposure $\simeq 10^6$ R), shows a similar maximum change in the response of peak III when annealed at 400°C for 1 h (see Fig. 5, curves 3 and 4). (The sample thus obtained is designated as YFs or CFs hereafter). Annealing at 300 or 500°C instead of 400°C also causes an increase in the sensitivity, but to a much smaller extent. Again the special role of 400°C annealing compared with that at 300 and 500°C is evident. Though the effect on peaks of group 1 is small, peak III is sensitized by a factor of 30 through the 400°C anneal and by a factor of 5 through the 300 and 500°C treatments. Even peak V is sensitized several-fold. The same treatment given to CF does lead to some recovery of the sensitivity which had been lost on 700°C heating. But the increased sensitivity is still less than in the natural sample and far less than in the natural 400°C annealed CF. Table 1 summarizes for peak III the results of annealing natural CF, and also the results for samples of YF which have been

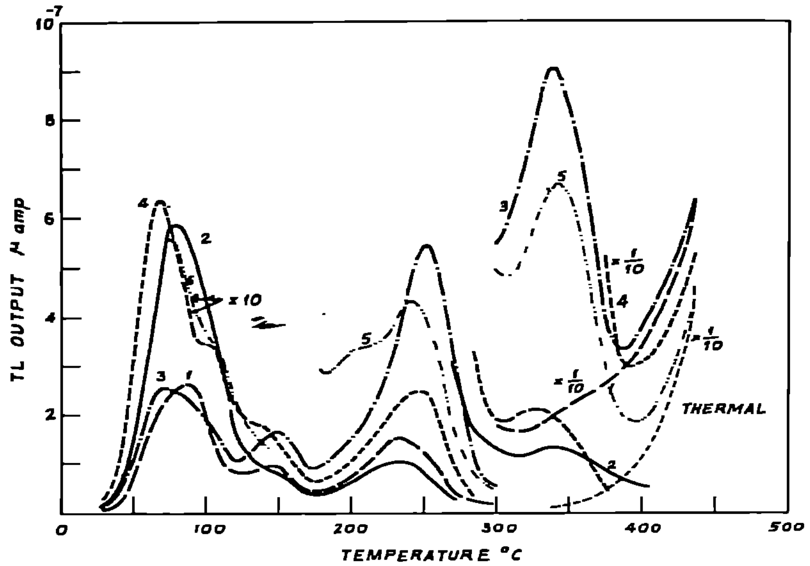

Fig. 5. TL glow curves of fluorite (yellow): annealed at 400°C for 1 h (1) and (2); annealed at 700°C for 1 h: (5); sample of (5) exposed to 7 × 10^6 R prior to annealing for 1 h at 400°C: (3) and (4). Exposures: (1) and (3) 5130 R; (2), (4) and (5) 7 × 10^4 R.

annealed at 700° C and then exposed to saturation and further annealed at 300, 400 and 500° C. Figs. 6a and 6b show the TL response of peaks I and III, and II and IV, respectively, for natural YF samples, and also for the 700° C-annealed and sensitized samples. Finally, the integrated TL output in the 700° C-annealed and sensitized YF samples, is drawn in Fig. 7.

TABLE 1

Effects of annealing and irradiation on the TL of samples of CF and YF, exposure 7 × 10^3 R

Treatment	Height of peak III for	
	CF	YF
Not annealed	3.6	0.2
Annealed for 1 h at		
700°C	0.12	0.28
300°C	4.0	
400°C	8.0	
500°C	4.6	
700°C-1 h Sample exposed to 4.6 × 10^6 R and further annealed at		
300°C		1.4
400°C		8.3
500°C		1.3

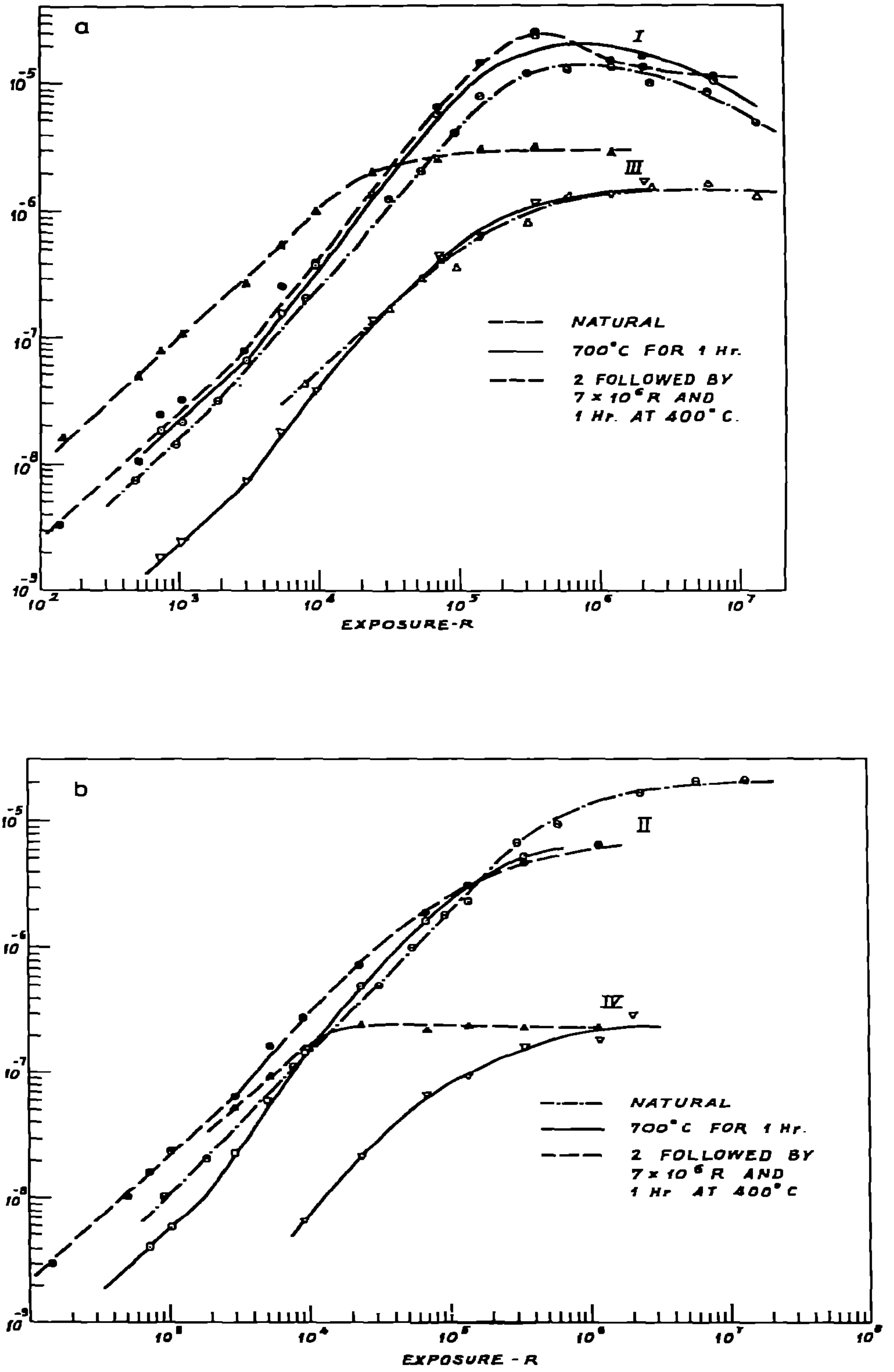

Fig. 6. (a) TL response of peaks I and III in yellow fluorite; and (b) TL response of peaks II and IV in yellow fluorite.

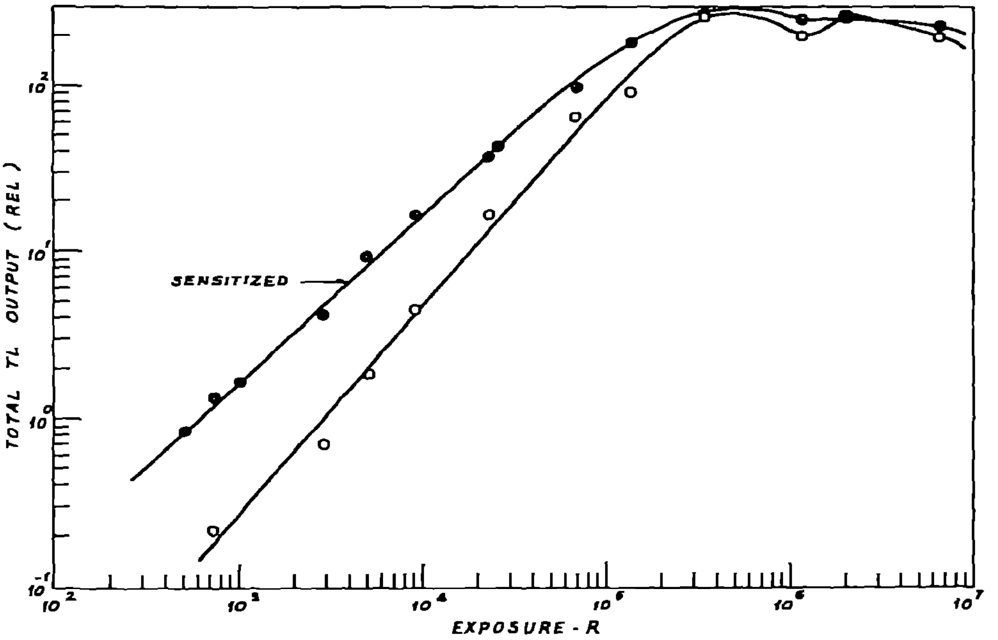

Fig. 7. Integrated TL response of 700°C-annealed and sensitized yellow fluorite.

DISCUSSION

The results presented above show that both yellow and colourless fluorite samples have TL curves which consist of several peaks over the temperature range 50—300°C. The peak temperatures shift with dose. The shifts are such that one might immediately think of second-order kinetics as being applicable. However, this would only be true if there were isolated peaks and if the temperature shift of each peak could be monitored individually. However, this is not so. In fact, attempts to anneal out various peaks by temperature/time adjustments lead to continuously varying peak positions. This has led researchers to suggest a model of continuous TL traps in fluorite [8]. The observations may be understood in terms of an array of TL active traps occurring almost continuously in the required temperature range. Since the sensitivities of the various traps also vary widely, either because of their differing numbers or because of differences in their recombination probabilities, or both, the resultant glow has peaks whose temperatures do not remain constant with dose. This phenomenon is more marked in colourless fluorite than in yellow fluorite. Annealing at 700°C too does not help very much, as the shift in peak temperature is still seen. This seems to be a general feature of fluorite samples, as shown by the results of other workers [1,3]. Even in synthetic CaF_2 : Dy, multiplicity of peaks and a very crooked TL response has been reported [9]. However, in the latter case the response becomes linear on annealing the phosphor at 600°C. In the fluorite samples used in the present work even annealing at 700°C for one hour does not make the glow curve stable. The TL peaks grow supralinearly (Figs. 6a and 6b) as does the integrated TL output (Fig. 7, curve 1).

A second peculiarity of these samples is the decreasing sensitivity of TL with peak temperature except at very high doses. At very high doses peak II overtakes peak I. A peak I′ in between peaks I and II and a peak at 210° C, slightly higher than the one at 250° C, emerge. This pattern holds for the YF annealed and unannealed samples. In the colourless natural fluorite a peak around 215° C remains prominent throughout. This indicates that some kind of trap adjustment or creation is definitely taking place as irradiation progresses. As noted earlier, the annealing at 400° C plays an important role in the sensitization process. This is true for all the samples, that is, for natural CF and YF as well as for CFs and YFs. But the effect does not occur to the same extent in each case. In yellow fluorite maximum sensitization is attained in the YFs and not in the natural YF. In colourless fluorite, on the other hand, maximum TL output is obtained in natural CF and not CFs, directly opposite to the behaviour of yellow fluorite. In fact the sensitization procedure does not fully restore the sensitivity lost on 700° C heating. Further, in the two sensitized samples the TL response becomes nearly the same, except for the peak around 340° C which remains very small in CF. It should also be noted that the sensitization on annealing is mainly for peaks III and V. There is no sensitization of other peaks in CF, and in YF the effect is small. Thus it is doubtful that the effect of 400° C annealing (both lower-temperature, 300° C, and higher-temperature, 500° C being much less effective) is merely that of emptying the traps; competition from higher-temperature traps having been eliminated by the high exposure. In YF, in addition to the role of 400° C annealing in enchancing the TL response, the sensitization treatment (700° C-1 h anneal followed by a dosage of 10^6 R) definitely helps to create more of the species responsible for the higher TL response. In colourless fluorite, on the other hand, these species seem to be present fully and the sensitization treatment greatly reduces the sensitivity.

In LiF these effects have been explained in terms of an increase in the recombination probability caused by the addition of luminescence centres. The latter is concomitant with the break-up on irradiation of a complex centre, TCLC, into a high-temperature trap (TC) and the luminescence centre (LC) [10]. However, this is unlikely to be the process in CaF_2. For peak III the TL output is higher (Fig. 6a) in the sensitized powder at saturation though the integrated TL output is not significantly different from that in the 700° C-annealed powder. This may be due to the fact that ultimately the contribution of peak III to the total TL output is less than 10%. The TL emission spectrum of fluorites, due to rare-earth impurities, is spread over a very wide wavelength-range for the first group of peaks, but is much simpler and dominated by 375-nm emission for peak III and V. The sensitization process may be making available more of the recombination centres.

Since Amba Dongar fluorites occur in association with carbonatites (a carbonate rock of igneous origin) which contain a fair amount of rare-earth elements and actinides (U and Th), the spontaneous radiations emanated since the explosive volcanism in that area (37.5 ± 2.5 My by K—Ar dating, cf. Deans and Powell [11]) may be responsible for the colour. γ-Irradiation from a 2000 Curie γ-source for 15 min made both the colourless and yellow samples intensely coloured. The spectrum (in CARY-14) of the CF exhibited an intense, broad peak around 610 nm and a weak band at 495 nm. For comparison, a synthetic CaF_2 crystal (manufactured by Harshaw Chemical Co., U.S.A.) was irradiated for 18 h and its spectrum recorded; there was no observable band in the range studied. These bands, however, get thermally bleached and therefore are not due to rare-earth (RE) ions as such. However, it is known that RE ions in CaF_2 function as electron traps which are stable to about 300°C. It may also be mentioned that substitutional impurities like O^{2-} and/or Na^+ can contribute to hole centres which are stable above room temperature. These impurities cause intense colouration in irradiated CaF_2 crystals. The trivalent RE ions are reduced to a divalent state on irradiation and these are again reoxidized to the trivalent ions on heating. The RE impurity ions act as electron trap centres. Heating involves the release of holes from lattice defects and their recombination at the RE impurity sites.

ACKNOWLEDGEMENTS

Our thanks are due to Dr. A.K. Ganguly, National Fellow, and Dr. S.D. Soman, Head of the Health Physics Division, both of Bhabha Atomic Research Centre, Bombay for their support and encouragement in this inter-institutional research; also to Dr. T. Subbaratnam of the Health Physics Division for his much valued co-operation. Field work and visits to Bhabha Atomic Research Centre by one of us (S.M.) were possible due to U.G.C. support of a research project on the carbonatites and fluorite deposits around Amba Dongar and other such areas in India.

REFERENCES

1 R. Schayes, C. Brooke, I. Kozlowitz and M. Lheureux, in F.H. Attix (Ed.), Luminescence Dosimetry, Conf 650637, Springfield USAEC, 1967, p. 249.
2 C.M. Sunta, Ph.D. Thesis, Agra University, India, 1971.
3 S. Watanabe and E. Okuno, in V. Mejdahl (Ed.), Proc. Int. Conf. Luminescence Dosimetry, 3rd, Risø, Denmark, Risø Report N. 249, Danish AEC and IAEA, 1971, p. 300.
4 M.T. da Cruz, M.R. Mayhugh and S. Watanabe, in T. Niewiadomski (Ed.), Proc. Int. Conf. Luminescence Dosimetry, 4th, Krakow, Poland, 1974, p. 61.
5 V.K. Jain, Phys. Status Solidi A, 38 (1976) K 65.
6 V.K. Jain and A.K. Ganguly, BARC Report, I — 466, Bhabha Atomic Research Centre, Bombay, 1977.
7 S.P. Kathuria, C.M. Sunta, R. Sasidharan and V.K. Jain, Proc. Natl. Symp. on Thermoluminescence and its applications, Kalpakkam, India, 1975, p. 690.
8 S. Watanabe and S.P. Morato, in V. Mejdahl (Ed.), Proc. Int. Conf. Luminescence Dosimetry, 3rd, Risø, Denmark, Risø Report. 249, Danish AEC and IAEA, 1971, p. 58.
9 W. Binder, S. Disterhoft and J.R. Cameron, Proc. Int. Conf. Luminescence Dosimetry, 2nd, Gatlinburg, Conf 680920 USAEC, 1968, p. 43.
10 V.K. Jain, S.P. Kathuria and A.K. Ganguly, J. Phys. C, 7 (1974) 3910.
11 T. Dean and J.L. Powell, Nature (London), 218 (1968) 750.