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ABSTRACT

Thermoluminescent response of natural Brazilian fluorite to ^{137}Cs gamma-rays has been studied, having in mind both the understanding of the supralinearity phenomenon and the utilization of this fluorite in radiation dosimetry.

Virgin fluorite was pre-annealed at 580°C for ten minutes followed by 400°C for two hours and then irradiated to different exposures between 25R and 1.2 MR. The response of glow peak II (pan temperature 180°C) is linear up to 3 kR, beyond which it becomes supralinear and finally saturates at about 300 kR. Under these conditions, the response of glow peak III (pan temperature 290°C) is not supralinear, and saturation is reached sooner, at about 100 kR.

The correlation between supralinear response and sensitization has also been studied. Samples irradiated to different exposures, as above, were individually annealed after irradiation for 15 minutes at 400°C and then exposed to 100R. Peak III exhibited sensitized response above 3 kR previous exposure, whereas peak II demonstrated only slight sensitization, and then only near 100 kR previous exposure. Thus, sensitization is anti-correlated with supralinear response for these two peaks.

Peak II was found to be sensitized, however, when the post-irradiation anneal was at 175°C instead of 400°C, and thus eliminated only peaks I and II, not I, II and III. Also supralinear response can be obtained from peak III when the virgin phosphor is annealed at 600°C for times longer than 10 minutes.

These results are qualitatively explained by the model postulating competing traps, although this model must be applied in a slightly altered form. Other existing models do not seem appropriate.

INTRODUCTION

The common thermoluminescent dosimeters exhibit linear response to low exposures, while at high exposure they demonstrate saturation effects where all traps are filled and response can not increase. In the intermediate region, say 500 to 1.000 R, these materials often exhibit supralinear response, that is, their emission per Roentgen of exposure begins to increase. Several phenomenological models have been proposed to explain this effect, but choosing between the models is usually difficult.

Supralinearity has been found experimentally for LiF:Mg[1], $Li_2B_4O_7$:Mn[2], and some other material[3], while CaF_2:Mn responds linearly from 0.1 to 3×10^5R. Schayès et al.[4] found that peaks II, III, IV, and V occurring at 175, 260, 385 and 525°C in the glow curve of Belgian natural calcium fluoride present non-linearity above 10 kR.

We have studied Brazilliam natural calcium fluoride, intending its application in dosimetry. The results indicate that its TL response as a function of exposure or absorbed dose is most likely caused by competing traps.

* Based in part upon portions of a thesis submitted by E. Okuno to the Institute of Physics, University of São Paulo, in partial fulfillment of the requirement for the Ph.D. degree.

THERMOLUMINESCENCE VS. EXPOSURE

The fluorite used in this work was collected near Criciuma, Santa Catarina State, Brazil, and was distinguished from other samples by its green color. Before use, the fluorite was crushed, powdered and sieved through 80 onto 200 mesh Tyler screens.

Irradiation was at room temperature using ^{137}Cs gamma-rays to expose samples contained in cylindrical polyethylene capsules. Unless otherwise noted, irradiation was preceded by annealing 10 minutes at 580°C and then 2 hours at 400°C, both followed by quick cooling (less than 3 minutes) to room temperature. This treatment largely eliminates TL induced during geological storage (we will call this natural TL), particularly that corresponding to peaks I through V.

Most TL measurements were taken on the CON-RAD model 5100 reader which uses constant current in the planchet.

RESULTS

a) Response to Gamma-Rays

Figure 1 shows typical glow curves and heating cycles for these experiments. The shape of the glow curve is largely insensitive to different pre-irradiation annealings, or cooling rates, although some heat treatment must be given to eliminate the natural TL.

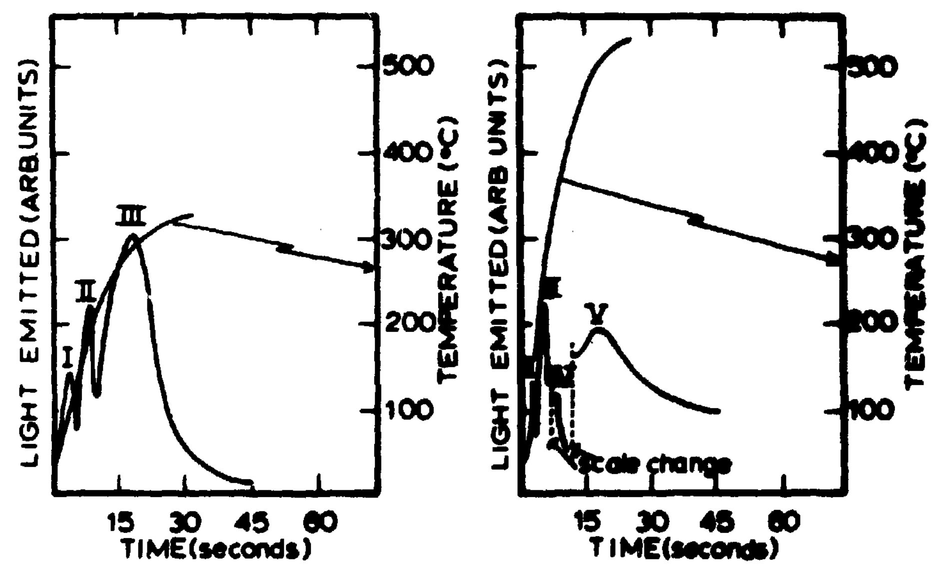

Fig. 1
Typical glow curves of fluorite for the two different heating cycles after a 100 R (left) and 10 kR (right) exposure to Cs-137.

Since peaks II and III are the important ones for dosimetry we concentrated on these peaks. Their heights as functions of exposure are shown in Fig. 2 where we plot TL/R against exposure, since this form is most easily read. For peak II we see that response is initially linear to about 3 kR, then supralinear to about 100 kR, and finally saturates beyond this value. Glow peak III is different; it responds linearly to about 200 R, then less than linearly to saturate at about 100 kR.

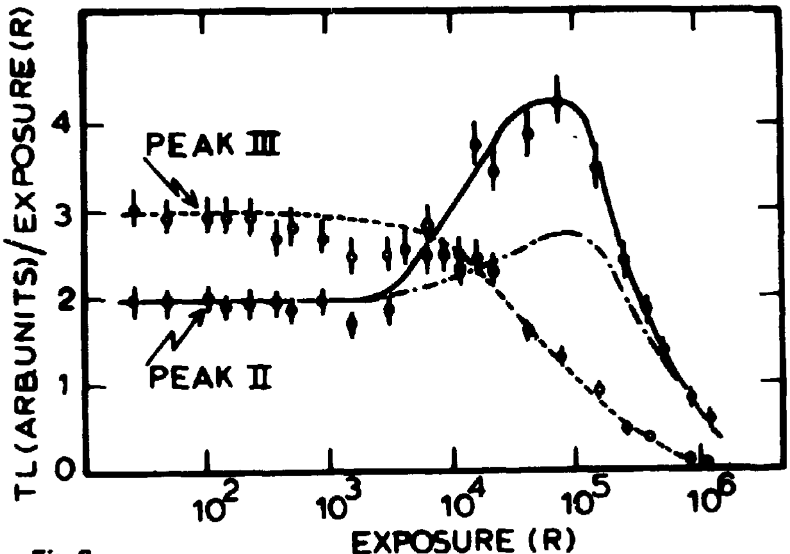

Fig. 2
TL/R as a function of exposure for peaks II (black circles) and III (open circles). The dashed line is the best fit obtained using eigther the traps creation or the competing traps model for peak III. The solid and the dot-dashed lines are the best fits obtained using the traps creation and the competing traps model for peak II, respectively. The competing traps model was applied in a restricted form.

Supralinear response in peak III can be obtained, however, if the pre-annealing is varied from the normal one. Figure 3 demonstrates the effect of pre-annealing for 10, 30, and 60 minutes at 600°C in the place of the normal 10 minutes at 580°C. After 10 minutes at 600°C the response is much as Fig. 2. Annealing for 30 minutes reduces the overall sensitivity, but the peak now demonstrates a slight supralinearity, as shown in the middle curve of the figure. Annealing for 60 minutes further reduces the sensitivity and increases the supralinearity, as seen in the bottom curve. Peak II on the other hand remains supralinear, but displays a decreasing sensitivity similar to that of peak III.

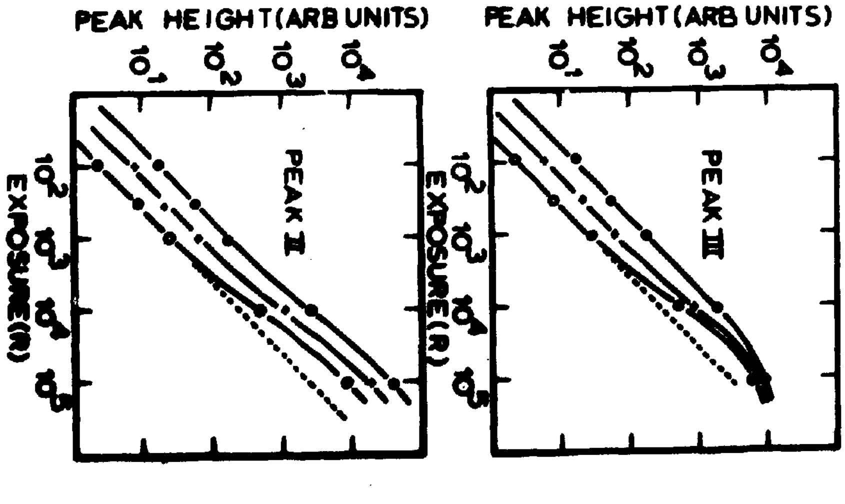

Fig. 3
Peak height as a function of exposure for samples pre-annealed at 600°C for 10 minutes (black circles), 30 minutes (crosses) and 60 minutes (open cicles). The dashed line represents linear response.

b) Sensitization

Some TL phosphorus irradiated to exposures able to cause supralinearity present an increased sensitivity to low exposures, once the high exposure TL is erased thermally. Such an increase in sensitivity is called sensitization[5]. In dosimetry LiF:Mg a direct correlation was found between supralinearity and sensitization.

Our samples exhibited a sensitization effect shown in Fig. 4. The samples were given the exposure shown on the ordinate, then annealed 15 minutes at 400°C to empty traps corresponding to peaks II and III. Before final read out they were irradiated to 100 R test exposure. The top curve shows that peak III is sensitized by previous exposures larger than about 3 kR. The sensitivity corresponding to 10^6 R previous exposure is close to 2.25 times larger than that corresponding to a previous exposure less than 1 kR. On the other hand peak II does not display a clear sensitization, except a small increase near 10^6 R, as shown by the bottom curve of Fig. 4. Comparison with Fig. 2 shows that the supralinear peak is not sensitized. and vice versa. It is also interesting to note that peak II begins to show its increased sensitivity only when peak III has begun to saturate.

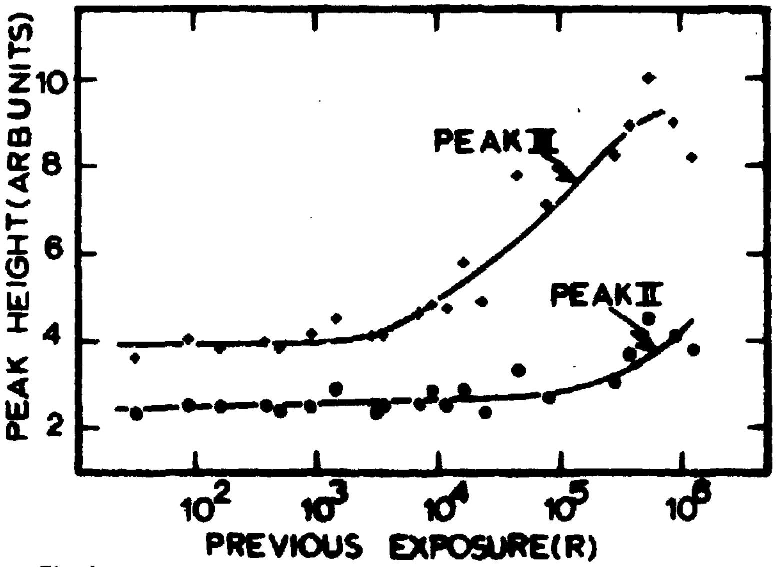

Fig. 4
Peak height induced by a 100 R test exposure as a function of previous exposure. Black circles correspond to peak II and crosses to peak III.

To test the idea that peak III might be a competing trap we measured the sensitivity of peak II with peak III filled, and compared with the case when peak III is empty. Figures 5, 6, and 7 show the results.

In each case the sample was given a previous exposure, as indicated in the figures. A portion of each sample was then given one of two treatments: 1) Annealing at 300°C for 30 minutes to empty II and III traps filled by the previous exposure; 2) Annealing at 175°C for 15 minutes to only empty II traps. The samples were then given a 1,000 R test exposure, and read to determine the effect of III filling on II's sensitivity. The three figures demonstrate clearly that filling III traps causes sensitization of peak II. The dot-dashed curve in each figure is the same as the solid one, except peak II has been eliminated by annealing 20 minutes at 145°C. This dot-dashed curve shows that changes in peak II's apparent height aren't due to overlap with peak III.

The measurements in this experiment were taken on the Harshaw reader with slow, externally controlled heating to resolve the peaks as well as possible. This better resolution indicates that the so called peak II may consist of two superimposed peaks.

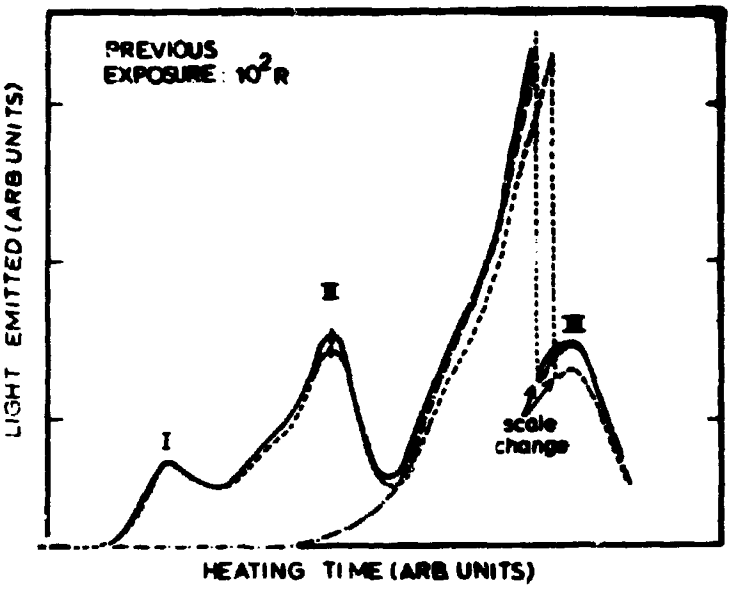

Fig. 5
Glow curves of samples irradiated to 1,000 R test exposure. These samples were given 100 R previous exposure. Solid line: the TL without emptying peak III traps, i.e., with 15 min anneal at 175°C. Dashed line: the TL for emptied III traps, i.e., 30 min at 300°C anneal. Dot-dashed line: Isolation of peak III with 20 min at 145°C anneal after 1,000 R test exposure, but with 15 min at 175°C anneal, before 1,000 R exposure.

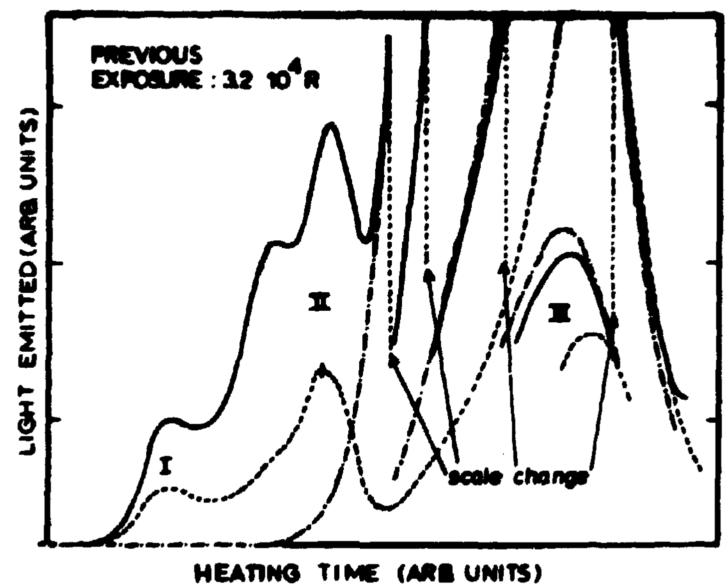

Fig. 6
Same as in Fig. 5 except for a 4 kR previous exposure.

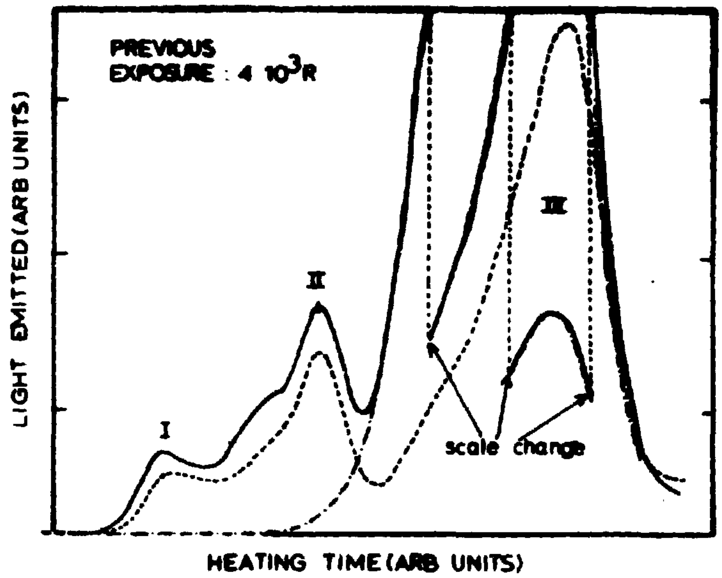

Fig. 7
Same as in Fig. 5 except for a 32 kR previous exposure.

DISPLACEMENTS OF PEAK POSITION

Peak position in the glow curve may change due to high exposure or post-annealing treatment. Figure 8 shows such a displacement of peak III to lower temperature (up to about 10°C) as the exposure increases beyond about 3 kR, while no such effect is observed for peak II. There seems to be some correlation between this effect and supralinearity. A different kind of displacement of peak III was found for sensitized material, while again peak II did not move. In this last case peak III first moved to higher temperature from about 3 kR up to about 15 kR, and then displaced to lower temperature above 15 kR.

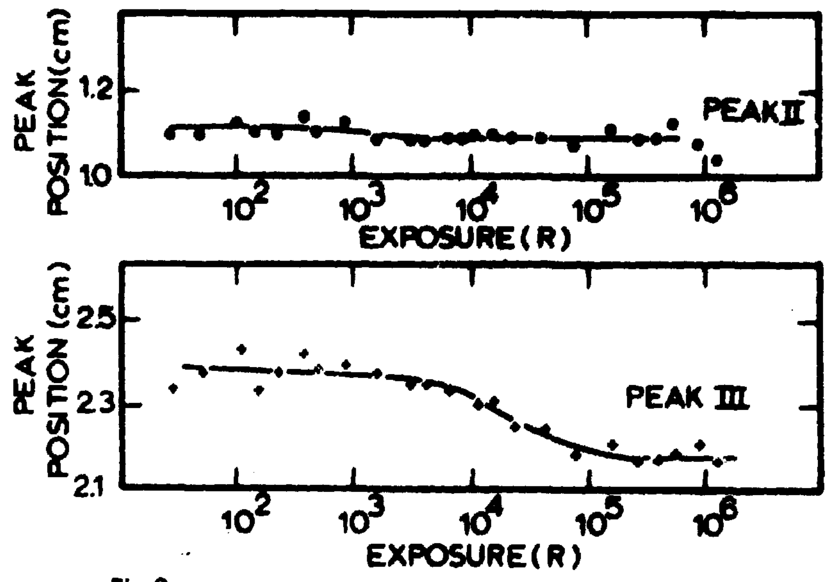

Fig. 8
Peak position as a function of exposure for peaks II and III.

In many instances the peak position shifts as the time of post-annealing increases. This effect will be discussed elsewhere[6].

MODEL CALCULATION

Cameron, Zimmermann, and Bland[1] proposed a mathematical model in which it was assumed that the radiation creates additional traps, giving rise to supralinearity. The principal argument against the model was the fact that the "created" traps appeared physically identical to the original traps. This seemed like an improbable coincidence. The competing traps model[7] already mentionned was next proposed.

The traps creation model predicts a TL proportional to

$$L(R) = [N_o \beta (e^{-\beta R} - e^{-\alpha R}) + N_F (\alpha(1-e^{-\beta R}) - \beta (1-e^{-\alpha R}))] / (\alpha - \beta) \qquad (1)$$

where L(R) is the number of filled traps at exposure R, N_o is the initial number of traps, N_F is the maximum number of traps, α is the probability constant for the creation of traps, and β is the probability constant for the filling of traps.

The competing traps model predicts a TL proportional to

$$L(R) = N_F (1 - e^{-\gamma R}) - N_{oc} (1 - e^{-\delta R}) \qquad (2)$$

where N_F is the maximum of traps to be filled, N_{oc} is the maximum number of competing traps, γ is the probability constant of creating an electron which is captured, and δ is the probability constant of filling a competing trap.

Numerical calculations were carried out to find parameters that fit the observed curves of Fig. 2. For peak III without supralinearity $\alpha = 0$ and $\delta = 0$, and both models give the same expression for L(R). The best fit is obtained for

$N_o = N_F = 1.1$ in the arbitrary units

$\beta = \gamma = 2.7 \times 10^{-5}\ R^{-1}$

For peak II we have

$N_F = 5N_o$

$\alpha = 0.5 \times 10^{-4}\ R^{-1}$

$\beta = 1.1 \times 10^{-5}\ R^{-1}$

in the model of traps creation, and

N_F = 8.5 in the arbitray units

N_{oc} = 0.13 N_F

δ = 2.7×10^{-5} R^{-1}

γ = 5.8×10^{-6} R^{-1}

in the competing traps model.

The theoretical curves are also represented in Fig. 2. The behavior of peak III can thus be fully predicted by both models, while for peak II the model of creation of traps provides a good fit, but the other one does not. This is due probably to the fact that we assumed only peak III traps as competing traps. The effect of deeper traps can not be quantitatively considered at this point since data on TL vs. R are lacking.

We also calculated the sensitization factor S/S_0 for peak II where S_0 is the TL reading of a non-sensitized sample after an arbitrarily chosen test exposure, and S is the TL reading of a sensitized one for the same test exposure. In Fig. 9 calculated values of the sensitization factor are plotted as a function of previous exposure. Since in the traps creation model the sets of solutions (α, β, N_0) and (β, α, $N_0\ \beta/\alpha$) are equally good ones as far as TL vs. R is concerned, S/S_0 were evaluated for these two sets. The first set gives the dashed curve, and the second set, the solid curve. Although neither of them predict the measured values, the second set is favored over the first set. The dashed curve in Fig. 10 is the predicted S/S_0 - curve from the competing traps model, which does not fit the experimental curve either, but it is as close as the solid curve to the measured values.

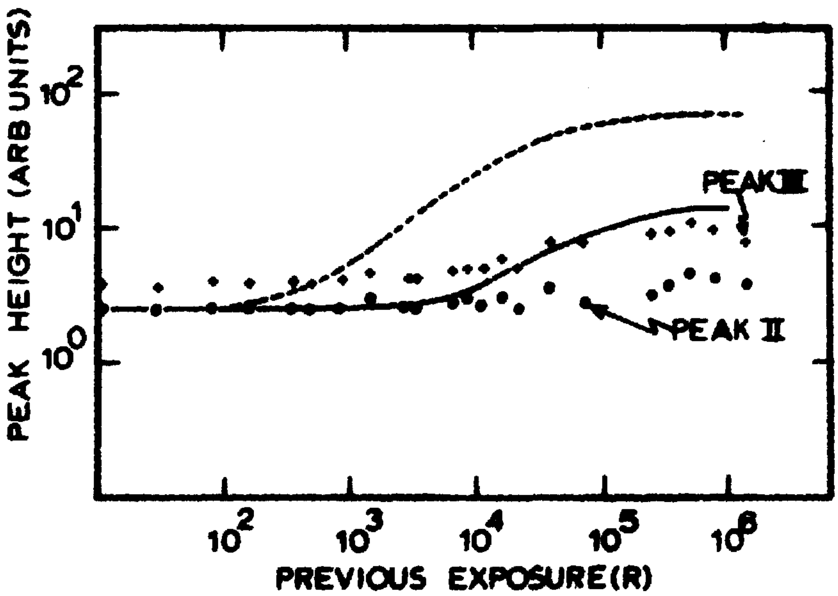

Fig. 9
Sensitization factor as a function of previous exposure. Theoretical curves were obtained using traps creation model for peak II. The dashed curve corresponds to $\alpha = 0.5 \times 10^{-4} R^{-1}$ and the solid one to $\alpha = 1.1 \times 10^{-5} R^{-1}$.

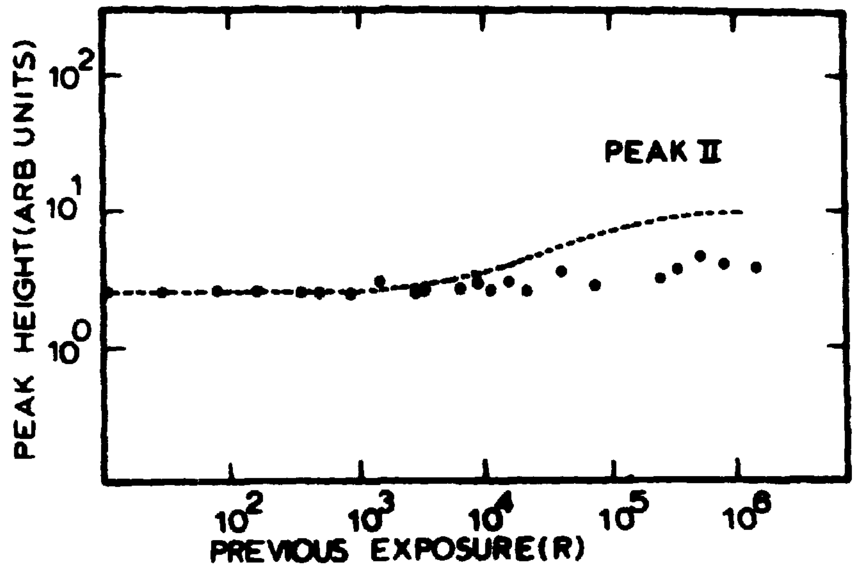

Fig. 10
Sensitization factor as a function of previous exposure. The theoretical curve was obtained using the competing traps model.

Both models predict, however, no sensitization effect for peak III although experimentally a considerable S/S_0 value was found.

CONCLUSIONS

We interpret the above results to favor the model of competing traps[7], although the model must be made more general to explain the data. Basically, the normal competing traps model postulate competitive traps of large cross section which trap charge carriers at relatively low exposures, then saturate, giving other centers a better chance to capture carriers; whence supralinearity is induced. Sensitization could then occur if the intervening treatment erases the low temperature TL, but does not empty the competing traps. We explain the above experiments as follows:

1. Deep competing traps cause supralinearity in peak III, if they are sufficiently emptied prior to irradiation. Ten minutes at 600°C does not sufficiently empty them, while 60 minutes does.

2. The Fig. 3 seems to show a non-influence of peak VI or deeper traps on peak II, since the shape of the TL vs. exposure curve of peak II was not changed by emptying peak VI although TL reading decreased due to longer annealing at 600°C.

3. Since peak III is only supralinear under special conditions (deep traps relatively empty), peak II traps and the deep traps must divide the available carriers during irradiation. Peak III is sensitized, therefore, when the deep traps are full, and this division does not take the carriers away from III traps.

4. Comparing Fig. 2 and Fig. 4 we see that, while peak II that is supralinear is not sensitized (for exposures less than 500 kR), peak III has an opposite behavior. This result contrasts the behavior of TL peaks in TLD-100. This result combined with the one shown in Fig. 3 indicates that peak III competes with peak VI since, both

peak III's sensitization and supralinearity occur when peak VI is filled and no supralinearity takes place for empty (or almost empty) peak VI. On the other hand figures 5, 6 and 7 show a sensitization of peak II when III is full and no sensitization when III is empty, indicating a competition of these two peaks.

To see whether the interim heat treatment influences or not the sensitization of fluorite, experiments are in progress wherein the interim annealing temperatures are varied from 300, 400 to 500°C, for times varying between 0 and 120 minutes for each temperature. The preliminary result indicates that there is no marked interim annealing effect, meaning that the behavior of peaks II and III is not essentially due to such a treatment, except for a decrease in sensitivity of both peaks for higher temperature as well as longer heating.

5. The displacement of the position of peak III in Fig. 8 seems to be correlated with the way the TL response behaves when the fluorite is irradiated to high exposure. If a continuous distribution[6] of peak III traps (in trap depth) is assumed, Fig. 8 indicates that high exposure predominnantly detroyes the deeper traps.

6. It should be noted that glow curves obtained with a very low heating rate (Figs. 5, 6, and 7) show a new peak between I and II not observed with faster heating rates.

7. Fitting peak III curve in Fig. 2 requires adjustment of one parameter, namely, β in Eq. (1) and γ in Eq. (2). To fit peak II curve we have to note, however, that in creation of traps model the parameters a, β and N_o/N_F must be adjusted independently of β-value found for peak III. Now in the case of the competing model, assuming that the supralinearity of peak II, is due to peak III, γ-value found for peak III must be used, therefore only two parameters δ and N_F/N_{OC} are left free to be varied. Thus, although the creation of traps model appears to give a better fit, we cannot be sure that this model is favored mainly because of the results shown in Figs. 5, 6 and 7.

In short, Figs. 3, 5, 6 and 7 favor the competing traps model, but, numerical results in Fig. 2 favor the creation of traps model.

ACKNOWLEDGEMENT

We are indebted to Dr. Michael R. Mayhugh for valuable discussions, to Departament of Biology of the University of São Paulo and Hospital A.C. Camargo for making available their Cs-137 and Co-60 sources, respectively, for irradiation of materials used in this work.

RESUMO

A resposta termoluminescente da fluorita brasileira e raios-gama de Cs-137 foi estudada, tendo em mente tanto a compreensão do fenômeno de supralinearidade como a utilização desta fluorita na dosimetria de radiação.

Fluorita virgem foi pré-recozida a 580°C durante 10 minutos seguido de 400°C por duas horas e depois irradiada a diferentes exposições entre 25 R e 1,2 MR. A resposta do pico II de emissão (temperatura da panelinha 180°C) é linear até de 3 KR, além do qual torna-se supralinear e finalmente satura a cêrca de 300 KR. Sob estas condições, a resposta do pico III de emissão (temperatura da panelinha 290°C) não é supralinear e a saturação é atingida mais depressa, a cêrca de 100 KR.

A correlação entre a resposta supralinear e sensibilização foi, também, estudada. Amostras irradiadas com diferentes exposições, como acima, foram recozidos após a irradiação, por 15 minutos a 400°C e depois irradiadas a 100 R. O pico III apresentou uma resposta sensibilizada para uma exposição prévia superior a 3 KR, enquanto que o pico III ficou sensibilizado muito pouco, e isto sòmente para exposição prévia perto de 100 KR. Segue-se que entre a sensibilização e a supralinearidade dêsses 2 picos, não há correlação.

Entretanto, o pico II é sensibilizado quando o recozimento pós irradiação é feito a 175°C no lugar de 400°C, tendo com isto eliminado sòmente os picos I e II, e não I, II e III. Do mesmo modo a resposta supralinear pode ser obtida do pico III quando o fósforo virgem é recozido a 600°C por tempos superiores a 10 minutos.

Ésses resultados são qualitativamente explicados pelo modêlo que postula a existência de armadilhas em competição, embora êste modêlo deva ser aplicado numa forma ligeiramente modificada. Outros modelos existentes não parecem concordar com os resultados experimentais.

RÉSUMÉ

La réponse thermoluminescente de la fluorite brésilienne aux rayons- α du Cs-137 fut étudiée en ayant présent à l'esprit aussi la compréhension du phénomène de supralinéarité de même que l'utilisation de cette fluorite en dosimétrie de radiations.

La fluorite vierge fut prérecuite à 580°C pendant 10 minutes puis à 400°C pendant 2 heures et après irradiée en diffèrentes expositions entre 25 R et 1,2 MR. La résponse du pic II de l'emission (tempèrature de la petite coupe étant 180°C) est linéaire jusqu'à environ 3 KR, au-de-lá elle est supralinéaire et finalement est saturée aux environs de 300 KR. Dans les mêmes conditions la résponse du pic III de l'emission (temperature de la petite coupe 290°C) n'est pas supralinéaire et se sature bien plus rapidement, et cela aux environs de 100 KR. La corrélation entre la résponse supralinéaire et la sensibilisation fut également étudiée, les échantillons irradiés en différentes expositions comme ci-dessus furent recuits après irradiation durant 15 minutes à 400°C puis irradiés à 100 R. Le pic III présenta une résponse sensibilisée par une exposition anteriéure supérieure à 3 KR, alors que le pic II resta très peu sensibilisé; il l'est seulement par une exposition antérieure proche de 100 KR. Il s'ensuit que entre la supralinéarité de ces 2 pics il n'y a pas de corrélation.

Cependant le pic II est sensibilisé lorsque le recuit post-irradiation est fait à 175°C au lieu de 400°C, de plus ne sont éliminés que les pics I et II et non pas le pics I, II et III. De la même manière la résponse supralinéaire peut être obtenue du pic III lorsque le phosphore vierge est recuit à 600°C pendant un temps supérieur à 10 minutes.

Ces resultats sont qualitativement expliqués par le modèle postulant l'existence de pièges en compétition, bien que ce modèle soit appliqué sous une forme légèrement modifiée. Les autres modèles qui existent, ne paraissent pas concorder avec les rèsultats expérimentaux.

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