

## Thermal decomposition of hydrated borates. Part 2. Thermal decomposition of kaliborite $\text{HKMg}_2\text{B}_{12}\text{O}_{16}(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$

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(Received 14 May 1992)

### Abstract

The structural mechanism of the thermal decomposition of kaliborite has been investigated. Kaliborite decomposition is an internal structural reconstitution process occurring in the whole volume of the crystal. The following stages of the process have been distinguished: (1) dehydroxylation; (2) dehydration; (3) recrystallization of the anhydrous amorphous substance and formation in succession of  $\text{MgB}_4\text{O}_7$ ,  $\text{Mg}_2\text{B}_2\text{O}_5$  and  $\text{KB}_5\text{O}_8$ . Dehydration precedes dehydroxylation and both of them consist of two independent stages: formation of free water molecules localized into the structural framework, and their release.

### INTRODUCTION

Kaliborite (hintzeite +  $\text{HKMg}_2\text{B}_{12}\text{O}_{16}(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$ ) crystallizes in a monoclinic system. It occurs mostly in grain aggregates: well-shaped plate crystals are rare.

The data referring to its chemical composition, structure and properties are divergent. Van't Hoff [1] gave the formula for this mineral as  $\text{KMg}_2\text{B}_{11}\text{O}_{19} \cdot 9\text{H}_2\text{O}$ ; Pardillo Vaquer [2], in contrast, assigned it the formula  $\text{KMg}_2\text{B}_{11}\text{O}_9 \cdot 15\text{H}_2\text{O}$ ; according to Christ [3] it is built of polyions of the  $[\text{B}_5\text{O}_6(\text{OH})_4]^-$  and  $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$  type and its chemical formula is  $\text{KMg}_2\text{B}_{11}\text{O}_{12}(\text{OH})_{14} \cdot 2\text{H}_2\text{O}$ . From another study [4] it follows that kaliborite belongs to pentaborates of chain structure containing an additional side chain. Its structure contains an anion of the type  $[\text{B}_5\text{O}_7(\text{OH})_3\text{OB}(\text{OH})_2]^{3-}$  in which there occur two boron atoms in threefold coordination with oxygen, three boron atoms in tetrahedral coordination and, moreover, an additional boron atom in triangular coordination. Such a structure is expressed by the formula  $\text{HKMg}_2[\text{B}_5\text{O}_7(\text{OH})_3\text{OB}(\text{OH})_2] \cdot 4\text{H}_2\text{O}$ .

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There also exists the opinion [5] that in the structure of kaliborite the boron–oxygen chains run parallel to the “*b*” axis. A single element in the chain is a double ring containing two triangles ( $\text{BO}_2(\text{OH})$  and  $\text{BO}_3$ ), three tetrahedra (two  $\text{BO}_4$  and one  $\text{BO}_2(\text{OH})_2$ ) and the additional triangle  $\text{BO}(\text{OH})_2$ . The double ring as repeating unit makes up a  $[\text{B}_6\text{O}_8(\text{OH})_5]_n^{3-}$  polyion, which is perpendicular to the chain direction. Between two screw-axis related double rings there are Mg-octahedra. Each Mg-octahedron shares four of its oxygen atoms with the boron atoms of a single chain. Potassium, however, fills the voids between four boron–oxygen chains linking them. The coordination polyhedron of potassium has one edge in common with the adjoining Mg-octahedron. In this way the bridges  $\text{Mg}-2\text{H}_2\text{O}-\text{K}-2\text{H}_2\text{O}-\text{Mg}$  are formed between pairs of neighboring boron–oxygen chains.

Kaliborite shows perfect (001) and  $(\bar{1}01)$ , and good (100) cleavages, all due to the weak K–O bonds and to the hydrogen bridges occurring between the boron–oxygen chains.

## EXPERIMENTAL

### *Materials and methods*

Kaliborite from Stassfurt was examined. The sample belonged to the Mineralogical Museum at Wrocław University. The monomineral nature of the sample has been confirmed by X-ray and IR examinations [6–8].

Thermal investigations were carried out with the microcomputer-controlled derivatograph C (MOM, Budapest) using the technique of dynamic heating and measurements under quasi-isothermal-isobaric conditions.

The changes in the structure of kaliborite during heating were examined by the X-ray investigation (DRON-3 apparatus) and by IR spectroscopic examinations (Zeiss MR-80). The examined samples were heated to temperatures 270, 295, 400, 600, 700, 750, 850 and 1000°C at a rate of  $2.5^\circ\text{C min}^{-1}$ . The behavior of the kaliborite grains during heating was observed in a heating Leitz microscope and in scanning electron microscope (Tesla).

## RESULTS

The DTA curve for kaliborite (Fig. 1) obtained under standard conditions (sample 100 mg; heating rate 10 and  $2.5^\circ\text{C min}^{-1}$ ; air atmosphere; Pt crucible) shows the endothermal effect within the temperature range 200–300°C with distinct inflection at 260°C. It is connected with the loss of 24.8 wt.% of  $\text{H}_2\text{O}$ , which is greater than the theoretical loss (23.90 wt.%), being probably caused by the liquid inclusions existing in the kaliborite crystals. At 679 and 729°C exothermal effects occur, not

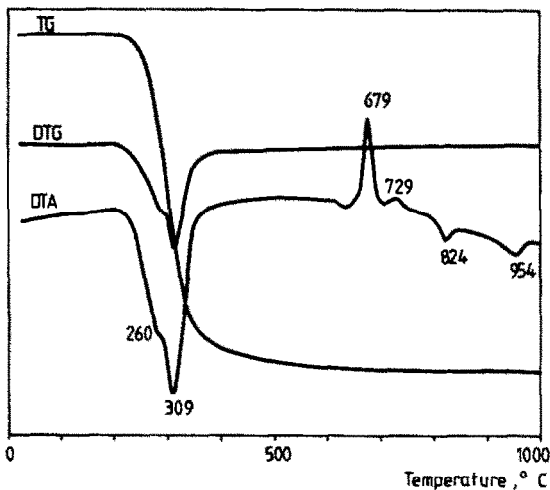


Fig. 1. TG, DTG and DTA curves for kaliborite.

accompanied by any change in the sample weight, preceded by endothermic inflection. At 824 and 954°C endothermic effects occur, not resulting in any change in the kaliborite either.

The Q-TG, Q-DTG and Q-DTA curves for kaliborite obtained under quasi-isothermal-isobaric conditions (Fig. 2) show that kaliborite heated up to 258°C loses 2.5 wt.% of H<sub>2</sub>O at constant rate. This is adsorption water and water filling the inclusions in the kaliborite crystals. The removal of water from the structure of kaliborite begins at 258°C and proceeds at a constant temperature; it is marked by the step on the Q-TG curve and the corresponding peaks on the Q-DTG and Q-DTA curves.

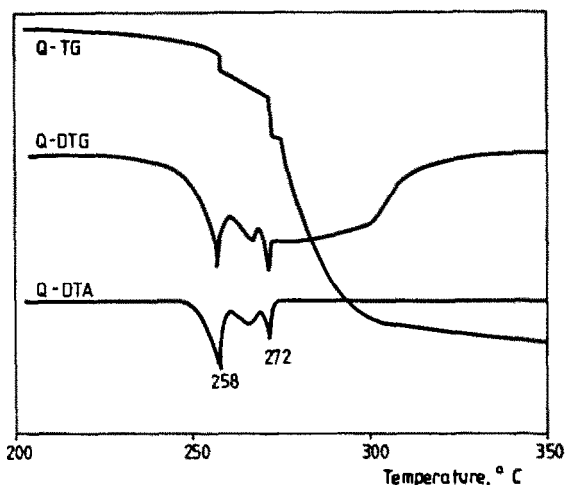


Fig. 2. Q-TG, Q-DDG and Q-DTA curves for kaliborite.

1 mol H<sub>2</sub>O is then released. For the further removal of water at the same rate (0.15 mg min<sup>-1</sup>) an increase of temperature up to 272°C is necessary. At this temperature a repeated rapid release of 2 mol H<sub>2</sub>O occurs. With increase of temperature 6 mol H<sub>2</sub>O escape continuously at the given constant rate.

X-ray patterns (Fig. 3) have revealed that with increasing temperature the essential framework of the kaliborite structure is retained. In contrast to the results obtained by Sajko et al. [9], an X-ray pattern of a sample heated up to 270°C still showed the lines of this mineral, the strongest being at 0.722, 0.622 and 0.310 nm, although of diminished intensity. This proves that the boron–oxygen chains built up of double [B<sub>6</sub>O<sub>8</sub>(OH)<sub>5</sub>]<sup>3-</sup> rings forming the main structural network of kaliborite have not been completely broken. At 295°C the main lines of kaliborite are still visible, but their intensity is very small. At 400°C the lines characteristic of this mineral disappear. There remains only a broadened band (about 20–22°C) typical of amorphous substances.

The kaliborite sample heated to 700°C has revealed the presence of well

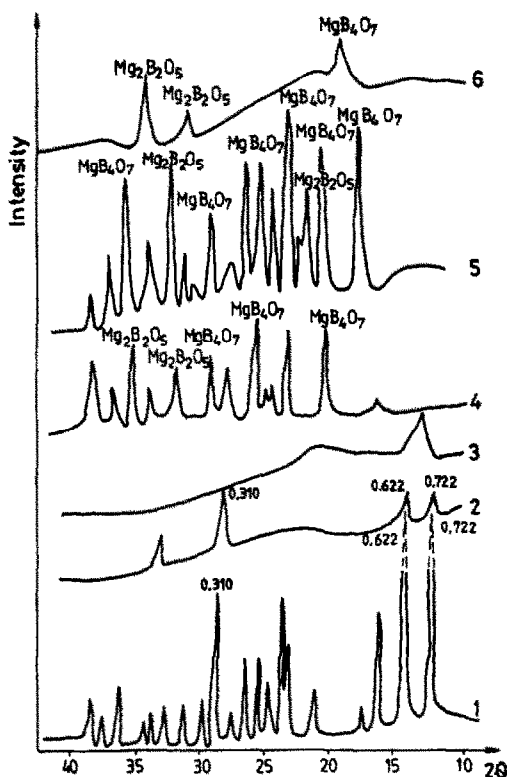


Fig. 3. X-ray diffraction patterns of kaliborite samples heated to (1) 270°C, (2) 295°C (3) 400°C, (4) 700°C, (5) 850°C, (6) 1000°C.

crystallized magnesium borate  $\text{MgB}_4\text{O}_7$  and a small amount of  $\text{Mg}_2\text{B}_2\text{O}_5$ . At  $750^\circ\text{C}$  the intensity of  $\text{Mg}_2\text{B}_2\text{O}_5$  lines increased, and, moreover, there appeared a new one of low intensity, indicating the existence of potassium pentaborate  $\text{KB}_5\text{O}_8$ . At  $850^\circ\text{C}$  the diffraction pattern did not change. At  $1000^\circ\text{C}$  the borate lines are disappearing, only the strongest lines  $\text{MgB}_4\text{O}_7$  and  $\text{Mg}_2\text{B}_2\text{O}_5$  being retained.

The IR absorption spectrum of kaliborite (Fig. 4) shows bands of borates in the range  $400\text{--}1700\text{ cm}^{-1}$  [7, 8]. They correspond to the valency and deformation vibrations of the B–O and B–O–B bonds. The absorption bands at  $890$ ,  $980$ ,  $1055$ ,  $1350$  and  $1390\text{ cm}^{-1}$  are caused by the vibration of  $\text{B}^{\text{III}}\text{--O--B}^{\text{IV}}$  bonds; the  $1110$  and  $1175\text{ cm}^{-1}$  bands are caused by the vibration of the  $\text{B}^{\text{IV}}$  atom; the bands at  $1290$  and  $1340\text{ cm}^{-1}$  are caused by the vibration of the  $\text{B}^{\text{III}}$  atom [10]. The appearance of several absorption bands in the range  $400\text{--}700\text{ cm}^{-1}$  is evidence of the complex structure of the boron–oxygen anion [8]. In the short wave part of the spectrum absorption bands occur at  $3200$ ,  $3420$  and  $3580\text{ cm}^{-1}$ . The bands at  $3200$  and  $3420\text{ cm}^{-1}$  with simultaneous presence of the band at  $1620\text{ cm}^{-1}$  are caused by vibration of the molecular water, whereas the sharp absorption band at  $3580\text{ cm}^{-1}$  is caused by vibration of the OH group. At  $270^\circ\text{C}$  the band of the OH group disappears completely, whereas the band of molecular water becomes broaden and shifted to  $3440\text{ cm}^{-1}$ , which with simultaneous decrease in the intensity of bands at  $3200$  and  $1620\text{ cm}^{-1}$ , is evidence of the splitting off of part of the water

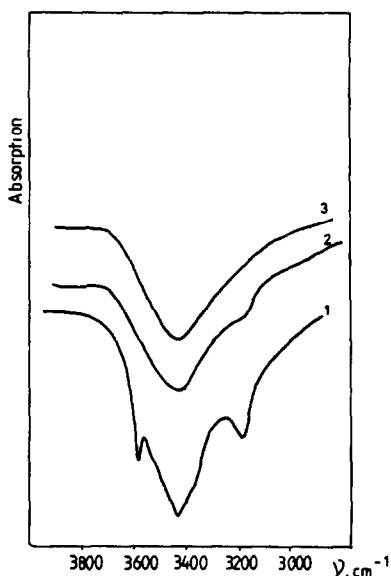


Fig. 4. OH and  $\text{H}_2\text{O}$  stretching bands of kaliborite heated to (1) room temperature, (2)  $270^\circ\text{C}$ , (3)  $340^\circ\text{C}$ .

particles from the borate rings. In the range  $400\text{--}1700\text{ cm}^{-1}$  of the IR absorption spectrum there can still be observed the characteristic bands of kaliborite, but of considerably reduced intensity. At  $400^\circ\text{C}$  the  $3200\text{ cm}^{-1}$  and  $1620\text{ cm}^{-1}$  bands of molecular water disappear.

#### DISCUSSION

The decomposition of kaliborite begins with splitting off of OH groups and the formation of water molecules which remain within the structure of the mineral and become located in the free spaces between the boron–oxygen chains as internal water. At  $258^\circ\text{C}$  the pressure produced by this water disrupts the borate crystal and part of it (about 1 mol) is released. Next, the hydrogen bonds which link the water particles with the borate structure become broken and simultaneously the released water is also retained in the voids between the chains. At  $272^\circ\text{C}$  the second violent release of accumulated water (about 2 mol) occurs. These processes proceed without any major changes in the external form of the kaliborite crystal. Only a small decrease of the sample volume is observed in a heating microscope. The remaining water molecules enclosed within the framework are gradually released up to  $400^\circ\text{C}$ . As a result of the dehydration process the borate chains become destroyed. The remaining material is anhydrous and X-ray-amorphous with pores visible in a scanning electron microscope arranged parallel to the direction of the

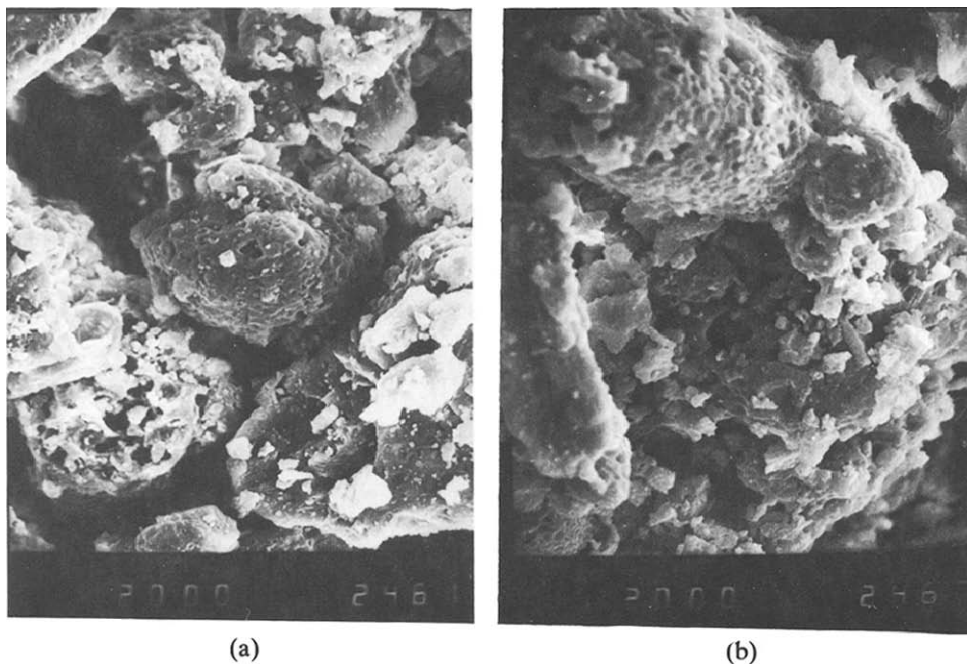


Fig. 5. Kaliborite heated to  $400^\circ\text{C}$ . Scanning electron microscope. Original magnification  $2000\times$ .

borate chains. Water particles have accumulated in these pores. With increasing temperature the internal pressure of the enclosed water caused a disruption of the kaliborite crystals and the release of vapor (Fig. 5).

During further heating the structure becomes denser and after the endothermal effect of its transformation (at 640°C) which is typical of amorphous substances, the magnesium borates  $MgB_4O_7$ , and next  $Mg_2B_2O_5$  (679°C) become crystallized. At 729°C the potassium pentaborate  $KB_5O_8$  is crystallized, which at 824°C exhibits a polymorphic transition; at 954°C the borates melt.

The thermal decomposition of kaliborite shows all the features characteristic of an internal process. As in the case of chain calcium borate-colemanite [11], the decomposition of kaliborite (Mg,K chain pentaborate with an additional side chain) proceeds in two separate stages: (1) formation of water from the OH groups and its removal from the structure; (2) removal of molecular water from the structure.

Both these processes proceed independently and are registered by separate peaks on the Q-DTA and Q-DTG curves. The disruption of the structural framework caused by release of water molecules accumulated in the voids of the framework in the case of kaliborite proceeds at a constant rate; in this it differs from the explosive dehydration of colemanite. As in the case of colemanite, it is not until water has been completely removed from the structure of kaliborite that the borate chains become destroyed and an amorphous substance formed.

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