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Annealing Cycle Effects on the TL Sensitivity of $\text{CaF}_2:\text{Tm}$ (TLD-300)

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Several thermal procedures have been studied to obtain the highest sensitivity with the lowest standard deviation. A thermal annealing at 400°C for 2 h has been found to be the best. It seems, however, that different thermal procedures suggested by other workers could be attributed to the different heating and cooling rates in the annealing procedures themselves.

1. Introduction

In view of the wide use of thulium activated calcium fluoride thermoluminescence dosimeters, we have investigated the effect of the annealing procedures on the sensitivity of this material. The dosimetric characteristics of this phosphor have already been studied in some papers.⁽¹⁻⁴⁾ The most important property of this material is the presence of two well separated glow peaks (peaks 3 and 5) which respond in different ways to low and high LET radiations.^(5,6)

Since the annealing procedure is always a very important parameter in thermoluminescence dosimetry and various thermal treatments have been reported in the scientific papers,^(1,2,4) our aim is to find the best thermal treatment which allows the highest sensitivity with the lowest uncertainty and maintains the individual calibration factors of the dosimeters with re-use. In the present paper we also report our experiment on the possible changes of the previously given parameters without and with thermal treatment between successive irradiations. The effect of a low-temperature annealing in addition to a high-temperature has also been investigated.

2. Materials and Methods

To evaluate the thermoluminescent emission from irradiated $\text{CaF}_2:\text{Tm}$ ribbons, purchased from Harshaw Chemical Company, U.S.A., a manual Harshaw Model 2000, coupled with a glow-curve analyser Model 2080, was used. With this instrumentation it has been possible to determine the total light as the integral of the glow-curve area, partial glow-peak areas, and glow-peak heights. A linear heating rate of about 10°C s⁻¹, from room temperature to about 300°C was used, and the total TL light itself was integrated in the temperature range from room temperature (~24°C) to 290°C. The readout time was 40 s.

For each experimental point ten dosimeters were used. A prompt readout was carried out at the end of the irradiation time. The annealing oven was a Vinten Annealing Facility, Model 622/E, which allows programmable temperature treatments. The annealing procedure consists of a heating cycle from room temperature to the desired annealing one. The temperature was kept constant for a given time; then

cooling at a slow rate (about 6 h) took place until room temperature was reached. The irradiations were carried out using a ⁹⁰Sr-⁹⁰Y β radiation source inserted in an automatically timed exposure apparatus from Alnor. The doses given are reported below for each experiment.

Since TLD-300 has a glow-curve composed of three peaks well resolved (peaks 2, 3 and 5 following the Lucas nomenclature), individual calibration factors for each of the three peaks of each sample, as well as for the total light, were determined. The individual calibration factors for each peak were determined for individual detectors at any annealing temperature as

$$f_{ik} = \frac{\sum_{i=1}^n k \frac{X_{ik}}{n}}{X_{ik}}$$

where X is the peak height or the peak area, k is the peak number, i the identity index for each sample, and n the number of detectors.

A similar expression was used to determine the calibration factor for the total light of any detector. A light source correction for changes in the PM tube sensitivity has also been taken into account. The sensitivity factors at any annealing temperature did not show appreciable variations as a function of thermal treatments. The individual calibration factors were then obtained as an average on the total number of factors.

3. Results and Discussion

To study the behaviour of TLD-300 without external annealing procedures, ten ribbons were irradiated at 1.67, 16.7 and 167 mGy and cycled thirty times at each dose to check the reproducibility of the TL response. Figure 1 shows

Fig. 1. Response of TLDs at different dose levels over thirty cycles of irradiation-readout without annealing.

Fig. 2. Second reading (residual TL light) over thirty cycles of irradiation-readout without annealing.

the results. The data from the second reading are reported in Fig. 2. From Fig. 1 it is possible to observe that a good reproducibility is obtained without external annealing. The TL light keeps itself constant enough during subsequent irradiation/readout procedures. These results have already been partially reported in a previous paper⁽⁵⁾ but the study was not very accurate. At first sight these results could suggest the use of this phosphor without external regeneration, although some growth in response is observed at 16.7 and 167 mGy, while the response decreases slightly at 1.67 mGy.

On the other hand, Fig. 2 clearly shows that the residual TL light (second readout after irradiation) is almost constant, and high for the 167 mGy irradiation level, and for the other two lower irradiations the residual light tends to become less and less with subsequent irradiation/reading cycles. A least square fit of the regression line shows very well the tendency of the second readings in the different cases.

Consequently, it seems to be impossible to use this phosphor without external thermal regeneration. Considering the residual light as background, the determination of the threshold dose, defined as $2\sigma_B S$, where σ_B is the standard deviation of the background and S the phosphor sensitivity, should be affected by the widely scattered values of background itself.

The second part of the experiment consists of trying different temperatures for different lengths of time. Temperatures of 200°C, 300°C and 400°C were used, keeping the phosphors at each temperature for 30 min, 1 h, 1.5 h, and 2 h. The results, shown in Fig. 3, are given as total TL sensitivity in percent. The standard deviation (SD) is plotted in the same way. Each experimental point is the average of ten readings. All dosimeters were irradiated with a test dose of 16.7 mGy.

Plot (a) shows that the sensitivities at 200°C and 300°C are low compared with that at 400°C annealing temperature. The sensitivity at 400°C for 30 min is marginally lower than that for 2 h, while it drops for 1 h and 1.5 h. It is very interesting to compare the corresponding standard deviations (plot b). In fact, the lowest SD is reached at 400°C for 2 h, although it is not much higher at the same temperature for 30 min.

It is thought that the different procedures suggested in Refs. (2,4) could be dependent on slight differences in the

chemical characteristics of different batches as well as in the heating and cooling rate during the annealing procedures themselves. It is possible to explain the difference in sensitivity at 200°C and 300°C. In fact the tail of the high temperature peak extends up to about 350°C, depending on the heating rate used. Thus the 200°C annealing is able only

Fig. 3. Results obtained after different annealing procedures. Plot (a): Sensitivity in percent; Plot (b): Standard deviation in percent; Plot (c): Peak height ratios (H_3/H_5); Plot (d): Threshold dose in μGy .

to transfer some trapped charges from the high temperature traps to the lower ones. These retrapped charges act as memory of previous irradiations and give a fictitious high sensitivity in comparison with that at 300°C. As the annealing time is longer and/or the temperature is higher (i.e. 300°C), the transfer effect is less evident compared with that of erasure. In any event the 200° and 300°C treatments are not satisfactory. The 400°C annealing procedure seems the best, providing the largest distribution of electron and hole trapping sites, at Tm^{3+} , interstitial F^{-1} and substitutional O^{2-} ions.⁽⁶⁾ At the same time, the transfer phenomenon disappears.

Plot (c) shows the peak height ratio behaviour (H_2/H_1) with the various annealing treatments. It can be seen that the peak height ratio is nearly constant at any temperature, with a maximum variation of 10%. The peak height ratio is almost independent of annealing temperature from 200° to 400°C. This behaviour is in good agreement with other results.⁽⁴⁾

In the same Figure, plot (d) shows the dose threshold D_0 at the 95% confidence limit. According to the sensitivity plot (a) the best threshold dose is achieved for 400°C thermal treatment with best values for 30 min and 2 h annealing time.

To check the effect of a fast cooling rate after annealing, the samples were annealed at 400°C for 2 h and then cooled in ventilated air from 400°C to room temperature in 10 min. While the peak height ratio drops by 15% of the value obtained with the slow cooling rate in the oven, the sensitivity drops by 11%. Hence a rapid cooling reduces both peak height ratio and total sensitivity. The discrepancies in thermal procedures among various workers could be attributed to the different cooling rates of the annealing, as already mentioned, but these data are not reported generally. In any event caution should be exercised to ensure the reproducibility of the cooling.

A thermal treatment at 500°C for 1 h has also been attempted. In this case the sensitivity dropped by 14% in comparison with the maximum sensitivity obtained for a 400°C annealing treatment. The 500°C thermal treatment does not only reduce the sensitivity but also the peak height ratio, which is reduced by 14%. Hence the 500°C procedure was found unsatisfactory and has not been studied further.

To check the effect of the low temperature annealing after the 400°C treatment, two different procedures have been

used. The first one was a 2 h treatment at 400°C followed by 2 h at 100°C. In both cases no significant change in the TL sensitivity and the peak height ratio was observed. The glow curve structure is not influenced by the 100°C annealing treatment and therefore it is possible to conclude that a thermal treatment at 400°C for 2 h is adequate for a full erasure of any stored information in the dosimeters.

4. Conclusions

The results obtained in this work are, generally, in good agreement with the results of other workers. The small differences among our data and the data given in different papers could be attributed to various factors such as (i) heating rate during annealing, (ii) cooling rate from annealing temperature to room temperature, (iii) different percentages of chemical impurities.

In any event, a temperature annealing of 400°C seems to be good enough to erase all stored information in the dosimeters. Owing to the different factors mentioned above, the duration of the annealing at 400°C can range from 30 min to 2 h without significant differences in the results. A low temperature annealing, i.e. 100°C for 2 h, following the one at 400°C, does not change the structure of the glow curve, nor does it result in appreciable differences in sensitivity or in the peak height ratio; it follows that a complex annealing procedure is not necessary for this material.

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