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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

CONTROLLED RATE THERMAL ANALYSIS OF HYDRATED BORATES

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Abstract

Quasi-isothermal-isobaric analysis was applied as a main method for investigation of thermal decomposition of borates. The structural mechanism of the dehydration and dehydroxylation of selected borates is considered. It has been found that they consist of two independent stages: formation of gaseous water molecules localized into the structural framework and their release. The internal pressure of gaseous water molecules is the factor influencing the course of these processes. The strengths of the chemical bonds of the components and the freedom of their displacement also determine thermal stability of hydrated borates.

Keywords: borates, CRTA, decomposition, structural mechanism

Introduction

Crystalline borates are compounds of boron, oxygen, metals and hydrogen atoms. They may contain water molecules and hydroxyl groups and in some cases also non-borate anions such as e.g. Cl^-, SO_4^{2-}. The basic elements forming the crystalline structure of borates are the $B\phi_3$ and $B\phi_4$ polyhedra ($\phi=O^{2-}$, OH^-) combined into clusters referred to as fundamental building blocks (FBB) [1]. FBB occur either as unconnected polyhedra or, after polymerisation, they form finite clusters, infinite chains, infinite sheets or infinite frameworks. The negative charge of boron-oxygen polyhedra is compensated by cations of much lower electronegativity force than that of boron cation (Ca, Mg, K, Na) occupying the interstitial positions in the structure of borates. In origin borates the FBB contain 1–12 boron atoms [2], while several synthetic compounds have 12 or more boron atoms in FBB [3].

Crystalline borates containing the same number of boron atoms in a boron-oxygen polyhedra often differ in the content of molecular water. Water molecules are suitable ligands for most cations; water participates also as a donor and acceptor of protons in the hydrogen bonds occurring in borates structures. There

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exists a correlation between the content of molecular water and the degree of polymerization of FBB [4]. Isolated, island structures of borates contain the greatest amount of hydrated water. With decreasing amount of molecular water they become transformed into chain and next into sheet structures – in case of total absence of molecular water there are formed infinite frameworks.

On account of the specific structure of borates their thermal decomposition is a complex process proceeding in several stages. Modern thermal analysis, X-ray diffraction and spectroscopic methods in connection with optical and electron microscopic techniques have created new possibilities for investigation of this process. Controlled rate thermal analysis method (CRTA) has proved particularly applicable in the investigations of the processes of the dehydration of borates.

In a variant developed by Rouquerol [5] the reaction rate is controlled through the measurement of the pressure of gaseous products of the decomposition reaction.

In a variant developed by Paulik, Paulik [6, 7] and applied in the present study, the parameter controlling the decomposition is the mass loss of the sample, and this is kept constant by controlling the heating rate. Constant rate of mass loss is responsible for the quasi-isothermal conditions of decomposition. A special sample holder ensures a self-generated atmosphere in the surroundings of the sample, by which quasi-isobaric conditions are produced. Such quasi-equilibrium conditions make very precise identification possible of the particular stages of thermal dissociation of hydrated borates.

Experimental

Materials

Coarse–crystalline, pure borate minerals from the collection of the Mineralogical Museum of the Wrocław University were selected for the examinations. They were hydrated borates of alkaline and alkaline-earth metals, which have different complex borate anions. They included:

colemanite – $Ca_2B_6O_8(OH)_6{\cdot}2H_2O$ (Turkey),
pandermite – $Ca_2B_5O_8(OH)_3{\cdot}2H_2O$ (Demir Kapu, Turkey),
ulexite – $NaCaB_5O_6(OH)_6{\cdot}5H_2O$ (Iquique, Peru),
kaliborite – $HKMg_2B_{12}O_{16}(OH)_{10}{\cdot}4H_2O$ (Stassfurt, Germany),
tincalconite – $Na_2B_4O_5(OH)_4{\cdot}3H_2O$ (San-Bernardino, California),
kernite – $Na_2B_4O_6(OH)_2{\cdot}3H_2O$ (Mohave, California) and
larderellite – $NH_4B_5O_7(OH)_2{\cdot}H_2O$ (Tuscany, Italy).
Synthetic, chemically pure borax – $Na_2B_4O_5(OH)_4{\cdot}8H_2O$ was also included in this examination.

The monomineral character of the samples has been confirmed by X-ray and FTIR examinations.

Methods

The thermal decomposition of the borates has been investigated by X-ray, FTIR and thermal methods. The thermal studies were carried out with a microcomputer controlled derivatograph C (MOM) using the technique of dynamic heating (TG, DTG, DTA) and quasi-isothermal-isobaric measurements (Q-TG, Q-DTG, Q-DTA). Q-measurements were performed in air, with a sample of 50 mg, in platinum labyrinth crucibles, which ensured quasi-isobaric conditions during the experiments. First, the sample was heated at a rate of 2.5°C min^{-1} as long as no changes were observed in the sample. When the mass loss took place in the sample, the heating control device reduced the temperature and kept it on such a level that the mass loss rate remained constant according to the programmed value of 0.15 mg min^{-1}.

The behaviour of the borate grains during heating was observed in a heating microscope and in a scanning electron microscope.

Results

Thermal dehydration and dehydroxylation of borates

Colemanite – $Ca[B_3O_4(OH)_3]{\cdot}H_2O$ is built of borate chains which are made up of FBB comprising two tetrahedra and one triangle [8]. The thermal decomposition of this calcium triborate proceeds in two separate stages marked on the Q-DTA curve as two endothermal peaks within the temperature range 300–400°C (Fig. 1). The first 363°C, has a distinct inflexion at 320°C. As revealed by the IR examinations (Fig. 2), the OH^- group band at 3620 cm^{-1} in the IR absorption spectrum disappears, while the broad band of the molecular water (3200–3400 cm^{-1}) remains. This means that thermal dissociation of colemanite begins with the splitting off of the OH groups, which form water molecules (320°C). Next, the bonds of molecular water with borate rings become broken (363°C). In the course of the next stage of the process, the water molecules formed during the initial decomposition stages are removed (1.5 mol). The removal of a part of this water (0.5 mol) proceeds rapidly as is evidenced by a step on the Q-TG and Q-DTG

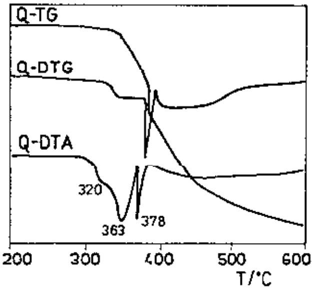

Fig. 1 Q-TG, Q-DTG and Q-DTA curves of colemanite decomposition

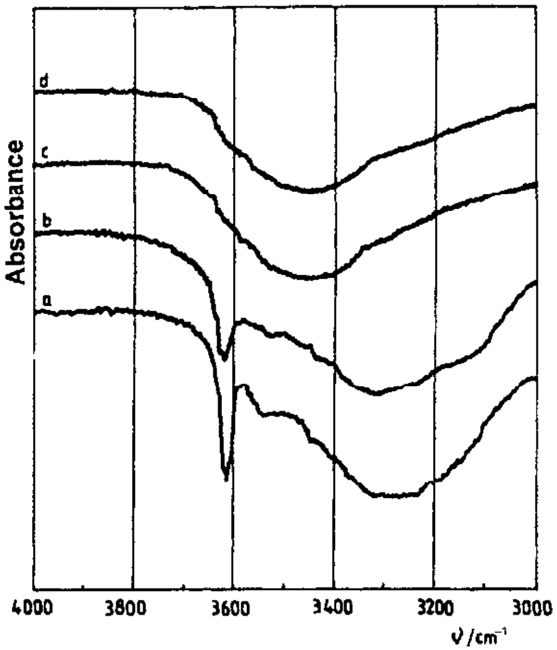

Fig. 2 Hydroxyl and H_2O stretching bands of colemanite heated at: room temperature (a), 345°C (b), 375°C (c), 405°C (d) [9]

curves (378°C). It is accompanied by an explosive disintegration of colemanite grains and spraying of the sample visible in a heating microscope. The remaining amount of water (3.5 mol) escapes slowly up to the temperature of 650°C, and this is accompanied by gradual amorphisation of the structure.

Pandermite – $Ca_2[B_5O_8(OH)_3]\cdot 2H_2O$ belongs to the pentaborates which probably have a layered structure [10]. The thermal decomposition of pandermite begins with the process of two-stage dehydration [11]. During the first stage, up to 438°C, 3.5 mol of water molecules are lost at a constant rate (Fig. 3). At 438°C a sudden release of the 0.5 mol of water molecules occurs. This process takes a violent course and is accompanied by spraying of a part of the powdered sample. When the amount of the removed water molecules exceeds a value of 3.5 mol, a rearrangement of the pandermite structure takes place [11]. This consists of the formation of a structure with smaller distances between the layers; however, the layered structure of pandermite is still preserved. As the temperature increases, the OH groups are gradually released and an X-ray amorphous substance is formed.

Ulexite – $NaCa[B_5O_6(OH)_6]\cdot 5H_2O$ is a sodium calcium pentaborate of island structure whose FBB are built of two six-membered boron-oxygen-hydroxide rings containing one triangle and two tetrahedra [12]. The thermal dissociation of ulexite begins with the removal of 1.5 mol of water molecules at a constant rate (118°C) (Fig. 4). This stage is accompanied by the rebuilding of the mineral structure [13]. The second stage of dehydration is characterised by an explosive release of a part of water (0.5 mol) at 144°C and next, the remaining water molecules (2.5 mol) are removed at constant rate. The solid product of dehydration of ulexite is the amorphous matrix containing OH groups in which calcium borates crystallise immediately.

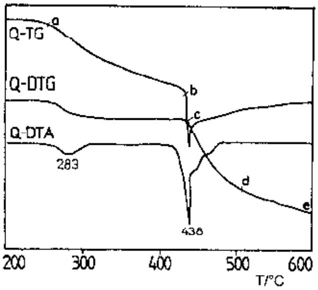

Fig. 3 Q-TG, Q-DTG and Q-DTA curves of pandermite decomposition

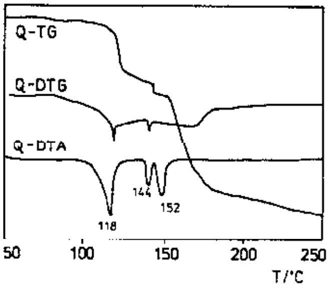

Fig. 4 Q-TG, Q-DTG and Q-DTA curves of ulexite decomposition

Kaliborite – $HKMg_2[B_5O_7(OH)_3OB(OH)_2]_2 \cdot 4H_2O$ belongs to pentaborates of chain structure containing the fundamental anions in which there occur two rings comprising one triangle and two tetrahedra and, moreover, an additional triangle [1]. The decomposition of kaliborite proceeds in several stages, separated from each other under quasi-isothermal-isobaric conditions (Figs 5, 6). It begins with splitting off of OH groups and the formation of water molecules which remain within the structure of the mineral [14]. At 258°C the removal of the retained water (1 mol) proceeds at a constant temperature. Next, the hydrogen bonds which link the water particles with the borate structure become broken and at 272°C the second violent release of accumulated water (2 mol) occurs. With increase of temperature the remaining water molecules (6 mol) escape continuously at a given constant rate up to 400°C.

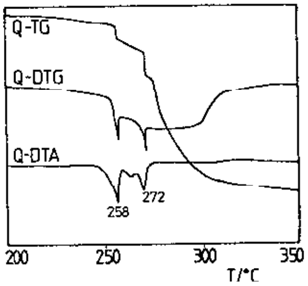

Fig. 5 Q-TG, Q-DTG and Q-DTA curves of kaliborite decomposition

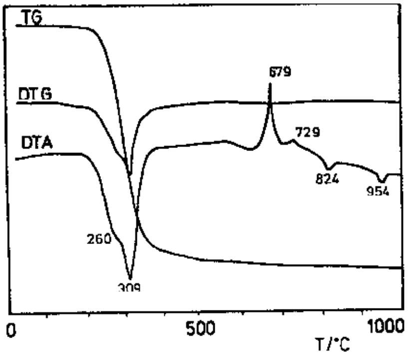

Fig. 6 TG, DTG and DTA curves of kaliborite decomposition

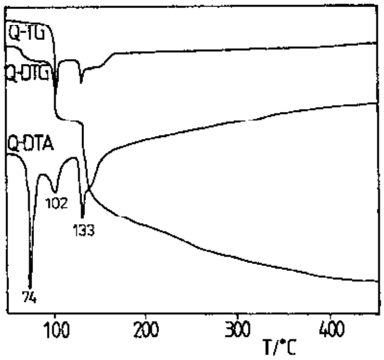

Fig. 7 Q-TG, Q-DTG and Q-DTA curves of borax decomposition

Borax – $Na_2[B_4O_5(OH)_4]\cdot 8H_2O$ is a tetraborate whose structure is made up of two constituent units, boron-oxygen polyions and chains formed by sodium atoms surrounded by water molecules [12]. During heating of borax at the temperature 74°C some of the molecules of the coordination water bound with the boron-oxygen anions and sodium cations are split off which is illustrated by the endothermal effect on the Q-DTA curve, not connected with a change in the sample mass (Fig. 7). The rapid release of the retained water molecules at the temperature 102°C (3.5 mol) and 133°C (1.5 mol) is accompanied by the rearrangement of the borax structure into a tincalconite one [15] and the spraying of the sample. Next, borax gradually loses the remaining molecular water (3 mol) up to the temperature 200°C. Dehydration is associated with amorphisation of the crystalline structure. The newly formed amorphous substance preserves all OH groups and further increase in temperature causes their gradual removal up to above 500°C.

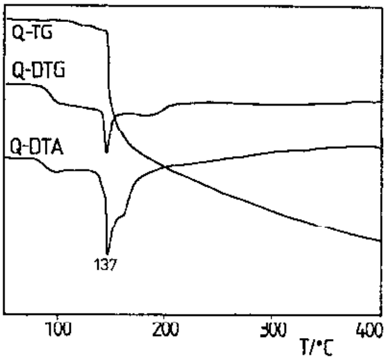

Fig. 8 Q-TG, Q-DTG and Q-DTA curves of tincalconite decomposition

Tincalconite – $Na_2[B_4O_5(OH)_4]\cdot 3H_2O$ structure contains the same kind of polyions as borax but its structure is more compact on account of a smaller number of water molecules [16]. Thermal decomposition of tincalconite proceeds in a way similar to that of borax (Fig. 8). As a result of heating at the temperature 137°C 1 mol of water is rapidly removed from its structure and the next amount of water (2 mol) is released continuously up to the temperature 200°C. The product of dehydration is the X-ray amorphous sodium diborate, containing in its structure OH groups which are removed from the amorphous matrix continuously up to the temperature of 500°C (2 mol H_2O).

Kernite – $Na_2[B_4O_6(OH)_2]\cdot 3H_2O$ a member of the borax family, contains in its structure the same polyions as borax or tincalconite, but the polyions are polymerized infinite chains [12]. The initial stage of the decomposition of kernite is associated with the splitting off of OH groups and molecular water from the borate structure. These processes are illustrated by the endothermal effects on the Q-DTA curves at the temperatures 84 and 100°C (Fig. 9). Part of the newly formed water is released from the structure of the mineral at constant rate up to the temperature 155°C (1 mol), and at the temperature 155°C the next part of water (0.5 mol) is suddenly released. In the course of further continuous heating up to a temperature of about 500°C the residual water is removed, the result of which is a complete destruction of the mineral structure.

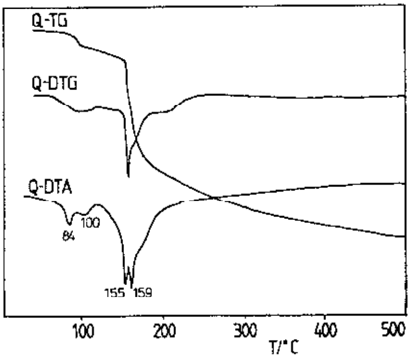

Fig. 9 Q-TG, Q-DTG and Q-DTA curves of kernite decomposition

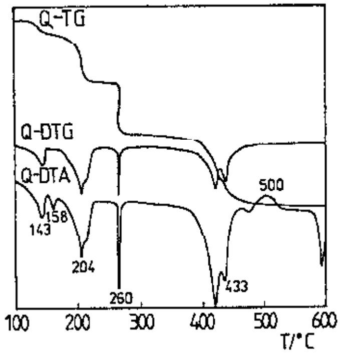

Fig. 10 Q-TG, Q-DTG and Q-DTA curves of larderellite decomposition

Larderellite – $NH_4[B_5O_7(OH)_2]\cdot H_2O$ belongs to pentaborates of chain structure with the FBB consisting of two rings, each containing two triangles and one tetrahedron in common [12]. Up to the temperature 300°C (Fig. 10) only water (simultaneous dehydroxylation and dehydration) is removed from the borate structure [17]. Part of the water molecules (1.3 mol) is removed from the structure of the mineral in a continuous way up to the temperature of about 200°C, and at the temperature 204°C a sudden release of 0.2 mol H_2O takes place. During further heating the next 0.7 mol H_2O is being removed from the larderellite structure continuously up to the temperature 220°C. At 260°C the next violent removal of 1.8 mol H_2O occurs. This process is accompanied by explosive disintegration of the larderellite grains resulting in spraying of a part of the powdered sample. Dehydroxylation and dehydration of larderellite does not cause any changes in its structure. In the temperature range 330–450°C 2 mol of ammonia and the accompanying water, formed as a result of the oxidation of ammonium ions to ammonia, are removed. The total removal of ammonia from the structure of larderellite causes the destruction of the boron-oxygen chains and the formation of X-ray amorphous, porous matrix, inside which a slow crystallisation of boron oxide is started [17].

Thermodynamic analysis

Since no data concerning the thermodynamic function of the formation of hydrated borates and the corresponding amorphous phase are available, an approximated method of their calculation has been applied [18], which consists in summing up the standard free energies of the formation of the respective oxides, OH groups and water molecules making up the structure of the respective reagents. The calculated free energy changes of the borates decomposition at various temperatures are shown in Table 1.

Table 1 Changes of the ΔG^0 for dissociation of borates at various temperatures

Reaction	ΔG^0/kJ mol^{-1}					
	25°C	127°C	227°C	327°C	427°C	527°C
$Ca_2B_6O_8(OH)_6 \cdot 2H_2O \rightarrow$ $2CaO \cdot 3B_2O_3 + 5H_2O$	73	43	23	–28	–72	–122
$Ca_4B_{10}O_{16}(OH)_6 \cdot 4H_2O \rightarrow$ $4CaO \cdot 5B_2O_3 + 7H_2O$	89	35	–5	–98	–186	–280
$2NaCaB_5O_6(OH)_6 \cdot 5H_2O \rightarrow$ $Na_2O \cdot 2CaO \cdot 5B_2O_3 + 16H_2O$	97	31	–19	–133	–243	–359
$2HKMg_2B_{12}O_{16}(OH)_{10} \cdot 4H_2O \rightarrow$ $K_2O \cdot 4MgO \cdot 12B_2O_3 + 19H_2O$	136.5	77.5	37.5	–63	–151	–250
$Na_2B_4O_5(OH)_4 \cdot 8H_2O \rightarrow$ $Na_2O \cdot 2B_2O_3 + 10H_2O$	102	2	–78	–252	–428	–608
$Na_2B_4O_5(OH)_4 \cdot 3H_2O \rightarrow$ $Na_2O \cdot 2B_2O_3 + 5H_2O$	62	22	–8	–77	–143	–213
$Na_2B_4O_6(OH)_2 \cdot 3H_2O \rightarrow$ $Na_2O \cdot 2B_2O_3 + 4H_2O$	43	5	–25	–91	–157	–225

Table 2 Thermal parameters of the decomposition of borates

Mineral	$T_{\mathrm{o\ thermod.}}$	$T_{\mathrm{o\ exp.}}$	$T_{\mathrm{end\ exp.}}$	Density/ mol cm^3
Colemanite	241	300	650	0.0117
Pandermite	196	250	550	0.0069
Ulexite	102	118	500	0.0049
Kaliborite	231	250	400	0.0029
Borax	109	100	500	0.0045
Kernite	118	85	500	0.0055

From the presented data it follows that with increasing temperature the probability of the decomposition of borates increases, although their thermal stability varies. Assuming the value $\Delta G^{\circ}=0$ for the beginning of the decomposition reaction, the thermodynamic temperatures of the beginning of the decomposition of hydrated borates ($T_{\mathrm{o\ thermod.}}$) have been determined. These values, were found to be close to those determined experimentally, or slightly lower (Table 2).

Discussion

Thermal decomposition of hydrated borates comprises two stages:

1. Formation of free water molecules occurring as a result of their splitting off from the borate framework (dehydration) or as a result of the splitting off of the OH groups from the hydrogen-oxygen anions (dehydroxylation),
2. Removal of water molecules towards the outside of the structure of the mineral.

These processes do not always occur simultaneously. For the dissociation of borates they are often independent processes (colemanite and borax) or coincide only in part (pandermite, ulexite, kaliborite, kernite).

Water molecules formed at the first stage of the decomposition of borates become completely (colemanite, borax) or partly (e.g. pandermite or ulexite) retained in the empty voids of their crystalline structure or they accumulate along the micro and macro-defects of the grains as gaseous internal water. With increasing temperature the pressure of confined gas molecules increases, resulting in the disruption of the framework and release of the retained water molecules.

Thus the course of thermal dissociation of borates becomes affected by the pressure of the gaseous products of the reaction (internal pressure) enclosed in their framework. The increase of the internal pressure causes the depression of the reaction equilibrium, hence under the experimental conditions, higher temperature is necessary for the beginning of the borates dissociation.

The specific course of thermal dissociation of borates is well illustrated by the sealed box model [19] whose walls are not permeable to the gaseous products of dissociation. The phenomenon of explosive release of water occurs in borates with large, well developed crystals (colemanite, borax), which prevent the escape of the gaseous molecules trapped inside them. In these minerals the processes of breaking up the weakest hydrogen bonds and removal from the structure of the newly formed water are separated from each other by a certain temperature interval. In fine grains the retaining of the dissociation products is less probable, and as a result the processes of their formation and removal from the structure proceed simultaneously and in a less violent way (pandermite or ulexite).

During the violent stage of the decomposition of borates a relatively small amount of water vapour (0.5–1 mol) is removed from their structure. A considerable part of the water trapped inside the structure of borates is released at a constant rate, and the course of its release depends also on the degree of development of the internal structure of the mineral as the structural defects offer an easy way for the enclosed gaseous molecules to escape. This is in accordance with the molar density of the borate structure and is evidenced by the values of temperatures at which the process of the water vapour comes to the end (Table 2).

Control rate thermal analysis is helpful in distinguishing the above stages of internal decomposition. Accordingly on the quasi-isothermal-isobaric thermal analysis curves the following sections may be determined: 1) a section of constant rate of water release through the structural discontinuities (a and b in Fig. 3), 2) a step of explosive release of the internal water (b and c in Fig. 3) and 3) a section of diffusional migration of residual water from the amorphous matrix (c and d in Fig. 3).

Another factor determining the course of thermal dissociation of borates is the strength of the chemical bonds occurring in the structure of these minerals. Their magnitude is estimated approximately by using, as a measure of atomic interaction, simple values such as the Pauling's electronegativity, electronegativity force [20] or effective nuclear charge of the atomic core values [21]. In crystalline borates the negative charge of complex boron-oxygen anions is balanced by the metallic cations. The temperature of the beginning of the borates decomposition increases with the increasing strength of the bonds between the metallic cation and the respective anion groups (Table 3). Calcium and magnesium borates are characterized by higher temperatures of the beginning of thermal decomposition (Table 2), since the Ca^{2+} and Mg^{2+} cations, present in their structure, exhibit high values of the electronegativity force or of the effective nuclear charge of the atomic core, interpreted as the bond strengths of the cations with negative ligands. On the other hand, the alkaline borates demonstrate lower temperature of the beginning of their decomposition since the cations occurring in their structure have lower ability to bind the boron oxygen anions.

Table 3 Selected crystallochemical properties of some cations

Property	Cation				
	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}
Electronegativity	0.9	0.8	≈0.9	1.0	1.2
Electronegativity force	8.07	5.04	–	19.02	34.44
Effective nuclear charge of the atomic core	0.615	0.565	–	0.934	1.051

The values of the strengths of the bonds: metal-boron-oxygen anion is in accordance to the values of the *M*–O lengths (Table 4). For example, the Mg^{2+} ions of high electronegativity force form in kaliborite shorter Mg–O bonds, i.e. stronger in comparison with K–O bonds occurring in the same mineral or with NH_4–O bonds occurring in larderellite.

Table 4 Lengths of the chemical bonds in borates

Borate	*M*–O	[•]	O–H[•]	H ...O[•]	Ref.
Colemanite	Ca–O	2.42	2.81	2.69	[22]
Ulexite	Na–O Ca–O	2.42 2.48	0.80	2.08	[23]
Kaliborite	K–O Mg–O	2.94 2.08	1.76	1.01	[24]
Borax	Na–O	2.43	0.98	1.92–2.03	[25]
Tincalconite	Na–O	2.43	–	–	[26]
Kernite	Na–O	2.41	–	–	[27]
Larderellite	NH_4–O	2.97	–	–	[28]

During thermal dissociation of hydrated borates the dehydration and dehydroxylation processes occur in different succession. This phenomenon is to be accounted also to the differences in the length of hydrogen bonds occurring in the structure of these borates (Table 4). The island structure of ulexite and borax is characterised by considerably longer hydrogen bonds, binding the water molecules with the structure of the minerals, hence, because of their weaker bonds, the water molecules are broken off as the first in the course of heating these minerals. In borates of chains structure (colemanite, kaliborite) the water molecules are bonded with the matrix structure by means of shorter hydrogen bonds as compared with the length of such bonds with respect to the OH groups. Hence their breaking off takes place after the breaking-off of the OH groups.

There are no data available concerning the length of the hydrogen bonds in the layered structure of pandermite. From the earlier results [10] it follows that during heating of pandermite, the molecular water is removed first followed by the formation of borate of lower H_2O content which still retains the layer structure, and next by removal of the OH groups. This multistage course corresponds to the varying strengths of the hydrogen bonds between the OH groups and the H_2O molecules in the pandermite structure. Thus the obtained results indicate the existence in this structure of longer hydrogen bonds linking the water molecules, present in-between the layers and shorter ones binding the OH groups located within the layers.

Conclusions

The processes of thermal decomposition of hydrated borates are of the nature of internal structure reconstitution reactions [29], which proceed within the rigid structure of a crystalline mineral as a reaction medium.

They comprise two processes: formation of free water molecules and removal of these towards the outside of the solid matrix. For internal decomposition of borates these processes occur often independently, at different temperatures.

The water molecules formed during the first stage become located in the empty voids of the structure and also accumulated along the macro- and microdefects of the grains. With increasing temperature, the pressure of accumulated water vapour increases, resulting in the disruption of the structure (often in an explosive way) and liberation of the gaseous molecules.

The remaining water molecules and OH groups bonded in the solid matrix migrate with temperature increase outwards. The above stages of the thermal decomposition can be easily distinguished by means of Q-derivatograph.

The thermal decomposition of hydrated borates is affected by the pressure of the gaseous products of the reaction trapped in their structure. It is also determined by the kind and strength of chemical bonds occurring in their structure.

* * *

Since this Special Issue of the Journal of Thermal Analysis and Calorimetry is dedicated to Professor Ferenc Paulik, I would like to appreciate his support during my staying at Technical University of Budapest. The experience obtained in Professor's Lab was very helpful in the study of thermal reactions of borates.

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