

## DYSPROSIUM DOPED CaSO<sub>4</sub> FOR HIGH SENSITIVITY X AND GAMMA-RAYS DETECTORS

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X-ray and gamma-ray detectors, based on Dy doped CaSO<sub>4</sub> crystals were produced. They are able to detect photons with energies within the range 30 keV – 3000 keV. The fading (loss of information) of a detector within a 30 days period is <5%. These detectors are constitutive parts of the thermoluminescent dosimeters.

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### 1. Introduction

The crystalline substances are the most used for Thermoluminescent Dosimetry (TLD) purposes. The crystalline structure allows for a controlled impurification with activators in order to improve their dosimetric parameters. The activators introduced into the crystalline network [1], enhance the number of electrons and hole traps inside the forbidden band. In the first step, immediately after the irradiation, the electrons and hole traps are populated, due to mobile charge carriers released by ionization; in the second step of heating the trap depopulation occurs and a light signal is emitted.

CaSO<sub>4</sub> becomes thermoluminescent if an activator, e.g. dysprosium, is introduced in the crystalline structure. The energy of the ionizing radiation, stored in the thermoluminophore after its irradiation can be maintained for a 3 months period, with a fading value of <5%. The main requirements imposed to a TL phosphor are the followings: (i) A high efficiency or sensitivity, defined as the ratio between  $E_{TL}$  and  $mD$ ,  $\eta_{TL}=E_{TL}/mD$ , where:  $E_{TL}$  is the energy emitted as luminescence,  $m$  is the phosphor mass and  $D$  is the absorbed dose value. (ii) Good dosimetric properties, such as linear response for a large interval of doses. (iii) Reproducibility and insensitivity to temperature, light, humidity etc. (iv) Easy to be handled

Generally, one thermoluminophore, cannot accomplish all these requirements at the same time. This is the reason why the choice of the luminophore and activator and the construction of the dosimeters are very important parameters in designing a dosimetric system.

The energy stored in the CaSO<sub>4</sub> luminophore is released as a light signal after its heating at a 360 °C temperature in a special oven, included in a TL -Reader; in our case a commercial TL -Reader, VICTOREEN 2800 type was used; the light spectrum contains two peaks at 478 nm and 571 nm.

The CaSO<sub>4</sub>:Dy dosimeters are used in a dosimetric system for the measurement of environmental absorbed dose in air produced by X and  $\gamma$  rays within the energy range 30 keV-3000 keV. They are exposed to the environment for a 30 days period. Due to their high sensitivity [1] CaSO<sub>4</sub>: Dy detectors are constitutive elements of the dosimetric systems used for the environmental survey of the Nuclear Power Plants, specially designed localities, or other Nuclear Objectives.

The present paper presents a new technology for getting CaSO<sub>4</sub>: Dy type TL detectors, as well as the results obtained during their testing.

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## 2. Technological procedure for obtaining the detectors

The technological procedure must be very carefully chosen and followed, as these detectors are very sensitive to the chemical composition [2,4], thermal treatment [3] etc. Our original procedure is described below:

The basic raw materials are: pure  $\text{H}_2\text{SO}_4$ , with  $1.840 \text{ g}\cdot\text{cm}^{-3}$  density,  $\text{CaSO}_4$ , 99.9% purity,  $\text{Dy}_2\text{O}_3$ , Merck, tridistilled water, obtained by two distillations in usual glassware, while the third one was carried out by the use of quartz.

The  $\text{CaSO}_4$  matrix is activated by a carefully controlled impurification procedure with Dy atoms, which play the role of thermoluminescence centers. To this purpose the  $\text{Dy}_2\text{O}_3$  powder is dissolved in diluted  $\text{H}_2\text{SO}_4$  (<30%) in tridistilled water. A dysprosium sulfate solution is obtained. The  $\text{CaSO}_4$  salt is dissolved in this solution, in such an amount as to ensure a controlled Dy impurification of 0.15%.

The mixture solution is evaporated very slowly for about 20 hours in a box, in air atmosphere at  $100^\circ\text{C}$ , until a solid crystal is obtained. The temperature is maintained by using a sand bed and is carefully controlled.

Thereafter, we introduced a supplementary thermal treatment, in order to remove the  $\text{H}_2\text{SO}_4$  traces and interstitial water from the crystalline matrix, which were detected in the usual procedures, having as a consequence a poor reproducibility of detectors. The treatment is carried out by keeping the material to a temperature of  $700^\circ\text{C}$  for two hours and at  $400^\circ\text{C}$  for 20 minutes. The heat treatment is carried out in quartz glassware closed in an electrical oven. The very pure  $\text{CaSO}_4:\text{Dy}$  is a hexagonal crystal, pink bright in color. The crystal is then crushed in an agate mortar and the powder is separated by sieving; crystals dimensions of  $70\div 200 \mu\text{m}$  are selected.

The thermoluminescence of the pure powder was checked by irradiation with a dose of  $10^{-1}$  Gy and the thermoluminescence curve was studied. According to literature data [5,6], the mean TL peak, must appear between  $190^\circ\text{C}$  and  $220^\circ\text{C}$ . The secondary TL peak must appear under  $90^\circ\text{C}$  in order to avoid the loss of information. In the next stage, the pure  $\text{CaSO}_4:\text{Dy}$  is mixed with teflon powder in equal proportions and a compact mixture is obtained. The mixture is then poured in special moulds and subjected to an external pressure of  $80 \text{ kgf}/\text{cm}^2$  in order to obtain solid pellets. The detectors, as pellets, have the dimensions :  $\Phi=10.0\pm 0.2 \text{ mm}$ ,  $h=0.8\pm 0.2 \text{ mm}$

## 3. Preliminary treatment of the detectors

Two successive types of thermal treatments proved to be necessary. The first one aims to provide mechanical resistance [4] of the pellets (detectors). It is achieved by subjecting the detectors to a temperature of  $350^\circ\text{C}$  for an hour, by ensuring a very slow temperature variation rate during the warming ( $20\text{-}350$ )  $^\circ\text{C}$  and cooling ( $350\text{-}20$ )  $^\circ\text{C}$  cycles. As a results, rigid, mechanically resistant pellets are obtained.

A supplementary second treatment was introduced by us in order to remove the surface traps. For the lowering and stabilization of the background counting rate values, an alternation of irradiations and thermal treatments were carried out. The irradiations were made at absorbed doses of about  $10^{-2}$  Gy, followed by subjecting the detectors to a temperature of  $(350\pm 10)^\circ\text{C}$  for an hour. A low rate of temperature variation was applied. The irradiation–thermal cycles were repeated 5-6 times.

## 4. Procedures of irradiation and measurement of dosimetric parameters

As the literature data show [5,6] and International Standards require [7] the dosimetric parameters of these detectors are very restrictive as they are designed to obtain dosimeters to be used in the very low environmental doses. The imposed dosimetric parameters are: the response value and homogeneity of the lot; linearity of the response within the interval and basic error; reproductibility of the dosimetric response and energy dependence of the response.

The experimental procedure to establish these parameters consists in the followings. The detectors are irradiated in a panoramic geometry in standard irradiation fields of: (i) Filtered X rays with energies of 29, 48, 80, 123 keV, for dose interval  $(10^{-2} \pm 2 \cdot 10^{-3})$  Gy, determined with uncertainties  $\pm 5\%$  (coverage factor,  $k=2$ ); (ii) 662 keV (<sup>137</sup>Cs) and 1250 keV (<sup>60</sup>Co) gamma rays, within the dose interval  $(10^{-5} - 10^{-1})$  Gy with uncertainties of  $\pm 5\%$  ( $k=2$ ). The responses of the detectors, expressed as measured values of the absorbed dose (Gy), are determined by using a calibrated TLD-Reader.

The irradiated detectors are introduced in the TLD-Reader oven and heated following a thermal cycle, depending on the used TL detector type. In this process, the dosimetric information is obtained as an ultraviolet radiation emission, having the intensity proportional with the absorbed dose; this light emission acts on the photocathode of the photomultiplier contained in the TLD-Reader. As a result, the TL peak area (impulses) is proportional with the absorbed dose [8].

A commercial VICTOREEN TLD-Reader was used, with a heating rate of 15°C/sec. The TLD-Reader contains the following constitutive parts: the system for heating and recording of temperature; the system for the light flux detection provided with a photomultiplier; the system for data processing and result display.

The reader is also provided with a system for pure gaseous nitrogen flow which maintains a constant work temperature for the photomultiplier and avoids the chemiluminescence, which results in false light signals and consequently the occurrence of erroneous results. The heating system contains also the voltage supply and a thermocouple for temperature monitoring, connected with the system for data processing. The heating is made according to a pre-set thermal cycle containing several steps: preheating, measurement, resetting and cooling. The TL curve of the CaSO<sub>4</sub>: Dy crystalline powder contains the main peak at about 210 °C and two secondary peaks at 70 °C and 90 °C. After short regeneration treatment, the 70 °C peak was eliminated.

## 5. Results

### 5.1 Response value (calibration factor) and homogeneity of the lot

A number of 50 different detectors were irradiated to a conventional true absorbed dose,  $D_{ct} = (10^{-2} \pm 5\%)$  Gy generated by the reference <sup>137</sup>Cs source.

Table 1 presents the number of impulses obtained,  $X_i$ , calculated with the relation:

$$X_i = E_i - B_i \quad (1)$$

where:  $E_i$  is the number of impulses of one detector and  $B_i$  is its background value.

Table 1. The determined value of response for CaSO<sub>4</sub>:Dy detectors irradiated to a conventional true absorbed dose,  $D_{ct} = 10^{-2}$  Gy.

Detector	$E_i$ [impulses]	$B_i$ [impulses]	$X_i$ [impulses]	Detector	$E_i$ [impulses]	$B_i$ [impulses]	$X_i$ [impulses]
1	72300	90	72210	26	72100	125	71975
2	73250	95	73155	27	70300	102	70198
3	72000	120	71880	28	71100	99	71001
4	70110	110	70000	29	71200	105	71095
5	69500	89	69411	30	70400	100	70300
6	69900	90	69510	31	69300	98	69202
7	70100	100	70000	32	69000	90	68910
8	71300	105	71190	33	69800	99	69701
9	71000	103	70897	34	71100	97	71003
10	71900	110	71790	35	70300	105	70295
11	69700	89	69611	36	71600	120	71480
12	67900	92	67808	37	72300	94	72206
13	69400	89	69311	38	71800	99	71701
14	69600	91	69509	39	71300	120	71180

Detector	E <sub>i</sub> [impulses]	B <sub>i</sub> [impulses]	X <sub>i</sub> [impulses]	Detector	E <sub>i</sub> [impulses]	B <sub>i</sub> [impulses]	X <sub>i</sub> [impulses]
15	70600	112	70488	40	70600	108	70492
16	71600	110	71490	41	69700	101	69599
17	71900	109	71791	42	69900	98	69811
18	72200	121	72079	43	68900	89	68811
19	69600	100	69800	44	70600	90	70510
20	69100	106	68994	45	71900	99	71801
21	70400	99	70301	46	69600	101	69499
22	71500	97	71403	47	70600	110	70490
23	71500	88	71412	48	71200	122	71078
24	70400	98	70302	49	72000	129	71871
25	71000	122	70878	50	71200	115	71085

The mean value from the Table 1 data is:  $\bar{X} = [70590 \pm 1410]$  impulses, with a coverage factor,  $k = 2$  (corresponding to a 95% confidence level)

Dividing this mean value with the conventional true absorbed dose value,  $D_{ct} = 10^{-2}$  Gy, the response value,  $R$ , is calculated as:

$$R = \frac{\bar{X}}{D_{ct}} = (7.059 \pm 0.141) \cdot 10^6 \text{ imp / Gy} \quad (2)$$

The homogeneity of the set is expressed as:

$$H_X = 100 \frac{X_{\max} - X_{\min}}{X_{\min}} [\%] \quad (3)$$

From the maximum and minimum  $X$  values of Table 1, one obtains  $H_X = 7.9\%$

## 5.2 Linearity of the response within the dose interval and basic error

All the selected detectors grouped on lots of 5 pieces were irradiated at various conventional true absorbed dose values,  $D_{ct}$ , within the interval:  $(10^{-5} - 10^{-1})$  Gy. The measured dose values,  $D_{meas}$ , versus the  $D_{ct}$  values are presented in table 2.

The basic error is defined as:

$$\varepsilon [\%] = [(D_{meas} - D_{ct}) / D_{ct}] \cdot 100 \quad (4)$$

$D_{meas}$  values were calculated as mean values from data obtained with the 5 exposed detectors, by using the relation (2)

Table 2 shows the measured absorbed doses, by using CaSO<sub>4</sub>:Dy detectors irradiated at various conventional true absorbed dose values within the interval 10 μGy-100 mGy

Table 2. The evaluated absorbed dose values of CaSO<sub>4</sub>:Dy type TL detectors, irradiated at various conventional true absorbed dose values within the range 10 μGy-100 mGy.

No.	D <sub>ct</sub> [Gy]	D <sub>meas</sub> [Gy]	ε [%]
0	1	2	3
1	1 · 10 <sup>-5</sup>	0.84 · 10 <sup>-5</sup>	-16.0
2	3 · 10 <sup>-5</sup>	3.37 · 10 <sup>-5</sup>	+12.3
3	5 · 10 <sup>-5</sup>	5.8 · 10 <sup>-5</sup>	+11.6
4	1 · 10 <sup>-4</sup>	0.92 · 10 <sup>-4</sup>	-7.6
5	5 · 10 <sup>-4</sup>	5.46 · 10 <sup>-4</sup>	+9.34
6	1 · 10 <sup>-3</sup>	1.08 · 10 <sup>-3</sup>	+8.0
7	5 · 10 <sup>-3</sup>	4.5 · 10 <sup>-3</sup>	-9.92

No.	D <sub>c.t.</sub> [Gy]	D <sub>meas</sub> [Gy]	ε [%]
8	12.5 · 10 <sup>-3</sup>	14.4 · 10 <sup>-3</sup>	+14.9
9	5 · 10 <sup>-2</sup>	4.71 · 10 <sup>-2</sup>	-5.7
0	1	2	3
10	7.5 · 10 <sup>-2</sup>	6.93 · 10 <sup>-2</sup>	-7.48
11	9.55 · 10 <sup>-2</sup>	8.84 · 10 <sup>-2</sup>	-7.4

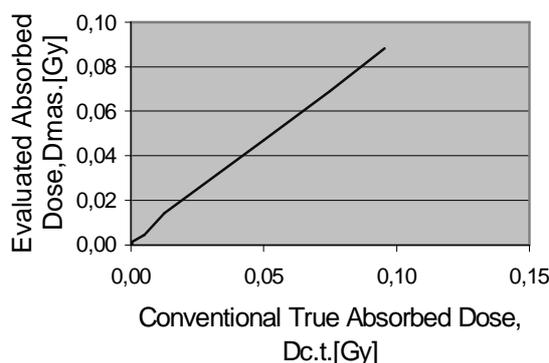


Fig. 1. The variation of the evaluated absorbed dose of CaSO<sub>4</sub>:Dy type TL detectors for different conventional true absorbed dose.

By analyzing the results from the Table 2, one may conclude: (i) Within the interval (10<sup>-5</sup>-10<sup>-4</sup>) Gy, the maximum error is 16%. This is a very good result for such low absorbed dose values, by comparison with literature data, when 50% error values are reported ; (ii) Within the interval (10<sup>-4</sup>-5×10<sup>-3</sup>) Gy, the maximum error is 14.9 % ; (iii) For absorbed doses higher than 5×10<sup>-3</sup> Gy, the error lowers to maximum 7.5 %; The general calibration curve, calculated as linear regression of Table 2 data, is : D<sub>meas</sub> = ( 0.925±0.008) D<sub>c.t.</sub>  
The final conclusion is that the obtained detectors measure the absorbed dose with high accuracy and are fully suitable to obtain environmental dosimeters. They prove the accomplishment of the standardization documents requirements [7].

### 5.3. Reproducibility of the response

The reproducibility is very important when measuring low absorbed dose values, within the (5·10<sup>-5</sup>-2·10<sup>-4</sup>) Gy interval. The Standard I.E.C. defines reproducibility of the responses and the upper allowed limits, by the following relations:

$$S_i = \frac{s_{R_i}}{\frac{1}{10} \sum_{i=1}^{10} R_i} \leq 0.075 \quad ; \quad S_j = \frac{s_{R_j}}{\frac{1}{10} \sum_{j=1}^{10} R_j} \leq 0.075 \quad (5a, 5b)$$

where: i=1.....10 (number of detector); j=1.....10 (number of irradiation)

This parameter was determined by irradiating 10 detectors, *i*, 10 times, *j*, at the same values of conventional true absorbed dose values, D<sub>c.t.</sub>: D<sub>c.t.</sub>= 5×10<sup>-5</sup>Gy and D<sub>c.t.</sub>= 2×10<sup>-4</sup>Gy.

The experimental values of reproducibility parameters, calculated as mean values of *f* the matrices of detectors and irradiations, and are presentd in Table 3.

Table 3. Reproducibility data, for 10 detectors, irradiated 10 times, to  $D_{ct.} = 5 \cdot 10^{-5}$  Gy and  $D_{ct.} = 2 \cdot 10^{-4}$  Gy.

$D_{ct.}$	$S_i$	$S_j$
$5 \cdot 10^{-5}$ Gy	0.062	0.063
$2 \cdot 10^{-4}$ Gy	0.037	0.039

From Table 3 one may conclude that the reproducibility requirement is fully accomplished.

#### 5.4. Energy dependence of the response

It is well known, that every detector, or dosimetric system has a specific response curve as function of radiation energy, as compared with the absorbed dose in air. The dependence factor, F, is calculated as the ratio between the obtained absorbed dose  $D_{mas}$  for various X and  $\gamma$  rays energy values, keV, and value corresponding to 662 keV (reference), for which  $F=1$ .

This is the reason why it is desirable to use detectors with an elemental composition, expressed as effective atomic number,  $Z_{eff}$ , as near as possible of the air one; an ideal example in the field of thermoluminescence is LiF. Various formulae are used to calculate  $Z_{eff}$ . In our case, the Miller's formula was chosen:

$$Z_{eff} = \frac{\sum_{i=1}^n (n_i A_i Z_i)}{M} \quad (6)$$

where  $n_i$  is the number of atoms,  $A_i$  is the atomic mass,  $Z_i$  is the atomic number of the element from the species  $i$ , respectively, and  $M$  is the molecular mass of the compound.

The values for  $Z_{eff}$  are respectively 7.6 and 16 for air and  $CaSO_4$ , and the dependence of energy is high.

The test was carried out as follows: The detectors, in groups of 5 pieces, were exposed to filtered X rays, with energies of 29 keV, 48 keV, 80 keV, 123 keV, reference gamma rays of 662 keV, and 1250 keV and the measured values of absorbed dose values,  $D_{meas}$  were registered. The nominal absorbed dose,  $D_{ct.}$  is about  $8.70 \cdot 10^{-3}$  Gy.

Table 4. The dependence of dosimetric response of the energy of X and gamma rays.

No.	Energy [keV]	$D_{ct.}, [Gy] \cdot 10^{-3}$	$D_{meas}, [Gy] \cdot 10^{-3}$	Factor, F
1	29	8.29	39.0	4.70
2	48	8.42	34.1	4.05
3	80	8.55	21.5	2.51
4	123	8.66	15.4	1.78
5	662	8.70	8.70	1.00
6	1250	9.56	9.08	0.95

As it is seen from Table 4, due to the appropriate choice of the mixture  $CaSO_4$ : Dy: Teflon proportion and of crystalline dimensions, F values vary only between 0.95 and 4.70 by comparison with the requirements of the standardization document [7]:  $F < 12$ . It is necessary to underline the more strict limitation, expressed as  $F < 2$ , for thermoluminescent dosimetric systems. This is the reason for which, various mixtures of  $CaSO_4$ : Dy and teflon are employed. At the same time in designing a dosimeter, the dosimetric case contains also a set of metallic energy filters [9], which allow the further reduction of energetic response values down to a value  $F \leq 2$ .

## 5. Conclusions

An original technology for obtaining CaSO<sub>4</sub>:Dy detectors for environmental measurements was developed. It consists in the use of an optimum physicochemical composition and of a special thermal treatments of the detectors. A new, preliminary treatment of the detectors was introduced, aimed to remove surface traps and to provide the mechanical resistance of the detectors. Further, by choosing an appropriate mass proportion between CaSO<sub>4</sub>:Dy and Teflon, the energetic dependence was reduced. The basic dosimetric parameters of the detectors, measured according to the international requirements, are superior to the reported literature data and fully accomplish the standardization requirements.

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