DEPENDENCE OF TL RESPONSE OF $CaSO_4$:Dy AND $CaSO_4$:Tm ON GRAIN SIZE

I. KÁSA

Department for Applied Chemistry,
Technical University, H-1521 Budapest

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Summary

$CaSO_4$: Dy and $CaSO_4$: Tm belonging to the most sensitive TLD substances have been prepared by crystallization from hot sulphuric acid containing a small amount of hydrogen peroxide. The addition of hydrogen peroxide has a special purpose because on the one hand, it hinders the greying of $CaSO_4$: Dy and $CaSO_4$: Tm caused by carbonization of the organic matter accidentally getting into the crystallization vessel, and on the other hand, it influences the grain size of the crystals produced. In the case of $CaSO_4$: Dy and $CaSO_4$: Tm phosphors the dependence of TL sensitivity upon grain size, first of all, in a grain size range higher than 63 μm has been examined. The fraction of grain diameter 63–200 μm was found to be the most sensitive and with increasing grain size the sensitivity decreased. For two samples the decrease in TL sensitivity was similar to that of activator concentration determined by the XRF method, while with the other two samples a significant change in the activator concentration with the grain size could not be stated. According to this, the TL response is influenced by several other factors, too. On the glow curve the TL peak at a temperature of about 110 °C decreased with the increase in grain size.

Introduction

In order to use the thermoluminescent (TL) phosphors for dosimetric purposes, the following parameters have to be examined: glow curve, sensitivity, dose characteristics, fading, energy dependence, TL emission spectrum. On the basis of the above mentioned parameters the phosphor to be applied in dosimetry is expected to remain chemically stable in air and also when heating up to about 300–500 °C involving also the fact that the shape of glow curve, the efficiency of TL, as well as the lower limit of measurement should not change upon longer storage, repeated irradiation and evaluation. An additional requirement is the resistance against environmental effects (light, humidity, organic solvents, vapours, gases, etc.). Finally, further important demands are the unexpensiveness of the TL phosphor, its simple and reproducible preparation, its easy handling without any toxic effect, etc.

The TL characteristics of a given phosphor are influenced by several factors, e.g. conditions of preparation, quality and concentration of activator, presence of a co-activator, and of contaminating ions, heat treatment, atmospheric effects, grain size, etc.

Calcium sulphate activated with dysprosium or thulium ($CaSO_4$:Dy, $CaSO_4$:Tm) exhibits excellent dosimetric features. For the time being, it belongs to the most sensitive thermoluminescent dosimetric materials (TLD), accordingly its application is wide-spread, especially in the measurement of small doses.

In 1971 Yamashita and coworkers [1] elaborated an excellent method to produce calcium sulphate activated with rare earth metals from hot concentrated sulphuric acid by crystallization. Becker [2], as well as Webb and coworkers [3] reported on a similar method.

In the production of phosphors, crystals of different grain size develop depending on the parameters of crystallization. For dosimetric purposes the grain size diameter of phosphor crystals is favourably between 60–200 μm. The grain size influencing the TL sensitivity has been examined by several authors [4–12].

Schmidt and coworkers [4] investigated the effect of $CaSO_4 \cdot 2H_2O$ concentration exerted upon the size of the crystals produced and the sensitivity of crystals thus obtained was measured. By increasing the $CaSO_4 \cdot 2H_2O$ concentration the crystal size as well as the sensitivity decreased.

Chandra and coworkers [5] studied the sensitivity of $CaSO_4$:Dy on gamma and UV-radiation, furtheron the dependence of the TL response upon the grain size in the case of both gamma and UV-radiation. The TL response was found to change inversely with grain size by the two radiations. These examinations were limited, however, first of all, to ranges below 200 μm grain size diameter.

By varying the parameters of crystallization from concentrated sulphuric acid TL phosphors $CaSO_4$:Dy and $CaSO_4$:Tm of different grain size were obtained. The effect of grain size upon the TL response has been studied, primarily in the range of grain size greater than 200 μm. This range can be of importance in the preparation of special dosimeters [13, 14].

Experimental

Production of TLD phosphors

$CaSO_4$:Dy and $CaSO_4$:Tm were crystallized from hot sulphuric acid containing a small amount of hydrogen peroxide. Hydrogen peroxide hinders the greying of the newly formed crystals caused by the carbonization of organic materials accidentally getting into the crystallization vessel. The newly formed crystals produced in the presence of hydrogen peroxide are nice snow-white. Although the grey colour of the crystals can generally be eliminated by heat treatment for 2 hours at a temperature of 700 °C, however, according to our data the sensitivity of $CaSO_4$:Dy and $CaSO_4$:Tm TL phosphors thus obtained does not reach that of the phosphors produced with the use of hydrogen peroxide [9].

Hydrogen peroxide serves also to control of crystal nucleus number. By adding a small amount of hydrogen peroxide to the clear solution before the spontaneous nucleus formation a great number of crystal nuclei are formed

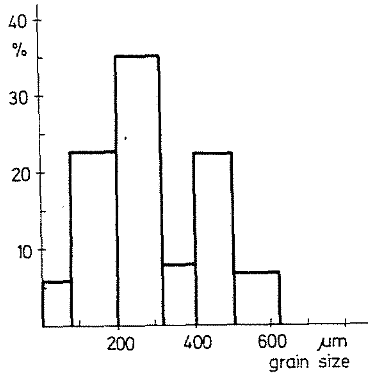

Fig. 1. No. 1. $CaSO_4$: Dy grain size distribution

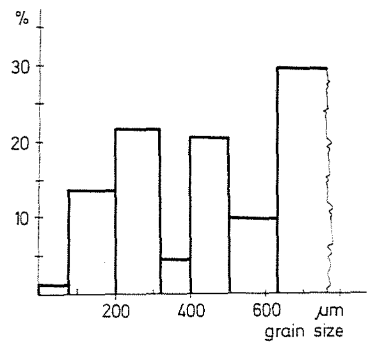

Fig. 2. No. 2. $CaSO_4$: Dy grain size distribution

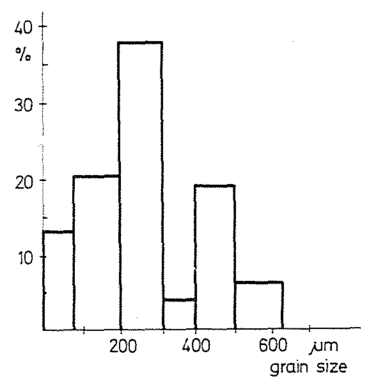

Fig. 3. No. 3. $CaSO_4$: Tm grain size distribution

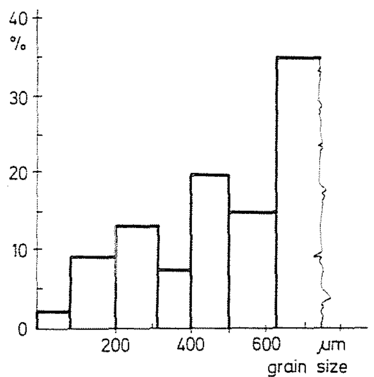

Fig. 4. No. 4. $CaSO_4$: Tm grain size distribution

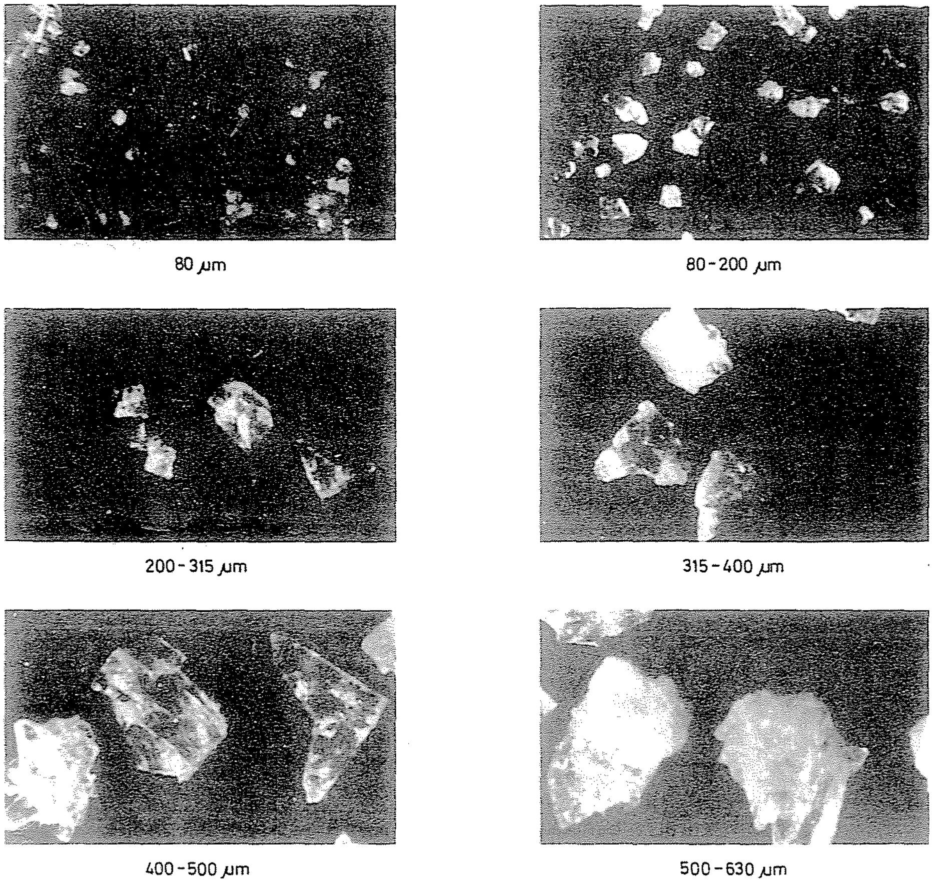

Fig. 5. Photograph of No. 1. $CaSO_4$: Dy grain fractions

which lateron do not re-dissolve fully, yielding the product with small grain size: No. 1. $CaSO_4$: Dy; No. 3. $CaSO_4$: Tm (Figs 1, 3, 5). If hydrogen peroxide addition is carried out earlier, the crystal nuclei developed by the addition are fully re-dissolved and in the course of later spontaneous nucleus formation only a smaller number of nuclei are produced resulting larger crystals: No. 2. $CaSO_4$: Dy; No. 4. $CaSO_4$: Tm (Figs 2, 4, 6).

Samples gained with the application of hydrogen peroxide have also been treated at a temperature of 700 °C for 2 hours, then fractions of different grain size were separated by sieving.

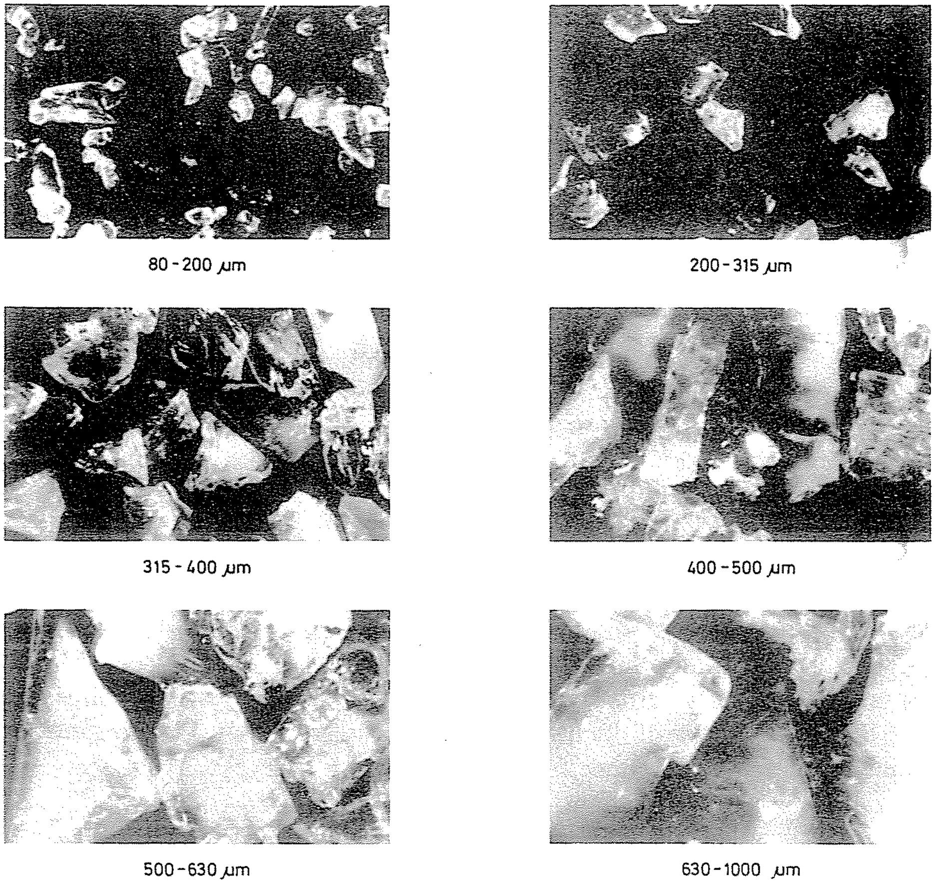

Fig. 6. Photograph of No. 2. $CaSO_4$: Dy grain fractions

Irradiation of TL phosphors and evaluation

The TL materials were irradiated with ^{60}Co-gamma radiation in a dose of 10 mGy (absorbed by air).

For the evaluation of the irradiated phosphors an instrument type TLD–04B produced by MTA–KFKI was used. At the evaluation the highest temperature of heating was 350 °C, duration of heating up 30 sec and duration of keeping at 350 °C was 5 sec. With the use of integral measurement, counting was started immediately after 100 °C had been reached and continued until the end of the cycle at a temperature of 250 °C. To the evaluation the method of double-heating was employed [15].

Determination of the activator concentration

The concentration of activator was determined by X-Ray Fluorescence (XRF) method. As an excitation radiation source a ^{109}Cd ring souree of 370 MBq activity has been applied. The L lines of dysprosium and thulium can be well excited with the 22.1 keV line of ^{109}Cd. The measuring cell was a Si(Li) detector, type 7313, Camberra product, whose resolution was about 180 eV (FWHM). Furtheron, a multichannel amplitude analysator, type Nuclear Data was applied.

Results and discussion

The typical grain size distribution of TLD materials produced in two ways is demonstrated in Figs. 1 and 2 in the case of $CaSO_4$: Dy and in Figs. 3 and 4 in the case of $CaSO_4$: Tm.

On the basis of Figs 1 and 3, as well as 2 and 4 it can be stated that the nature of the activator (Tm instead of Dy) has practically no effect upon the grain size distribution of the phosphors produced.

The photographs of $CaSO_4$: Dy TL crystals of different grain size, produced by two kinds of crystallization No. 1 and No. 2 can be seen in Figs 5 and 6. Similar results were obtained in the case of $CaSO_4$: Tm TLD phosphor.

The glow-curves of the fractions of No. 2 $CaSO_4$: Dy TL phosphor are shown in Figs 7–13.

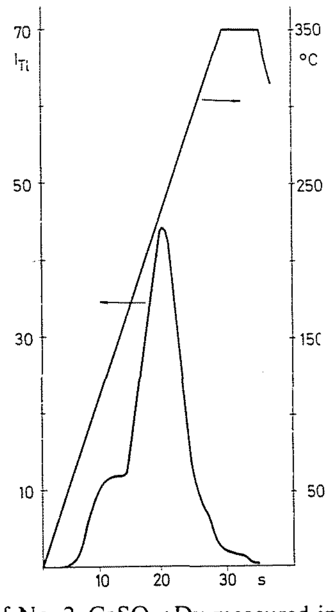

Fig. 7. Glow curve of No. 2. $CaSO_4$: Dy measured immediately after irradiation
Grain size: d < 63 μm

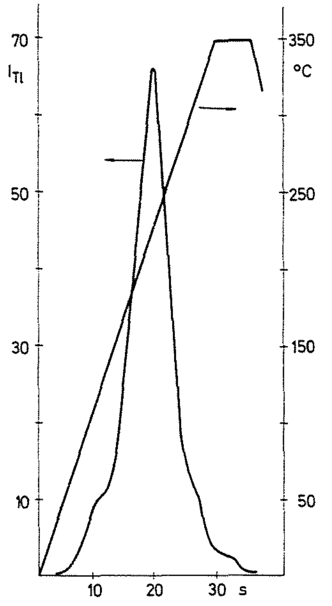

Fig. 8. Glow curve of No. 2. $CaSO_4$: Dy measured immediately after irradiation Grain size: d = 63–200 μm

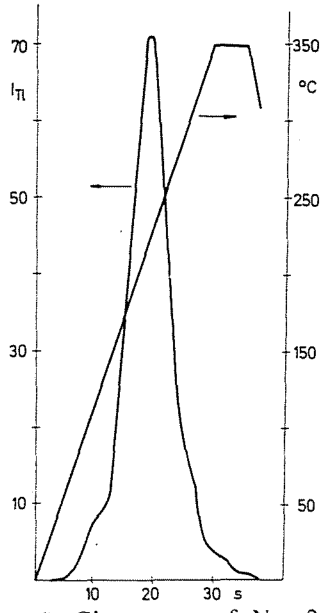

Fig. 9. Glow curve of No. 2. $CaSO_4$: Dy measured immediately after irradiation Grain size: 200–400 μm

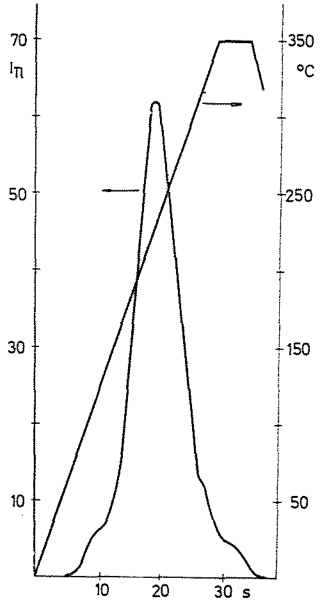

Fig. 10. Glow curve of No. 2. $CaSO_4$: Dy measured immediately after irradiation Grain size: d = 400–500 μm

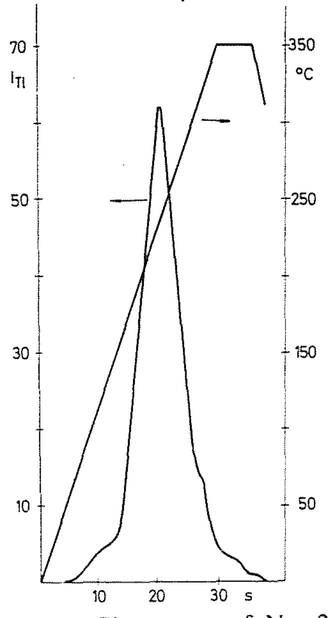

Fig. 11. Glow curve of No. 2. $CaSO_4$: Dy measured immediately after irradiation Grain size: 500–630 μm

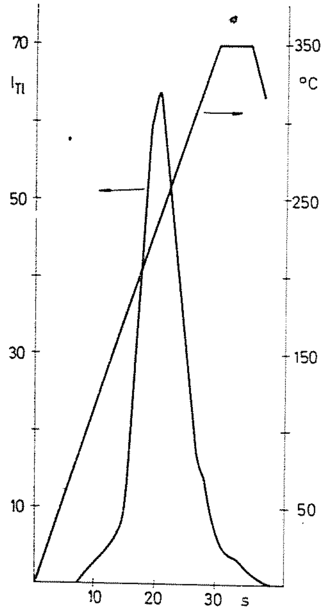

Fig. 12. Glow curve of No. 2. $CaSO_4$: Dy measured immediately after irradiation
Grain size: 630–1000 μm

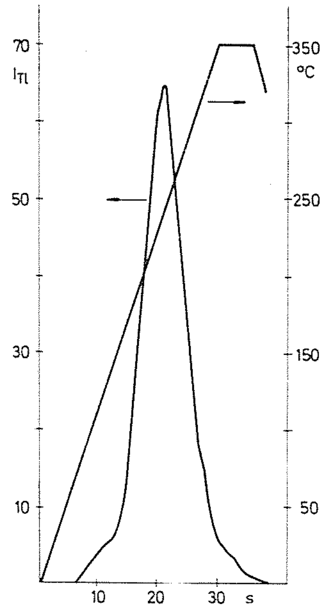

Fig. 13. Glow curve of No. 2. $CaSO_4$: Dy measured immediately after irradiation
Grain size: above 1000μm

On the basis of Figs 7–13 one can state that by increasing the grain size, the peak at about 110 °C gradually decreases. The temperature of the main peak at 230 °C shifts towards higher temperatures (235 °C and 240 °C, resp.) in the case of very big grains (d > 630 μm) (Figs 12 and 13). Due to the great grain size, the heating rate in the sample changes and the small shift of the main peak temperature (5–10 °C) is assumed to be the consequence of this fact.

The relative TL responses of fractions of different grain size in the case of all the 4 samples studied are given in percentage of fractions being in the interval of 63–200 μm in Table 1 and 2, as well as in Figs 14–15.

According to Tables 1 and 2, as well as to the data of Figures 14 and 15 the sensitivity of the examined $CaSO_4$:Dy and $CaSO_4$:Tm TLD phosphors changes with the grain size. In the case of all the four samples the most sensitive fraction is that being in the diameter interval 63–200 μm. The sensitivity of samples with "small grain size" decreases somewhat more rapidly in the range above 200 μm compared to that of "great grain size". Another fact to be considered is that the sensitivity of samples activated with thulium — in the case of both methods of preparation — decreases in a smaller degree with the increase in grain size, than of samples activated with dysprosium (Figs 14, 15).

Table 1

Relative TL responses of fractions of different grain size in the case of "small grain size"
($S_{TL\,63-200\,\mu m} = 100$)

Grain size interval (μm)	No. 1. $CaSO_4$:Dy	No. 3. $CaSO_4$:Tm
	Relative TL response %	
0–63	77.6	79.8
63–200	100.0	100.0
200–315	93.5	87.8
315–400	85.5	91.6
400–500	75.5	86.2
500–630	66.6	78.4

Irradiation: ^{60}Co; measured 24 hours after irradiation

Table 2

Relative TL responses of fractions of different grain size in the case of "great grain size"
($S_{TL\,63-200\,\mu m} = 100$)

Grain size interval (μm)	No. 2. $CaSO_4$:Dy	No. 4. $CaSO_4$:Tm
	Relative TL response %	
0–63	70.2	78.8
63–200	100.0	100.0
200–315	97.4	97.5
315–400	96.2	96.8
400–500	92.1	92.8
500–630	88.2	90.8
630–1000	84.9	86.7
above 1000	72.8	82.8

Irradiation: ^{60}Co; measured 24 hours after irradiation

The results obtained can be explained by several factors, e.g. the uneven distribution of the activator concentration in fractions of different grain size, the grain size dependence of the absorption of the exciting irradiation, light absorption and scattering phenomena, photonenergy dependence of the absorption of TL substances, surface and atmospheric effects, etc.

From among the above-listed possibilities the distribution of the activator concentration in fractions of various grain size has been studied by us. The activator concentration was measured by X-Ray Fluorescence method (XRF) [11].

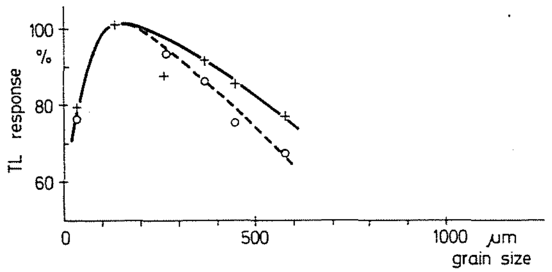

Fig. 14. TL response of No. 1. $CaSO_4$: Dy (ooo) and No. 3. $CaSO_4$: Tm (+ + +) fractions of different grain size measured 24 hours after irradiation

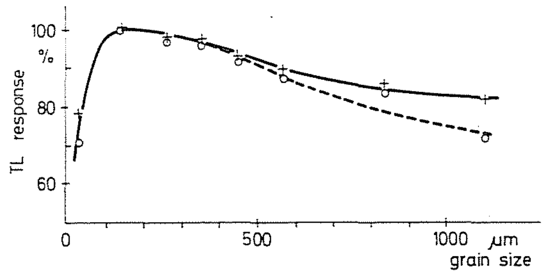

Fig. 15. TL response of No. 2. $CaSO_4$: Dy (ooo) and No. 4. $CaSO_4$: Tm (+ + +) fractions of different grain size measured 24 hours after irradiation

On the basis of our results the activator concentration decreases with the increase in grain size and also with the change of sensitivity in TLD samples No. 1 $CaSO_4$: Dy and No. 4 $CaSO_4$: Tm. With the two other samples, however, no similar tendency could be detected. In fractions of various grain size the activator concentration was found to be almost similar.

This observation suggests that the TL light is influenced also by other factors and phenomena. Accordingly, the examination of TL light requests also the simultaneous study of other factors, too, in addition to the activator concentration measurement, thereby representing a quite composed task.

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Dr. Imre KÁSA H-1521 Budapest