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DEVELOPMENT OF A SOLID STATE DOSIMETER BASED ON THERMOLUMINESCENT $CaSO_4$:Dy CRYSTALS *

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A new technique to obtain a solid state dosimeter based on the thermoluminescent properties of $CaSO_4$: Dy is described. It consists of preparing pellets by cold pressing the mixture of $CaSO_4$: Dy as the active TL material and NaCl as the binder. The method of preparation and main dosimetric characteristics such as reproducibility and linearity are studied. A filter combination for achieving an energy independent response for the dosimeter is studied and a filter configuration giving a nearly energy independent response from 20 keV to 1.25 MeV was obtained. The dosimetric characteristics from the point of view of introducing this dosimeter into the routine personnel monitoring are discussed.

1. Introduction

Thermoluminescence dosimetry is now widely used for personnel and environmental monitoring. Especially the lithium fluoride phosphor has attracted great interest because of its nearly tissue-equivalent response and its good long-term stability. In recent years great progress has been made in the development of new highly sensitive phosphors with low fading, e.g. CaF_2: Dy and $CaSO_4$: Dy, which are particularly favourable for application for low-dose measurements [1-5].

Naturally occurring CaF_2 mineral shows a strong TL response [6-8] attributed to the rare-earth impurities present in this mineral. The natural CaF_2 can, therefore, be used as a TL dosimeter. It has, however, three main disadvantages: (a) it has an energy dependent response like the film dosimeter [9], (b) it is sensitive to light due to the presence of photochromic centres, (c) as it occurs naturally, the impurity contents are not controlled or evenly distributed in the sample. The type and amount of impurities also, vary from sample to sample. Thus natural CaF_2 is not very suitable for use as a TL dosimeter, when one has to use the dosimeter in large scale and for environmental and personnel monitoring.

Work on laboratory grown rare-earth doped $CaSO_4$ samples shows that $CaSO_4$: Dy and $CaSO_4$: Tm give the best TL response [10]. These phosphors can easily be prepared in the laboratory [10-12]. They have a better TL response than CaF_2 (natural) and do not show any sensitivity to visible light [13]. A disadvantage, is an energy dependent response due to a high Z. It was found by many researchers that a proper combination of filters can give a nearly energy independent response and still retain the advantage of the higher sensitivity. Filter combination studies on the film dosimeter have been carried out by others with good results [14].

With this in view, we conducted a study on the possibility of introducing a new TL dosimeter for the environmental and personnel monitoring in order to replace ultimately the present film badge system. This is a report of the various aspects of this study.

2. Experimental procedures

2.1. Phosphor preparation

The method used for the preparation of the rare-earth doped $CaSO_4$: Dy phosphor consists mainly in obtaining a solution of the calcium sulphate and the rare-earth sulphate in excess of concentrated sulphuric acid. Various workers have used different calcium salts as starting material. The methods used by them differ from each other, only in small details [10,13].

The starting material used in this laboratory is the commercially available calcium carbonate (Baker Analysed Reagent). Specpure dysprosium oxide (99.999% from Materials Research) and concentrated sulphuric acid (from Merck) were used for this preparation. Dysprosium oxide is mixed with calcium carbonate in the ratio of 15 mg to 8.093 g. This proportion has been found to give the optimum concentration of dys-

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prosium in calcium sulphate phosphor, to give the best TL response [12]. This powder mixture is slowly added to a predetermined amount of concentrated sulphuric acid (250 ml) and allowed to dissolve. A saturated solution thus formed is heated at slightly elevated temperature to achieve complete dissolution of the calcium sulphate formed in this reaction. This results in a clear solution of $CaSO_4$: Dy in sulphuric acid. The solution is filtered through a millipore filter to remove the undissolved impurities. It is then evaporated slowly to dryness in a PVC fume-hood at 300°C. The resulting sample is in the form of microcrystals. The sample is then washed repeatedly with distilled water to remove traces of acids and then heated again to dryness. Finally the crystals were pulverized and sieved through 80 to 200 mesh tyler screens to be used in the experiments. Samples from a freshly prepared batch are given a heat treatment for one hour at 300, 400, 500 and 600°C. Ten aliquots from each treated batch were exposed to 275 mR from a ^{60}Co source and read out in a Harshaw Thermoluminescent Detector model 2000 A, with fixed settings of preheat and heating rate by using a fixed amount of powder. The high voltage used for the photomultiplier was 850 V. The data obtained are given in table 1.

It was observed that the response increases with temperature of treatment. Treatment of the phosphor at still higher temperatures could destroy the TL [13] and increase the intrinsic UV sensitivity [15], due to partial conversion of $CaSO_4$ to CaO. The heat treatment is therefore fixed to a one-hour heating at 600°C.

The amount of phosphor needed for the whole study is around a few hundred grams and the present facility allows preparation of only a few grams at a time. It is therefore essential to check the reproducibility of the phosphor preparation. Ten aliquots taken from each batch were exposed to a known exposure as given above and the results are shown in table 2. The individual δ values of various batches illustrate the uniformity of the impurity distribution and the average value for all batches shows a reproducibility within 10%.

Table 1
Effect of primary heat treatment on TL response of $CaSO_4$: Dy exposed to 275 mR and treated for 1 h.

Batch no.	Temp. of treatment (°C)	Average TL output $\pm\delta$ ($\times 10^{-10}$ A)
1	[a]	40 ± 2.6
2	300	41 ± 2.4
3	400	48 ± 2.7
4	500	60.4 ± 3.5
5	600	71.8 ± 2.4

[a] Freshly prepared sample. Temperature of evaporation ≈ 300°C.

Table 2
Reproducibility of various batches of $CaSO_4$: Dy.

Batch no.	Average TL output $\pm\delta$ ($\times 10^{-10}$ A)
01	81 ± 3
02	81 ± 1
03	78 ± 3
04	79 ± 5
05	78 ± 2
06	74 ± 5
07	77 ± 3
08	76 ± 3
09	65 ± 4
10	74 ± 2
11	71 ± 2
12	75 ± 2
13	74 ± 3
14	72 ± 3
Average	77 ± 7.7

2.2. Form of the dosimeter

TL properties of cold-pressed pellets of natural CaF_2 and of $CaSO_4$: Dy mixed with NaCl were previously studied in our laboratory and this form of dosimeter seems to be very useful. Cold pressed pellets with alkali halides, can be quite strong and semitransparent. Cold pressing with LiF as the binder was not possible (a pellet with LiF can only be produced if the pressing is done at temperatures in the range of 200°C). A lot of previous experimental work on this form of dosimeter was carried out and we arrived at the following conclusions:

1) The ratio of the phosphor to binder should be less than unity to obtain a semi transparent and a good, strong pellet that would stand routine handling.

2) TL response of the pellet for a fixed weight and geometry varies linearly with phosphor concentration up to 1:1. For higher concentrations the TL response saturates and even decreases. At these higher concentrations the pellet also becomes fragile.

3) The mixture of phosphor to binder in the ratio of 1:2 by weight gives a resistent pellet with a high TL response with minimum amount of phosphor.

Considerations of handling, economy and TL response lead us to the following parameters for the dosimeters to be used for the monitoring purposes:

1) Size: 6 mm diameter and 1.5 mm thickness.
2) Weight of the mixture: 75 mg.

Table 3
TL response average values and standard deviation δ for various batches.

Batch no.	No. of pellets	Average TL output $\pm\delta$ ($\times 10^{-10}$ A)
01	9	37.78 ± 1.93
02	28	34.7 ± 3.17
03	31	31.8 ± 2.73
04	24	36.08 ± 2.38
05	24	36.75 ± 2.6
06	39	32.13 ± 2.74
07	27	32.67 ± 2.22
08	36	35.39 ± 2.0
09	34	35.2 ± 2.22
10	40	34.6 ± 2.78
11	36	36.95 ± 2.32

3) Proportion of the phosphor to binder: 1 to 2 by weight.
4) Pressures used for pellet fabrication: 4000 lbs/pellet.
5) Binder used: NaCl.
6) Phosphor used: $CaSO_4$:Dy (with concentrations as described above).

A die for cold-pressing the above mentioned mixture was designed and built. It consisted of a cylindrical block of hardened stainless steel with three holes of 6 mm diameter, equally spaced at the vertices of an equilateral triangle. By this construction three uniform, reproducible and equally resistant pellets can be produced at a time.

Powder samples of $CaSO_4$:Dy and NaCl were sieved and the portion with grain size between 85 and 185 μm were collected for use. The two powder samples thus collected were mixed together in the weight proportion of one $CaSO_4$:Dy to two NaCl. Only about a total of 3 g was prepared each time to get a uniform mixture. This mixture was then treated at 600°C for one hour before use. Aliquots of 75 mg were weighed from this mixture and pellets were prepared. It has been observed that if the die is not cleaned properly after each use, it can not be operated smoothly. Moreover the pellets some times turned black due to die contamination thus leading to loss of sensitivity. The prepared pellets were given a heat treatment of one hour at 600°C.

Pellets prepared from different batches of 3 g mixtures were exposed to ^{60}Co irradiation and results are given in table 3. The individual δ values for the various batches show the uniform nature of the mixture.

3. Performance and characteristics of the dosimeter

Before introducing any new dosimetry system into field use, one has to test the system thoroughly for its various characteristics. The properties to be tested are its linearity of response, repeated usability, reliability to low dose measurements, performance under various storing environments and energy dependent characteristics.

3.1. Linearity

A dosimeter to be used in the field should have a linear TL response with the exposure. Batches of 15 dosimeters each were given a standard heat treatment of half an hour at 600°C. These batches were exposed from one mR to a few tens of R from a ^{60}Co source. Average TL output of the fifteen dosimeters with the standard deviation is plotted in fig. 1. It can be seen that the TL response of the dosimeter is quite linear and that an exposure as low as 1 mR can be estimated by this dosimeter.

3.2. Reliability in low exposure measurements

Fig. 2 shows the glow curve from a dosimeter exposed to 1 mR and the curve taken subsequently by reading the same dosimeter without any further exposure. It can be seen that the TL peak is clearly visible even for this low exposure level. A batch of 20 dosimeters was exposed to 1 mR and read out. The TL output for a 1 mR exposure measured for 20 dosimeters gave a standard deviation of 20% and an average TL reading of $(8.9 \pm 1.7) \times 10^{-12}$ A.

3.3. Reusability

A main advantage of the TL dosimetry system is its reusability. A batch of 15 dosimeters was given the primary heat treatment of one hour at 600°C then exposed to 200 mR and readout. The dosimeters were then treated for half hour at 600°C and again given the same exposure and readout. This procedure was successively repeated and the results are shown in table 4. It is seen that for a total of 8 h of thermal treatment, the TL sensitivity of the dosimeter does not change significantly. For longer periods of treatment a slight decrease of sensitivity is observed. This is possibly due to to the partial conversion of the $CaSO_4$:Dy to CaO. Thus the dosimeter could be used at least for 10 times without an individual recalibration. For environmental use, the dosimeter receives only a few tens of mR exposure at a time and hence it can be treated at lower temperatures and for shorter periods thus increasing its life cycle.

3.4. Study of energy dependent characteristics

The dosimeters were exposed to X and gamma rays of various energies, varying from 20 keV effective to 1.25 MeV effective. The machine used is the 'Stabilipan

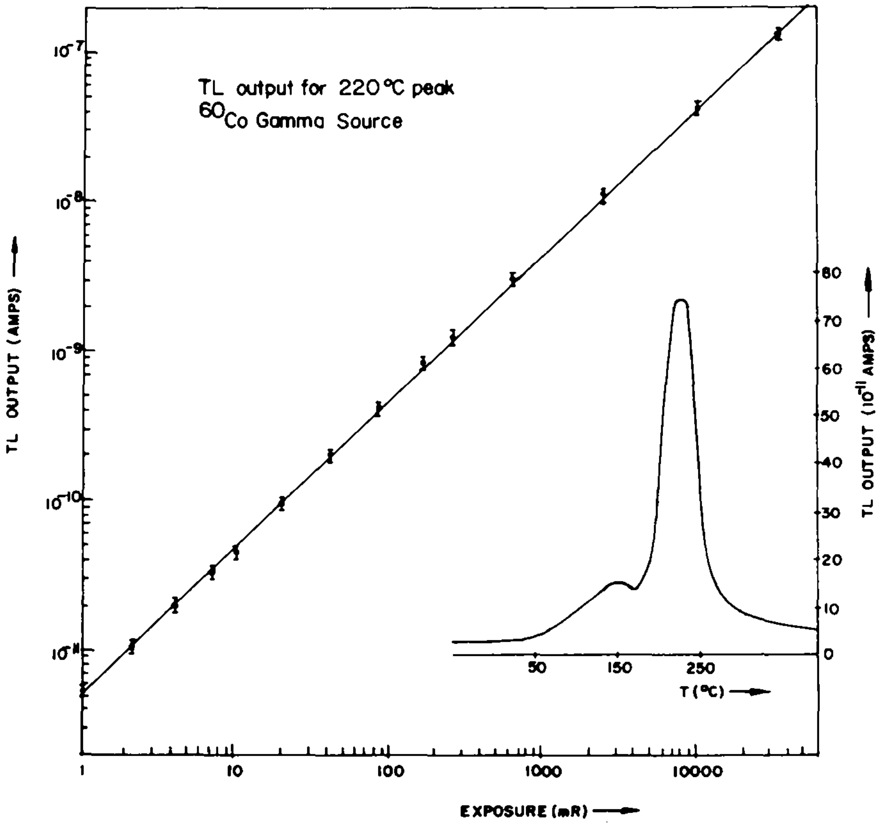

Fig. 1. Linearity of 220°C peak of $CaSO_4:Dy+NaCl$ pellet for exposures to ^{60}Co gamma rays.

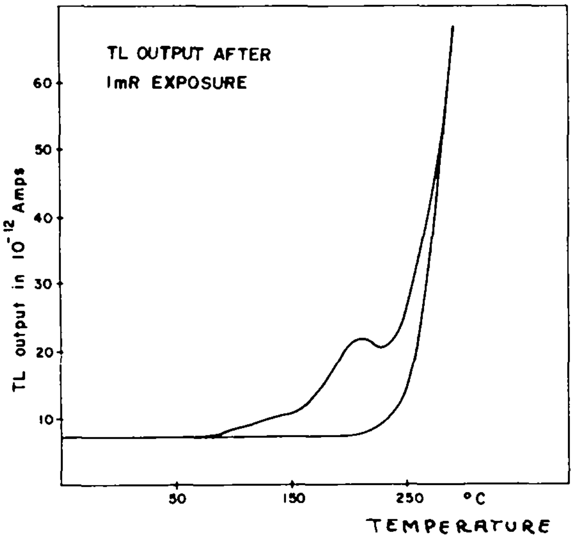

Fig. 2. Sensitivity for low doses of the $CaSO_4:Dy+NaCl$ pellet. The 220°C peak is shown against the background.

300' from Siemens, which is provided with various filter sets and variable voltages to obtain X-ray of different effective energies. The filter–voltage combinations used in the experiments are given in table 5. Data on dose

Table 4
Data on the reusability of 15 dosimeters.

Utilization no.	Accumulated period of treatment at 600°C (h)	Average TL output $\pm \delta$ ($\times 10^{-10}$ A)
01	2.0	18.3 ± 1.1
02	3.5	18.7 ± 1.7
03	4.0	18.9 ± 1.5
04	4.5	17.7 ± 1.2
05	5.0	17.0 ± 1.75
06	5.5	18.6 ± 1.6
07	6.0	18.3 ± 2.1
08	6.5	16.9 ± 1.7
09	7.0	16.6 ± 1.4
10	7.5	16.7 ± 1.3
11	8.0	17.0 ± 1.8

Table 5
Details of the parameters used for irradiations with 'stabilipan 300 X-ray machine from A.C. Camargo Hospital.

Sr. no.	Voltage (kV)	Filter (mm)	HVL (mm)	*E* (keV)	Current (mA)	Distance (cm)	Dose rate (R/h)
1	80	2.0 Al	2.1 Al	20	20	50	28.7
2	120	0.2 Cu	0.35 Cu	55	20	50	35.1
3	160	0.5 Cu	0.7 Cu	70	20	50	40.0
4	200	1.0 Cu	1.43 Cu	96	20	50	42.6
5	250	Th [a]	2.4 Cu	126	15	50	51.2
6	300	Th [b]	4.0 Cu	155	12	50	40.4

[a] 0.4 mm Sn, 0.25 mm Cu and 1.0 mm Al.
[b] 1.2 mm Sn, 0.25 mm Cu and 1.0 mm Al.

rates, HVL thicknesses and calculated effective energies used for the irradiations are given in table 5.

Preliminary filter studies on this dosimeter showed that a 0.8 mm thick lead filter with a hole of 2 mm diameter and with a 3 mm thick plastic filter can give a nearly energy independent response. A filter of 1 mm thick lead foil gave a low energy cutoff at around 100 keV. Detail studies on the response of the dosimeter under the above filters were carried out. A batch of 25 dosimeters were exposed to radiation of different energies. Plot of TL response per R against energy of the radiation is given in fig. 3. The filter used in this experiment was made of 1 mm thick lead foil with a 2 mm diam. hole at the centre and with the 3 mm plastic. It can be seen from the figure that the energy response of the dosimeter is quite uniform; however a better response can be achieved if one uses a 0.8 mm thick lead foil with a 2 mm diam. hole together with the three millimeter thick plastic filter.

3.5. *Effect of ambient light*

Batches of ten dosimeters were stored under normal illumination conditions in the room as well as under normal strong sunlight and another batch was stored in light tight container. All the dosimeters were read out after storage under the various conditions for a period of six hours.

It was observed that the dosimeters stored in the room light (consisting of tungsten filament lamps) as well as the dosimeters stored in the light tight container did not show any accumulation of TL signal. The dosimeters stored in the strong sunlight, however, showed slight accumulation of TL, of the order of 20 mR (^{60}Co equivalent). This is due to the slight intrinsic UV sensitivity developed in the phosphor due to the partial conversion to CaO. Therefore it must be noted that direct exposure of the dosimeter to unfiltered sunlight or to other UV sources should be avoided, especially when low exposure levels are involved. It was also observed that exposure to normal room light does not induce any fading of the TL signal.

3.6. *Effect of moisture*

To study the effect of moisture, batches of ten dosimeters were (a) stored in a desiccator (20% relative

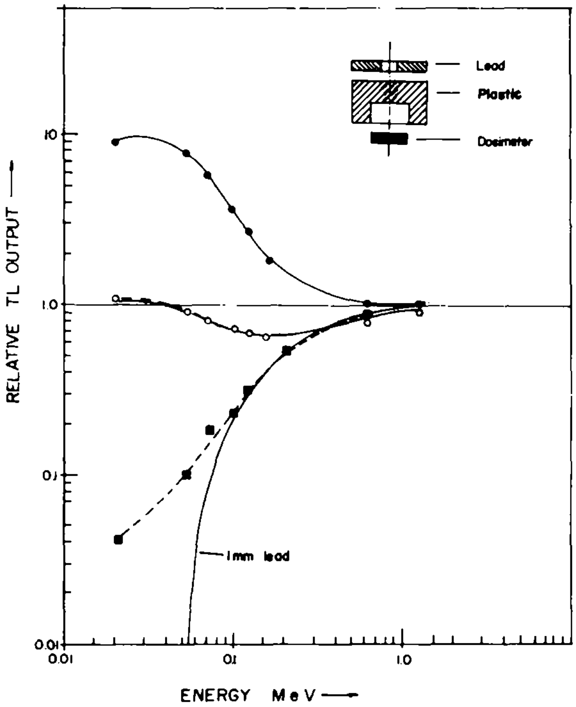

Fig. 3. Energy dependence of the TL response from the $CaSO_4$:Dy+NaCl pellet after exposure to different energies and filter combinations. Responses are normalized to the unfiltered dosimeter response to ^{60}Co gamma exposure. (●) Response for 3 mm thick plastic badge. (■) Response for 3 mm thick plastic and 0.8 mm thick lead filter–solid line: calculated for 1 mm thick lead filter. (○) Response for the combination of 3 mm thick plastic 0.8 mm thick lead filter with a 2 mm diameter hole.

humidity), (b) kept in the open in the laboratory (average relative humidity of 60%) where they were sealed in PVC plastic sheets. All these dosimeters received a known exposure before. The dosimeters were stored for a period of one month and then read out. It was observed that the dosimeters in the sealed PVC sheet were not affected even though they were stored in the open environment. The dosimeters stored in a desiccator did not show any effect of moisture. Dosimeters left in the open on a table top did not show any deterioration of their TL characteristics under ambient conditions. Only when the humidity levels were extremely high (as high as 80%) the dosimeters showed some sign of deterioration when stored in the open.

Thus it became clear from the above tests that the dosimeters will not be affected by environmental moisture conditions if they are used in the normally sealed conditions. In case the dosimeters are to be used in the environmental monitoring in the open then it is essential that they are kept in sealed containers and protected from the sunlight.

3.7. Fading characteristics

It is already known from a detailed study of the thermoluminescent characteristics of this phosphor that the dosimetric peak to be used in this case is quite stable at room temperature and one can not observe any significant fading even in a period of one month.

3.8. Response of dosimetry badge to photons of different energies

Batches of ten badges were exposed to 300 mR of ^{60}Co irradiation, to 300 mR of X-rays of effective energy of approximately 45 keV (50 keV with 5 mm Al filter) and to both exposures at the same time. The dosimeters were read out and the individual doses due to low energy photons, high energy photons and the mixed field were estimated from the calibration curves for the used filter conditions. It was observed that the doses could be estimated accurately (within 10%). In case of radiation of energies less than 100 keV even the approximate effective energy of the radiation field could be determined.

3.9. Background exposure accumulation

As the dosimeters should be used for a period of 15 days, it is essential to know the total TL accumulation of the dosimeters over this period compared to that caused by the normal background radiation alone. It was observed that the accumulation in the dosimeter over a period of one month does not exceed the normally expected value of 10 to 15 mR. Thus with use of NaCl as the binder material one can use this dosimeter for low exposure level measurements.

3.10. Dosimetry badge

The final TL badge will consist of four dosimeters under the following filter conditions.

1) Open window. (With the normal dosimeter packing for sealing and protecting from direct sunlight.)
2) 3 mm thick plastic.
3) 3 mm plastic with 1 mm lead.
4) 3 mm plastic with 0.8 mm lead with 2 mm diam. hole.

The dosimeter under the open window will accumulate exposure from hard beta rays and gamma rays (soft as well as hard). The dosimeter under the plastic filter will accumulate exposure from gamma photons only. The dosimeter under the third filter will accumulate exposure from hard gamma rays (with energies above 100 keV) and the fourth dosimeter will give the energy independent response for exposures from gamma rays with energies above approximately 15 keV. Depending on the need, only one of the above dosimeters could be used in this badge. A combination of readings could also allow the energy determination for an unknown source.

4. Conclusions

The combination of $CaSO_4$:Dy powder bound with NaCl in a pellet form with an appropriate filter to ensure energy independence resulted in a practical, sensitive and reliable dosimeter for multipurpose dosimetry utilization. This preliminary study showed the potential of this badge for introducing it in personnel and environmental routine dosimetry. It was also demonstrated that the dosimeter can easily be produced on a mass scale what makes it even more promising for industrialization and, due to its low cost, to widespread commercialization. Further work is being carried out for testing this badge in the field and data on an intercomparison study are being collected. These results will published elsewhere.

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