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PUBLICAÇÃO IEA N.° 253
Novembro — 1971

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UV INDUCED THERMOLUMINESCENCE IN NATURAL CALCIUM FLUORIDE*

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ABSTRACT

Samples of a green variety of fluorite found at Criciuma, Brasil, annealed at 580°C for 10 minutes and then at 400°C for two hours were exposed to 365 nm UV light. The transferred TL from deep trap to lower temperature trap gives rise to a glow curve containing peaks I, II, III', III and IV in a readout up to 400°C. This TL response was measured as a function of UV exposure time t and the result is not a saturation curve, but; TL tends to zero for large t indicating a simultaneous bleaching effect.

The curve of TL vs. the number n of identical cycles in a exposure readout cycle was obtained for different durations of exposure in each cycle, showing that for large n the rate of decrease of log (TL) is independent of the exposure duration. The effect of duration and temperature of pre-annealing on TL transfer under UV exposure as well as the dependence of transferred TL on previous gamma radiation were investigated. Finally a mathematical model is proposed

INTRODUCTION

Schayes et al[1] discussed some of the thermoluminescent properties of M.B.L.E. (Manufacture Belge de Lampes et de Materiel Electronique S.A., Bruxelles, Belgium) natural CaF_2 submitted to a complete heat treatment at 600°C to empty all traps formerly filled through the action of natural radioactivity; subsequently irradiated to γ -(or β- or α) rays, annealed at 400°C (to empty all traps up to number IV) and exposed to light (300 to 500 nm) present TL reading for peaks I to IV, with the exception of peak III, which is displaced to a higher temperature peak referred to as peak III' (~ 275°C). This result was interpreted as a transfer of charge carriers from traps corresponding to peaks V and VI to lower temperature traps.

Wilson, Lin, and Cameron[2] and McCullough and Cameron[3] discussed additional properties, having in mind possible use as a UV dosimeter. The high sensitivity to UV light, the stability of peak III', and the relative mechanical simplicity are considered advantages of natural CaF_2 over other UV dosimeters. Light effects in $CaSO_4$: Mn have been studied for some time[4], and more recently CaF_2: Mn was also suggested as a UV dosimetry system[5].

We have extended the study of thermoluminescent properties of fluorite found at Criciuma, Santa Catarina State, Brasil. This work concerns the effect of UV light on the TL of "green" fluorite.

TL RESPONSE AS A FUNCTION OF UV EXPOSURE TIME

Samples of green coloured virgin fluorite were first annealed at 580°C for 10 min and then at 400°C for 2 hours were used in this experiment. Then for illumination a small amount of the sample was spread out homogeneously in an aluminum pan and exposed to 365 nm UV light, which was obtained with Corning Glass filters 7-37 and 0-52 and Osram HWL-250w

*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.

mercury Lamp. The light intensity at the samples was 12μ w/cm^2. The light and the aluminum pan were enclosed in a box to avoid room light. Since the temperature inside the box reached about 60°C, peak I decayed quickly and we consequently ignore it. Such procedures were repeated for time of exposure varying from I min to 780 hours. The reading of TL response of peaks II and III was carried out in CON-RAD TL reader model 1500, keeping the PMT voltage at 860V. The right hand curve in Fig. 1 is the glow curve of green fluorite irradiated to 100 R γ-rays from ^{137}Cs source, while on the left we have a glow curve of a sample exposed to 365 nm UV light for 6 min. In the last case III' was observed at about 242 ± 4°C with a height much smaller than that of peak III, which appears at ~ 290°C.

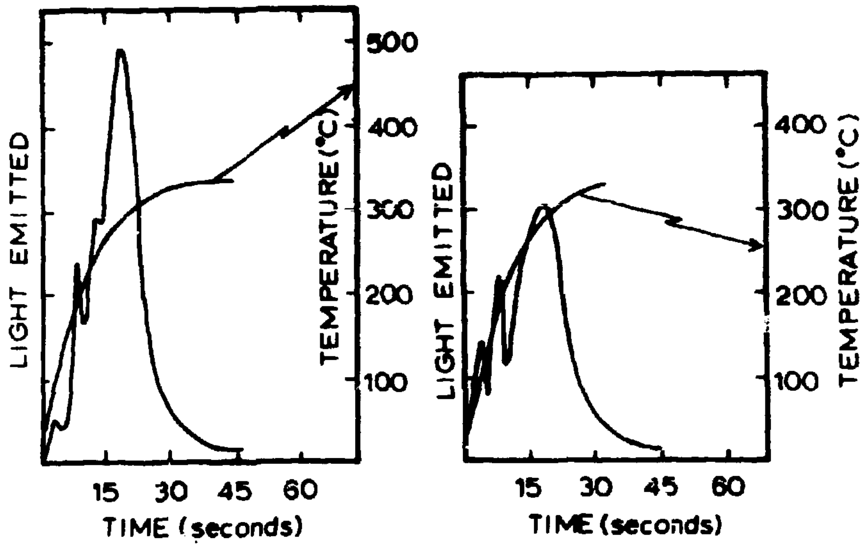

Fig.1
Right side. Glow curve of green fluorite irradiated to 100R γ-rays of ^{137}Cs. Virgin phosphor was preannealed at 580°C for 10 min then at 400°C for 2 hours. Left side - Glow curve of similary treated material exposed to 365 nm UV light for 6 minutes.

Figure 2 shows the TL response vs. exposure time. In contrast to the case of M.B.L.E.

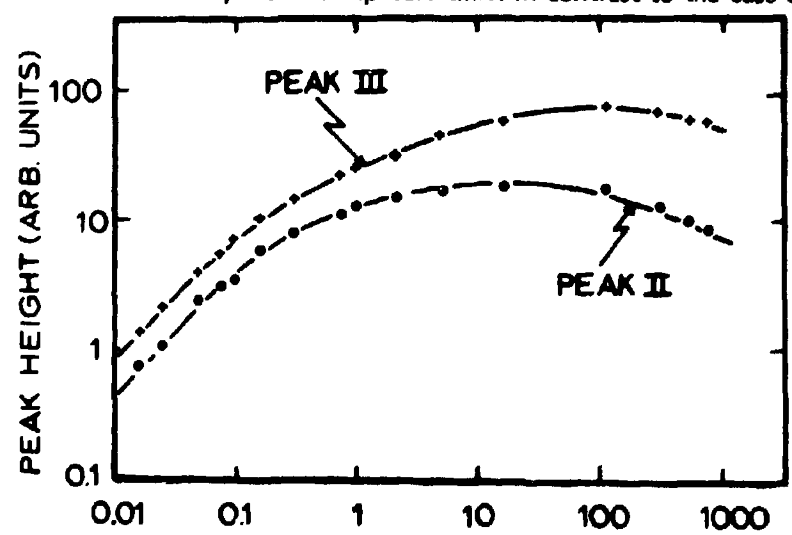

Fig.2 ILLUMINATION TIME (h)
Peak height vs. time of exposure to 365 nm UV light. Primary current I = 0,8 A. Pre-annealing 580°C/10 min plus 400°C/2 hr.

fluorite, we always found peak III to be much more prominent than peak III', therefore we considered only peaks II and III. Linear response is not observed unless as an approximation for very short time interval (of the order of 5 min). the overall behaviour of this curve suggests that the filling of low temperature traps is accompanied by a simultaneous bleaching by UV light. Thus in the beginning, trap filling predominates and peaks II and III grow, but as the traps are filled, bleaching becomes large. Since the population of deep traps decreases as the filling of shallow traps proceeds, there is a time when the rate of both filling and bleaching becomes equal so that finally bleaching predominates, and peaks II and III start to diminish. In the last section a mathematical model is proposed to describe this result.

At this point we should recall that the samples used in this measurement were pre-annealed at 580°C for 10 min. This means that traps corresponding to peaks IV and V were emptied, hence any charge carriers that are transferred must come from peak VI or a deeper one.

Samples treated as described previously, were irradiated to UV light for 0.25 to 130 hours. The planchet current was kept at 1.25 amperes so that peaks IV and V could also be read. Figure 3 presents the heights of peaks II, III, IV and V as functions of exposure time. While peaks II, III and IV have the behaviour described above, peak V only decreases.

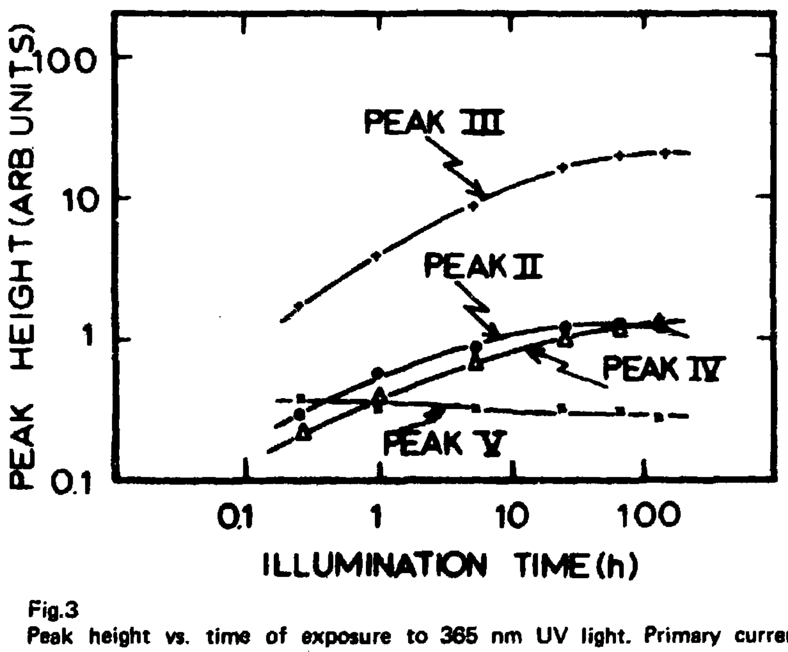

Fig.3
Peak height vs. time of exposure to 365 nm UV light. Primary current I = 1,25 A.

Peak III' could be resolved for short exposure only. As the exposure times becomes longer peak III grows faster and masks peak III'. It was found, however, that peak III' can be better resolved if the fluorite is pre-annealed at a temperature higher than 550°C, because as we will see later high temperature annealing diminishes peak III while peak III' is less affected.

The question of why peak III' is induced by UV radiation but not by X or γ rays is unanswered yet. It is possible that UV light first creates a new kind of trapping center and then fills it by transferring charge carriers from deep traps.

EXPOSURE-READOUT CYCLES

Virgin samples of green fluorite annealed at 580°C for 10 minutes and then at 400°C for

2 hours were subsequently subjected to:

1. Exposure to 365 nm UV light for 15 min;
2. Readout (primary current I = 0.8 A)
3. 400°C anneal for 15 min.

Let us call these three operations one cycle. The first experiment included series of eighteen such cycles. The result is shown in Fig. 4 where (x) indicates the height of peak III and (+) that of peak II. We see that after the fifth cycle log (TL) decreases by a constant amount for each cycle. The slope of this line reflects the rate at which deep traps are emptied by incident photons.

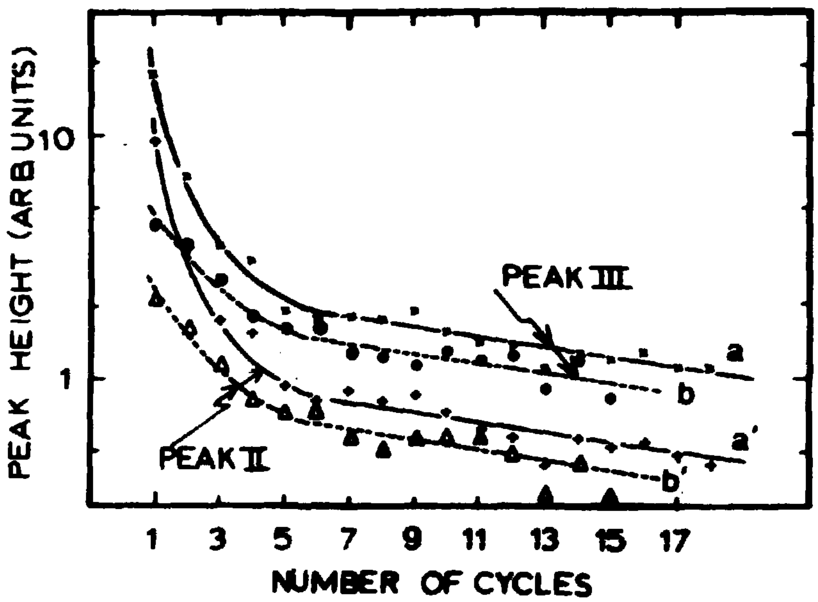

Fig.4
Peak height vs. cycle number. UV exposure for 15 min, readout and then 400°C anneal for 15 min for each cycle. (X) - peak III and (+) - peak II for virgin material; ( ) - peak III and (o) - peak II for material used in the previous measurement, but then irradiated to 10 kR cobalt γ-rays before continueing.

In a second experiment, the material used in the above experiment without further treatment was irradiated to ^{60}Co γ-rays with an exposure of 10^4R. Next, fifteen new cycles were carried out and the result is also shown in Fig. 4, where black circles stand for peak III and white ones for peak II. We see that a high γ-exposure tends to restore initial conditions, probably by refilling deep traps, and that decaying behaviour continues for each cycle.

In the next experiment the annealing at 400°C for 15 min in each cycle was eliminated. We found that it made no difference because each readout emptied the low temperature traps.

Next, we investigated the effect of longer exposure times to UV light in each cycle. In Fig. 5 the results for 5 min, 15 min, 1 hr, 5 hr, and 17 hr exposure are represented for peak III. It is interesting to note that the slope of lines for large numbers of cycles is independent of the cycle's exposure time. The peak height depends, of course, upon the exposure time in each cycle. The peak II has the same behaviour as peak III.

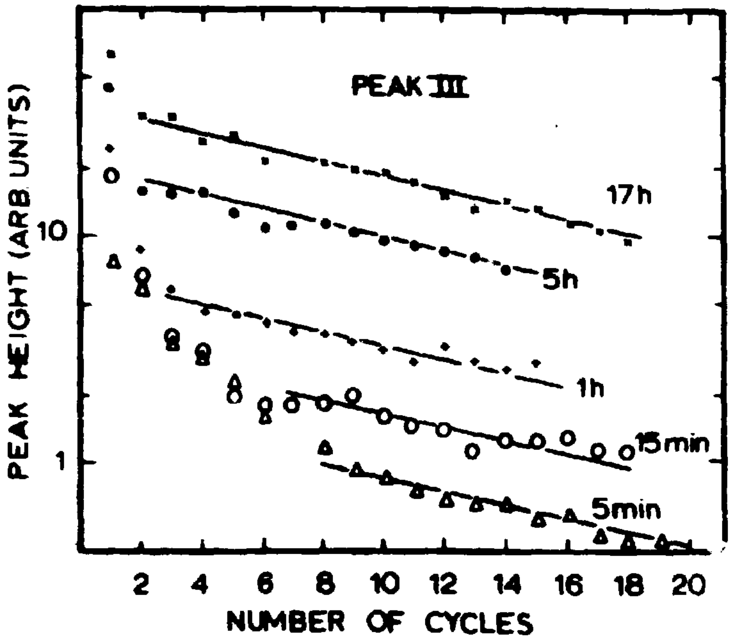

Fig. 5
Peak height vs. cycle number for different exposure time intervals in each cycle.

EFFECT OF DURATION AND TEMPERATURE OF PRE-ANNEALING

It is well known that the TL sensitivity for X- or γ-rays of fluorite decreases as the isothermal pre-annealing temperature is kept above 450°C. For such a high temperature it decreases also with the duration of the heat treatment. Since usually a TL dosimeter is pre-annealed at some high temperature to be used or re-used, we have to investigate the dependence of TL sensitivity to UV light on these factors.

Virgin samples of green fluorite were pre-annealed at 400, 450, 500 and 550°C for 10 and 30 min. For comparison's sake each group of sample was divided into two. One was irradiated to 10 R X-rays and the other one was exposed to UV radiation for 15 min. The way the sensitivity decreases is illustrated in Fig. 6 and 7. The reading for the sample pre-annealed at 400°C was taken as 100%. We see that the sensitivity decreases very fast for temperature above 450°C, and as expected, if the time of annealing is longer, there is a larger decrease of sensitivity. Furthermore, it can be seen that the UV sensitivity drops faster than that for X-rays.

Two causes can account for this drop in the UV sensitivity; (1) the higher the temperature of pre-annealing the smaller is the number of electrons left in the deep traps that contribute to transferred TL, (2) the annealing may thermally damage traps corresponding to peaks II and III. In fact, as we already mentioned, peak III' suffers less heat effect than peak III.

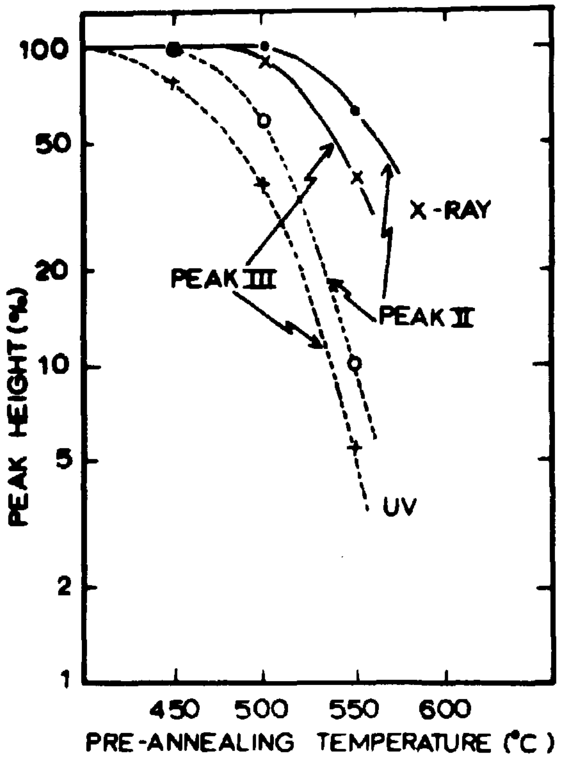

Fig. 6
Sensitivity decrease with pre-annealing temperature for a 10 min annealing. Normalized to TL response for 400°C anneal.

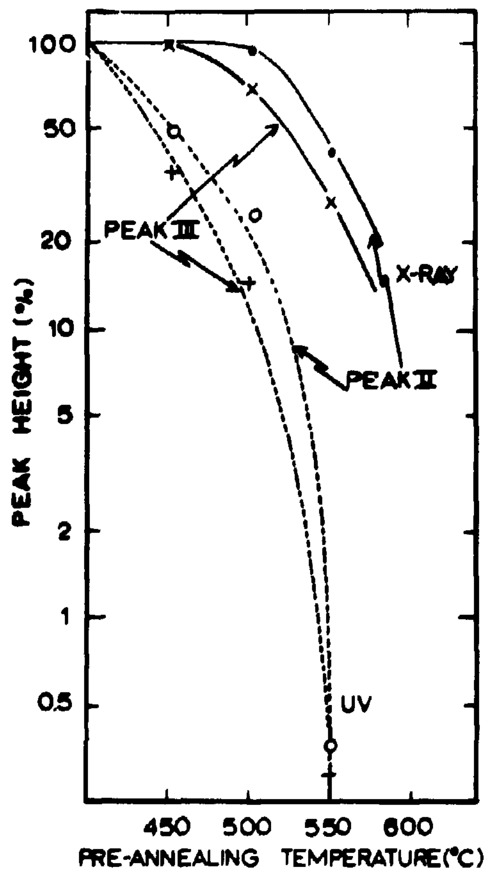

Fig. 7
Sensitivity vs. pre-annealing temperature for a 30 min annealing. Normalized to TL response for 400°C anneal.

DEPENDENCE OF TRANSFERRED TL ON PREVIOUS γ - EXPOSURE

Samples of fluorite were exposed to cesium γ-rays from 35 R to 10^6R. After usual readout they were annealed at 400°C for 15 min and then exposed to 365 nm UV light for 15 min. The transferred TL of peaks II and III was subsequently read.

Figure 8 shows that previous γ-exposure has no effect on peak II up to about 2 x 10^5R while the peak III height increases steadily starting at ~ 3 x 10^3R. No saturation above 10 kR was observed.

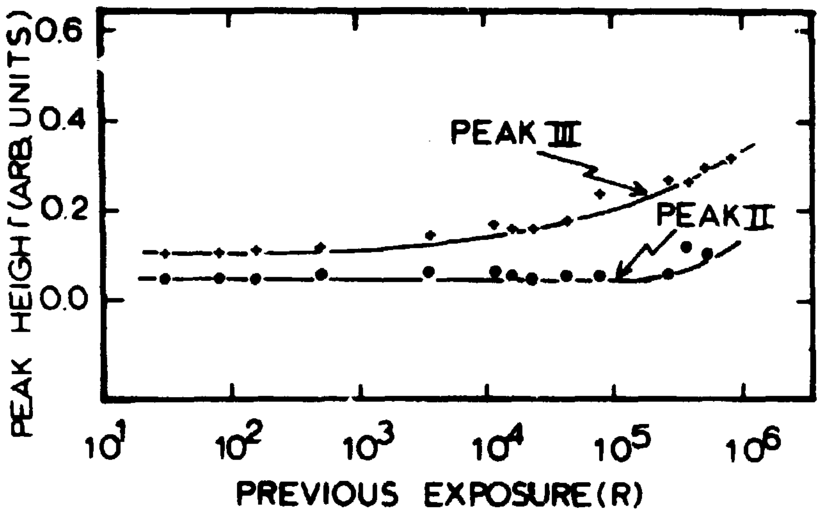

Fig.8
Transferred TL vs. previous γ-exposure.

In connection with this result it was found that the position (peak temperature) of peak II remains unchanged while that of peak III shifts to higher temperature starting at about 3 x 10^3R.

One might think that the growth of deep traps account for the increase in the peak III height as the γ-exposure increases. On the other hand this assumption does not explain why peak II remains constant. It is more reasonable to assume that the sensitization effect on γ-induced TL holds also for transferred TL.

Mathematical model.

We proposed the following model to describe the mechanism involving transferred TL. Let us denote by:

N'_{od} = initial number of filled deep traps (one kind),

N_d = number of deep traps that remain filled after time t of illumination to UV light,

a_d = constant probability factor per unit time for liberation of charge carriers from a deep trap,

N_3 = number of filled traps corresponding to peak III after time t,

β_3 = probability per unit time for the filling of traps III,

N_{3f} = maximum number of available traps III that are filled or not,

α_3 = probability per unit time for emptying of traps III.

Now we assume that

$$\frac{dN_d}{dt} = -\alpha_d N_d \longrightarrow N_d(t) = N_{od} \exp(-\alpha_d t)$$

$$\frac{dN_3}{dt} = \beta_3 (-dN_d/dt)\ (N_{3f} - N_3) - \alpha_3 N_3$$

The solution $N_3(t)$ has the following form

$$N_3(t) = \beta_3 N_{od}\, \alpha_d N_{3f} \exp(-\alpha_3 t + \beta_3 N_{od} \exp(-\alpha_d t)) \int_0^t \exp((\alpha_3 - \alpha_d)t' - \beta_3 N_{od} \exp(-\alpha_d t'))\ dt'$$

N_3 vanishes as t goes to zero or to infinity in agreement with the experimental data. For very small values of t

$$N_3 \approx \beta_3 N_{od}\ \alpha_d N_{3f} t$$

The numerical calculation for determination of parameters is under way and the result will be reported elsewhere.

CONCLUDING REMARKS

In the present work we found peak III' at a temperature below that of peak III. Both peaks can be observed after short exposures to UV light. Peak III being always larger than peak III' its height should be used in UV dosimetry.

The decrease of the height of peaks II and III in each cycle, described in third Section is due to the reduction of the number of electrons captured in traps VI. Therefore the rate at which log (TL) decreases in each cycle measure the rate for emptying of traps VI.

No evidence for direct induction of thermoluminescence by ultraviolet light was found. However the appearance of peak III' for UV light but not for γ-rays can be interpreted as creation of traps III' by UV light and subsequent filling by charge carriers transferred from deep traps.

The linearity of transferred TL with UV light is not observed.

The fluorite has a high sensitivity to UV induced thermoluminescence.

ACKNOWLEDGEMENTS

Thanks are due to Dr. Michael R. Mayhugh for discussions. The ^{137}Cs γ-ray source used in this work belongs to the Instituto de Biociências of the University of São Paulo.

RESUMO

Amostras de fluorita esverdeada, obtida em Criciuma, Santa Catarina, Brasil, recozidas a 580°C por 10 minutos e depois a 400°C por duas horas, foram expostas a luz UV de 365 nm. A TL transferida de armadilhas profundas para as de temperatura mais baixa, dá lugar a uma curva de emissão contendo picos I, II, III', III e IV, numa leitura até cêrca de 400°C. Esta resposta TL foi medida em função do tempo t de exposição a UV e, o resultado não apresenta saturação, mas, um valor que cai a zero para t grande, dando indicaçao de um efeito simultâneao de esvaziamento e preenchimento.

A curva de TL vs. o número n de ciclos idênticos de exposição - leitura foi obtida para durações diferentes de exposição em cada ciclo; ela mostra que para n grande a razão de decréscimo de log (TL) é independente da duração da exposição. O efeito da duração sôbre a transferência de TL devido à luz UV, assim como a dependência da TL transferida com a exposição gama prévia foram investigadas. Um modêlo matemático é proposto no fim.

RÉSUMÉ

Les échantillons de fluorite verte, obtenus à Criciuma (Santa Catarina, Brésil) ont été recuits à 580°C pendant 10 minutes, puis à 400°C pendant deux heures; ensuite ils ont été exposés à la radiation ultraviolette de 365 nm de longueur d'onde. La thermo-luminescence issue de pièges profonds pour des tempèratures plus basses donne lieu à une courbe d'émission comportant les pics I, II, III', III et IV pour une lecture jusqu'à 400°C. Cette réponse TL fut mesurée en fonction du temps d'exposition aux ultra-violets et les résultats ne présentent pas de saturation, mais passent par un maximum avant de décroitre jusqu'à zéro, pour t grand; cela nous indique qu'il y a un effet d'évacuation et de remplissage simultanés.

La courbe de thermoluminescence en fonction du nombre n de cycles identiques de l'exposition et de la lecture fut obtenue pour des temps d'exposition différents pour chaque cycle; elle montre que pour n grand la raison du décrément logarithimique de TL est indépendante du temps d'exposition. L'effet du temps et de la température de prérecuit avant l'irradiation sur la transférence de la TL du à la lumière UV ainsi que la dépendance de TL transfèrée avec une exposition gamma antérieure, furent étudiés. Nous avons proposé un modéle mathematique pour cet effet.

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