NEW METHOD FOR PREPARATION OF $CaSO_4$: Mn SUITABLE FOR DOSIMETRY II*

THERMOLUMINESCENT AND DOSIMETRIC CHARACTERISTICS OF PHOSPHORS PRODUCED BY $CaCl_2$ DEHYDRATION

By

I. KÁSA and I. TÖRÖK**

Department of Applied Chemistry, Technical University Budapest

Received April 15, 1975

Presented by Prof. Dr. E. Pungor

In a previous paper [1] investigations into the dehydration of calcium sulfate in the presence of calcium chloride and sulfuric acid were reported. The aim of these experiments was to produce manganese-activated calcium sulfate of good quality and more suitable for dosimetry. In the course of dehydration carried out in sulfuric acid in excess, calcium sulfate of orthorhombic modification was found to develop. With calcium chloride as dehydrating agent, the sample contained also some dihydrate and hemihydrate in addition to the orthorhombic calcium sulfate, resulting in hexagonal calcium sulfate through β-hemihydrate, transformed in turn to orthorhombic calcium sulfate by exothermal coloration at about 350 to 380 °C. The crystal grains produced by thermal treatment at 800 to 900 °C are not so closely packed and no sticky at all, so they are more convenient to apply in powder form than are samples dehydrated in excess of sulfuric acid which are rather sticky.

Experimental

1. *Sample production by $CaCl_2$ dehydration*

Samples were produced as described in [1]. Concentrated sulfuric acid was diluted to about triple, then 1 mole % of manganese sulfate — related to calcium sulfate — was dissolved within. Afterwards purified $CaCl_2$ stock solution [2, 3] more than needed stoichometrically was added. The precipitate was evaporated to dryness on a water-steam bath, then missing quantity of sulfuric acid was added and kept in air at a temperature of 800 to 950 °C for 30 minutes. After cooling, the coloured parts were removed from the porous block, powdered in a mortar and sifted. This way white, non-sticky powder was obtained, suitable for dosimetric purposes both with [2, 3] and without after-treatment.

* Dedicated to Prof. G. Schay on the occasion of his 75th birthday.

** Clinic of Radiology, Semmelweis University for Medicine, Budapest

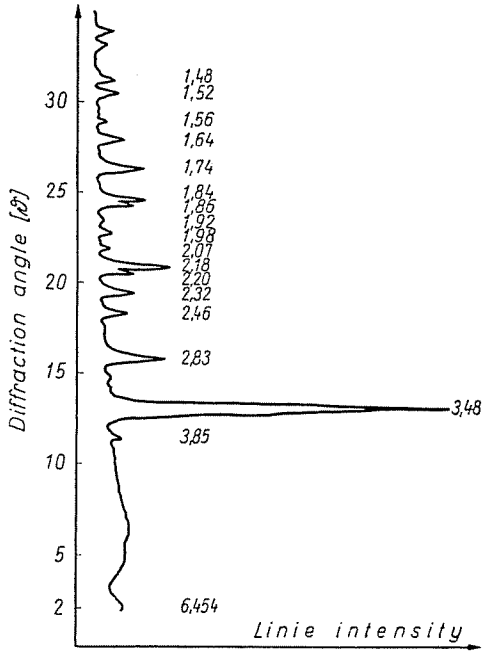

Fig. 1. X-ray diffractogram of the sample produced by dehydration in the presence of sulfuric acid

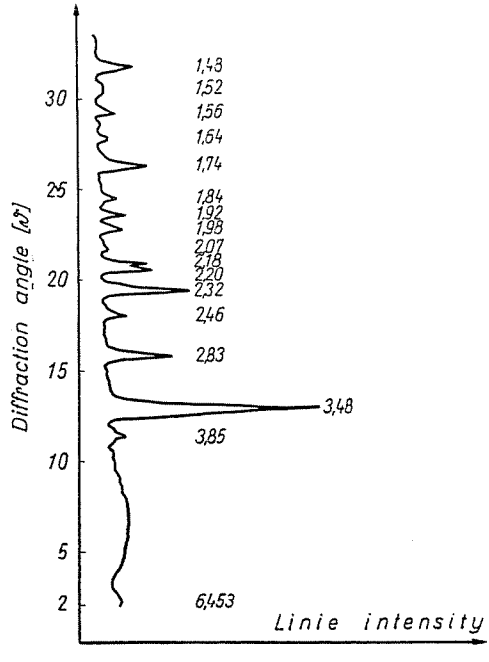

Fig. 2. X-ray diffractogram of the sample produced by dehydration in the presence of calcium chloride

2. *X-ray diffractometry*

X-ray diffractometry was done by means of an X-ray diffractometer made by Rigaku Denki Co. The recordings were taken with Cu K_α rays under accelerating voltage of 32 kV and current intensity of 24 mA. In the diagrams the deviation angles (ϑ) are plotted on the ordinate and the intensities on the abscissa. The numbers written to peaks indicate the distances of the lattice in Å. The peaks were identified by using the ASTM catalogue.

3. *Recording of the glow curves, dosimetry*

After irradiation with X- or γ-rays, the glow curves were recorded partly by means of the experimental thermoluminescent dosimeter (TLD) developed in the "Frédéric Joliot-Curie" Radiobiological and Radiohygiene Research Institute, and partly by an apparatus type Vacutronik VA-M-30 domestically transformed [4] for recording TL-curves. The glow curves were recorded at a heating rate of 40 °C/min.

The dosimetric measurements (fading, dose characteristics, energy dependence) were made in a Vakutronik-VA-M-30 apparatus.

Results and discussion

1. *X-ray diffractometry*

Luminescent phosphors prepared by dehydration in the presence of sulfuric acid or calcium chloride in excess do not differ by crystal structure. Samples produced by both methodes are calcium sulfate of orthorhombic modification.

Figs 1 and 2 show X-ray diffractometry of the samples produced each way. The place and intensity of the curves are in a fairly good agreement with data found in the ASTM catalogue. The light intensity belonging to the lattice distance of 1.74 Å of the sample dehydrated in the presence of $CaCl_2$, found before treatment at 900 °C to be the multiple of that in the ASTM-catalogue [1], dropped after heat treatment. Place and intensity of the curve correspond to the values found in the catalogue. Thus, the orthorhombic calcium sulfate is transformed by heat treatment to a crystal "normal" from the point of view of crystal structure.

2. *Glow curve*

No significant difference can be observed between the glow curves of the samples gained each way (Figs 3, 4). Neither do the samples produced by dehydration in the presence of calcium chloride differ if exposed to an after-treatment (Figs 4, 5).

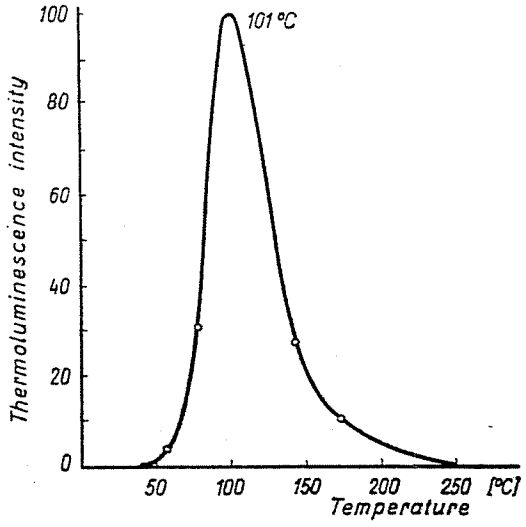

Fig. 3. Glow curve of the sample produced by dehydration in the presence of sulfuric acid (after-treated)

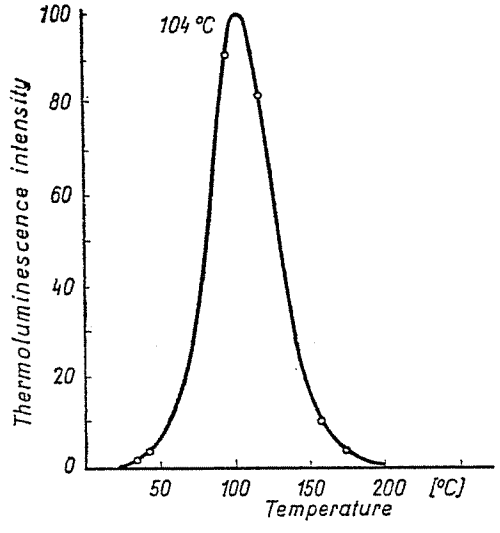

Fig. 4. Glow curve of the sample produced by dehydration in the presence of calcium chloride (after-treated)

3. *Fading*

Fading of phosphor prepared by dehydration in the presence of calcium chloride was examined at different temperatures. The results are demonstrated ni Fig. 6. The fading of the samples dehydrated each way at room temperature

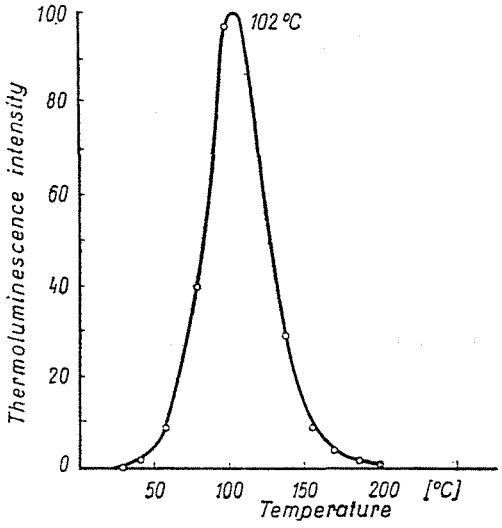

Fig. 5. Glow curve of the sample produced by dehydration in the presence of calcium chloride (without after-treatment)

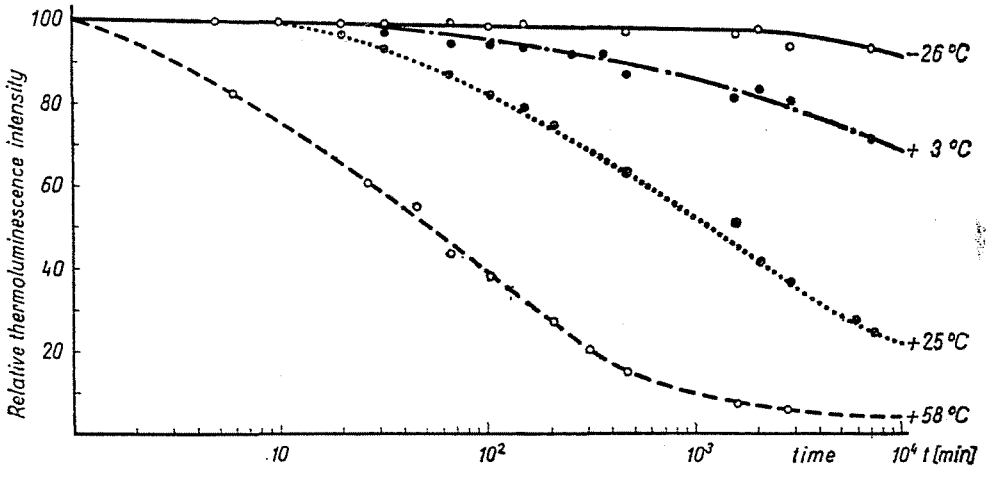

Fig. 6. Fading of the sample produced by dehydration in the presence of calcium chloride at different temperatures

is presented in Fig. 7. The results show an agreement between fadings of the samples produced in two ways as well as the results published by Bjärngard [7].

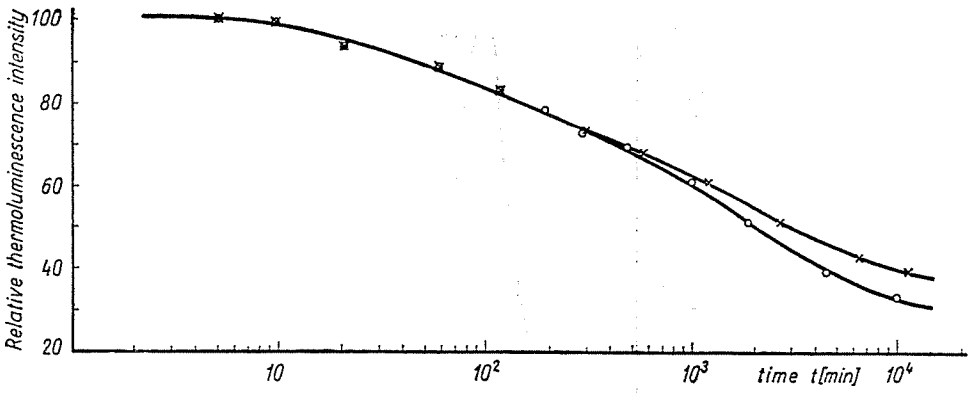

Fig. 7. Fading of samples dehydrated in different ways at room temperature

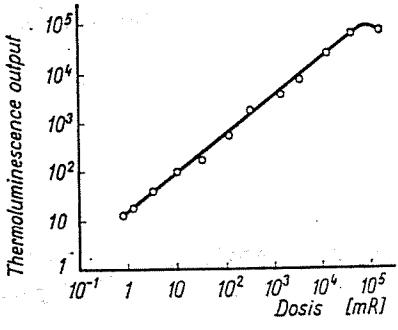

Fig. 8. Thermoluminescent signal-dose correlation of the sample produced by dehydration in the presence of calcium chloride

4. *Dose characteristics*

The TL-dosimeters have generally application ranges of 4 to 8 orders of magnitude ($\approx 10^{-3}$ to 10^5 R) depending on the TL-phosphor used and on the evaluating apparatus.

Literature data, relevant to the upper and lower limits of the dosimetric application of $CaSO_4$: Mn thermoluminescent phosphor, are rather divergent, obviously depending on the thermoluminescent phosphor produced in different ways, as well as on the evaluating devices [5 through 11].

In the evaluating apparatus type Vakutronik VA-M-30, our sample produced a well-measurable signal even on the effect of 1 mR radiation. Our samples exhibited a linear relationship in the radiation range 1 to 10^5 mR, that recessed above it (Fig. 8).

This shows a good agreement with the data of the samples produced by dehydration in the presence of sulfuric acid in excess [3].

5. *Energy dependence*

The energy dependence of the samples was essentially not related to the production conditions — in conformity with expectations. The energy dependence of the $CaSO_4$: Mn phosphor was found to be maximum in the 50 to 70 keV range (Fig. 9).

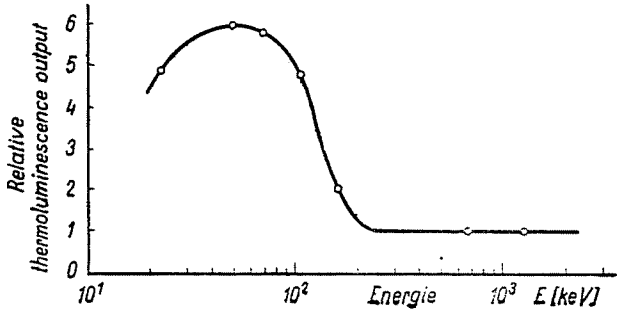

Fig. 9. Energy dependence of the sample produced by dehydration in the presence of calcium chloride

Our measuring results are in agreement with those of Bjärngard, with the difference that he found the maximum sensitivity in the 50 to 100 keV range [7].

Summary

The thermoluminescent and dosimetric characteristics of $CaSO_4$: Mn thermoluminescent phosphor produced by two different dehydration processes have been investigated and compared to each other and to literature data. The examined characteristics (crystal structure, glow curve, fading, dose characteristic, energy dependence) of the thermoluminescent phosphor produced by each method did not differ significantly and our results fairly agreed with those found in the literature.

Advantages of the $CaSO_4$: Mn thermoluminescent phosphor produced by dehydration in the presence of calcium chloride excess consist in simple production, no special reducing atmosphere required by heat treatment, and applicability without after-treatment. They possess the same good dosimetric characteristics as phosphor produced by other methods, in addition they are non-sticky, and easy to handle (to dose).

References

1. KÁSA, I., BUZÁGH-GERE, É.: Periodica Polytechnica Chem. Eng. 19 (1975) No. 4. 263—274.
2. KÁSA, I., PORUBSZKY, I., KISS, L.: Acta Chim. Hung. **68**, 11 (1971).
3. KÁSA, I., RÓKA, O., KISS, L.: Magyar Kémiai Folyóirat **77**, 126 (1971).
4. TÖRÖK, I.: Application of Solid-Body Dosimeters in Clinical Practice and Experiments. (In Hungarian). Candidate's Thesis, Budapest 1972.
5. ARKANGELSKAYA, V. A., VAYNBERG, B. J., RAZUMOVA, T. K.: Opt. i. Spektr. **4**, 681 (1958).
6. BJÄRNGARD, B.: Rev. Sci. Instr. **33**, 1129 (1962).

7. BJÄRNGARD, B.: Aktibolaget Atomenergi Report, Stockholm, Sweden No AE—109 (1963).
8. BJÄRNGARD, B.: Aktibolaget Atomenergi Report, Stockholm, Sweden No AE—118 (1963).
9. ATTIX, F. H.: NRL Report No 6145 (1964).
10. IKEYA, M.—ITOH, N.: J. Nucl. Sci. Tech. **6**, 132 (1969).
11. IKEYA, M.—ISHIBASHI, M.—ITOH, N.: Health Physics **21**, 429 (1971).

Dr. Imre KÁSA
Dr. István TÖRÖK } H-1521 Budapest