

Thermal decomposition of hydrated borates. Part 1. Thermal decomposition of pandermite $\text{Ca}_2\text{B}_5\text{O}_8(\text{OH})_3 \cdot 2\text{H}_2\text{O}$

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Abstract

Thermal decomposition of pandermite monocrystals has been investigated by thermal, X-ray and IR methods, SEM and optical microscopy. Investigations have revealed that it is a multi-stage internal process, realized by gradual reconstitution of the mineral structure. The following stages have been distinguished: (1) a two-step release of interlayer water; (2) internal structure reconstruction; (3) dehydroxylation and amorphization of crystal structure; (4) recrystallization of amorphous solid and successive formation of CaB_2O_4 and then CaB_4O_7 .

INTRODUCTION

Borates are a large group of substances of complex chemical composition and structure. They are distinguished by a structural framework formed of polymerized boron–oxygen–hydroxyl tetrahedra or triangles, which are linked to each other by means of cations. This framework makes borates similar to other inorganic substances of polymeric structure, such as silicates or phosphates.

Borates differ from each other in the basic structural element, which may contain 1, 2, 3, 4, 5, 6 and 9 boron–oxygen–hydroxyl polyhedra (tetrahedra and triangles). These elements may combine, forming chains or larger units. The crystallochemical structure of borates contains accordingly as anions isolated groups of polyhedra, chains or layers.

The structure and the properties of many hydrated borates have not yet been adequately studied. Their thermal decomposition is not sufficiently known either. It takes a complex multi-stage course which comprises the processes of dehydration, dehydroxylation and crystallization of new compounds.

Our earlier investigations of some hydrated borates [1, 2] have revealed

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that the processes of their thermal decomposition are of the nature of internal structure reconstitution reactions. The reactions of internal reconstitution (intraframework or internal reactions) are defined as chemical processes taking place in the whole bulk of a solid body. The solid products of these reactions are formed inside the structural framework of the parent substance through the rebuilding or displacement of its elements [3, 4].

These reactions proceed through the diffusion transport of ions, atoms or molecules, which is slow, and in crystalline solids it is occasionally directional. The consequence is usually a multi-stage course for these reactions, the state of equilibrium being attained through several intermediate stages.

The distinct connection between the structure of the parent substance (precursor) and the structure of the solid product with reference both to their constitution and their mutual orientation (topotaxis) are a special feature of these reactions.

In the course of the internal decomposition, the thermal dissociation reaction accompanied by the formation of the molecules of the gaseous product and their release may be quite a separate process occurring at a different temperature. In that case the gas molecules remain temporarily enclosed in the voids of the structural framework of the solid body until their pressure (internal pressure) disrupts the framework, causing the gas to escape.

The release of the gaseous products of the internal thermal decomposition occasionally has a violent or even explosive character. These and other specific phenomena associated with the internal decomposition can be explained using a sealed box containing compressed gaseous decomposition products as a model of this process. This model has already been postulated in a previous paper [4].

Earlier investigations of two borates—colemanite [1] and ulexite [2]—allowed us to establish several specific phenomena accompanying their decomposition.

Calcium tetraborate (colemanite $\text{CaB}_6\text{O}_{10}(\text{OH})_6 \cdot 2\text{H}_2\text{O}$) is built of borate chains. These are made up of units comprising two BO_4 tetrahedra and a $[\text{B}_3\text{O}_4(\text{OH})_3]^{2-}$ ring. The chains are linked to each other by the Ca^{2+} cations to form sheets. The system of hydrogen bonds formed by the OH group chains and water molecules ties sheets together into a three dimensional spatial framework.

Thermal dissociation begins with the splitting off of the OH groups, which form water molecules (343°C). The next step is the splitting off of the water molecules bound with the rings (363°C). Both types of water molecules remain enclosed in the empty voids (internal water). Part of it (0.5 mol) becomes released in an explosive way at 378°C. The remaining amount escapes slowly up to a temperature of 650°C, and this is

accompanied by gradual amorphization of the structure. From the amorphous glass-like anhydrous matrix there the crystallization of $2\text{CaO} \cdot 3\text{H}_2\text{O}_3$ occurs.

Sodium calcium pentaborate (ulexite $\text{NaCa}[\text{B}_5\text{O}_6(\text{OH})_6] \cdot 5\text{H}_2\text{O}$) is built of isolated polyanions having the form of six-membered boron–oxygen–hydroxide rings. The Ca^{2+} and Na^+ cations are coordinated by the water molecules and the OH groups. Their coordination polyhedra form chains bonding the borate chains into a three-dimensional framework.

The decomposition of ulexite begins with the removal of the water molecules. This is a two-stage process. The first dehydration (118°C) is accompanied by the rebuilding of the ulexite structure, the second (159° and 181°C) brings its decomposition. The second stage of dehydration is characterized by explosive release of water. $\text{CaO} \cdot \text{B}_2\text{O}_3$ and $2\text{CaO} \cdot \text{B}_2\text{O}_3$ are crystallized from the anhydrous amorphous substance remaining. Crystals are confined in an amorphous matrix formed by the retained borate anions and the OH groups, linked with strong bonds with the Na^+ cations. Above 550°C the OH groups are gradually removed and NaB_3O_5 is crystallized. Next, calcium borates disappear and NaCaBO_3 crystallizes.

The complex and diversified course of the decomposition of these borates caused the authors to extend their investigations and include other hydrated borates in order to find the relation between the chemical composition and structure of these minerals and the structural mechanism of thermal reactions. These studies are the subject of this paper.

Exact data about the structure of pandermite are still unavailable. According to the available literature pandermite belongs to the group of pentaborates of layer structure. Layers are formed of the anions $[\text{B}_5\text{O}_8(\text{OH})_3]^{2-}$ which contains probably four tetrahedra and one triangle, forming two six-membered rings. They are linked by a boron atom of fourfold coordination [5].

The data concerning the thermal decomposition of pandermite are divergent. Investigations carried out under isothermal conditions have revealed differences in the mode of water release by minerals of various origin [6–9]. As yet it is considered [5, 9] that up to a temperature of 400°C the water of crystallization releases from the pandermite, and that above 400°C the escape of water formed as a result of the removal of the OH groups takes place from the structure. At a temperature of 740°C a rhombic modification of $\text{CaO} \cdot \text{B}_2\text{O}_3$ crystallizes from the amorphous anhydrous pandermite and persists up to 1000°C .

EXPERIMENTAL

Material and methods

Sample of coarse-crystalline pandermite from a deposit in Demir Kapu (Turkey) has been obtained from the collection of the Mineralogical

Museum at Wrocław University. Its purity has been confirmed by X-ray diffraction patterns and IR spectra [10, 11].

TG, DTG, DTA, Q-TG, Q-DTG and Q-DTA were carried out with a Q-1500 D derivatograph and microcomputer-controlled derivatograph C (MOM, Budapest). Pandermite 100 mg samples were heated in Pt crucibles in air at a rate of 10 or 2.5°C min⁻¹. Quasi-isothermal-isobaric measurement of the decomposition of pandermite was carried out in labyrinth crucibles at the constant mass loss rate of 0.15 mg min⁻¹.

To study the nature of the structural changes during heating, samples of pandermite at temperatures of 340, 400, 580, 760 and 800°C were subjected to X-ray diffraction and IR spectroscopic examinations. X-ray powder patterns were made with a DRON-3 diffractometer, using Cu K α radiation. Absorption IR spectra were obtained with a Zeiss Ur-10 spectrometer, and the samples were prepared as KBr discs. The behavior of pandermite during heating was observed in a heating Leitz microscope. Samples heated to different temperatures were also examined with a scanning electron microscope (Tesla).

RESULTS

Thermal investigations carried out under conventional and under quasi-isothermal-isobaric conditions have shown that the decomposition of

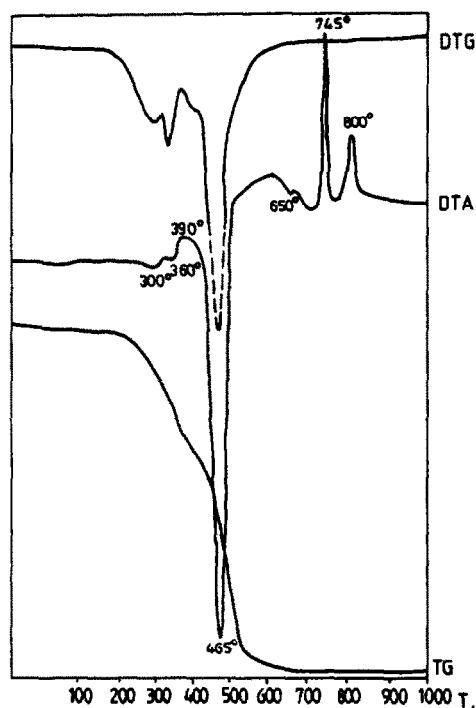


Fig. 1. TG, DTG and DTA curves of pandermite.

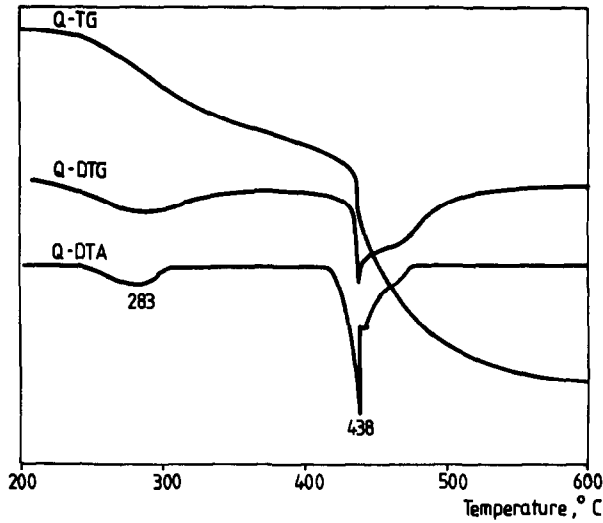


Fig. 2. Q-TG, Q-DTG and Q-DTA curves of pandermite.

pandermite proceeds in several separate stages. The endothermal effect at 300°C (Fig. 1) is accompanied by the loss of 2 mol H₂O, and next, at 360°C by the removal of 1.5 mol% H₂O. At 390°C there takes place an exothermal effect, which should be assigned to the rebuilding of the structure. The endothermal effect, the maximum of which occurs at 465°C, is accompanied by the release of 3 mol H₂O. At 650°C the endothermal effect of the framework rearrangement occurs, typical of amorphous substances (transformation temperature T_g) and at 745 and 800°C the exothermal effects of the crystallization of new compounds occur.

The Q-TG, Q-DTG and Q-DTA curves of pandermite obtained under quasi-isothermal-isobaric conditions are shown in Fig. 2. It follows from these curves that pandermite heated to 438°C loses mass at a steady rate of 9.90 wt.% (3.5 mol of H₂O). At 438°C a sudden release of 1.90 wt.% H₂O (about 0.5 mol H₂O) occurs, which is marked by a step on the Q-TG curve and peaks on the Q-DTG and Q-DTA curves. For further release of water from the structure of pandermite at the same rate (0.15 mg min⁻¹) a temperature increase is necessary, and then about 3 mol H₂O are released in a continuous way up to 580°C.

Water release in the course of the first stage of dehydration does not produce any changes in the structure of pandermite. On the X-ray pattern of a sample heated up to 340°C the main lines of pandermite are still visible, with the strongest line at 1.08 nm (of diminishing intensity, however) (Fig. 3). There also appears a new unidentified line at 0.316 nm, probably corresponding to the formation of a borate of lower H₂O content which still retains the layer structure. At 400°C some of the lines characteristic of pandermite disappear completely while others are pre-

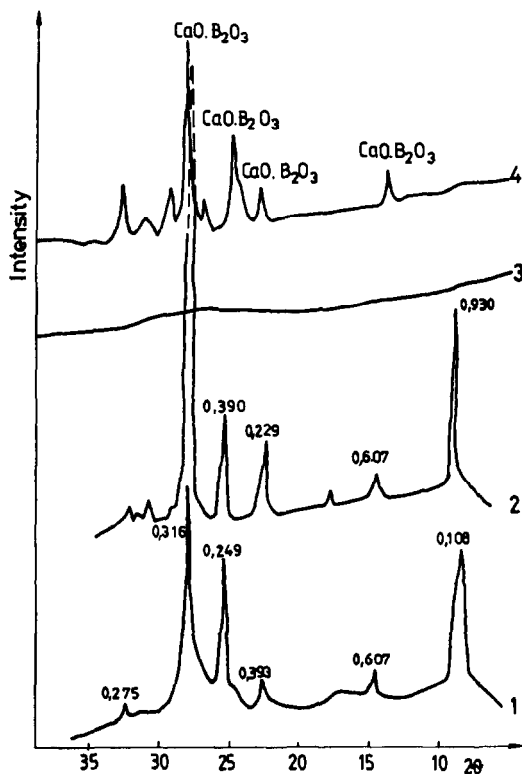


Fig. 3. X-ray diffractograms patterns of pandermite samples heated to (1) 340°C, (2) 400°C, (3) 580°C, (4) 760°C.

served; in contrast, new lines appear (0.316, 0.930 and 0.390 nm) and their intensity increases. At 580°C both the lines of pandermite and those attributed to the new form of calcium borate formed during heating disappear. However, a broad band at about $2\theta \approx 30^\circ$ typical of an amorphous substance appears. X-ray patterns of pandermite heated in the range 760–820°C have shown that calcium borate $\text{CaO} \cdot \text{B}_2\text{O}_3$ crystallizes from the amorphous substance (exothermal effect on the DTA curve at 745°C); next, at 800°C $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ crystallizes, in agreement with the stoichiometry of the chemical composition of the amorphous phase.

The IR absorption spectrum of natural pandermite shows the bands in the region $400\text{--}1600\text{ cm}^{-1}$ characteristic of borates, responsible for the symmetric and asymmetric stretching vibrations of the boron atoms of three- or four-fold coordination [12, 13]. In the short-wave part of the spectrum there appear the absorption bands at 3100, 3470, 3570 and 3590 cm^{-1} connected with the stretching vibrations of the OH groups and water molecules [11]. The appearance in the spectrum of the effect of splitting off the vibration levels of the OH groups (the bands at 3570 and 3590 cm^{-1}) is evidence of the existence of hydrogen bonds in the structure [14, 15].

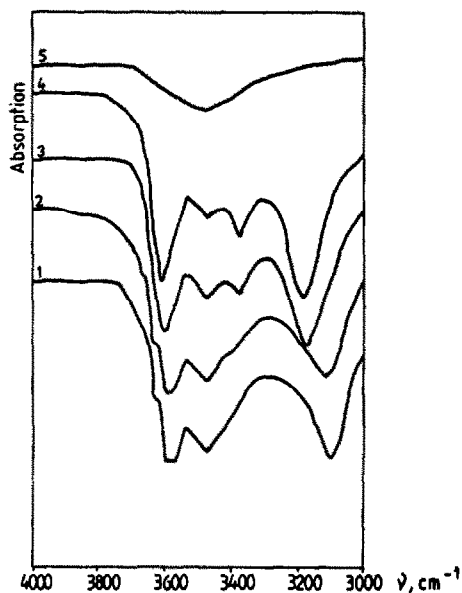


Fig. 4. Hydroxyl and H_2O stretching bands of pandermite heated to (1) room temperature, (2) 265°C, (3) 340°C, (4) 400°C, (5) 580°C.

A pandermite sample heated at 340°C (Fig. 4) shows OH group bands, whereas the band of molecular water is shifted to about 3165 cm^{-1} , which with the simultaneous considerable decrease in the intensity of the 1660 cm^{-1} band indicates the splitting off the water molecules from the borate rings [16]. The absorption spectrum of pandermite heated at 340°C, both in the region of $400\text{--}1600\text{ cm}^{-1}$ and in the short-wave range, compared with the spectrum of pandermite in its original state, shows additional bands deriving from the newly formed (probably less hydrated) form of this mineral. At 400°C, the band at 1660 cm^{-1} connected with molecular water is no longer visible, and the band at 3165 cm^{-1} is shifted and broadened, which is evidence of continuous splitting off of the water molecules from the borate rings. In a sample heated to 580°C the OH group band disappears completely.

DISCUSSION

The thermal decomposition of pandermite begins the process of two-stage dehydration. First, 2 mol and then 1.5 mol water molecules localized between the layers of the mineral are lost. The first to become released are the water molecules at those surfaces in immediate contact with the atmosphere (crystal faces, cracks). Next, those water molecules situated in the deeper layers of the crystal (altogether 3 mol H_2O) leave. Some of the water molecules splitting off from the framework remain enclosed in the voids between the layers as internal water. At 360°C the pressure created by these water molecules disrupts the borate crystal and

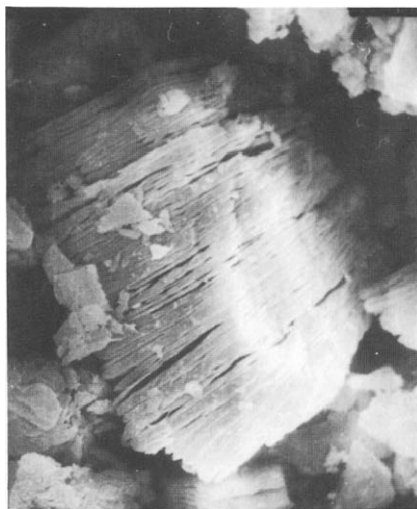


Fig. 5. Scanning electron micrograph of pandermite heated to 340°C. Original magnification 200×.

a considerable part of the internal water is released (1.5 mol H₂O). This process takes a violent course and is accompanied by spraying of part of the powdered sample. It is visible in a heating microscope. When the amount of the removed water molecules exceeds a certain value (3.5 mol), rearrangement of the pandermite structure takes place. This consists of the formation of a structure with smaller distances between the layers. However, the layer structure of pandermite (it seems) is still preserved. This reconstruction is accompanied by an exothermal effect (390°C) like a crystallization process. At 438°C a sudden release of the rest of the internal water occurs; next, as the temperature increases, the OH groups are gradually released (dehydroxylation). The pressure of the liberated water vapor in the above processes causes the exfoliation of the pandermite crystals parallel to the borate sheets and an increase of their volume (Figs. 5 and 6).

The dehydroxylation of pandermite results in the formation of an anhydrous X-ray-amorphous substance with preserved fragments of the initial framework in its structure. This is shown by a broad band on the X-ray diffraction pattern at the place of the strongest pandermite line. The amorphous substance has spherical pores in which the water particles accumulated (Fig. 7) before the internal pressure causes disruption of the grain and their release.

The X-ray-amorphous product of dehydration and dehydroxylation retains to a considerable degree the initial plate form of the pandermite crystals. The crystals became merely split into a series of parallel layers, making them porous. During the further heating the material becomes denser and the distance between the layers diminishes, until they



Fig. 6. Scanning electron micrograph of pandermite heated to 500°C. Original magnification 500×.

disappear completely (Fig. 7). At 630°C the endothermal effect of transformation—typical of amorphous substances—takes place, caused by the breaking of some of the elements retained in the framework. Next, at 745°C, calcium borate $\text{CaO} \cdot \text{B}_2\text{O}_3$, and afterwards, at 800°C, calcium diborate $\text{CaO} \cdot 2\text{B}_2\text{O}_3$ crystallize.

The decomposition of pandermite is an internal process realized in the bulk of the crystal. Its multi-stage course is a consequence of the specific structure of this mineral, and is also closely related to the varying

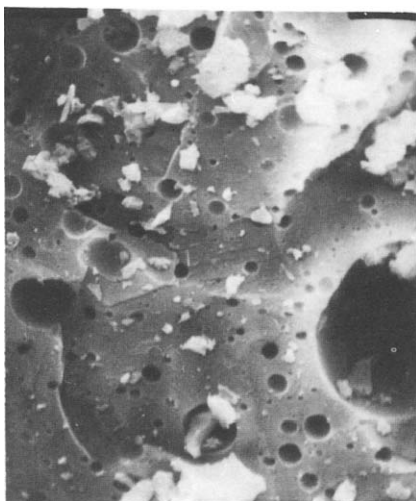


Fig. 7. Scanning electron micrograph of pandermite heated to 700°C. Original magnification 5000×.

strengths of the hydrogen bonds between the OH groups and the H₂O molecules in the boron–oxygen layers. In the structure of pandermite there exists a distinct difference between the strong hydrogen bonds between OH groups within the layer and the weaker hydrogen bonds of H₂O between the layers. As a result, in the course of heating, the molecular water is removed first, followed by the rearrangement of the structure, and next by removal of the OH groups. The other phenomena characteristic of internal processes are accumulation of liberated water molecules in the voids of the structural framework, its disruption at higher temperature accompanied by violent release of the retained water and the low sensitivity of this process to the external pressure of the gaseous decomposition products, amorphization of the primary framework and its reconstitution, and subsequent crystallization of new compounds according to the principle of structural similarity [3, 4]. All of these processes take place during heating of the pandermite crystals.

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