

Easy Synthesis of CaB_2O_4 Via Pyrolysis of Calcium Fructoborate

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The investigation of the thermal behavior of calcium fructoborate samples of composition $\text{Ca}(\text{C}_6\text{H}_{10}\text{O}_6\text{BO})_2 \cdot 3.5\text{H}_2\text{O}$ showed that CaB_2O_4 is generated as the final solid pyrolysis residue. On the basis of these observations a new, very easy, synthetic procedure for the preparation of high purity samples of this calcium borate is proposed. The material was characterized by X ray powder diffractometry and IR spectroscopy.

Keywords: calcium fructoborate, CaB_2O_4 , new synthetic procedure, X ray analysis, IR spectra

1. Introduction

Crystalline inorganic borates constitute a technologically important class of oxide materials which display widespread application in high-performance devices¹⁻³.

Besides, the structural chemistry of solid borates is characterized by a considerable diversity that comes from the ability of the boron atoms to bind to three or four oxygen atoms, viz. by forming isolated trigonal planar BO_3 or tetrahedral BO_4 groups. The condensation of these groups also generates a vast array of oligomeric or polymeric structures⁴.

Most of these borates are usually prepared by solid state reactions between boric acid or boron oxide and metallic oxides or carbonates ("ceramic method")^{5,6}.

Recently, we have investigated the general physicochemical properties and the structural peculiarities of calcium fructoborate, $\text{Ca}(\text{C}_6\text{H}_{10}\text{O}_6\text{BO})_2 \cdot 3.5\text{H}_2\text{O}$, an interesting compound just introduced in the market for boron supplementation⁷. During the investigation of its thermal behavior we found that CaB_2O_4 was generated as the final thermolysis residue. Therefore, we have now additionally investigated this process in order to explore the possibility of developing a new and simple synthetic procedure for the synthesis of this calcium borate.

2. Experimental

The synthesis of calcium fructoborate was performed according to Miljkovic's procedure⁸ using boric acid from Carlo Erba, D-fructose from Sigma and CaCO_3 and acetone from Merck. D-fructose (2.16 g; 12 mmol) were dissolved in 10 mL of distilled water at room temperature and boric acid (0.372 g; 6 mmol) were then added to this solution. Finally, calcium carbonate (0.246 g; 2.46 mmol) were added in small portions, under constant stirring. After the CO_2 evolution has ceased, 40 mL of acetone were added to the reaction mixture, whereupon a colorless oil was separated at the bottom of the reaction vessel. The two layers were separated using a separatory funnel. The lower oily layer, containing the crude boron complex was treated again with 40 mL of acetone. Upon standing for one hour, crystallization was induced with a glass rod, and the oil slowly turned into a white crystalline solid. The product was filtered

off, washed with small portions of acetone and air dried. Analysis: Calcd. for $\text{Ca}(\text{C}_6\text{H}_{10}\text{O}_6\text{BO})_2 \cdot 3.5\text{H}_2\text{O}$ (MW = 512.7): C, 28.09; H, 5.27; Ca, 7.82%. Found: C, 28.22; H, 5.50; Ca, 7.75%.

Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a Shimadzu system (models TG-50 and DTA-50, respectively) using platinum crucibles, working in an oxygen flow of 50 mL/min and at a heating rate of 5 °C/min. Sample quantities ranged between 10 and 20 mg. Al_2O_3 was used as a DTA standard. One of the obtained thermograms is shown in Figure 1. The hydration water was given off, up to about 130 °C (experimental mass loss = 12.26%, theoretical mass loss = 12.29%) and this process was accompanied by a very weak DTA endothermic signal at 67 °C. The degradation of the anhydrous compound occurs in three successive TG steps located between 130 and 220 °C (mass loss = 17.10%), 220 and 410 °C (mass loss = 30.85%) and finally between 410 and 600 °C (mass loss = 23.87%). These thermolysis steps were related to DTA-signals at 181 °C (endothermic), 315 °C (exothermic), and 452 °C (strong exothermic). The total experimental mass loss of 84.08% suggested the final generation of CaB_2O_4 as the solid residue (theoretical mass loss = 84.34%):

The formation of this borate was additionally confirmed through the IR spectra and X ray-powder analysis of the residue. The X ray powder diagram, obtained with a Philips PW 1710 diffractometer, using Ni-filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5425 \text{ \AA}$), matched exactly that of the respective JCPDF file (32-0155) for CaB_2O_4 . The IR spectrum of the residue, recorded in the range 4000-400 cm^{-1} with a FTIR-Bruker-EQUINOX-55 instrument, using the KBr pellet technique, is also characteristic for this borate, as shall be discussed below.

On the basis of this information we developed the following synthetic procedure: a sample of about 1.00 g of $\text{Ca}(\text{C}_6\text{H}_{10}\text{O}_6\text{BO})_2 \cdot 3.5\text{H}_2\text{O}$ poured in a platinum crucible was slowly heated, during about 40 minutes, in a muffle furnace in air, up to 550 °C and maintained during 15 min. at this temperature. After that, the product was milled in an agate mortar and finally heated again, 30 minutes more, at 600 °C.

3. Results and Discussion

Calcium fructoborate, $\text{Ca}(\text{C}_6\text{H}_{10}\text{O}_6\text{BO})_2 \cdot 3.5\text{H}_2\text{O}$, which can be prepared by a very simple procedure, is an adequate precursor for

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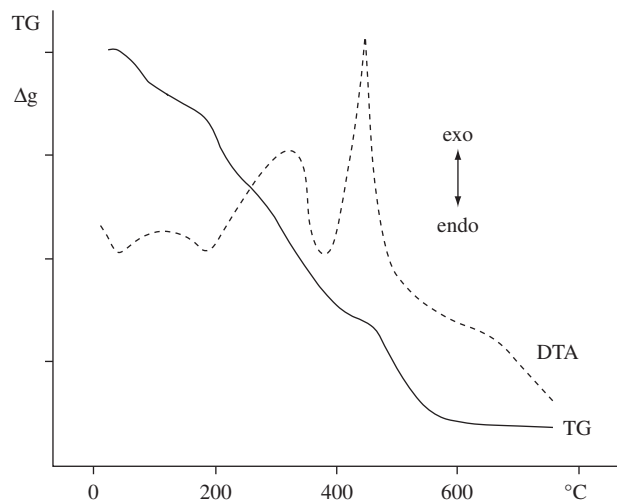


Figure 1. TG and DTA traces of the thermal decomposition of a calcium fructoborate sample.

the synthesis of CaB_2O_4 as it presents the correct Ca/B proportion and its thermal decomposition occurs at moderate temperature⁶. After short heating, the generated borate is obtained in the form of a very finely divided black powder.

The structure of CaB_2O_4 was first determined by Zachariassen⁹ and refined thirty years later¹⁰. It crystallizes in the orthorhombic space group Pnca with $Z = 4$ and the structure is conformed by triangular BO_3 -groups that shared pairs of O-atoms generating infinite $-\text{O}-\text{B}-\text{O}-\text{B}-\text{O}-$ chains running parallel to $[001]$.

As mentioned above, the obtained samples presented a well-defined and characteristic X ray powder diagram which only shows the typical reflections of CaB_2O_4 .

The IR spectrum of these samples is also very characteristic and allows the rapid characterization of the material. One of the recorded spectra is shown in Figura 2. It compares very well with previously reported spectral information¹¹ and complements it in certain aspects. The very strong band located at 1444 cm^{-1} with a shoulder at 1497 cm^{-1} originates in B-O stretchings involving the external O-atoms. The other very strong band, found at 1200 cm^{-1} , is related to B-O chain stretchings. The remaining band multiplet observed in Figura 2 (773 (shoulder), 739 (strong), 712 (shoulder), 688 (very strong) and 643 (strong) cm^{-1}) is related to different deformational modes¹¹.

4. Conclusions

The proposed synthetic procedure, using calcium fructoborate as a precursor, allows a quick and easy preparation of the CaB_2O_4 chain-like metaborate. The material can be rapidly characterized by means of its X ray powder diagram or by its very characteristic IR spectrum.

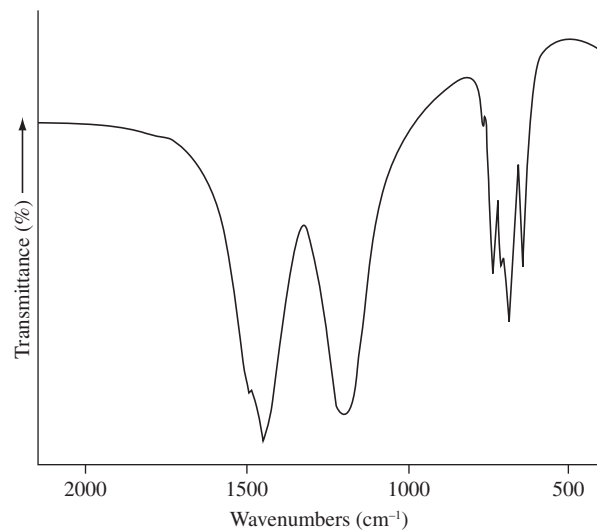


Figure 2. FTIR spectrum of one of the prepared CaB_2O_4 samples, in the spectral range between $2000\text{--}400\text{ cm}^{-1}$.

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