EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

TIS-RP/169/PP

5 February 1986

**SOME THERMOLUMINESCENT PROPERTIES OF A NEW
PREPARATION OF $\text{CaSO}_4:\text{Dy}$ PHOSPHOR**

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ABSTRACT

A new batch of $\text{CaSO}_4:\text{Dy}$ sintered pellets from Boris Kidric Institute has been studied. From this study it appears that the new product can be very useful in environmental dosimetry if a simple annealing procedure is performed before irradiation. A pre-readout annealing is also suggested to erase the first peak, which fades very quickly.

To be published in
International Journal of Applied Radiation and Isotopes

1. INTRODUCTION

High sensitivity thermoluminescent materials such as calcium fluoride and calcium sulphate are not tissue-equivalent. They over-respond at low photon energies because of their high Z value. On the other hand, their high sensitivity makes them a very good material for environmental dosimetry applications where the exposure rate is very low and the strong energy dependence of the dose reading can be improved by using suitable filters. It has been pointed out by Lindeken et al. [1] that a negligible fraction of the radiation dose from natural background arises from photons with energies less than 100 keV so that the use of dosimeters without filters is always possible.

Because of the long term measurements in environmental dosimetry, the TLDs have to be very stable, accurate and reliable.

The most popular thermoluminescent materials for environmental dosimetry are $\text{CaF}_2:\text{Dy}$ and $\text{CaSO}_4:\text{Dy}$. Owing to the simplicity of preparation of the latter, this material has a wide diffusion. From time to time the environmental laboratories produce their own calcium sulphate, with slight or sometimes large differences in physical properties from material already available.

The present study concerns measurements on a new batch of $\text{CaSO}_4:\text{Dy}$ sintered pellets, obtained from M. Prokic, Boris Kidric Institute (BKI), Belgrade, Yugoslavia.

2. EXPERIMENTAL METHODS

This study involves making measurements to establish some characteristics of this material, such as annealing, background, sensitivity, short term fading, etc. A Harshaw manual reader has been used throughout the experiment. The heating rate was about $10^\circ\text{C sec}^{-1}$ and the maximum temperature about 350°C .

Glow-curve structure

At the first step the glow-curve structure of $\text{CaSO}_4:\text{Dy}$ from BKI was compared with those of $\text{CaSO}_4/\text{LiF}:\text{Dy}$ and $\text{CaSO}_4:\text{Dy}$ (TLD-900) from Harshaw Chemical Co. The dosimetric properties of the latter two materials are well known [2-5]. Figure 1 shows the three glow-curves.

The glow-curve of the $\text{CaSO}_4:\text{Dy}$ (BKI) shows two well resolved peaks. The first peak has a temperature at the maximum of about 60°C , the second one about 210°C . As expected from the very low temperature of the first peak, the peak itself is affected by rapid fading. The results about fading will be reported later in the paper.

Behaviour without annealing

It has been suggested [6] that this material could be used without any thermal regeneration between readout and subsequent irradiation. To test the behaviour of this material without annealing, four samples were irradiated and read out without any external annealing. A second reading was performed to check the background level as residual TL light. In our case, because no annealing was performed before irradiation, the second reading should be used as only available data to find the threshold dose. The said procedure was repeated twenty times to check any variation in the TL response as well as in the second reading. Two levels of β dose (^{90}Sr - ^{90}Y) from a calibrated β source, Studsvik type, were used: 1.67 mGy and 16.7 mGy respectively. Due to the low temperature peak, the readings were carried out immediately after irradiation - maximum 2 minutes later - to avoid any inaccuracy in the TL response. Table 1 shows the results. From this table it can be seen that the reproducibility is very good over all cycles both for 1.67 mGy and 16.7 mGy; the linearity is also respected. On the other hand the second reading was very stable within each irradiation level, while it increases from the low to the high irradiation level. As the memory of the previous irradiations does not seem to affect subsequent readings, it is obvious at this stage that the material could be used without any external annealing.

To check better the behaviour of the second reading, a set of inhomogeneous irradiations were performed. They were made in the order

they are listed in Table 2. In the same table the first and the second readings are also reported with the associated values of σ . Each point represents the average of four readings. It is relevant to observe the increase of the response when the 1.67 mGy irradiation was performed after that at 33.4 mGy: the percentage difference between the maximum and minimum readings is about 60%. The second reading for high dose levels of irradiation, i.e. 50.1 mGy, represents about 1% of the first reading, whereas for low dose it represents about 15% of the former. Moreover, the responses for low doses seem to be affected by the previous high-dose irradiations. This is evident for group B following group C, as well as for group B following E. The sensitivity values give a clearer evidence of the memory effect.

From the values obtained by this experiment, it is evident that a second reading is not enough to erase all information concerning previous irradiations. To check the effect of subsequent readings, nine readings were performed on the same sample after the first readout. Two dose levels were used and the results are shown in Fig. 2. In the case of 1.67 mGy irradiation, the tenth reading is 3.2% of the first one ($= 100$), while for 16.7 mGy the tenth readout is 0.23% of the first one. It can be concluded that the percent residual TL light after low dose irradiation is always much higher than that after high dose irradiation.

Coming back to the data reported in Table 2: in order to find the lower detection limit D_{LDL} [7], defined at the 98% confidence level as $3\sigma/S$, where S is the sensitivity expressed as nC/mGy, we used the standard deviation of the mean second readings instead of the standard deviation of the mean background, having considered the second reading as the zero dose reading.

Using the mean value of sensitivity and the σ of the mean second reading (see Table 2), we get $D_{LDL} = 400 \mu\text{Gy } ^{90}\text{S}-^{90}\text{Y}$ beta equivalent that is not a really good value, especially for environmental dosimetry applications. Obviously we can conclude that the use of this material without any external annealing treatment will fail to produce real information about the environmental dose levels. Figure 3 clearly shows the residual TL glow after the second readout. Let ϕ_1 , ϕ_2 and ϕ_3 be the glow-peak areas as indicated in the figure, and ϕ_3' the

residual glow-peak areas after the second reading. For a dose level of about 8.4 mGy the ratio $\phi_3/\phi_3' = 1.6$, and this means that 37% of the third peak is still available.

Annealing

A 400°C annealing temperature, the normal one for such types of phosphor [2,4,5], for 1 hour was used. After cooling to room temperature, a set of ten dosimeters were read out in the manual reader and the background was measured. The mean background level or zero dose reading was equivalent to about 2 µGy. The standard deviation (1σ value) of the zero dose reading of the unexposed dosimeters was 0.6 µGy. After that the same dosimeters were irradiated at 16.7 mGy and read out immediately to check if any sensitivity change occurs with annealing: the sensitivity was almost the same and in good agreement with the sensitivity calculated during the procedure without annealing. Now, the threshold dose D_{LDL} is given by 1.8 µGy. This value is in very good agreement with the data given in Ref [7] for the $CaSO_4$ system. Furthermore, according to the IEC protocol [8], the detection threshold for detectors used in environmental dosimetry must not exceed 10 µGy for a minimum period of use of seven days, or 30 µGy for thirty days of use. Moreover, the following relation has to be fulfilled:

$$t_n \cdot \sigma_{H_e} < H$$

where H is one of the values already given (10 or 30 µGy), σ_{H_e} is the standard deviation of $\bar{H}_e$ (mean of the evaluated dose of the unirradiated dosimeters), and t_n is the Student's t for n-1 degrees of freedom, with n equal to the number of dosimeters used. In our case $n = 10$ and $t_n = 2.26$, with $\sigma_{H_e} = 0.6$ µGy. So we get from the previous relation 1.4 µGy $< H$. The performance requirement is then fulfilled.

Comparing this value with that obtained without annealing, it is evident that external annealing is necessary to achieve good results in environmental monitoring. On the other hand, the lower detection limit D_{LDL} may vary from day to day. Due to this, the D_{LDL} value was checked over 25 times of repeated exposures and annealings. The results are plotted in Fig. 4. The average D_{LDL} over 25 runs was found to be 0.85 µGy, with a standard deviation of 47%.

Short term fading and pre-readout annealing

The low temperature peak fades very rapidly and it is necessary in such a case to use pre-readout annealing to erase the first peak. Before carrying out the pre-read annealing, a short term fading was studied. Due to the rapid fading of the first peak, it seems appropriate to use a pre-readout annealing to erase it. A thermal treatment of 100°C for ten minutes is good enough to erase the first peak. The sensitivity in this case is only 20% less than that without pre-readout annealing. Figure 5 shows both the fading effect and the glow-curve effect pre-readout annealing.

3. CONCLUSIONS

The new $\text{CaSO}_4:\text{Dy}$ from BKI satisfies the general requirements for a phosphor used for environmental measurements. The only precaution that has to be taken is to apply an external annealing which produces a very low threshold dose. Also, pre-readout annealing is necessary before readout because of the strong fading of the first peak.

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FIGURE CAPTIONS

Fig. 1 Glow-curves of three different preparations of dysprosium activated calcium sulphate.

(A) CaSO_4/Dy from BKI

(B) $\text{CaSO}_4/\text{LiF:Dy}$ from Harshaw

(C) $\text{CaSO}_4:\text{Dy}$ (TLD-900) from Harshaw.

Fig. 2 Residual TL light, in percent, after subsequent readings. TL light from first reading = 100.

Fig. 3 Glow-curves after first and second readings. ϕ_1 , ϕ_2 and ϕ_3 are the glow-peak areas. ϕ_3' is the residual glow-peak area.

Fig. 4 D_{LDL} of $\text{CaSO}_4:\text{Dy}$ (BKI) during the runs of repeated exposures and annealing procedures.

Fig. 5 Glow-curve shape at different times elapsed since irradiation and after pre-readout annealing at 100°C for 10 minutes.

TABLE 1

Mean thermoluminescent readings for four $\text{CaSO}_4:\text{Dy}$ pellets,
mean second readings, and σ in per cent

Cycle	1.67 mGy				16.7 mGy			
	Mean reading	1 σ	Mean second reading	1 σ	Mean reading	1 σ	Mean second reading	1 σ
	nC	%	nC	%	nC	%	nC	%
1	143.3	5	2.98	13	1320	1	13.7	12
2	141.7	5	2.93	23	1300	3	13.1	8
3	138.4	4	2.98	8	1360	2	13.4	6
4	139.6	1	2.73	9	1360	1	14.1	12
5	138.2	2	3.08	5	1360	1	14.5	13
6	140.4	4	2.99	15	1330	2	18.	10
7	138.4	3	3.24	3	1350	4	18.2	9
8	140.7	3	3.04	11	1360	4	18.1	10
9	144.3	11	2.64	14	1400	3	19.	17
10	142.1	4	2.75	8	1330	7	21.1	12
11	143.1	2	2.83	12	1310	2	20.8	10
12	142.5	1	2.91	15	1330	3	20.	10
13	147.	1	2.96	18	1300	3	21.5	7
14	146.1	7	2.63	13	1340	3	21.2	2
15	143.7	2	2.75	24	1330	1	24.8	16
16	142.2	2	3.17	33	1410	3	26.1	4
17	128.1	5	2.66	26	1430	3	21.2	16
18	138.1	3	2.67	10	1380	2	20.6	12
19	137.7	3	2.71	14	1430	4	19.1	8
20	136.	5	2.87	18	1350	7	18.6	10
Mean	140.6		2.88		1358		18.9	
1 σ (%)	3		6		3		19	

TABLE 2

Inhomogeneous irradiations.
TLDs received the irradiations in the order they are listed

Group	Dose mGy	Mean 1st reading nC	σ %	Mean 2nd reading nC	σ %	Sensitivity nC/mGy
A	16.7	1320	2	20.9	9	79
	16.7	1360	4	18.1	10	81
	16.7	1410	2	25.4	5	84
	16.7	1350	6	17.2	11	81
	16.7	1360	5	19.3	10	81
B	1.67	144.4	3	14.3	13	86
	1.67	160.2	6	15.3	23	96
	1.67	147.3	3	8.4	4	88
C	33.4	2730	3	29.	7	82
	33.4	2590	3	39.8	13	78
	33.4	2660	4	43.1	14	80
	33.4	2580	5	42.4	16	77
B	1.67	221.7	21	23.1	25	133
	1.67	147.7	7	12.9	31	88
	1.67	140.	4	10.	18	84
D	8.35	671.8	4	16.5	18	81
	8.35	706.6	3	18.1	22	85
	8.35	707.	2	16.9	15	85
	8.35	710.5	3	14.6	14	85
E	50.1	4000	3	35.7	6	80
	50.1	4000	1	40.7	3	80
	50.1	4030	2	43.5	4	80
	50.1	4020	1	49.8	4	80
B	1.67	179.2	6	25.8	6	107
	1.67	164.8	4	16.5	21	99
	1.67	154.3	4	11.5	30	92
Average					24.2 $\pm$ 12.1	84 $\pm$ 20

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5