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Thermochimica Acta 374 (2001) 51–54

thermochimica acta

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Thermal decomposition of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$

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Received 25 August 2000; received in revised form 23 February 2001; accepted 24 February 2001

Abstract

Thermal decomposition of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ has been investigated by isothermal, non-isothermal methods. X-ray and FT-IR spectra determined the isothermal dehydrated products. The results showed that it is a multi-stage course. Structure and thermal decomposition mechanism of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ were discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermal decomposition; Thermal dehydration; Hydrated borate

1. Introduction

The thermal analyses of most of hydrated borates have already been reported, however, different results exist even for the same borate compound, particularly in double salts. Gao [1,2], Gode [3] and Stock [4–8] indicate that when a hydrated borate was heated, dehydroxylation, amorphization of crystal structure and recrystallization of amorphous solid would happen. $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ was synthesized by the institute of chemistry of Latvia [9] and would be useful for production of enamels and ceramic colors. They reported that the salt loses 8 mol water after 5 days at 70°C, 1.5 mol water after 6 days at 100°C, and the others would be lost at higher temperature. There were not more thermal properties of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ in references. In this paper, the thermal decomposition of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ was studied by isothermal and non-isothermal methods. We have also studied the crystal structure, dissolution and thermochemistry of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ in other papers [10,11].

2. Experimental

2.1. Preparation and composition

Solution A: 50 g H_3BO_3 and 25 g KOH dissolved in 400 ml H_2O. Solution B: 4.5 g $CaCl_2{\cdot}6H_2O$ dissolved in 15 ml H_2O. Solution A and B were mixed and stirred at 298 K for 2–4 days, then allowed to stand for 10 days during which the white amorphous precipitate was transformed into crystals. The precipitate was washed with distilled water, and then with alcohol and ether, and finally dried at room temperature to constant weight.

The sample was analyzed, and characterized by X-ray powder diffraction and FT-IR spectroscopy. The results of analyses were K_2O: 14.59%, CaO: 8.70%, B_2O_3: 43.19%, H_2O: 33.52%. The synthetic sample is thus a pure compound of formula $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}$ $12H_2O$ and suitable for thermal decomposition experiments.

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PII: S0040-6031(01)00494-4

2.2. Isothermal and non-isothermal analysis

The samples were placed in thermostat or furnace at 70, 80, 90, 100, 250, 400, 600, 800 and 1000°C and the weight loss recorded at regular intervals (t versus ΔW), until samples were constant weight, and then X-ray (D/MAX-IIIB, Cu Kα) and FT-IR spectra (Nicolet 170sx) of dehydrated products recorded.

The TG and DTA curves of the samples were recorded on a TA Instrument 2100, with different heating rates. During heating, N_2 of flow rate of $1\,l\,h^{-1}$ was used. Samples were loaded in Al_2O_3 crucible.

3. Results and discussion

The isothermal t–ΔW curve is displayed in Fig. 1. From these thermal dehydration data, $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ did not dehydrate under 70°C, and dehydrated entirely above 400°C.

To study the nature of the structural changes during heating, samples at temperatures of 70–1000°C were subjected to X-ray diffraction and IR spectroscopic examinations. X-ray and FT-IR spectra of samples are displayed in Figs. 2 and 3.

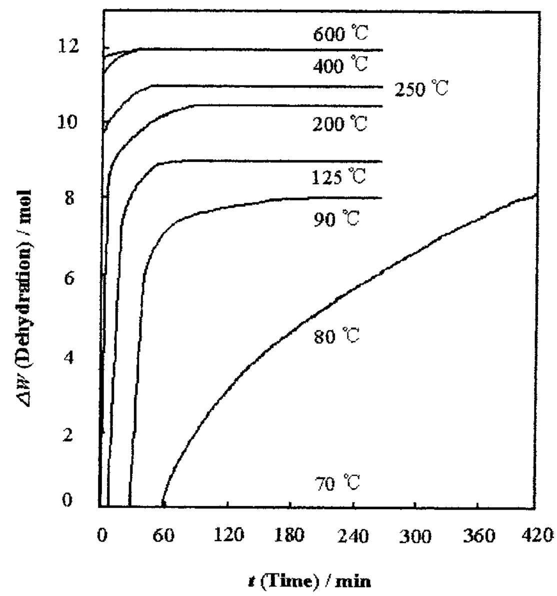

Fig. 1. Isothermal dehydration (curve t vs. ΔW) of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$. X-axis label: time in min; Y-axis label: dehydration in mol.

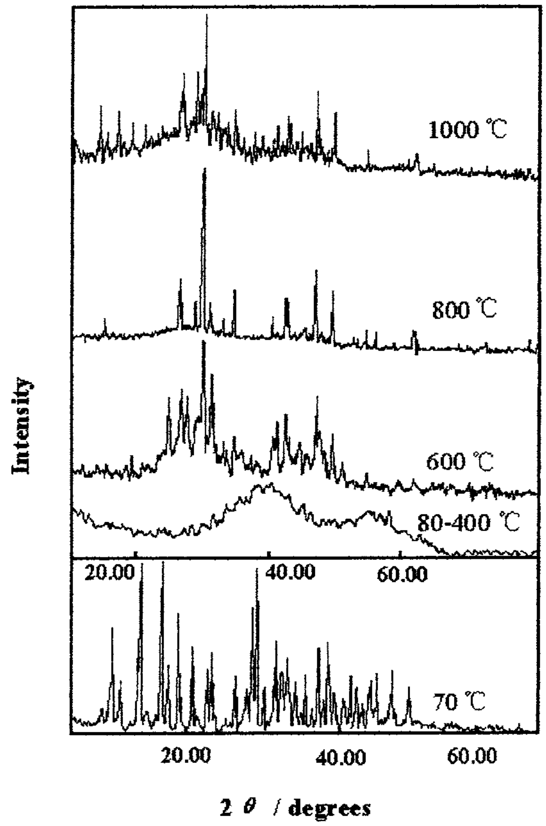

Fig. 2. X-ray of mid-products of isothermal dehydration of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$. X-axis label: 2θ in degrees; Y-axis label: intensity.

On the X-ray pattern of the sample heated at 80°C, the lines of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ disappear. The dehydration transforms the structure into an X-ray-amorphous substance. From 600–1000°C, there appear new lines and their intensity increases. X-ray patterns of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ heated up to 600°C have shown that calcium borate ($CaO{\cdot}B_2O_3$) crystallized from the amorphous substance.

From X-ray results, $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ transformed into amorphous from crystal when dehydrated 8 mol H_2O at 80°C. It did not recrystallize until 600°C. The recrystallization sample was CaB_2O_4.

FT-IR spectra of sample at 70°C. H–O–H bending modes exist at 1636 and 1691 cm^{-1}. B(3)–O asymmetric stretching was 1345, 1407 and 1445 cm^{-1}. The

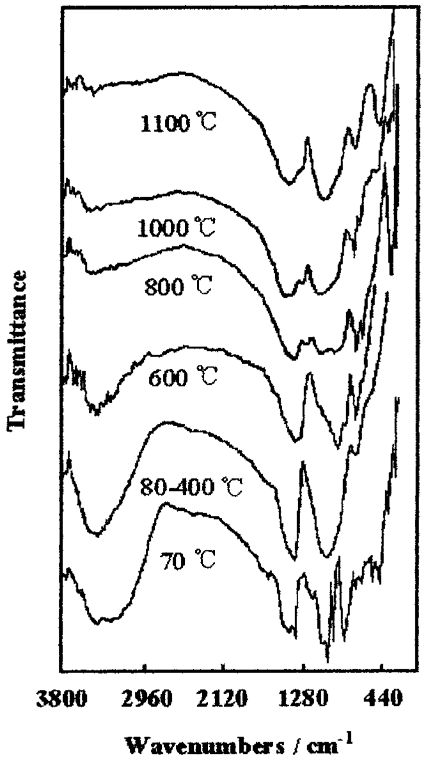

Fig. 3. IR spectra of mid-products of isothermal dehydration of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$. *X*-axis label: wavenumbers in cm^{-1}; *Y*-axis label: transmittance.

peaks at 1165 and 1267 cm^{-1} were assigned B–O–H bending modes. B(4)–O asymmetric stretching was 1038, 1071 and 999 cm^{-1}. B(3)–O symmetric stretching was 945 cm^{-1}. The value of B(4)–O symmetric stretching was 833 cm^{-1}. The band at 583 cm^{-1} was characteristic of tetraborate anions. 705, 657 and 531 cm^{-1} were assigned to B(3)–O bending modes, while the bending of B(4)–O occurs at about 461 cm^{-1}. At 80–400°C, the samples were amorphous. Most of peaks of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ in FT-IR spectra disappear and only peaks in zone of 1350 and 1000 cm^{-1} were remained and broaden. At 600°C, there occur lines of 910 and 824 cm^{-1}, which were assigned to B(3)–O and B(4)–O symmetric stretching, respectively. At 800–1000°C, there appear a peak of 706 cm^{-1}.

The decomposition of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ begins with the removal of the water molecules. This dehydration is accompanied by the rebuilding of the $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ structure. Up to a temperature of 400°C, the water of crystal is released from the $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$, and the escape of water formed as a result of the removal of the OH groups takes place from the structure. At a temperature of 600°C, $CaO{\cdot}B_2O_3$ crystallizes from the anhydrous amorphous substance remaining and persists up to 1000°C. Investigations carried out under isothermal conditions reveal difference in the mode of water release. This is in accordance with the structure of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$, eight water molecules are coordinated to potassium and calcium cations, the other four water molecules come from OH groups in the borate polyanion. $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ is built of isolated polyanions having the form of boron–oxygen–hydroxide rings, the anions $[B_4O_5(OH)_4]^{2-}$ which consists of two BO_4 tetrahedrons and two BO_3 triangles that form two six-member rings. The Ca^{2+}, K^+ cations are coordinated by the water molecules and the OH groups.

Thermal investigations carried out under non-isothermal method. The endothermic effect at 80–90°C was accompanied by the loss of 8 mol H_2O, and the other water removed slowly at higher temperature.

The DTA, DTG and TG curves were recorded at 0.5, 1, 5, 10, 15 and 20°C min^{-1}. The curves at 5, 10, 15 and 20°C min^{-1} are shown in Fig. 4(A). It exhibits a step change in heat flow at about 80°C, which was single endothermic peak of dehydration. The exothermic peak, which should correspond to the recrystallization of amorphous products after dehydration, did not occur in DTA curve.

Three small endothermic peaks were present in DTA curve at low heating rate (1°C min^{-1}) and two small peaks were present in DTA curve at 0.5°C min^{-1}. Those show that the eight structure water molecules have three different places. These endothermic peaks, which merged on obvious distinguishable shoulder, overlapped to be a peak because at high heating rate.

In the course of heating, the eight structural water molecules were removed first, accompanied by the rearrangement of the structure and formed amorphous substance. Next, removed the OH group, and subsequent recrystallization of new compounds.

According to the density values of borates, $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ should lose water at low temperature because of small molar density. Colemanite

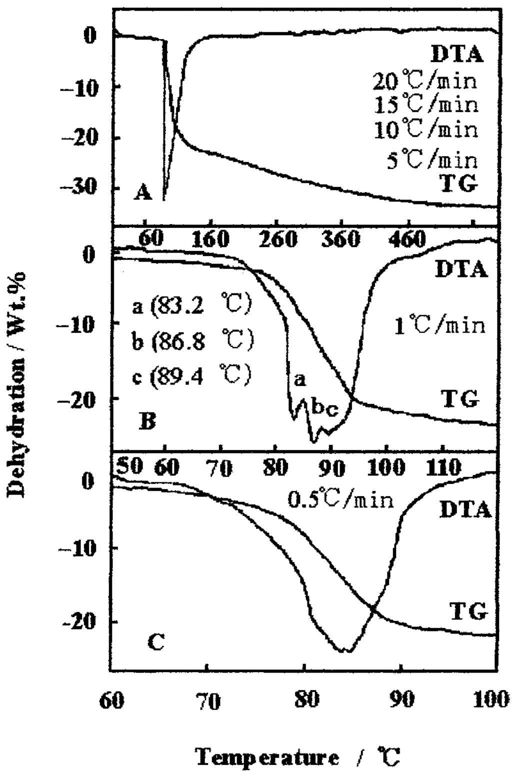

Fig. 4. DTA and TG curves of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ at different heating rates. *X*-axis label: temperature in degrees; *Y*-axis label: dehydration in wt.%.

($Ca_2B_6(OH)_6{\cdot}2H_2O$) begins to lose water at 340°C (molar density $0.0117\ mol\,cm^{-3}$), Pandermite ($Ca_2B_5O_8(OH)_3{\cdot}2H_2O$) begins to lose water at 300°C (molar density $0.0069\ mol\,cm^{-3}$), Ulexite ($NaCa[B_5O_6(OH)_6]{\cdot}5H_2O$) begins to lose water at 118°C (molar density $0.0048\ mol\,cm^{-3}$) [6–8]. The molar density of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ is $0.0028\ mol\,cm^{-3}$, so its lost water temperature is low at 83°C.

The course of the thermal decomposition of $K_2O{\cdot}CaO{\cdot}4B_2O_3{\cdot}12H_2O$ is as follows:

$$K_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O\,(\text{cryst.}) \xrightarrow[\text{Endo.}]{83.2^\circ C} K_2CaB_8O_{13} \cdot 9.5H_2O + 2.5H_2O \xrightarrow[\text{Endo.}]{86.8^\circ C} K_2CaB_8O_{13} \cdot 8H_2O + 1.5H_2O\uparrow \xrightarrow[\text{Endo.}]{89.4^\circ C} K_2CaB_8O_{13} \cdot 4H_2O\,(\text{amorph.}) + 4H_2O\uparrow \xrightarrow{\sim 600^\circ C} CaB_8O_4(\text{cryst.}) + K_2B_6O_9\,(\text{amorph.}) + 4H_2O\uparrow \xrightarrow{\sim 1000^\circ C} K_2CaB_8O_{14}\,(\text{melt})$$

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