



FTIR spectroscopy of calcium and zinc borate compound modified by fructose

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Abstract: The solid form of the neutral trigonal form of boron organic ester with fructose, calcium carbonate (CaCO_3), and zinc carbonate (ZnCO_3) is prepared and modified in solution. The borate compounds are investigated by FTIR spectroscopy upon modification with ZnCO_3 or CaCO_3 or both. FTIR spectroscopy is developed to determine different types and the amount of borate derivatives present in products. The modifier portion from ZnCO_3 and fructose is consumed for boron transformation from BO_3 to BO_4 coordinated units. Limited borate units are formed upon modification by ZnCO_3 and fructose. But on the other hand, modification with CaCO_3 and fructose leads to higher transformation. The concentration of free boric acid (H_3BO_3) in the prepared sample cannot be transformed totally to its derivatives upon modification with zinc carbonate.

keywords: Calcium zinc borate, Bio-application, FTIR analysis, Borate groups.

1. Introduction

B_2O_3 is considered to be essential for all plant and animal life [1-4]. The interaction of calcium (Ca), zinc (Zn), or both with boron (B) has been observed in a variety of living tissues, including the human body and plants [1-7]. The precise extent of the Ca/B interaction, on the other hand, is still being investigated experimentally [7, 8]. Calcium and fructose in borate structure have been studied for their biological and biochemical action, and it has been realized that it has a chemical structure similar to natural boro-carbohydrates found in edible plants [4-8]. Boron is found in plants as sugar esters [9, 10], the most effective chemical form for assimilation into cells. Natural boron complexes have previously been revealed as an isolated boric acid ester with fructose (fructose-B-fructose), glucose, and sorbitol (glucose-B-glucose) [9-11]. Boron supplementation has traditionally been accomplished using boric acid and some inorganic borates [4-9]. Other boron

compounds with the same goal have recently been introduced in the pharmaceutical industry market. CaFB (calcium fructoborate) has recently been shown to have intriguing antioxidant, anti-tumor, and anti-inflammatory properties [8-12]. Boron, in addition to its role in promoting healthy bones and joints, may play an underappreciated role in protecting men against prostate cancer [13]. Fortunately, the clinical trial discovered that boron may help prevent prostate cancer and that higher levels of boron were associated with a lower risk of prostate cancer in a dose-response pattern. Recent studies suggested that boron has a chemopreventive role in prostate cancer. Another recent study realized that boric acid inhibits the proliferation of some human prostate cancer cells. Recent research has confirmed that when omega-3 fatty acids are combined with the critical trace mineral boron, the bone health benefits of these essential fats

may be greatly enhanced. Laboratory animals fed a diet high in omega-3 fatty acids and boron, for example, had higher bone mineral density and stronger bones than animals fed other dietary fats and boron. These results suggest that omega-3 fatty acids and boron may work together to support dense, strong bones [7-12]. The goal of this study was to look into the molecular composition of borate compounds that had been modified with both mixed $ZnCO_3$ and $CaCO_3$ and fructose to provide the material in bioactive forms.

2. Experimental

2.1 Sample preparation

Ca- and Zn-fructoborate: (2.16 g) D-fructose was dissolved in 4 ml distilled water and (0.372 g). Boric acid is then added and followed by (0.246 g) calcium carbonate or zinc carbonate. 20 ml of acetone was added after the complete evolution of carbon dioxide from the reaction results in the formation of colorless oil at the bottom of the conical flask separated using a separation funnel. The final obtained material was then triturated by a glass rod to induce crystallization resulting in the formation of white crystalline solid material washed again by acetone. The solvent allowed to evaporate at room temperature resulting in the formation of pure Ca-Zn fructoborate with about 0.78% yield.

2.2 Measurements

FTIR absorption spectra were recorded in the range of $400-4000\text{ cm}^{-1}$ and 2 cm^{-1} step resolution at temperature (20°C), by KBr pellets technique, using an FTIR spectrometer (type Mattson 5000, Fine Measurements Laboratory), Mansoura University, Egypt.

Measurements were applied in the ratio 1:100 on powder sample mixed with KBr. To get a disc-like shape, the weighed mixture was subjected to a load of 5 tons/cm^2 . The absorption spectra of IR were

immediately performed to avoid moisture attack. Using the two-point baseline correction, the spectra were corrected for the dark current noises and background. Then, the spectra were normalized by making the absorption of each spectrum vary between 0 and 1 arbitrary unit. Such normalization is necessary to eliminate the concentration effect of the powder sample in the KBr disc. Each band, width, position, and amplitude are adjustable automatically by using the standard curve fitting program to minimize the squares of deviations between the experimental and the simulated curves.

3. Results and discussion

The infrared spectra are being used to define the matrix of the investigated compound material and to identify distinct functional groups that comprise the glass network. Figure 1, displays the FTIR spectra of all examined compositions. The difference in these FTIR spectra of the investigated samples indicates that $CaCO_3$ plays a different role than $ZnCO_3$, as the substitution of $CaCO_3$ with $ZnCO_3$. The whole FTIR wide band between 800 and 1200 cm^{-1} is divided into two main peaks, at 950 and 1140 cm^{-1} . Splitting occurs at a slow rate in $CaCO_3$ enriched samples. The modification of the borate network by decreasing BO_3 concentrations results in the formation of short chains, which can be reflected in this composition region by decreasing the amplitude of the FTIR spectra representing the BO_3 unit. This behavior confirms that $CaCO_3$ ions act as a strong modifier, but $ZnCO_3$ acts as an intermediate differently.

In more detail, the spectrum contains two major absorption band features. First, tetrahedral structural units made up of BO_4 and BO_3 that can be assigned to stretching vibrations of B-O in the $800-1200\text{ cm}^{-1}$ range [14, 15]. Second, in asymmetric BO_3 units, $1200-1600\text{ cm}^{-1}$ is related to B-O stretching vibrations [16-18]. Furthermore,

a vibration of B–O–B bonds involving BO_4 tetrahedral and cationic components in (ZnO_6) units is attributed to the small band identified around 950 cm^{-1} [19, 20]. Usually, the absorbed band in the low-frequency region is assigned to cationic vibration which modifies the well former species. In all investigated glasses, there is a very wide FTIR band centered at 600 cm^{-1} was resolved. The broadness of this band is due to mixed vibration between the two types of modifiers Ca and Zn vibrations [21, 22].

To investigate the role of ZnCO_3 in fructoborate glasses, a comparison of the IR spectra of ZnCO_3 free glass and CaCO_3 rich matrix is presented in figure 2 and figure 3. These figures depict deconvolution of two FTIR spectra for samples free of ZnCO_3 and glass containing and free of CaCO_3 . When more Zn is added, both the intensity and relative area of these bands decrease, implying that Zn ions would occupy boron sites and act to reduce the concentration of the B-O-B bonds in tetrahedral coordination.

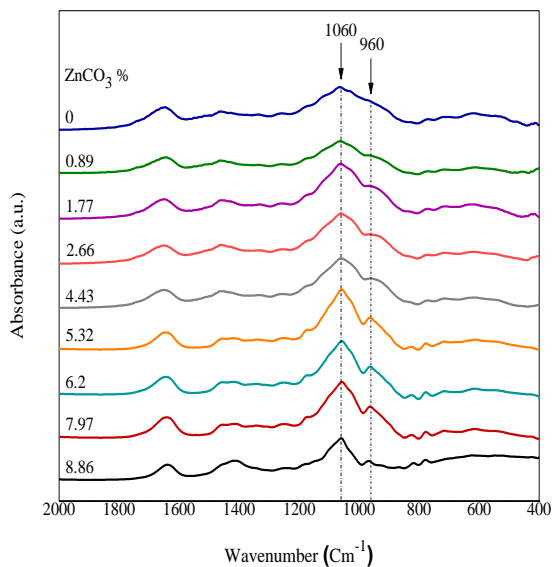


Fig. 1. FTIR spectra of fructoborate powder upon substitution of CaCO_3 with ZnCO_3 .

Figure 2 and figure 3 show that there are significant differences in the relative area (800 cm^{-1} and 1200 cm^{-1}) of the ZnCO_3 and

CaCO_3 samples. The relative area of Ca-F-B composition is greater than that of Zn-O-B composition. This implies that CaCO_3 has a greater ability to convert BO_3 or H_3BO_3 to tetrahedral born coordination. .

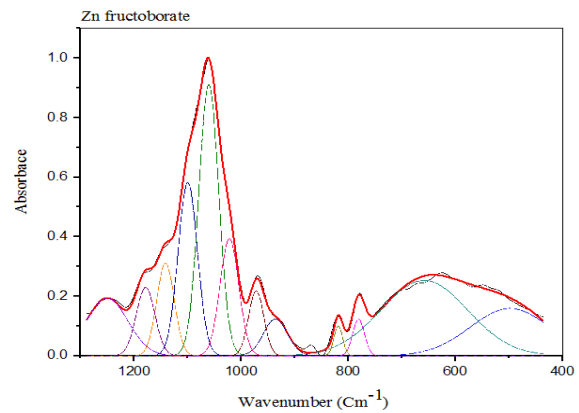


Fig. 2. Deconvoluted spectrum of zinc fructoborate (ZnFB)

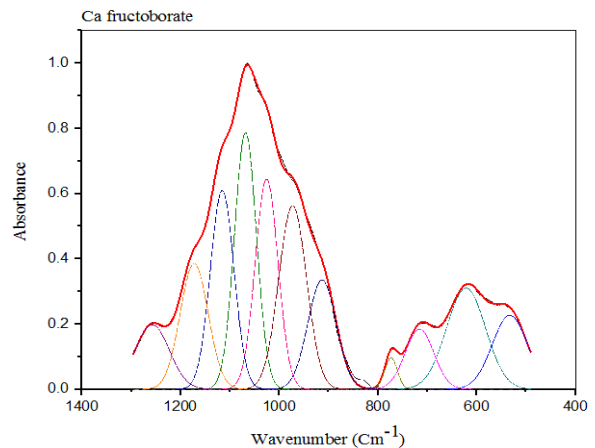


Fig. 3. Deconvoluted spectrum of calcium fructoborate (CaFB)

Furthermore, the effect of CaCO_3 reduces free boric acid. But in the case of ZnCO_3 , however, the free boric acid and derivatives of borate units such as N_4 are limited. This distinction can be explained by the fact that CaCO_3 can act as a strong modifier to the borate matrix. The fraction of N_4 has increased a higher value as a result of the modification. However, Zn has more than one valence state; one can form BO_4 units and acts as a modifier, while the other valence state can resist the transformation process. As a result, the relative area is smaller than that of Ca borate.

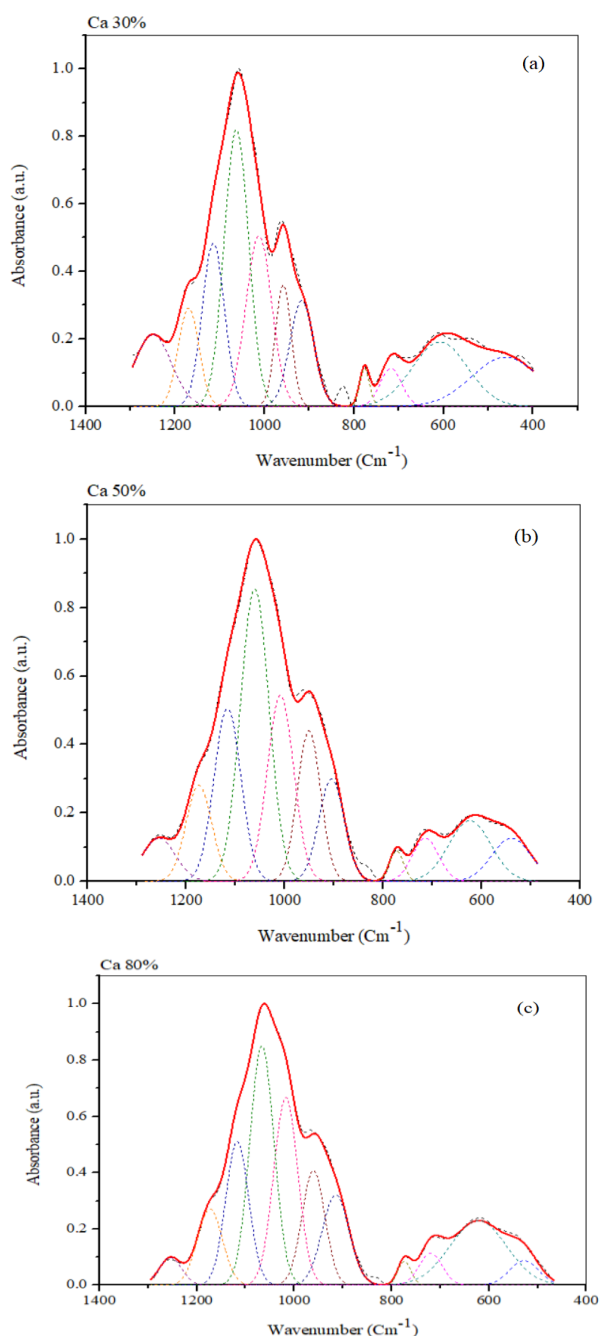


Fig. 4. The deconvoluted spectra (a), (b), and (c) for different concentrations of the prepared samples

The highest transformation process of boric acid to other borate derivatives is not recommended in the field of bio-applications, since boron ions release is high and causes toxicity of the compound. Also, the limited transformation of the boric acid to its derivative upon the presence of

ZnCO₃ cause more toxicity, since the boric acid becomes free and causes free radical which leads to cancer [23,24]. The properties of mixed ion effects should be used to solve such problems. In other words, ZnCO₃ should be added instead of CaCO₃. As a result, an intermediate transformation of boric acid to its derivative is preferred. The spectra of mixed Zn and Ca ions are depicted in figure 4. The results of the analysis are listed in table 1 and are parenthesized by figure 5.

Table 1 and Fig. 5 summarize the percentages of Boric acid, BO₃, BO₄, and the fraction of boron tetrahedral units. Upon substitution of CaCO₃ with ZnCO₃, it can be observed that the fraction of N₄ decreases with increasing ZnCO₃ content.

Table 1 shows boron derivatives as a result of the transformation of Boric acid to BO₃ and BO₄ units.

Table 1. Analysis results of the examined compounds by FTIR spectroscopy.

	Boric acid	BO ₃	BO ₄	N ₄
Ca fructoborate	7.6%	64.1%	28.3%	0.306 %
Ca 90% Zn 10%	9.3%	64.7%	26%	0.287 %
Ca 80% Zn 20%	11.9%	64.2%	23.9%	0.271 %
Ca 70% Zn 30%	13.4%	64.2%	22.4%	0.259 %
Ca 50% Zn 50%	14.1%	64.1%	21.8%	0.254 %
Ca 40% Zn 60%	14.45 %	64.33 %	21.22 %	0.248 %
Ca 30% Zn 70%	19.6%	61.8%	18.6%	0.231 %
Ca 10% Zn 90%	20.18 %	61.97 %	17.85 %	0.224 %
Zn fructoborate	77.6%	12.1%	10.3%	0.103 %

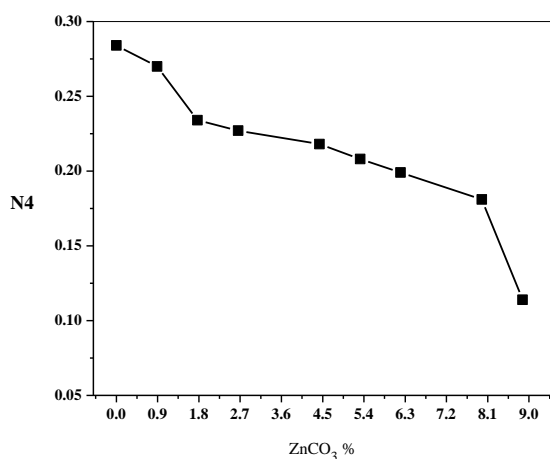


Fig. 5. The change of N₄ with increasing of ZnCO₃ at expense of CaCO₃

4. Conclusion

The trigonal form of boron organic ester with fructose, CaCO₃, and ZnCO₃ was studied using the FTIR technique. Different borate compounds are formed and determined upon modification with ZnCO₃ or CaCO₃ or both. Limited borate units are formed, the low transformation of boron to its derivatives, upon modification by ZnCO₃. In contrast, modification with CaCO₃ leads to higher transformation. But releasing of a high amount of boron ions during the dissolution process might cause some toxicity. To avoid this problem, small concentrations from boron ions should be controlled to be released. The mixed Zn and Ca carbonate has the most proper advantage for the formation of boron species useful for medical uses.

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