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THERMAL DECOMPOSITION OF COLEMANITE

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ABSTRACT

Thermal decomposition of colemanite $Ca[B_3O_4(OH)_3]H_2O$ monocrystals has been investigated by thermal, X-ray, IR and optical microscopy methods at normal as well as at elevated temperatures. Investigations have revealed that thermal decomposition of colemanite occurs in the whole volume of the crystal and is divided into two independent stages: (1) formation of H_2O from OH groups and (2) breaking of H_2O and borate chains bonds and then removal of both kinds of water from the anhydrous phase of the preserved borate structure. Each process corresponds to a separate DTA peak, the second being accompanied also by loss of weight due to explosive water escape.

This represents a rare event of dehydroxylation with distinct separation of H_2O formation and removal of water molecules from the parent substance.

INTRODUCTION

The thermal decomposition of colemanite is complex because of the interference of different reactions. Calcium borate mineral colemanite $Ca[B_3O_4(OH)_3]H_2O$ forms monoclinic prismatic class $2m$ crystals. Its structure contains infinite boron–oxygen chains parallel to the a axis. The chain elements consist of two BO_4 tetrahedra and a ring of the composition $[B_3O_4(OH)_3]^{2-}$. The chains are joined to each other laterally by ionic bonds through the Ca^{2+} ions to form sheets extending parallel to (010). A system of hydrogen bonds involving the hydroxyl groups in the chain and the water molecules ties the sheets together [1].

Thermal decomposition of colemanite has been investigated by many authors [2–18] and by various thermoanalytical methods; the conclusions were different both with respect to the crystal structure and from the point of view of the mechanism of the thermal decomposition.

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Hartung and Heide [2], when examining the behaviour of colemanite during heating, found that in the temperature range 60–430 °C dehydration of colemanite occurs. X-Ray examinations revealed that after dehydration the substance has an amorphous form which at about 680 °C shows a characteristic effect of crystallization of new phases, and at 1000 °C becomes molten.

The investigations by Sattler [3] have confirmed the above conclusions and demonstrated that above 800 °C crystallization of $CaO \cdot B_2O_3$ and $CaO \cdot 2B_2O_3$ takes place; these melt at 930 °C.

Frischat and Herr [4] correlated the endothermic effects occurring within the temperature range 50–400 °C with the loss of the crystallization water of colemanite. They ascribed the endothermal effects at 650–800 °C to the decomposition of calcite admixture.

Karazanov and Gabdzanov [5] carried out a more detailed examination of low-temperature transitions occurring during colemanite heating. They found that within the temperature range 300–355 °C the chains in the structure of colemanite are broken (endothermic peak), whereas the release of the crystallization water is visualised in the form of two endothermic peaks at 385–400 °C and 400–750 °C.

The subject of the present paper is the thermal decomposition of colemanite monocrystals.

EXPERIMENTAL

Material

Selected samples of colemanite from Turkey occurring in montmorillonized volcanic tuffs have been subjected to investigation. They form short, prismatic crystals elongated along 001 (Fig. 1).

Microscope observations of thin sections cut out from selected fragments of colemanite crystals revealed the inclusions of colemanite grains with different optical orientation and parallel cleavage. Irregular or fissure-like pores which are arranged along cleavage planes are visible inside the crystals. No detectable contaminations of other minerals were found.

The mineral composition of colemanite samples was determined by X-ray and IR investigations. The samples appeared to be pure colemanite.

Methods

Conventional TG, DTG, DTA and Q-TG, Q-DTG and Q-DTA measurements were carried out with the microcomputer controlled derivatograph C (Hungarian Optical Works) [19]. Simultaneous TG, DTG and DTA examinations were performed using a sample of about 100 mg and a covered

Fig. 1. Scanning electron micrograph of prismatic crystals of colemanite.

platinum crucible, in an air atmosphere and at a heating rate of 2.5 °C min^{-1}. In the *Q* measurements the labyrinth, a covered and an open crucible, the multiplate sample holder and a sample of about 100 mg were used with a decomposition rate of 0.2 mg min^{-1}.

To ascertain the changes in the colemanite structure during heating, X-ray investigations were carried out. Samples of colemanite heated at the temperatures 330, 345, 360, 375, 405, 665, 740, 760 and 820 °C were examined. X-Ray powder patterns were obtained with a Dron-3 (U.S.S.R.) diffractometer using Cu K_α radiation.

To find out the temperatures of the OH group loss and the molecular water loss, IR spectroscopic examinations were performed. Natural colemanite and colemanite heated at 345, 375 and 405 °C were examined. A Zeiss UR-10 spectrometer was used and the samples were prepared as KBr discs. IR spectra were recorded in the wavenumber range 4000–3000 cm^{-1} at a speed of 50 cm^{-1}.

Changes in shape of a colemanite sample during heating were observed in a heating Leitz microscope. Cylindrical 2 × 3 mm samples of powdered colemanite shaped by pressing were heated at a constant rate of 5 °C min^{-1}.

RESULTS

DTA curves for colemanite samples examined under the standard conditions show two endothermic peaks within the temperature range 320–400 °C (Fig. 2). The first, 369 °C, has a distinct inflexion at 340 °C. The peak at 386 °C is accompanied by a 24.1 wt.% loss due to the release of water. The excess water content in the colemanite sample examined over the theoretical water content (21.8 wt.%) is the result of the occurrence of small inclusions of aqueous solution in its crystals. At a temperature of 741 °C there occurs

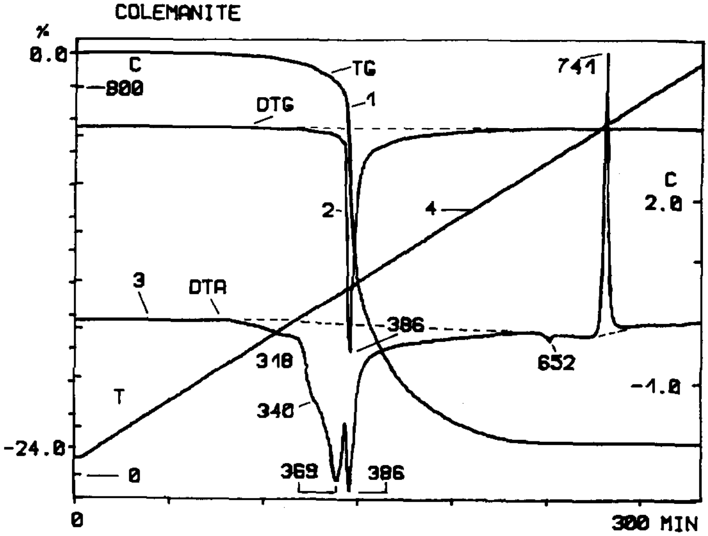

Fig. 2. Simultaneous TG, DTG and DTA curves of the thermal decomposition of colemanite.

an exothermic peak not accompanied by any change in the weight of the sample, preceded by a weak endothermic peak. Its shape indicates that it is caused by crystallization.

The curves T, Q-TG, Q-DTG and Q-DTA of colemanite obtained under quasi-isothermal and quasi-isobaric conditions are shown in Figs. 3–5. It is seen from the curves that water is removed from colemanite at various rates.

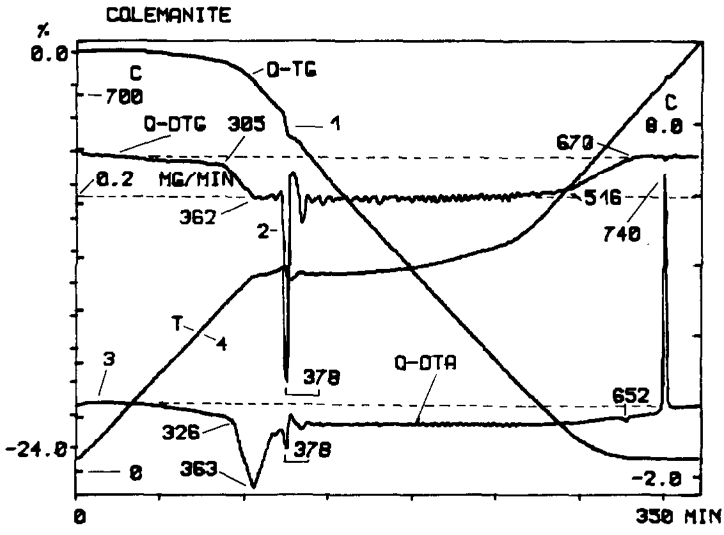

Fig. 3. Simultaneous Q-TG, Q-DTG and Q-DTA curves of the thermal decomposition of colemanite.

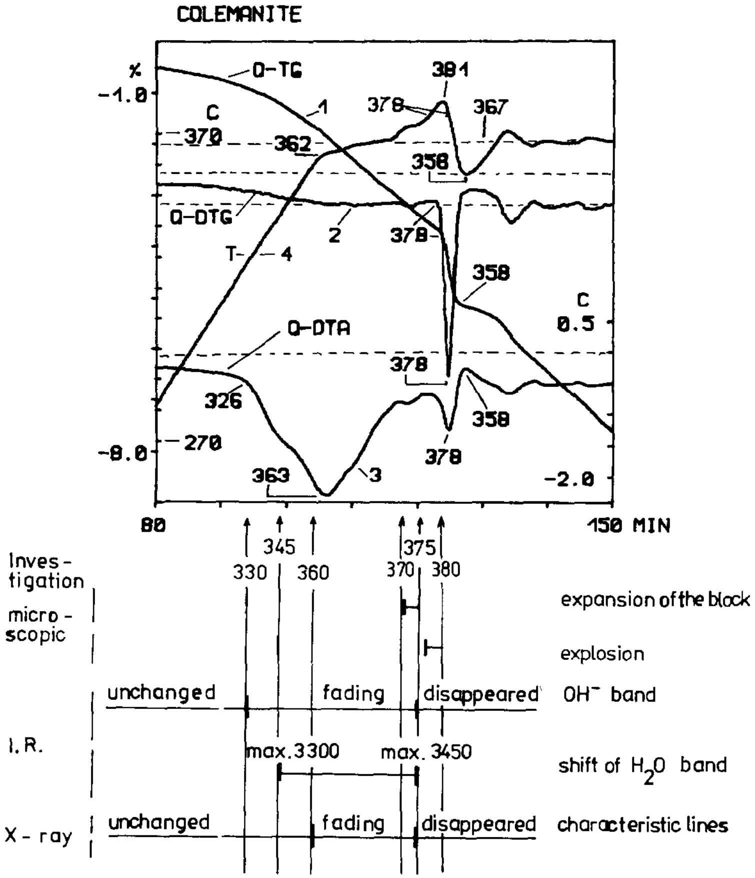

Fig. 4. Correlation between the microscopic, IR and X-ray results and the corresponding enlarged parts of the Q–TG, Q–DTG and Q–DTA curves illustrated in Fig. 3.

The removal of water begins at 364 °C and proceeds up to 378 °C at a constant rate. The amount of the removed water equals 3.3 wt.% which corresponds to the amount of water filling the inclusions in the colemanite crystals. For further removal of water at given rate of 0.2 mg min^{-1} a temperature increase is necessary. When the value of 378 °C is reached a sudden removal of water, about 1.5 wt.% occurs. This is indicated by a step on the Q-TG curve, with a peak Q-DTG and Q-DTA (Figs. 3 and 4). This process, by means of the quasi-isothermal heating control system, begins to reduce the temperature until it reaches 358 °C; this inhibits the further rapid removal of water and is marked by a backward bend on the Q-TG curve (Fig. 5). However, when the heating controller goes into action again and the temperature of the samples increases to 367 °C, further isothermal removal of water at the given rate commences and continues, until all has been removed. At this stage about 20 wt.% of water has been released.

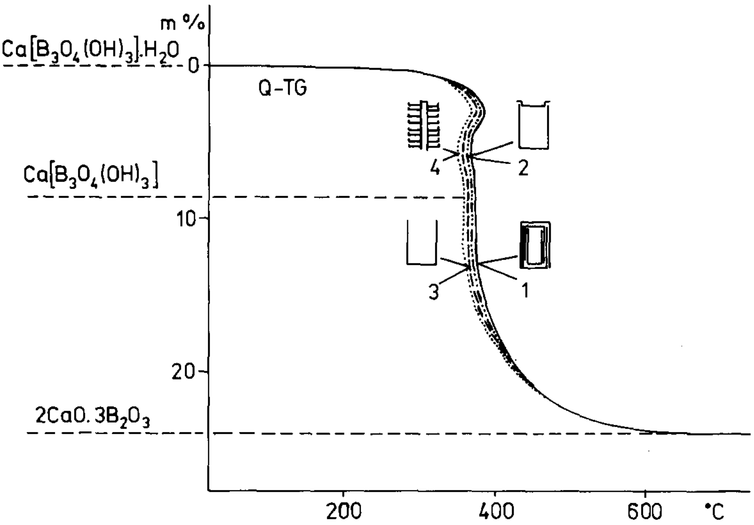

Fig. 5. Q-TG curves of the colemanite decomposition: (1) labyrinth crucible, (2) covered crucible, (3) open crucible, (4) multiplate holder.

In order to check whether the processes giving the peak at 369 ° C with an inflexion at 340 ° C on the DTA curve shown in Fig. 2, have the character of a reversible physical transformation, the TG, DTG and DTA curves were obtained by applying the experimental conditions given above. The measurements were carried out in such a way that the sample was heated to 360 ° C (Fig. 6, curve 1, point a) then the temperature was decreased to 230 ° C (point b) and afterwards increased again. The interrupted transformation proceeded when the sample reached the temperature of 360 ° C again (point c). A similar result was obtained when the heating was stopped at 375 ° C (Fig. 6, curve 2, point d). In neither case did the exothermic peak indicating a reverse process appear on the cooling curves or on the repeated heating curves, indicating the endothermic process started at the temperature at which the first heating was stopped (points c or f). This means that the process marked by the first endothermic DTA peak does not have the character of a reversible physical transformation.

The TG curves were also traced under quasi-isothermal quasi-isobaric conditions using four different sample holders, in order to obtain various partial pressures of the gaseous decomposition products in the atmosphere surrounding the sample. The following sample holders were used in succession: labyrinth, covered and open crucible and multiplate holder; these give the respective partial pressures 100, 25, 5 and 1 kPa. The curves obtained (Fig. 5) show that differences in the pressure of the gaseous decomposition products have a very small effect on the dehydration temperature of colemanite. According to our experience [20–23] this means that the process of water release by colemanite proceeds in an irreversible way. In the case of a

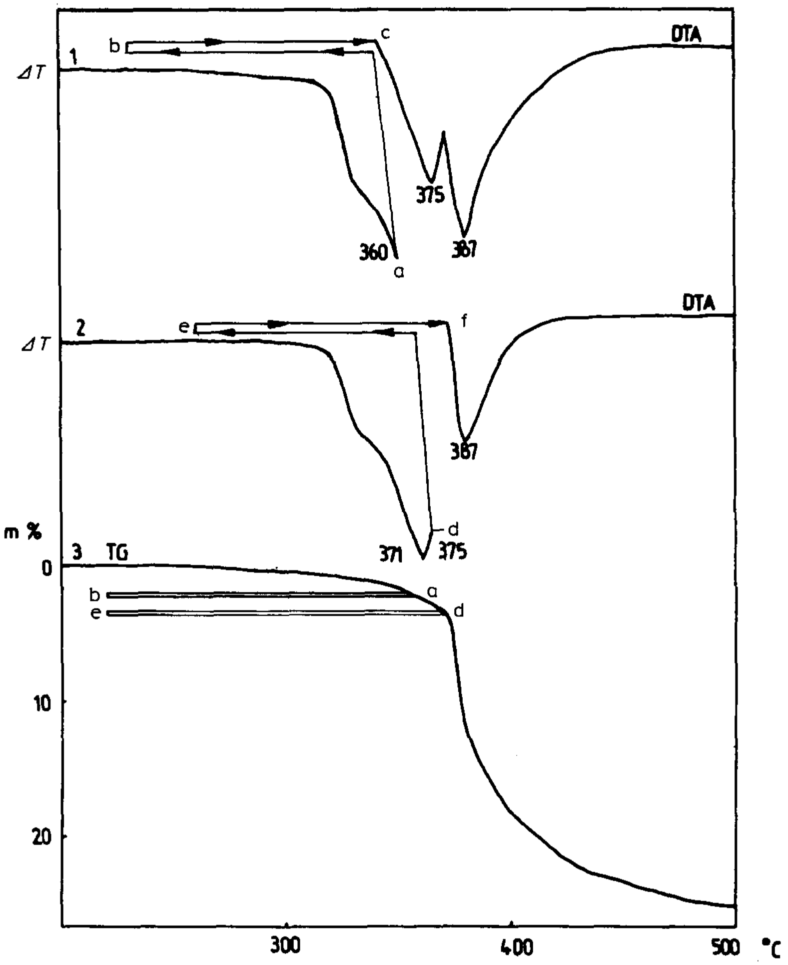

Fig. 6. TG and DTA curves of colemanite during the heating–cooling–heating cycle.

reversible * thermal dissociation the difference between the decomposition temperature in the labyrinth and that in the multiplate sample holder sometimes amounts to 300 ° C. On the Q-TG curves no step or inhibition indicating a two-stage release of water has been observed. The quasi-isothermal quasi-isobaric technique detects the overlapping decomposition steps when their temperatures differ by as little as 5 ° C [20,23].

The X-ray patterns show (Fig. 7) that with increasing temperature the essential framework of the colemanite structure is retained. On an X-ray pattern of a sample heated to 360 ° C the main lines of this mineral with the

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* The term reversibility of a reaction is used here in a kinetic sense and it means that the reverse reaction of the recombination of the gaseous decomposition products by a solid product proceeds at a measurable rate.

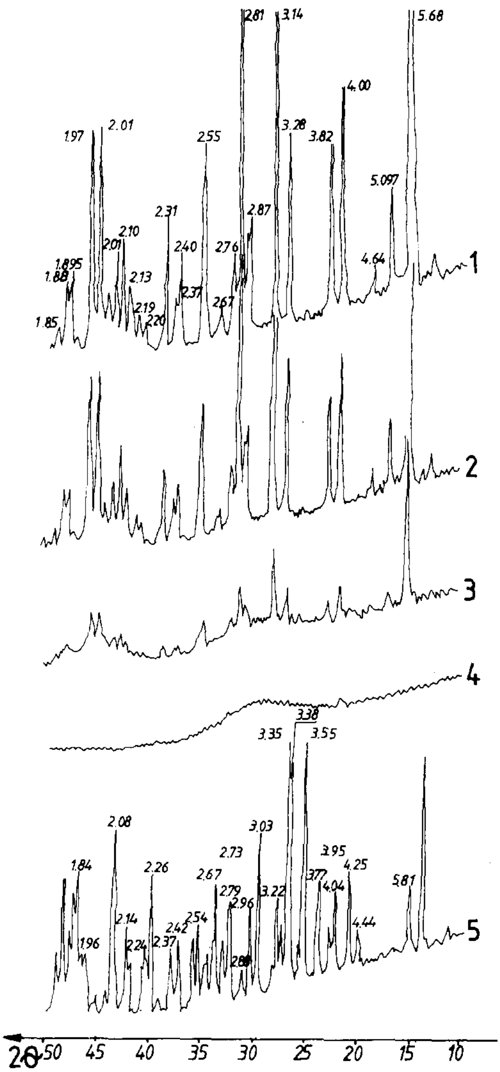

Fig. 7. X-ray diffractograms of colemanite heated at: (1) 330 ° C, (2) 345 ° C, (3) 360 ° C, (4) 375 ° C, (5) 820 ° C.

strongest line 020 (5.61 Å) are still visible. At 375 ° C the lines characteristic for the colemanite structure disappear. There remains only a broadened band about $2\theta = 30°$ typical of amorphous substances with only short-range order preserved in the arrangement of atoms.

X-ray examinations of colemanite samples preheated up to temperatures of 665, 740 and 820 ° C have shown that $2CaO \cdot 3B_2O_3$ has crystallized from the amorphous substance. Its crystal structure [24] is similar to that of hydrated borates (see Fig. 7).

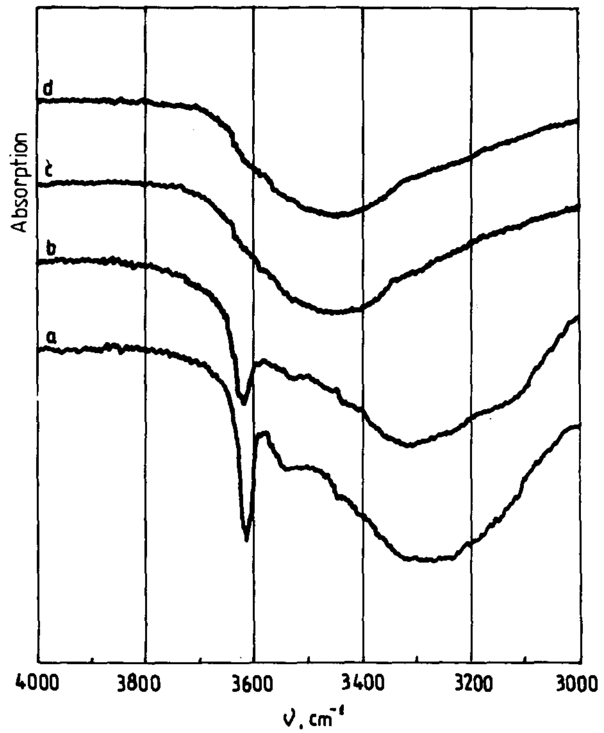

Fig. 8. Hydroxyl and H_2O stretching bands of colemanite heated at: (1) room temperature, (2) 345 ° C, (3) 375 ° C, (4) 405 ° C.

The IR absorption spectrum of natural colemanite [25] has a sharp absorption band at 3620 cm^{-1} caused by OH stretching vibrations and a broad band at 3200–3400 cm^{-1} associated with the fully symmetric and antisymmetric stretching vibrations of H_2O molecules (Fig. 8.). At 345 ° C the intensity of the OH absorption band decreases, while the broad band of molecular water is retained. At 375 ° C the band of the OH groups disappears, whereas the broad band of molecular water is shifted to about 3450 cm^{-1}. At 405 ° C this band is still visible, but its intensity is lower.

Observations made in a heating microscope have shown that the reaction at 386 ° C is accompanied by disintegration of the sample into small particles and their spraying. This process has a sudden, explosive character.

DISCUSSION

The results of the investigations have shown that the thermal decomposition of colemanite proceeds in two clearly separated stages marked on the DTA curves by two endothermal peaks.

As revealed by the X-ray and IR examinations during the first stage, there occur significant changes in the structure of colemanite. The OH group band in the IR absorption spectrum disappears, while the broad band of molecular water remains. This means that the OH groups split off to form water molecules. Moreover, bonds of molecular water with borate rings become broken, as is indicated by shifting of the H_2O band to 3450 cm^{-1} at 375 ° C.

Each process proceeds independently; hence the first endothermic peak of colemanite is a double one. The breaking of the molecular water bonds, it seems, occurs at a temperature higher than the splitting off of the OH groups. The molecular water is bound by relatively strong hydrogen bonds within the borate framework. This provides an explanation for the relatively high temperature at which this process occurs. The free water molecules formed during both processes, however, do not leave the structure of the mineral, as is evidenced by the absence of any changes in the sample mass, visible on the TG curves.

In spite of these changes the essential framework of the colemanite structure is retained, since on the X-ray pattern there can still be observed the main lines of this mineral [26] together with the strongest line 020. This proves that the boron–oxygen chains built up of the $[B_3O_4(OH)_3]^{2-}$ rings forming the main structural network have not been broken.

In the course of the next stage of the process, the water molecules formed during the initial decomposition stages are removed. This process is accompanied by a loss of the sample mass. The removal of part of this water proceeds rapidly as is evidenced by a step on the Q-TG curve. It is accompanied by an explosive-like disintegration of colemanite grains and spraying of the sample. The remaining water molecules confined in the preserved framework are released in a continuous way with increasing temperature.

The decomposition of colemanite has features characteristic for intracrystalline thermal dissociation, i.e. of a process proceeding in such a way that the decomposition centres are distributed uniformly throughout the whole volume of a crystal grain [27,28]. This dissociation proceeds in two separate stages, as follows: (1) water formation from the OH groups in the structure; (2) release of the water molecules formed.

Water molecules formed by the broken-away OH groups and those separated from the borate chains remain enclosed within the structure, probably filling the free spaces between the borate chains. With increasing temperature the pressure of the enclosed water molecules increases so much that it disrupts the framework and they are released. Accordingly, the rate of this process is not controlled by temperature changes and is only influenced by a distinct temperature drop, which is visible on the Q-TG curves.

The final decomposition stage is relatively slow. It can be assumed that there then takes place gradual release by diffusion of the remaining water molecules from the structure.

The water-removing process is responsible for the destruction of the retained borate structure and on the X-ray pattern of a sample heated to 375 °C the lines characteristic for colemanite disappear and a broadened band about $2\theta = 30°$ of amorphous substances is created.

Thermal dissociation of colemanite is distinguished by clear separation of the stage of dehydroxylation and formation of water molecules from the stage of the release of main part of the water. In cases of intracrystalline dissociation recognized so far, in which the essential structure framework has been retained (such as the decomposition of layered silicates of the kaolinite group) both these stages overlap fairly precisely (kaolinite) or are merely shifted (dickite).

Above 650 °C sintering of the sample takes place, evidenced in a high-temperature microscope by a rapid contraction in the sample volume. At higher temperatures crystallization of calcium borate takes place. On an X-ray pattern of a colemanite sample heated to 665 °C the strongest lines, characteristic of calcium borate $2CaO \cdot 3B_2O_3$, already appear. An intensive crystallization of this compound takes place at about 740 °C, which is revealed by the exothermal peak.

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