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THERMAL DECOMPOSITON OF BORAX

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Abstract

Thermal decomposition of borax has been researched by thermal, XRD and FTIR methods as well as SEM microscopy. Study have revealed that it proceeds according to the mechanism of internal reactions in the structure of the precursor as a medium.

The following stages of the process have been distinguished: (1) dehydration, (2) internal structure reconstitution – formation of tincalconite, (3) amorphization of crystal structure, (4) gradual dehydroxylation and crystallization of $Na_2O \cdot 2B_2O_3$ inside the amorphous matrix.

Keywords: borax, FTIR, TG–DTG–DTA, XRD

Introduction

The thermal decomposition of some substances (hydrated borates, phosphates, silicates) involves the destruction of their primary structure. The temperature induced gradual transformation of crystalline solids is accompanied by the breaking up of the chemical bonds in the structure of the precursor, caused by the formation of particles of the gaseous products of thermal decomposition [1].

The present study brings the description of the course of thermal decomposition of hydrated sodium tetraborate – borax, in the result of which an amorphous phase is formed as well as high temperature processes of its internal rearrangement leading to crystallization of new compounds.

The hydrated sodium borate: borax – $Na_2B_4O_5(OH)_4 \cdot 8H_2O$ belongs to the group of tetraborates of islands structure [2]. Two constituent units, boron-oxygen polyions and chains formed by sodium atoms surrounded by water molecules, make up the borax structure. The polyions are formed by two $BO_2(OH)$ triangles and two $BO_3(OH)$ tetrahedra sharing some of the oxygen atoms to form a group of composition $[B_4O_5(OH)_4]^{2-}$. The polyions are placed between the chains and linked to them by hydrogen bonds to form sheets parallel to (100) [3]. The results of NMR study [4, 5] have confirmed the presence of B^{11} atom of three and four-fold coordination in the borax structure.

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Experimental

The object of research was synthetic, chemically pure borax. It crystallizes in a monoclinic system forming crystals which constitute a combination of prisms and dihedrons along the 'z' axis (Photo 1).

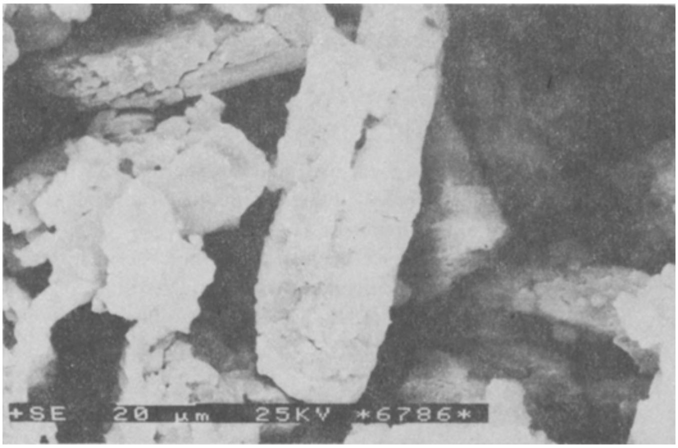

Photo 1 Scanning electron microscope of synthetic borax

The purity of the examined compound has been confirmed by X-ray and IR examinations.

Methods

Thermal study were carried out with a microcomputer controlled derivatograph C (MOM) using the technique of dynamic heating and measurements under quasi–isothermal–isobaric conditions (labyrinth crucibles, constant mass loss rate of 0.15 mg/min). Changes in the borax structure during heating were determined by X-ray diffraction method: XRD(DRON-3 diffractometer) as well as infrared spectroscopy FTIR (Fourier Spectrophotometer Digilab). The behaviour of the borax grains during heating was observed in scanning electron microscope (TESLA).

Results

The Q-TG, Q-DTG and Q-DTA curves of borax obtained under quasi–isothermal–isobaric conditions are shown in Fig. 1. It follows from these curves that at the temperature 74°C the endothermal effect takes place which is not ac-

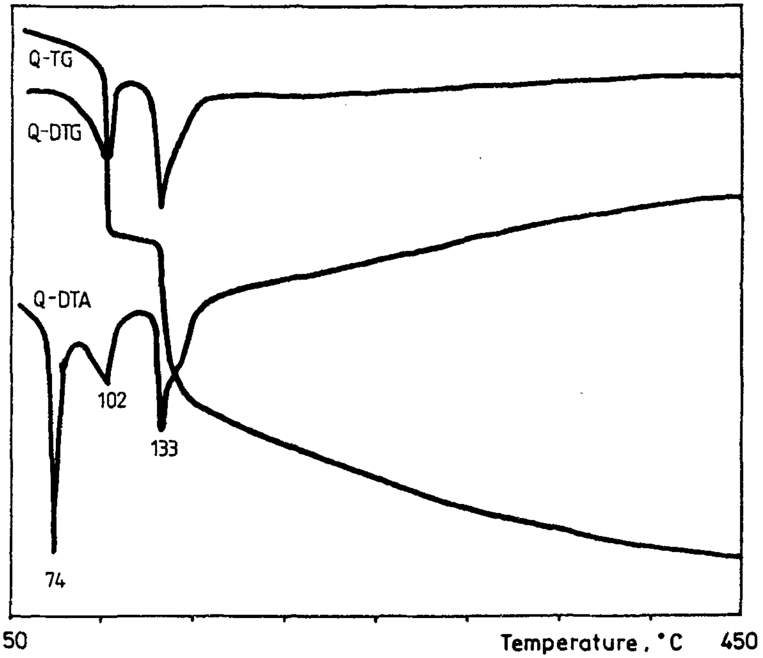

Fig. 1 Q-TG, Q-DTG and Q-DTA curves for borax

companied by any change in the sample weight. At the temperature 102°C a sudden release of 17 wt% H_2O (about 3.5 mole H_2O) 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 borax at the same rate (0.15 mg/min) an increase of temperature up to 133°C is necessary. At this temperature a repeated rapid release of 1.5 mole H_2O occurs. With the increase of temperature up to 200°C 3 mole H_2O are released, and then the remaining 2 mole H_2O are escaped continuously up to about 500°C. At 575°C exothermal effect occurs which is not accompanied by the change in TG curve, preceded by endothermal effect at 520°C (Fig. 2). At 730°C the endothermal effect of borax melting is recorded.

From the X-ray study it follows that water release during the first and second stage of dehydration produces changes in the structure of borax. On X-ray pattern of borax heated up to 140°C (Fig. 3) there appear bands typical of synthetic tincalconite. At 220°C the main lines of tincalconite disappear and a broadened bands characteristic of amorphous phase appear. The borax sample heated tc 420°C has revealed the presence of strongest diffraction lines of sodium diborate $Na_2O{\cdot}2B_2O_3$. At 650°C the intensity of the sodium diborate lines is dis-

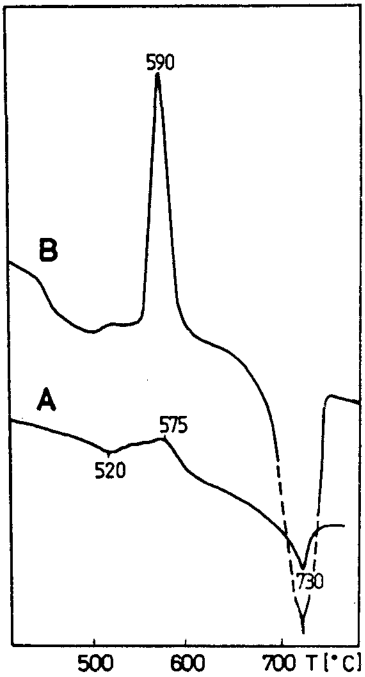

Fig. 2 DTA curves of borax (A) and glass of borax composition (B)

tinctly increased indicating the presence of well-crystallized $Na_2O·2B_2O_3$ (Fig. 3).

The IR absorption spectrum of borax (Fig. 4) shows the bands in the range 800–1400 cm^{-1} characteristic of borates, responsible for the stretching vibrations of the B–O–B bonds. In the short wave part of the spectrum there appear the absorption bands at 3200, 3350, 3500 and 3580 cm^{-1} connected with the stretching vibrations of the OH groups and water molecules [6]. At 220°C the 3200, 3350 and 1650 cm^{-1} bands of molecular water disappear and one broad band about 3500 cm^{-1} is observed, which intensity is reduced during heating of borax up to higher temperatures.

In the range 800–1400 cm^{-1} of the IR absorption spectrum there can still be observed the remainders of the absorption bands, characteristic of crystalline structure. The IR absorption spectrum of borax heated at 300°C in the range 800–1400 cm^{-1} shows bands characteristic of alkali borate glasses [7, 8].

Discussion

Thermal decomposition of borax proceeds, consistent with the research results [9–12] in several stages, separated from each other. At the temperature

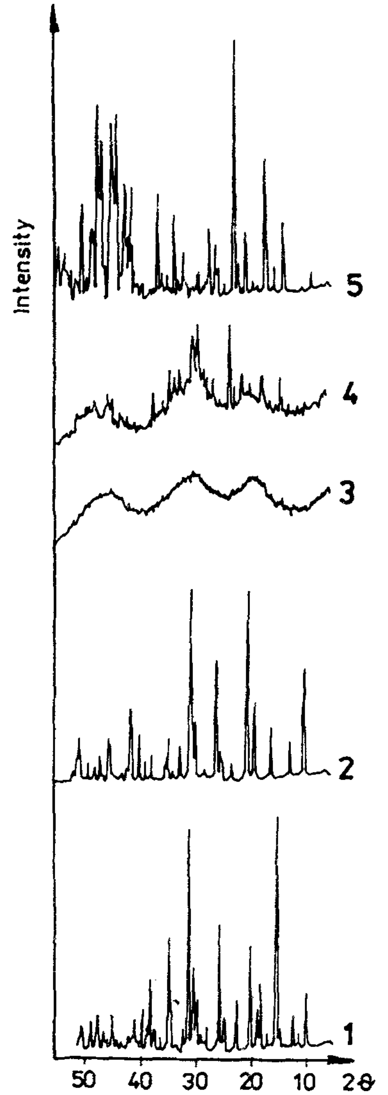

Fig. 3 X-ray diffraction patterns of borax samples heated to (1) room temperature (2) 140°C, (3) 220°C, (4) 420°C, (5) 650°C

74°C some of the molecules of the coordination water bound with the boron-oxygen anions and sodium cations are split off and enclosed inside the framework in the space between the chains as internal water. These processes are illustrated by the endothermal effect on the Q-DTA curve, not connected with a change in the sample mass (Fig. 1).

From the X-ray study it follows that the essential framework of the borax structure is preserved. The release of the retained water molecules at the temperature 102°C (3.5 mole) and 133°C (1.5 mole) is accompanied by the rearrangement of $Na_2B_4O_5(OH)_4\cdot 8H_2O$ structure into $Na_2B_4O_5(OH)_4\cdot 3H_2O$ one of smaller distance between the chains. On X-ray pattern of borax heated up to 140°C (Fig. 3) the lines characteristic of borax disappear completely, and instead there appear bands typical of synthetic tincalconite. These processes are accompanied by a distinct decrease of the grain size of borax, visible in a scanning electron microscope (Photo 2).

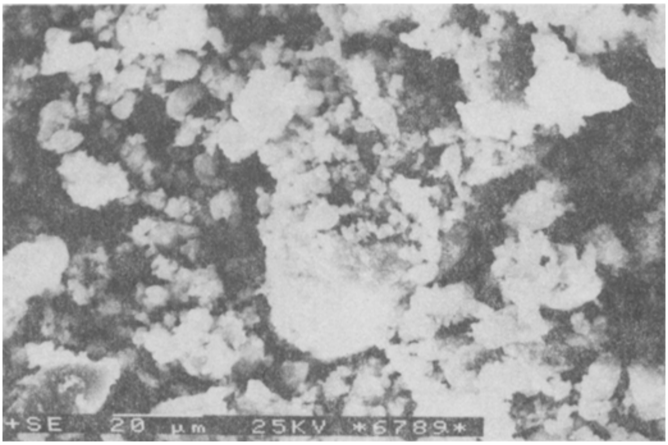

Photo 2 Scanning electron microscope of borax heated to 140°C

The remaining coordination water (about 3 mole) is removed up to the temperature 200°C, and the product of dehydration is the X-ray amorphous sodium borate with preserved elements of the primary borax structure. This is evidenced by the diffuse bands on the X-ray pattern replacing the strongest lines of crystalline tincalconite (Fig. 3). The preserved domains of the crystalline structure are too small or too defected to produce a measurable effect of X-ray diffraction. Their existence is yet confirmed by the IR absorption spectrum of borax heated above 200°C (Fig. 4). It shows in the range 800–1400 cm^{-1} the remainders of the absorption bands, characteristic of crystalline structure, indicating the presence of vibrations of the boron atoms of thre- and four-fold coordination. Amorphous sodium borate contains in its structure the OH groups which stabilize the amorphous matrix, and bind together by strong bonds with the sodium cations.

During the heating of the amorphous decomposition product of borax its internal structure gradually changes. Up to above 500°C the OH groups are

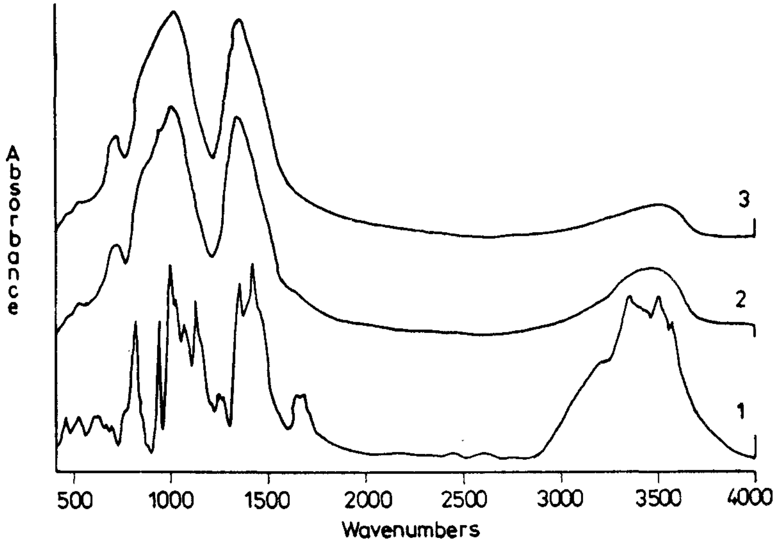

Fig. 4 IR spectra of borax samples heated to (1) room temperature, (2) 220°C, (3) 300°C

gradually removed from the amorphous matrix of the composition $Na_2B_4O_5(OH)_4$, which is accompanied by a sample weight loss (Fig. 1) and a distinctly decrease in the intensity of the 3500 cm^{-1} band is observed in IR study (Fig. 4).

As the OH groups are being removed there takes place slow crystallization of sodium diborate $Na_2O{\cdot}2B_2O_3$. Already at the temperature 400°C there appear

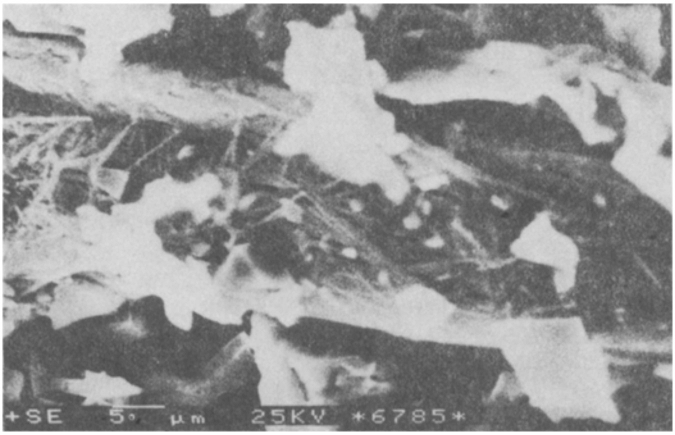

Photo 3. Scanning electron microscope of borax heated to 400°C

the first, strongest X-ray diffraction lines of this compound and the small amounts of sodium diborate, which is being formed, can be seen in a scanning electron microscope in the form of thin needles crystallizing from the amorphous matrix (Photo 3).

At the moment the OH groups are completely removed from the amorphous framework on the DTA curve of amorphized borax at the temperature 520°C there appears the endothermal, reversible effect of the internal structure rebuilding preceding its crystallization. Glass of the borax-like composition obtained by melting oxides mixture yields a similar transition effect (T_g) (Fig. 2).

The amorphous product of thermal decomposition of borax of the composition $Na_2O\cdot 2B_2O_3$ crystallizes at the temperature 575°C forming a compound of the same composition. This is the process of the internal rearrangement of an amorphous precursor structure occurring below the melting temperature of sodium diborate (735°C). Glass of the composition $Na_2O\cdot 2B_2O_3$ crystallizes rapidly what is evidenced by the sharp exothermal effect on the DTA curve, but at a higher temperature than that of amorphous borax.

In the light of the above results the thermal decomposition of borax may be illustrated as follows:

$$Na_2B_4O_5(OH)_4\cdot 8H_2O \xrightarrow{74^\circ C} Na_2B_4O_5(OH)_4\cdot 4.5H_2O\ (3.5H_2O)_{\mathrm{int.}} \xrightarrow{102^\circ C}$$

$$Na_2B_4O_5(OH)_4\cdot 4.5H_2O + 3.5H_2O\uparrow \xrightarrow{133^\circ C} Na_2B_4O_5(OH)_4\cdot 3H_2O$$

$$+\ 1.5H_2O\uparrow \xrightarrow{133-200^\circ C} \underset{\text{(amorph.)}}{Na_2B_4O_5(OH)_4} + 3H_2O\uparrow \xrightarrow{200-500^\circ C}$$

$$\underset{\text{(cryst.)}\quad\text{(amorph.)}}{[(Na_2B_4O_7)(Na_2B_4O_5)]} + 2H_2O\uparrow \xrightarrow{575^\circ C} \underset{\text{(cryst.)}}{Na_2B_4O_7} \xrightarrow{723^\circ C} \underset{\text{(melt)}}{Na_2B_4O_7}$$

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Zusammenfassung Mittels thermischen, XRD- und FTIR-Methoden als auch SEM Mikroskopie wurde die thermische Zersetzung von Borax untersucht. Die Untersuchung ergab, daß dies entsprechend dem Mechanismus interner Reaktionen in der Struktur des Präkursors als Medium erfolgt.

Folgende Stufen des Prozesses wurden unterschieden: (1) Dehydratation, (2) interne Strukturrückbildung zu Tinkalkonit, (3) Amorphisierung der Kristallstruktur, (4) stufenweise Dehydroxylierung und Kristallisation von $Na_2O2B_2O_3$ innerhalb der amorphen Matrix.