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DTA STUDIES ON THE BARIUM SULPHATE–CALCIUM SULPHATE EUTECTOID MIXTURE

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Samples of a nearly eutectoid mixture of 60 mole% $BaSO_4$ – 40 mole% $CaSO_4$, a highly effective system for the selective sorption of strontium, were studied using the DTA method. The effects of the time of thermal treatment and the number of thermal cycles of two different types on the homogenisation degree and thus on the formation of the metastable barium—calcium sulphate were examined. The conditions of the thermal decomposition of the metastable sulphate, the activation energy and the heat released during this process were estimated.

Previous studies of the heat-treated $BaSO_4-CaSO_4$ mixture suggested the advantage of such substances for the sorption of strontium ions [1, 2]. The most promising eutectoid mixture (actually a nearly eutectoid mixture: 60 mole% $BaSO_4$–40 mole% $CaSO_4$) was more carefully studied and the physico-chemical properties of a newly-formed structure were estimated [3, 4]. The results of IR and X-ray measurements gave evidence of the formation of a metastable, crystalline compound $BaSO_4-CaSO_4$. The instability of this form was proved by annealing which gave back the original components. The energy released during this process was found to correspond to the amount of the active form created by heat treatment and subsequent rapid cooling, i.e. to the content of the metastable sulphate. Thus the DTA method was used to compare samples prepared by various treatments. The effects of the time of heat-treatment at 1200° and the type of thermal cycle were studied in detail.

Experimental

The DTA measurements were carried out using a MOM Derivatograph. The powdered specimens were placed in platinum crucibles and measured in an air stream of 200 ml/min volumetric flow rate at a heating rate of 11°/min.

The weight of sample was approximately 250 mg.

The temperature of a specimen was measured in the centre of a sample layer using a Pt/PtRh (10%) thermocouple separated from the sample by a platinum protection tube mounted in the bottom of the crucible. As reference material for DTA measurements Al_2O_3 or $BaSO_4$ were used.

The peak areas on the DTA curves were measured with a planimeter. A calibration measurement of the transitional enthalpy change of potassium sulphate was carried out for the estimation of enthalpy changes from the DTA peaks. The value of this inversion enthalpy change has been reported to be 12.3 cal/g at 583°.

A 60 mole% $BaSO_4$–40 mole% $CaSO_4$ mixture was used for the preparation of samples. Both compounds were of analytical purity (Lachema), but this was checked by spectroscopic analysis. Special pellets in the form of hollow cylinders ($r = 9$ mm, $h = 25$ mm, wall thickness = 3 mm) were prepared from the wet mass after a thorough homogenization in a ball mill. These cylinders were then used for various thermal treatments: one series of samples was heated at 1200° for 5, 20, 45, 65, 150 and 270 min, respectively, with subsequent rapid cooling in water saturated with $CaSO_4$ (series D). The samples of series E were heated at 1200° for 20 min with slow increase and decrease of temperature, repeated 1 to 8 times (thermal cycling) and followed by subsequent cooling in water saturated with $CaSO_4$. The samples of series F differ from those of series E in that the rates of increase and decrease of temperature were higher.

All preparations were air-dried, ground to powder and the sieve fraction of <60 μm was used for measurements.

Results and discussion

The original mixture of 60 mole% $BaSO_4$ and 40 mole% $CaSO_4$ was examined by the DTA method in order to find the conditions of thermal treatment which lead to the selective sorbent. The typical DTA curve (Fig. 1, curve 1) of the

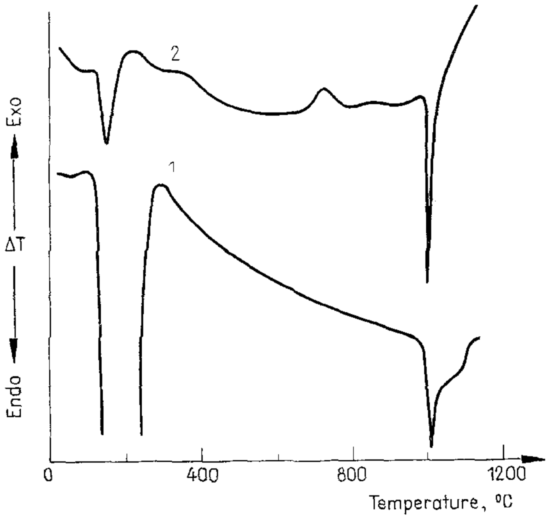

Fig. 1. DTA curves of a $BaSO_4$–$CaSO_4$ mixture (60 mole% $BaSO_4$). 1 — original mixture, 2 — metastable sulphate

initial mixture shows a broad endothermic peak corresponding to the dehydration of calcium sulphate dihydrate with no evident peak up to about 1000° where a doublet of endothermic peaks appears. These peaks correspond to the well-known transition of the eutectoid $BaSO_4-CaSO_4$ mixture from its orthorhombic state to its cubic state. The first sharp part of the doublet can be explained by the phase transition while the second part is due to the same process taking place in the less homogenized parts of the sample.

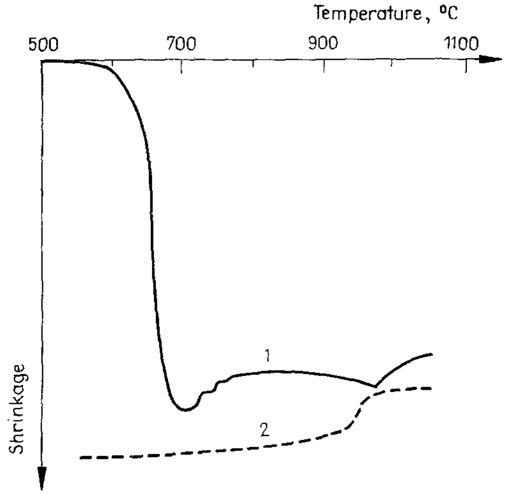

Fig. 2. The dilatometric curves of an original $BaSO_4-CaSO_4$ mixture pellet (arbitrary units). 1 — heating curve, (10°/min), 2 — cooling curve

This interpretation of the nature of the two endothermic peaks was confirmed by repeated DTA measurements on the same sample. It was shown that the second slow effect gradually disappeared during the thermal cycling, while the first sharp effect increased to a certain limit, as shown in Table 1. The DTA curves obtained during cooling of the samples show sharp exothermic peaks at about 930°.

The average value of the enthalpy change corresponding to the sharp endothermic effect was roughly estimated from the peak area measurements to be about 3.6 kcal/mol. The activation energy was calculated with the use of the equation [5]:

$$\ln \frac{1}{(1-\alpha)_m} = 1 - \frac{2RT_m}{E} \qquad (1)$$

where T_m = peak temperature (°K),
α = fraction converted,
E = activation energy (kcal/mol),
R = 1.987 kcal/mol, deg,
m = index for peak extremum values.

The activation energy value for $\alpha_m = 0.51$ and $T_m = 1263$ °K was found to be 16.3 kcal/mol.

A typical DTA curve of the specially heat-treated Ba, Ca/SO_4 specimens (the sample after the heat-treatment at 1200° was cooled rapidly in water) is shown in Fig. 1, curve 2. This curve is almost analogous to that of the initial sulphate mixture (curve 1) with the exception of a new, exothermic peak at about 730°. The temperature at the beginning of this exothermic effect (about 630) is in good agreement with the temperature of the largest volume change found by dilatometric measurements on the original mixture, demonstrated in Fig. 2. The dilatometry of pellets pressed at 1400 kp/cm^2 shows the most significant change (shrinkage) at about 650°. The thermal emanation measurement of analogous material [6] gives an effect corresponding to contraction at about the same temperature (about 700°). The ion mobilities at this temperature (diffusion rates) probably reach a value sufficient for an easier motion of the crystal components followed by contraction of the studied specimen. Therefore the metastable barium–calcium sulphate undergoes a decomposition to its original components in this temperature range. The structural properties of the mixture before and after the annealing were studied by X-ray and IR analysis [3]. It was found that

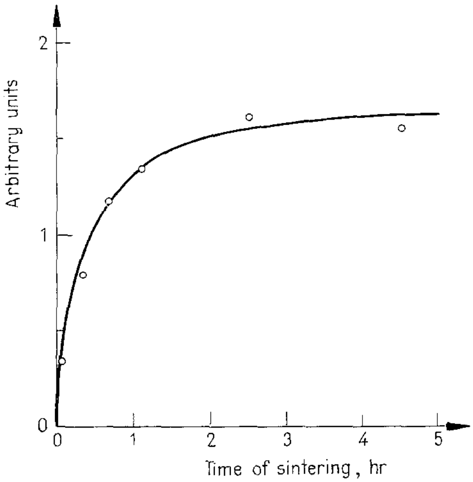

Fig. 3. Effect of the sintering time on the metastable sulphate content (Arbitrary units: DTA peak area—sample weight ratio)

the metastable sulphate results in a mixture of the pure original components, baryte and anhydrite.

An attempt using Eq. (1) to estimate the activation energy corresponding to the described exothermic effect gives a value of 12.8 kcal/mol.

The dependence of the fraction of the metastable sulphate on the time of heating at 1200° is shown in Fig. 3; the corresponding values for two types of thermal cycling (series E and F) are shown in Fig. 4. It can be seen from Fig. 3 that the amount of the metastable structure increases with the time of heat treatment to a certain limit, reached after approximately 2 hours. An analogous dependence for the series E and F demonstrates a very similar effect of both types of thermal cycling on the metastable phase formation. A certain limit of the size of the heat effect is reached after approximately two cycles. Having reached this magnitude the dependence on the number of further thermal cycles shows a very slight increasing tendency. The maximum heat effect obtained by the thermal treatment used was 1.27 kcal/mole. This value was estimated from the DTA curves and peak area measurements.

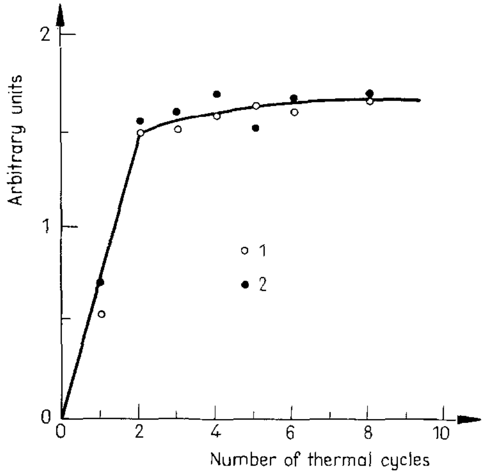

Fig. 4. Effect of the thermal cycling on the metastable sulphate content. (Arbitrary units: DTA peak area—sample weight ratio). 1 — series E, 2 — series F

As can be concluded from the results shown in Table 1, the continuous growth of perfectly homogeneous areas from the starting mixture was observed. The existence of these areas is a necessary prerequisite for the formation of metastable sulphate. The larger this area the bigger the expected size of the resulting crystals. In view of this assumption the sorbents prepared by thermal cycling would contain crystals whose size depends on the number of cycles.

The surface areas of the studied specimens (series F) were measured using the BET method, to confirm this assumption. The results are presented in Table 2.

Table 1

Thermal cycling of the $BaSO_4-CaSO_4$ mixture

Cycle No.	Endothermic effect peak area (arbitrary units)
1	0.333
2	1.63
3	2.13
4	—
5	2.93
6	2.90
7	3.16
8	3.33
9	3.50
10	3.66

As the particle size is inversely proportional to the specific surface area, the results obtained are a good confirmation of our consideration.

Table 2

The surface areas of the specimens of series F

Number of cycles	Surface area (m^2/g)
1	4.17
2	2.76
3	2.67
4	2.70
5	2.23
6	1.92

The specimens studied in this paper were used as strontium sorbents for sorption rate measurements [7]. The results of strontium sorption kinetics as well as of the calcium ion dissolution rate – both processes being strongly surface dependent – led to the above-mentioned conclusions.

Conclusions

1. It was proved experimentally that the nearly eutectoid mixture of $BaSO_4$ and $CaSO_4$ underwent a process of homogenization during the described thermal treatment. The polymorphic transformation at approximately 1000° proved to be of great importance for the homogenization.

2. The (Ba, Ca)SO_4 is thermally metastable and is decomposed into its original components by heating at about 630°.
3. The enthalpy changes calculated from DTA measurements can be used to evaluate the metastable sulphate content. This method was found to be useful for the characterization of sorbents prepared by various thermal treatments.

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Résumé — Etude par ATD d'échantillons provenant d'un mélange $BaSO_4$ 60 moles % — $CaSO_4$ 40 moles %, de composition voisine de celle de l'eutectoide et très efficace pour la sorption sélective du strontium. Etude de l'influence de la durée du traitement thermique et du nombre de cycles thermiques (de deux types différents) sur le degré d'homogénéisation, c'est-à-dire sur la formation de sulfate de baryum-calcium métastable. On a estimé les conditions de la décomposition thermique du sulfate métastable, l'énergie d'activation et la quantité de chaleur dégagée par le processus.

Zusammenfassung — Eine durch ihre selektive Fähigkeit zur Sorption von Strontium ausgezeichnete, beinahe eutektische Mischung von 60 Mol% $BaSO_4$ und 40 Mol% $CaSO_4$ wurde differentialthermoanalytisch geprüft. Der Einfluß der Zeit der thermischen Behandlung und von zwei verschiedenen thermischen Zyklen auf den Homogenisierungsgrad, und so auch auf die Bildung des metastabilen Barium—Kalzium Sulfates wurden untersucht. Die Bedingungen der thermischen Zersetzung des metastabilen Sulfats, die Aktivierungsenergie und die während des Vorgangs freigesetzte Wärme wurden ermittelt.

Резюме — Исследована почти эвтектическая смесь, состоящая из 60 мол% $BaSO_4$—40 мол% $CaSO_4$. Система обладает высокой эффективностью при избирательной сорбции стронция. Изучено влияние времени термической обработки и числа двух различных типов термического цикла при гомогенизации на образование метастабильного сульфата бария и кальция. Дана оценка условий термораспада метастабильного сульфата и определены энергия активации и теплота, выделяющаяся при этом процессе.