NEW METHOD FOR PREPARATION OF $CaSO_4$: Mn SUITABLE FOR DOSIMETRY. I

STUDIES ON PREPARING $CaSO_4$: Mn THERMOLUMINESCENT PHOSPHORS BY DEHYDRATION

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The modifications of calcium sulphate containing waters of crystallization ($CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 1/2H_2O$) are not luminescent, whereas the anhydrous orthorhombic modification is. The preparation should endeavour to produce this modification, and also, an appropriate amount of a suitable activator ion in the crystal lattice. This is achieved most easily by igniting calcium sulphate dihydrate mixed with the activator ion at 800 to 1000 °C. Orthorhombic calcium sulphate is formed according to the following reaction equation [1]: $CaSO_4 \cdot 2 H_2O \rightarrow CaSO_4 \cdot 1/2 H_2O \rightarrow CaSO_4$ (hex) $\rightarrow CaSO_4$ (ortho).

Earlier the preparation was really conducted in this way [2, 3], both dehydration and formation of orthorhombic calcium sulphate were due to high temperature.

Attempts have been made to prepare the anhydrite modification from calcium sulphate dihydrate at a lower temperature, using a dehydrating agent (cc. H_2SO_4) [4—6]. In this case — probably due to the better conditions for the incorporation of the activator — the efficiency of thermoluminescence increases. The results are even better if the formation of orthorhombic calcium sulphate and the introduction of the activator proceed simultaneously [7—11]. Our previous papers [10—11] surveyed the methods developed for the preparation of calcium sulphate activated with manganese applicable for dosimetry, and also our investigation results in determining the optimum conditions for the introduction of the activator simultaneously with the formation of calcium sulphate. Dehydration was effected with a small excess of sulphuric acid. An aftertreatment permitted the sensitivity of the samples heat-treated in air to approach or even reach that of samples prepared in a reducing atmosphere. This way a good quality but slightly sticky luminous powder was obtained, somewhat awkward in application.

Therefore, a new dehydration procedure was developed, keeping the way of activator introduction, heat treatment in air and aftertreatment, found to be effective during the earlier studies. This method permitted to improve the thermoluminescent properties of $CaSO_4$: Mn.

Experimental

1. *Preparation of samples*

Stock solutions were prepared and purified as described earlier [10, 11]. Twelve samples have been prepared as compiled in Table I.

The reagents were mixed slowly under stirring. The solution was evaporated to dryness on a steam bath and the residue pulverized, washed chloride-free with distilled water, dried at room temperature and powdered again.

Table I

Conditions of sample preparation

No. of sample	Reagent in excess	Additive	Temperature of precipitation	Drying
1	H_2SO_4	—	room temp.	Evaporation on a steam bath
2	H_2SO_4	—	room temp.	Evaporation on a steam bath. Washing free from chloride
3	$CaCl_2$	—	room temp.	Evaporation on a steam bath
4	$CaCl_2$	—	room temp.	Evaporation on a steam bath. Washing free from chloride
5	H_2SO_4	1 mole% $MnSO_4$	room temp.	Evaporation on a steam bath
6	$CaCl_2$	1 mole% $MnSO_4$	room temp.	Evaporation on a steam bath
7	H_2SO_4	—	boiling temp.	Evaporation on a steam bath
8	H_2SO_4	—	boiling temp.	Evaporation on a steam bath. Washing free from chloride
9	$CaCl_2$	—	boiling temp.	Evaporation on a steam bath
10	$CaCl_2$	—	boiling temp.	Evaporation on a steam bath. Washing free from chloride
11	H_2SO_4	1 mole% $MnSO_4$	boiling temp.	Evaporation on a steam bath. Washing free from chloride
12	$CaCl_2$	1 mole% $MnSO_4$	boiling temp.	Evaporation on a steam bath. Washing free from chloride

2. *Thermoanalytical investigations*

The thermal properties of the calcium sulphate samples prepared as described above were studied by thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA). The measurements were made in a PAULIK—PAULIK—ERDEY MOM Derivatograph [12], with

300 to 350 mg samples, using platinum crucible as sample holder and a heating rate of 5°/min, in air atmosphere.

3. X-ray diffraction studies

X-ray diffraction studies were carried out in a Rigaku Denki Co. Ltd. Japanese X-ray diffractometer, using CuKα radiation, 32 kV accelerating voltage and 24 mA current.

In the diagrams the diffraction angles ϑ are plotted on the ordinate and the intensities on the abscissa. Figures at the peaks represent the distances between crystal planes in Å. The peaks were identified by means of the ASTM catalogue.

Results and discussion

WEST and SUTTON [13] have shown as early as 1954 that five peaks appear on the DTA curve of calcium sulphate dihydrate if the measurement is made in air atmosphere. This finding was confirmed by later investigations [14—18].

The first marked endothermic peak ($\sim$180 °C) indicates the transformation of the dihydrate into hemihydrate, the second one ($\sim$215 °C) the transformation of the hemihydrate into hexagonal calcium sulphate (γ-CaSO₄, anhydrite III; soluble calcium sulphate).

The third narrow exothermic peak ($\sim$360 °C) shows the hexagonal → orthorhombic transformation, in which orthorhombic calcium sulphate (β-CaSO₄, anhydrite II; insoluble calcium sulphate) is formed.

The transformation of β-CaSO₄ into α-CaSO₄ is indicated by a narrow endothermic peak (1225 °C). Above this temperature the thermal decomposition of calcium sulphate starts. The melting of the eutectic CaO—CaSO₄ is indicated by a narrow endothermic peak at 1385 °C.

From our point of view only the first three peaks are of importance, since CaSO₄ : Mn suitable for dosimetry is obtained from a thermal treatment at 800 to 1000 °C.

The data obtained from the thermal curves of our samples are compiled in Table II.

It is obvious from the tabulated data that in the case of precipitating and dehydrating in presence of sulphuric acid excess the second DTG and DTA peaks at 260 to 270 °C disappear after washing the product (sample 2), hence these peaks belong to the sulphuric acid excess. If this is removed by washing, the corresponding DTG and DTA peaks disappear. The phenomenon persists even for precipitating in boiling solution or in the presence of 1 mole per cent of MnSO₄. The first DTG peak (80 to 90 °C) is hardly noticeable with the

2*

Table II

Data obtained from the thermal curves

No. of sample	Step 1		Step 2		Exo-thermic DTA peak, °C	Dehydration, composition, after treatment
	DTG peak, °C	Weight loss,* %	DTG peak, °C	Weight loss,* %		
1	80	6.8	260	4.5	—	H_2SO_4 excess
2	tailing	0.47	—	—	—	H_2SO_4 excess washed out
3	70	2.43	130	1.7 (0.13 mole H_2O)	—	$CaCl_2$ excess
4	—	—	125	2.6 (0.19 mole H_2O)	350	$CaCl_2$ excess washed out
5	98	10.4	275	11.6	—	H_2SO_4 excess 1 mole % $MnSO_4$
6	80	3.9	140	1.99 (0.15 mole H_2O)	350	$CaCl_2$ excess 1 mole % $MnSO_4$
7	85	10.6	270	9.8	—	H_2SO_4 excess, precipitated in boiling solution
8	tailing	0.39	—	—	—	H_2SO_4 excess, precipitated in boiling solution, washed out
9	95	6.6	140	2.66 (0.2 mole H_2O)	370	$CaCl_2$ excess, precipitated in boiling solution
10	—	—	130	7.6 (0.58 mole H_2O)	380	$CaCl_2$ excess, precipitated in boiling solution, washed out
11	90	10.7	270	6.4	—	H_2SO_4 excess, 1 mole % $MnSO_4$, precipitated in boiling solution
12	50	0.5	130	1.0 (0.08 mole H_2O)	—	$CaCl_2$ excess, 1 mole % $MnSO_4$, precipitated in boiling solution

* Weight loss in percentage of the dry matter.

washed samples, and the weight loss of 7 to 10% diminishes to less than 0.5% (Fig. 1). This shows that this water is bound by capillary forces rather than to be water of crystallization.

To demonstrate the correlations, the thermal curves of samples 1, 2 and 11 are presented in Figs 1 and 2. Also X-ray diffraction studies have shown that dehydration effected with excess sulphuric acid, results in orthorhombic calcium sulphate, unable of binding water, which means that neither dihydrate nor hemihydrate is present in appreciable amount (Fig. 3). This way good quality fine-grained crystals could be obtained, which were applicable for dosimetry, nevertheless somewhat sticky [10—11].
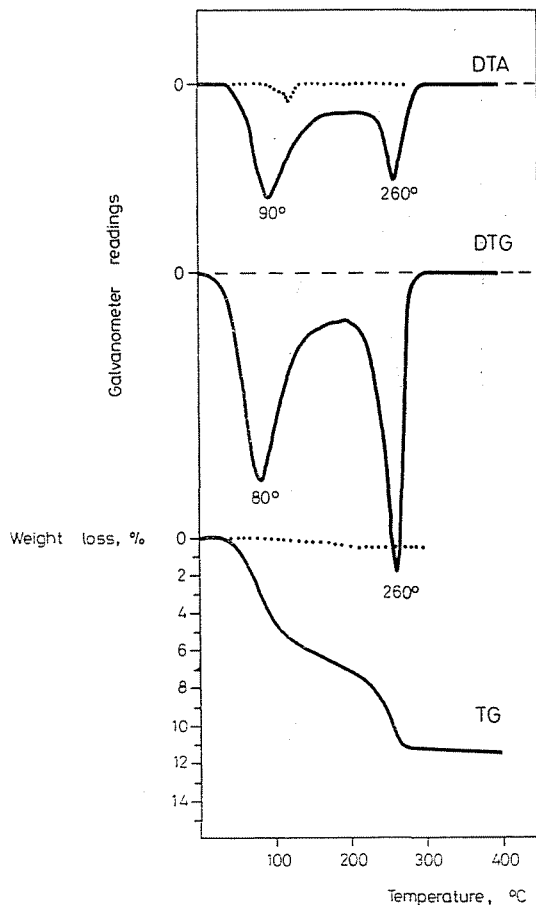
Fig. 1. TG, DTG and DTA curves of calcium sulphate precipitated at room temperature with sulphuric acid excess (samples 1 and 2). ——— Sample 1.; . . . . . . Sample 2

The situation is different if the dehydration is carried out in the presence of a small excess of calcium chloride. In this case only the first DTG peak (70 to 95 °C) by a weight loss of 2 to 6% of the unwashed sample disappears after washing (Table II).

This finding is unaltered by precipitating in boiling solution or in the presence of 1 mole % of MnSO$_4$. In this case also, capillary water rather than water of crystallization is present. In case of dehydrating in the presence of a small excess of CaCl$_2$, the second DTA and DTG peaks appear at a much lower temperature, 125 to 140 °C, and the corresponding weight loss of about 1 to 2.6% (Figs 4, 5 and 6).

The nature of this peak is, however, different from that of the second DTG peak of samples dehydrated with sulphuric acid excess. In this case it
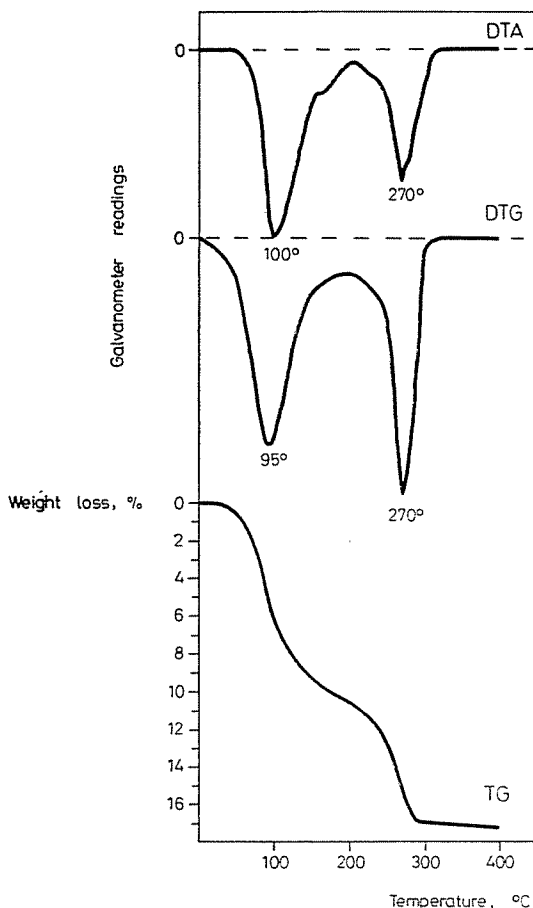
Fig. 2. TG, DTG and DTA curves of calcium sulphate precipitated in boiling solution with sulphuric acid excess containing 1 mole% MnSO$_4$ (sample 11)

does not disappear after washing the sample but even increases to some extent. This leads to the assumption that here waters of crystallization are involved. The sample dehydrated this way contains also some dihydrate, as indicated by the DTA and DTG curves and X-ray diffraction studies (Fig. 7).

The DTG and DTA curves of a sample dehydrated with calcium chloride excess and washed indicate two directly consecutive processes. This is in accordance with the case discussed by LEHMAN and RIEKE [18], namely that the decomposition of the dihydrate proceeds in two steps if the water of crystallization is not immediately removed (Fig. 5).

An increasing vapour pressure shifts the second peak towards higher temperatures and the separation becomes more pronounced. In this case the small amount of dihydrate present in the sample is transformed into hemi-hydrate and the latter into anhydrite.
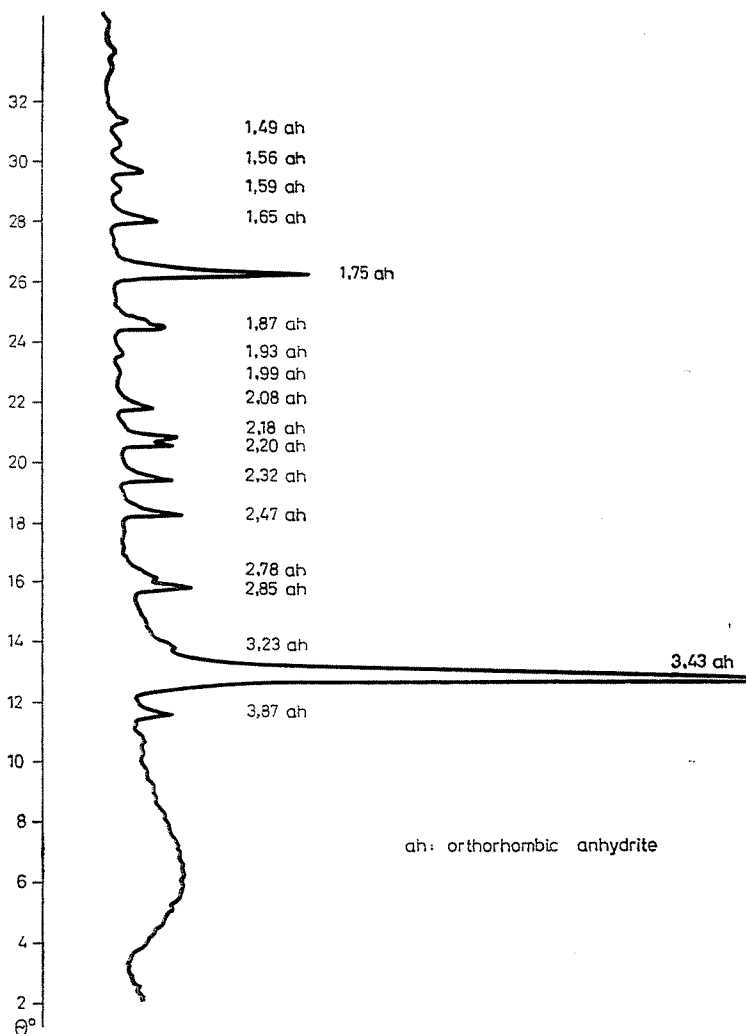
Fig. 3. X-ray diffractogram of calcium sulphate precipitated at room temperature with sulphuric acid excess containing 1 mole % MnSO₄ (sample 5)

The slight water uptake leads to the conclusion that the sample also contains some hemihydrate in addition to the insoluble anhydrite present in oriented form (Fig. 7). The DTA curve of calcium sulphate prepared and dehydrated in the presence of calcium chloride excess exhibits a narrow exothermic DTA peak between 350 and 380 °C, indicating the transformation of hexagonal calcium sulphate (soluble anhydrite, γ-CaSO₄; anhydrite III) containing traces of water and formed from calcium sulphate dihydrate by dehydration, into orthorhombic CaSO₄ (anhydrite II, β-CaSO₄) (Table II).
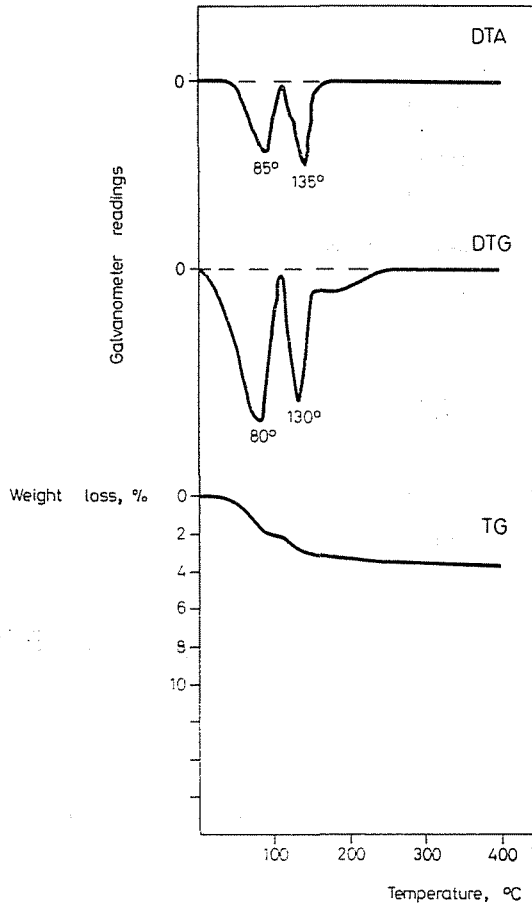
Fig. 4. TG, DTG and DTA curves of calcium sulphate precipitated at room temperature with calcium chloride excess (sample 3)

The temperature of occurrence and shape of the peak (sharp or flat) depends, in addition to the structure of the starting material on the degree of crystallinity of the developing soluble anhydrite and on the presence of impurities [15, 17].

The fact that the exothermic peak is distinct from the endothermic one and appears at a higher temperature shows it to form through a hemi-hydrate known in the literature [16, 18] as β-hemihydrate (porous micro-crystalline form).

Namely, two endothermic peaks of dehydration of α-hemihydrate are closely followed by the exothermic peak by dehydration in the presence of water [15, 17]. The contradiction that the hexagonal modification formed trough the β-hemihydrate is transformed into the orthorhombic modification
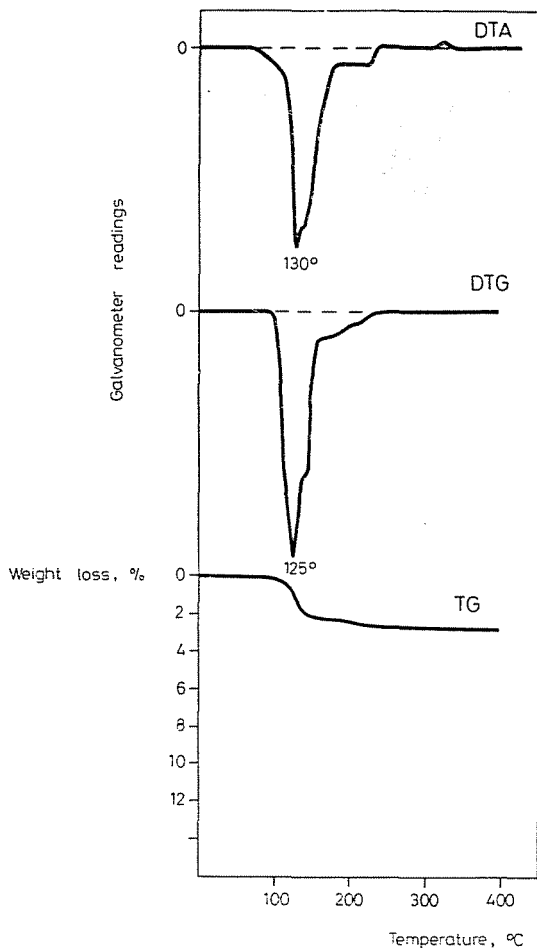
Fig. 5. TG, DTG and DTA curves of a sample precipitated at room temperature with calcium chloride excess and washed free from chloride (sample 4)

at higher temperature than the hexagonal $CaSO_4$ formed through the (solid, well crystallized) α-hemihydrate, as against expectations from the micro-crystalline nature of the β-hemihydrate, has been accounted for by LEHMAN and RIEKE [18] as follows:

The driving force of the transformation is the difference between the free enthalpies of the original and final modification. Provided the precipitation proceeds from gas or liquid phase, this is composed of two terms (volume and phase boundary). If the transformation of the solid modification is accompanied by a change in the geometry of the crystal lattice, a further term enters (lattice deformation).
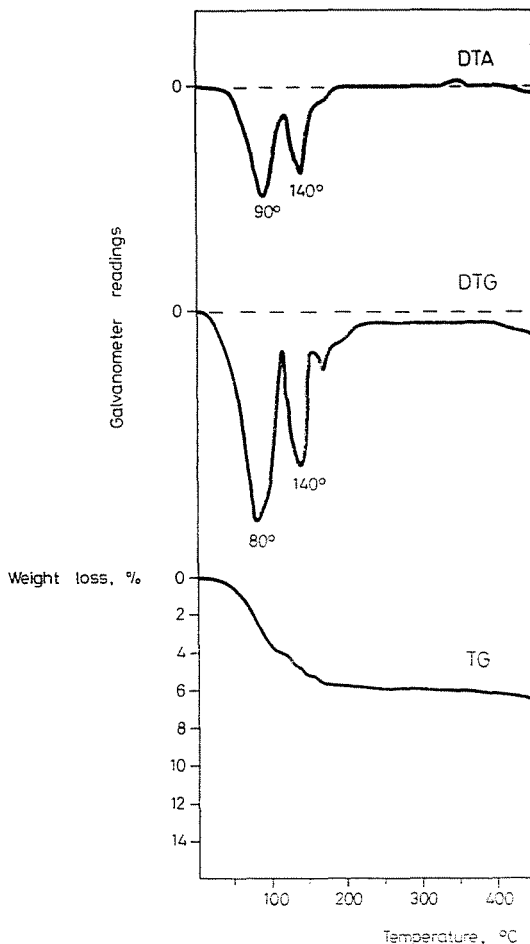
Fig. 6. TG, DTG and DTA curves of calcium sulphate precipitated at room temperature with calcium chloride excess containing 1 mole % $MnSO_4$ (sample 6)

The α-hemihydrate crystal has a greater specific volume. The high probability of nucleation and the term *volume* permits the partial transformation of the crystal at relatively low temperatures.

The transformation of the β-crystals of smaller size starts only at a higher temperature. Due to this fact and to the uniform size of the crystals, the transformation proceeds by exothermic reaction, within a typical narrow temperature range at a temperature higher than that necessary for the anhydrite (II) to be formed. Here the lattice strains hinder the complete transformation less than that of the α-modification, since the irregularity of the β-lattice reduces the strains.
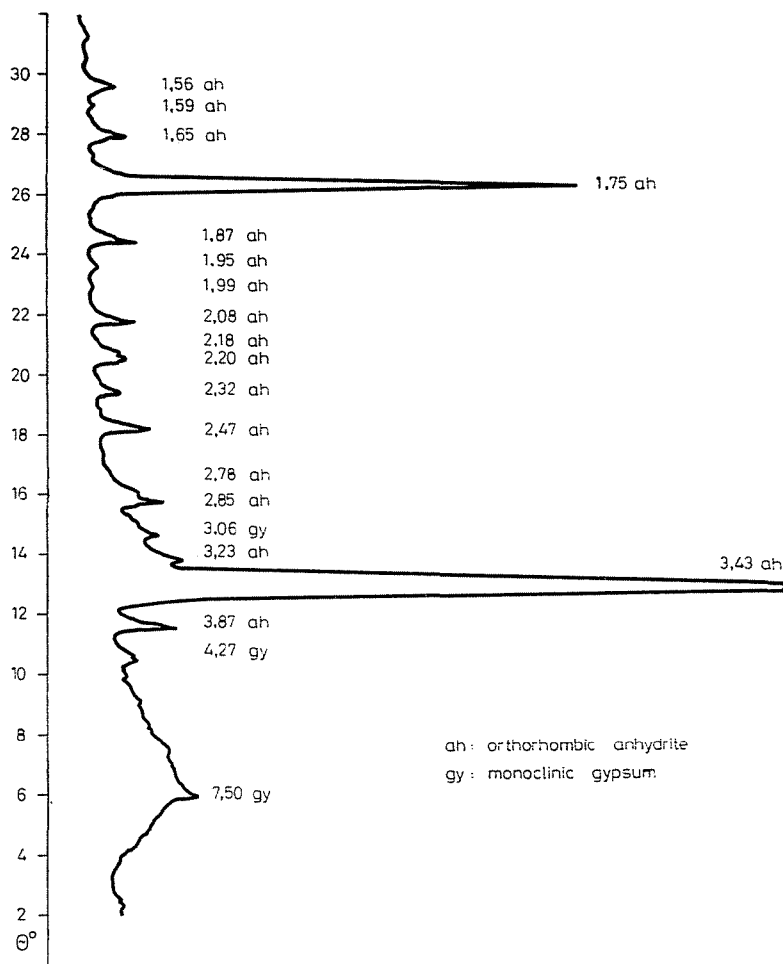
Fig. 7. X-ray diffractogram of calcium sulphate precipitated at room temperature with calcium chloride excess containing 1 mole % MnSO₄ (sample 6)

After finishing the dehydration in the presence of calcium chloride, the lacking amount of sulphuric acid is added prior to thermal treatment at 800 to 900 °C in air atmosphere. After cooling, the porous block is cleaned from the coloured parts, powdered, sieved and either after-treated [10—11] or used without aftertreatment. In both cases a nice white, non-sticking powder is obtained which is well suited for dosimetry.

The thermoluminescent and dosimetric properties of the resulting CaSO₄ : Mn phosphor will be described in a subsequent paper.

Summary

The conditions of the precipitation and dehydration of $CaSO_4$ have been investigated with the purpose of preparing $CaSO_4$: Mn phosphor suited for dosimetry.

By precipitation and dehydration with sulphuric acid excess, orthorhombic, anhydrous calcium sulphate is obtained in a single step. A heat treatment at 800 to 900 °C results in tiny compact crystals which can be used in dosimetry but are a little sticky.

The material formed by dehydration in the presence of a slight excess of calcium chloride contains some dihydrate and hemihydrate in addition to orthorhombic calcium sulphate, of which hexagonal calcium sulphate is formed through β-hemihydrate. The hexagonal form is transformed to orthorhombic calcium sulphate at about 350 to 380 °C in an exothermic reaction. The crystalline particles are less compact in this case, are not sticky at all and have excellent dosimetric properties.

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