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Thermal decomposition of hydrated borates. Part 3. Structural mechanism of thermal decomposition of borates

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Abstract

The structural mechanism of the thermal decomposition of hydroborates containing various boron–oxygen anions and of varying degrees of polymerization, and containing Ca^{2+} and Na^+ or K^+ cations, is considered.

The temperature of the reaction, its rate and the ordering of the removal of H_2O molecules and OH groups are determined by the strength of their bonds with anion rings or cations, and in considerable degree by the permeability of the structure to water molecules. Reconstitution of the amorphous solid products of the thermal decomposition of borates and their recrystallization as related to the precursor structure is discussed.

INTRODUCTION

Investigations of borates containing various boron–oxygen anions, varying degrees of polymerization, and containing the Ca^{2+} and Na^+ or K^+ cations, reveal certain relations between the structural mechanisms of their thermal decompositions and the structures of these compounds. The thermal decomposition of all the borates examined comprised several distinguishable processes.

(1) Splitting off of the H_2O groups bound with the boron–oxygen anion and of those coordinating the metal cations.

(2) Splitting off of the OH groups from the borate anions and formation of free water molecules.

(3) Release of water molecules formed as a result of both the above processes (the water molecules do not usually escape from the structure immediately after they have been formed but remained enclosed in it as internal water filling the voids).

(4) Rearrangement of the structure accompanying the removal of water molecules and OH groups.

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(5) Amorphization of the structure following dehydration and dehydroxylation (this process is accompanied by removal of the remaining water molecules and/or OH groups preserved within the framework).

(6) Crystallization of anhydrous borates connected with the reconstruction of boron–oxygen anions and redistribution and displacement of the metal cations.

DEHYDRATION AND DEHYDROXYLATION

During the decomposition of hydrated borates the processes of dehydration (splitting off of the structural water molecules) and dehydroxylation (removal of the OH groups) occur in varying sequences. In the cases of ulexite and pandermite, the molecular water is released and removed from the structure first, whereas the removal of the OH groups takes place at a higher temperature. During the heating of colemanite, the OH groups are the first to break off from the borate anions and the water molecules split off at a higher temperature. In the case of kaliborite, the OH groups and H_2O molecules release at the beginning simultaneously, but dehydroxylation is completed much earlier than dehydration.

A lower temperature of thermal dissociation of a solid is usually caused by a smaller bond strength of the respective groups of anions. In view of the considerable similarity of the structures of boron–oxygen anions, the reason for the varying behavior of the borates examined should also be looked for in other factors. One of these factors, seems to be the facility with which water molecules may be removed from the structure. This depends on the packing density of the framework atoms in their surroundings. When applying the sealed box model [1, 2] it can be imagined that in the case of the borate structure or the part of it (domain) which is hardly permeable to water molecules, the local internal pressure of H_2O increases strongly inhibiting the dissociation process. Domains act here as microautoclaves. In this case the splitting off of water molecules and their subsequent release becomes shifted to higher temperatures; it may exceed the dehydroxylation temperature if the nearest surrounding OH groups are permeable to H_2O molecules. In particular, the water molecules bound to the boron–oxygen anions should find themselves in such a situation. Similar behavior is observed in the chain structures of colemanite and kaliborite. In kaliborite, large K^+ cations and small Mg^{2+} cations occur between the chains, and this can make the structure more permeable to H_2O molecules: dehydration will then start simultaneously with dehydroxylation. In the pandermite structure, the spaces between the boron–oxygen layers provide a convenient route of escape for the H_2O molecules localized there. This makes the structure permeable to them so dehydration precedes dehydroxylation. This is in accordance with the molar density values of borates: the density of colemanite

(0.0117 mol cm^{-3}) is higher than that of pandermite (0.0069 mol cm^{-3}).

Water coordinating the metal cations which link the chains of the boron–oxygen anions appears to be easily released: ulexite begins to lose water at 118°C (molar density 0.0048 mol cm^{-3}).

One of the other factors influencing the dehydroxylation temperature of the borates examined is the strength of the bonds between the OH groups and the metal cations. OH groups are particularly strongly bound with sodium and, accordingly, pure NaOH becomes decomposed at a considerably higher temperature than its melting point (318°C). At elevated temperatures, hydrogen bound with the boron–oxygen anions may be formally regarded as a component of an HBO_2 molecule. Pure HBO_2 melts at 236°C [3]. In a molten state it retains stability until relatively high temperatures. The removal of the OH groups from molten HBO_2 requires the use of a special procedure such as a flow of gaseous Cl_2. This may explain the fact that the removal of the OH groups from the Na, Ca borate ulexite takes place as high as 550°C and is associated with a reaction between sodium and the boron–oxygen anions and the progressive synthesis of NaB_3O_5. In this case, the sodium cations act simultaneously as stabilizers of the ring borate anions bound to them. Borate anions may form new compounds with metal cations above 550°C as the OH groups are released.

The rate of release of various kinds of water at various stages of borate decomposition is varied. The constant rate thermal analysis (among others, the quasi-isothermal-isobaric method) helps to indicate this [4]. On the Q-TG curves of borates there may be distinguished: (a) sections of constant rate of water release from layers near the surface and macrodefects, remaining in direct contact with the atmosphere, (b) the step of explosive release of internal water; (c) a rectilinear section indicating the stage of slow removal of water molecules and remaining OH groups, confined in the framework of the amorphous decomposition products, proceeding at a constant rate.

A considerable part of the water (even most of it in the case of colemanite) removed in the course of the entire process of thermal decomposition escapes at stage (c). The phenomenon of the explosion of the grains (stage (b)) is caused by a relatively small amount of water vapour, equal to about 0.5–1 mol H_2O.

AMORPHIZATION AND RECRYSTALLIZATION

The dehydration and dehydroxylation processes cause the transformation of the borate structure into an X-ray-amorphous substance. This exhibits considerable stability, which may be attributed to the existence of preserved groups of polymerized boron–oxygen coordination polyhedra. They represent the remains of the structure of the precursor solid.

Removal of the remaining OH groups from the amorphous substance is usually finished just before the endothermal effect of the rearrangement of the structure (transformation point) preceding its recrystallization. The endothermal effect of transformation appears characteristic of all amorphous substances formed by amorphization in the solid phase, and of glasses [5]. The exothermal effect of the crystallization of amorphous anhydrous borates (which have been examined) occurs at a temperature higher by about 100°C than the transformation peak. This indicates their relatively small crystallization ability. Their recrystallization proceeds by the rearrangement of the borate framework elements and redistribution of the metal cations. This determines both the kind and the sequence of the formation of new compounds with increasing temperature.

The amorphous product of the thermal decomposition of colemanite has exactly the chemical composition of the compound $2CaO \cdot 3B_2O_3$ and this compound crystallizes at 741°C. This process is a rearrangement of the internal structure occurring in the solid state much below the melting point of the compound (950°C).

The point corresponding to the chemical composition of anhydrous pandermite in the $CaO–B_2O_3$ phase diagram lies in the area of the coexistence of $CaO \cdot B_2O_3$ and $CaO \cdot 2B_2O_3$. Both these compounds are formed during crystallization of amorphous anhydrite but they are not created simultaneously. The state of equilibrium of the solid is attained gradually. The compound $CaO \cdot B_2O_3$ (745°C) crystallizes first.

This may be explained as follows. According to the principle of structural similarity, the first to crystallize from the amorphous phase are the compounds whose structures are close to the chemical composition and structure of precursor or some microregions (domains) of it [6]. The newly formed crystals of calcium borate, as is seen, form themselves inside the anhydrous matrix, with composition close to the compound $CaO \cdot 2B_2O_3$. It recrystallizes next into a compound of this composition at 800°C. The higher temperature of $CaO \cdot 2B_2O_3$ crystallization may be explained by the difficulties in the formation of a more complex boron–oxygen anion, which involves greater displacements of the pieces of matrix structure. It must be added that both processes take place in the solid state, below the solidus temperature (823°C), which is the upper limit of the coexistence of both compounds.

The thermal amorphization of anhydrous kaliborite proceeds in a step-by-step mode as all the OH groups are released. When this process is completed there follows the rebuilding of the amorphous framework (endothermal effect of transformation). Within this framework the crystallization processes begin, leading to the formation of the two magnesium borates $MgO \cdot 2B_2O_3$ and $2MgO \cdot B_2O_3$ (679°C). Their simultaneous formation seems to be a consequence of the similarity of their structure to the precursor framework. The matrix with a composition close to KB_7O_{11}

remains amorphous. At 729°C $K_2O \cdot 5B_2O_3$ crystallizes in it. Its formation required considerable displacement of the K^+ ions localized in the parent structure between the magnesium–oxygen coordination polyhedra, and the formation of a complex pentaborate anion. The excess B_2O_3 is retained as an amorphous phase.

The rearrangement of the ulexite structure is especially complex. The crystallization of new compounds $CaO \cdot B_2O_3$ (chain borate) and $2CaO \cdot B_2O_3$ (pyroborate with anions composed of boron–oxygen triangles) follows immediately after the removal of the molecular water coordinating the metal cations. They are formed in the amorphous matrix $NaB_{3.4}O_{3.7}(OH)_{3.8}$, which has a complex multi-domain inhomogeneous structure. To express this, its formula may be written as $(NaOH) \cdot (HBO_2)_{2.8} \cdot (B_2O_3)_{0.3}$.

The removal of the remaining OH groups leads to the reconstitution of the matrix. Reactions also take place between boron oxide and the crystalline calcium borates. An amorphous calcium borates matrix appears, with simultaneous crystallization of NaB_3O_5. With increasing temperature, the chemical composition of the system becomes homogenized. Above 700°C, one equilibrium compound $NaCaB_3$ is formed, while the excess B_2O_3 remains amorphous.

According to the results of our investigations the course of the thermal decomposition of the particular borates is as follows.

Colemanite

$$Ca_2B_6(OH)_6 \cdot 2H_2O \xrightarrow[\text{Endo}]{340°C} Ca_2B_6O_{11} \cdot 2H_2O\ |3H_2O|_{\text{int}} \xrightarrow[\text{Endo}]{368°C}$$

$$Ca_2B_6O_{11} \cdot |5H_2O|_{\text{int}} \xrightarrow[\text{Endo}]{368°C} Ca_2B_6O_{11}(\text{amorph.}) + 5H_2O \uparrow \xrightarrow[\text{Endo}]{650°C}$$

$$Ca_2B_6O_{11}(\text{amorph.}) \xrightarrow[\text{Exo}]{741°C} Ca_2B_6O_{11}(\text{cryst.})$$

Pandermite

$$2[Ca_2B_5O_8(OH)_3 \cdot 2H_2O] \xrightarrow[\text{Endo}]{300°C} 2[Ca_2B_5O_8(OH)_3\ |H_2O|_{\text{int}}]$$

$$+ 2H_2O \uparrow \xrightarrow[\text{Endo}]{360°C} 2[Ca_2B_5O_8(OH)_3\ |0.25H_2O|_{\text{int}}] + 1.5H_2O \uparrow \xrightarrow[\text{Exo}]{390°C}$$

$$2[Ca_2B_5O_8(OH)_3\ |0.25H_2O|_{\text{int}}] \xrightarrow[\text{Endo}]{438°C} 2[Ca_2B_5O_8(OH_3]$$

$$+ 0.5H_2O \uparrow \xrightarrow[\text{Endo}]{438\text{–}580°C} Ca_4B_{10}O_{19}(\text{amorph.}) + 3H_2O \uparrow \xrightarrow[\text{Endo}]{650°C}$$

$$Ca_4B_{10}O_{19}(\text{amorph.}) \xrightarrow[\text{Endo}]{745°C}$$

$$[|3CaB_2O_4(\text{cryst.})|\ |CaB_4O_7(\text{amorph. matrix})|] \xrightarrow[\text{Exo}]{800°C}$$

$$[3CaB_2O_4(\text{cryst.}) + CaB_4O_7(\text{cryst.})]$$

Kaliborite

$$\mathrm{HKMg_2B_{12}O_{16}(OH)_{10}\cdot 4H_2O} \xrightarrow[\text{Endo}]{258^\circ\text{C}} \mathrm{KMg_2B_{12}O_{21}\cdot 4H_2O}\ |4.5\mathrm{H_2O}|_{\text{int}}$$

$$+\,\mathrm{H_2}\uparrow \xrightarrow{258\text{–}272^\circ\text{C}} \mathrm{KMg_2B_{12}O_{21}}\cdot n\mathrm{H_2O}\ |(8.5-n)\mathrm{H_2O}|_{\text{int}} \xrightarrow[\text{Endo}]{272^\circ\text{C}}$$

$$\mathrm{KMg_2B_{12}O_{21}}\cdot n\mathrm{H_2O}\ |(6-n)\mathrm{H_2O}|_{\text{int}} + 2.5\mathrm{H_2O}\uparrow \xrightarrow{272\text{–}400^\circ\text{C}}$$

$$\mathrm{KMg_2B_{12}O_{21}}(\text{amorph.}) + 6\mathrm{H_2O}\uparrow \xrightarrow[\text{Endo}]{554^\circ\text{C}} \mathrm{KMg_2B_{12}O_{21}} \xrightarrow[\text{Exo}]{679^\circ\text{C}}$$

$$[|\mathrm{MgB_4O_7} + 0.5\mathrm{Mg_2B_2O_7}(\text{cryst.})|\ |\mathrm{KB_7O_{11}}(\text{amorph. matrix})|] \xrightarrow[\text{Exo}]{729^\circ\text{C}}$$

$$[|\mathrm{MgB_4O_7}(\text{cryst.}) + 0.5\mathrm{Mg_2B_2O_7}(\text{cryst.})$$

$$+\,\mathrm{KB_5O_8}(\text{cryst.})|\ |\mathrm{B_2O_3}(\text{amorph. matrix})|]$$

Ulexite

$$\mathrm{NaCa[B_5O_6(OH)_6]\cdot 5H_2O} \xrightarrow[\text{Endo}]{118^\circ\text{C}} \mathrm{NaCa[B_5O_6(OH)_6]}\ |0.5\mathrm{H_2O}|_{\text{int}}\cdot 3\mathrm{H_2O}$$

$$+\,1.5\mathrm{H_2O}\uparrow \xrightarrow[\text{Endo}]{144^\circ\text{C}} \mathrm{NaCa[B_5O_6(OH)_6]\cdot 3H_2O} + 0.5\mathrm{H_2O}\uparrow \xrightarrow[\text{Endo}]{152^\circ\text{C}}$$

$$\mathrm{NaCa[B_5O_6(OH)_6]\cdot 0.5H_2O} + 2.5\mathrm{H_2O}\uparrow \xrightarrow[\text{Endo}]{152\text{–}260^\circ\text{C}}$$

$$[|0.5\mathrm{CaB_2O_4}(\text{cryst.})$$

$$+\,0.25\mathrm{Ca_2B_2O_5}(\text{cryst.})|\ |\mathrm{NaB_{3.4}O_{3.7}(OH)_{3.8}}(\text{amorph. matrix})|]$$

$$(=(\mathrm{NaOH})(\mathrm{HBO_2})_{2.8}(\mathrm{B_2O_3})_{0.3}) + 1.5\mathrm{H_2O}\uparrow \xrightarrow[\text{Endo,Exo}]{550^\circ\text{C}}$$

$$[|\mathrm{NaB_3O_5}(\text{cryst.})|\ |(\mathrm{Ca_2B_2O_4})_{0.5}(\mathrm{Ca_2B_2O_5})_{0.25}(\mathrm{B_2O_3})_{0.2}(\text{amorph. matrix})]$$

$$+\,2\mathrm{H_2O}\uparrow \xrightarrow{>700^\circ\text{C}} [|\mathrm{NaCaBO_3}(\text{cryst.})|\ |(\mathrm{B_2O_3})_2(\text{amorph.})|] \xrightarrow[\text{Endo}]{854^\circ\text{C}}$$

$$\mathrm{NaCaB_5O_9}(\text{melt})$$

FINAL REMARKS

The thermal decomposition of borates appears to be complex process proceeding through a step-by-step rearrangement of the internal structure of the mineral. Gradual transformation of the parent structure is a long, but as it seems energetically most convenient, way of attaining the state of equilibrium by the given solid body.

Processes of this type take place in many substances. However, they have not been given sufficient consideration in traditional solid state chemistry, being contradictory to established opinions and rules.

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