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Characterization Studies on Calcium Borate Compound Modified by $ZnCO_3$, $CaCO_3$ and Fructose

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Abstract:

Calcium fructoborate solid materials of formula $Ca(C_6H_{10}O_6BO)_2 \cdot 3.5H_2O$ were prepared by chemical wet technique. The neutral trigonal form of boron organic ester with fructose, under the solid form, is prepared and modified in solution in the anionic tetrahedral form; the borate compound is investigated by XRD spectroscopy. An ideal strong amorphous forming material is obtained upon modification with $ZnCO_3$ or $CaCO_3$. ^{11}B NMR solids and solution and Raman spectroscopy were developed to determine different types and the amount of borate derivative present in products. The modifier portion from calcium carbonate and fructose are consumed for boron transformation from three to four coordinated units. Raman spectra of pure B_2O_3 confirm the presence of the borate boroxol ring as the main structural units. But different borate units are formed upon modification by calcium carbonate and fructose. Modification by $ZnCO_3$ had a few effects on boron transformation. The chemical shift of ^{11}B NMR spectra is remaining unchanged upon its addition.

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1. INTRODUCTION

The element boron is essential for all plant and animal life [1-4]. The interaction of calcium (Ca) and boron (B) has been observed in plants, bacteria, animals, and humans, and has been documented in several papers [1-7]. However, the specific nature of the Ca/B interaction is still under experimental investigation. The characterization of this complex has been reported previously. The biological and biochemical action of calcium fructose in borate structure has been studied and found that it has a chemical structure similar to that of natural boro-carbohydrates found in edible plants [4-8]. The chemical status of boron in nutrition is very important. In plants, boron is found in the form of sugar esters [9,10]. The boron sugar esters are the best chemical form for assimilation into cells. There are previous studies that show that the natural complexes of boron have been isolated as a boric acid ester with fructose (fructose-B-fructose), glucose, and sorbitol (glucose-B-glucose) [9-11]. The first isolated soluble complexes from higher plants can represent these boric acid esters. Traditionally, boric acid and some of the inorganic borate have been used for boron supplementation [4-9]. Recently, some other boron compounds have been introduced in the pharmaceutical industry market, with the same objective. Recently, calcium fructoborate (CFB) has shown an interesting antioxidant effect, anti-tumor, and anti-inflammatory activity [8-12]. In addition to the role CFB in promoting healthy bones and joints, boron may play an underappreciated role in protecting men against prostate cancer. Fortunately, in the clinical trial, the study indicates that boron may help prevent prostate cancer and showed that boron's increased contribution has been associated with a reduced risk of prostate cancer with a dose-response pattern. Recent studies suggested that boron has a chemopreventive role in prostate cancer. Another recent study found that boric acid inhibits the proliferation of some human cells of prostate cancer. In recent studies, it has been confirmed that the bone health benefits of omega-3 fatty acids may be greatly magnified when these essential fats are combined with the critical trace of mineral boron. For instance, when laboratory animals consumed a diet rich in both omega-3 fatty acids and boron, they demonstrated greater bone mineral density and stronger bones compared to animals fed other dietary fats and boron. These findings suggest that omega-3 fatty acids and boron may work together to support dense, strong bones [7-12].

The objective of this study was to investigate the molecular composition of borate compounds under modification with both $CaCO_3$ and $ZnCO_3$ to provide the relative distribution of boron in free and chelated forms.

2. EXPERIMENTAL

2.1. Sample Preparation

Ca-fructoborate: D-fructose (2.16 g) was dissolved in 4ml distilled water and 0.372g Boric acid is then added and followed by 0.246 g by calcium carbonate. 20 ml of was acetone 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-fructoborate with about 0.78% yield. The same procedure was repeated for the formation of Zn-Ca-Fructoborate.

2.2. Measurements

X-ray diffraction measurements are carried out with a Shimadzu X-ray diffract meter (Dx-30, Metallurgy institute, El Tebbeen-Cairo). The peak position and intensity values used to identify the type of material were compared with patterns in the international powder diffraction file (PDF) database compiled by the joint committee for powder diffraction standards (JCPDS). NMR measurements were carried out at ambient temperature on a JEOL RESONANCE GSX-500 spectrometer operating at a high external magnetic field (11.747 T). ^{11}B NMR spectra were measured, using a 3.2 mm MAS-NMR probe operated at a rotor frequency of 15 kHz. Typical pulse lengths were 2.5 µs and 60 s delay time was sufficient to enable relaxation. The ^{11}B NMR solution was carried out on the same NMR technique. Raman spectra were recorded with a Jobin Yvon — HR640 spectrometer equipped with an Andor CCD detector (DU420A-BR-DD model). A laser source working at 532 nm with an average power of 63.02 mW was used during the experiment. The spectra were recorded at room temperature and an exposure time of 10 minutes.

3. RESULTS AND DISCUSSION

3.1. XRD Spectroscopy

It was known that boron oxide is considered an ideal strong amorphous forming material [3,8,13]. This is because B_2O_3 or H_3BO_3 cannot be crystallized under normal circumstances or at ambient pressure. This property can be reflected in Figure **1** which shows XRD spectra of H_3BO_3 modified by ZnO or by CaO. It can be observed that, the crystallization cannot be occurred because of completion between several borate units or phases which eventually induce the amorphization of the system. Besides, boron oxide which is extracted from boric acid has also the highest network formation tendency even at high concentrations. This feature has led to suggest that B_2O_3 material has abnormal behavior which can be termed as boron oxide crystallization anomaly [14, 15]. Therefore, refer to the fact that B_2O_3 never crystallizes at ambient pressure makes it even better than SiO_2 [39]. This is may because the glass formation region becomes wider than that of silicate glasses.

The XRD presented in Figure **1** leads that the investigated B_2O_3 network involves a stable amorphous structure which consists of boroxol borate rings $[BO_{3/2}]$ units in a hexagonal arrangement, as a main forming species.

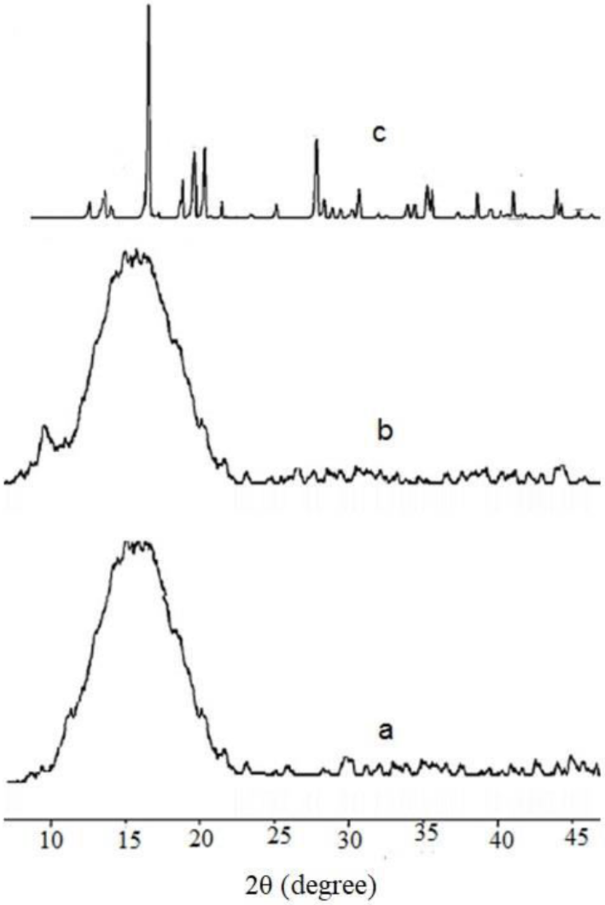

Figure 1: XRD spectra of fructoborate glass containing ZnO (**a**) and CaO (**b**). The XRD of fructose is shown in (**c**).

On the other hand, when B_2O_3 contains a major concentration of planner BO_3 which is distributed as a chain-like form [4-12], then (B_2O_3) can simply be crystallized. In our case, the vitreous B_2O_3 matrix consists only of the stable boroxol borate rings which consist of three $[BO_{3/2}]$ units in a hexagonal arrangement.

3.2. Raman Spectroscopy

The above consideration is characterized by resolving of Raman band located at ≈ 806 cm^{-1} for pure H_3BO_3 or B_2O_3 as shown in Figure **2**. The Raman spectra of the boroxol ring have shown only one resolved peak around 806 cm^{-1} which leads to the presence of the boroxol ring as the main species. On the other hand, when B_2O_3 is modified by both $CaCO_3$ and fructose molecules, non-ring (chain BO_3), planner BO_3 and BO_4 groups are the well-formed species see Figure **3**. Besides, some concentrations from boroxol ringed units are still present. The broader Raman peak at 800 cm^{-1} is assigned to B-O vibrations in the boroxol ring distributed in between planer, tetrahedral borate units. Transformation of boroxol BO_3 ring to both planner BO_3 and BO_4 is confirmed via the appearance of the more resolved peak around 1100 cm^{-1}.

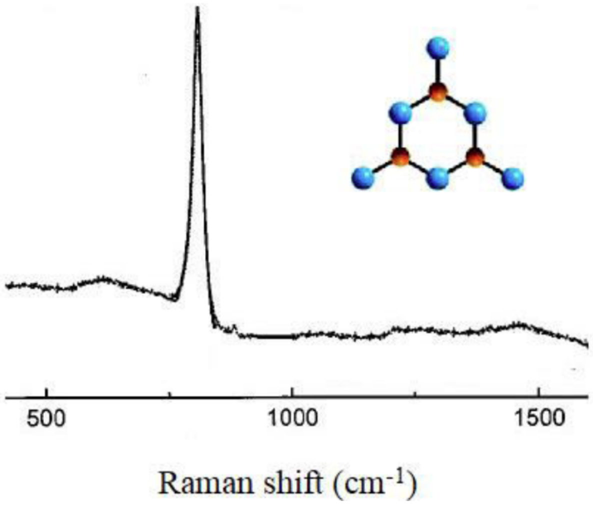

Figure 2: Raman spectra for pure B_2O_3.

Then, the addition of a modifier to the B_2O_3 or H_3BO_3 network leads to some modifications which can be clarified as H_3BO_3 can be transformed to B_2O_3 and H_2O molecules. The modifier of type $CaCO_3$ or $ZnCO_3$ can be transformed to CaO, ZnO, and CO_2. Then both hydrogen and carbonate groups should interact with B_2O_3 as a former species, forming mono or di-ester groups. Besides, boron-oxygen-boron (B-O-B) bonds may be broken by oxygen anions that come from the

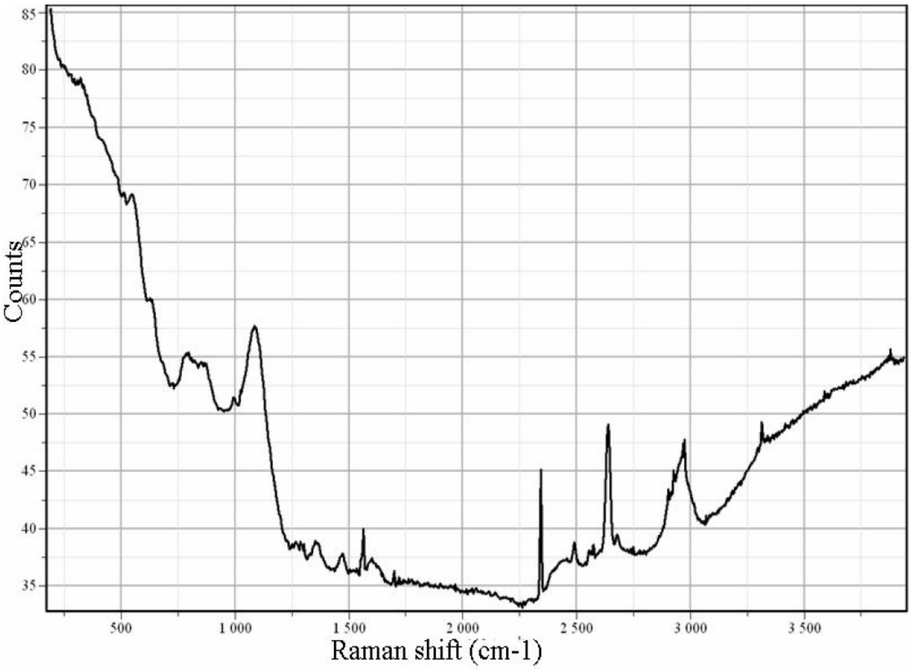

Figure 3: Raman spectra of pure borate glass matrix modified by fructose and $CaCO_3$.

modifier (Ca^{++} / -O-B). At high concentration from the modifier, the arrangement of ($BØ_3O$) tetrahedron with three bridging (Ø) and one non-bridging oxygen (O) ion can be formed. Then the structural role of the modifier differs in telluride, phosphate, and silicate structures. The reverse changes in the B_2O_3 structure are considered when it compared with that of phosphate and silicate network. The network of both SiO_2 and P_2O_5 consists of tetrahedral units that depolymerize with the addition of even low content of modifiers. However, the borate network consists of trigonal ($BO_{3/2}$) structural units and when the network modifier is incorporated in the borate network, the charged $[BØ4]^-$ tetrahedral units with bridging oxygen are well-formed species. The different coordination changes which were considered in the borate matrix cause some anomalous behaviors in the B_2O_3 network. This interest is mainly because of the anomalous behavior of the B_2O_3 matrix in that it forms superstructural units. The latter is considered as well-defined arrangements of the basic BO_3 and BO_4 structures Figure **4**.

As shown in Figure **4**, B_2O_3 can form a closed ring in boroxol B_3O_6 structure (s). It can form a planar triangle BO_3, whereas BO_4 has a tetrahedral arrangement of oxygen around the boron atom. An interesting parameter of borate glasses is the N_4 fraction, which is the amount of 4-coordinated boron compared to the total amount of boron:

$$N4 = \frac{B_4}{B_3 + B_4}$$

The pure B_2O_3 has an N_4 fraction of zero. When B_2O_3 is modified by any type of modifier oxide, the N_4 fraction becomes 50% and the will dominant units in such a case are called diborate. The proportion of 4-coordinated boron is detectable mainly by NMR spectroscopic technique [16,17]. In addition, Raman spectroscopy is considered amongst other means that characterize the borate network structure. It has previously shown that the maximum N_4 fraction was usually is around 33-40 mol% alkali oxide with a proportion of approximately 0.45 BO_4 to 0.55 BO_3.

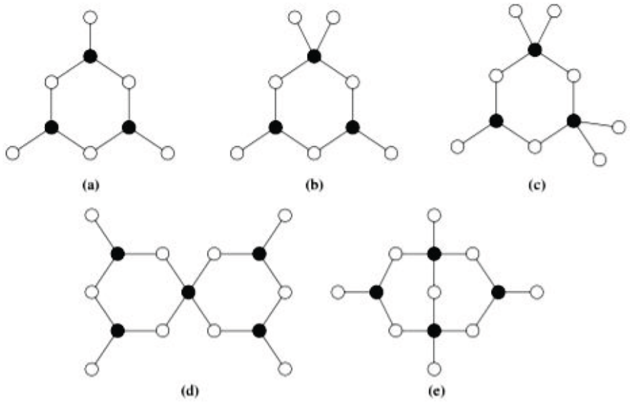

Figure 4: A selection of superstructural units composing of boron (●) and bridging oxygens (○) (**a**) boroxol ring, B_3O_6; (**b**) triborate, B_3O_7; (**c**) di-triborate, B_3O_8; (**d**) pentaborate, B_5O_{10}; (**e**) diborate, B_4O_9.

The new in this work is to correlate the change of N_4 fraction given by NMR spectroscopy to the well-formed BO_3, BO_4 units as derivative from free H_3BO_3. We relate the non-linear change in N_4 value to boron anomaly. The anomaly of B_2O_3 (derived from H_3BO_3) could be understood in terms of the coordination change of the boron atom that causes also a change in the connectivity of the B_2O_3 network with the addition of modifier oxides such as CaO or ZnO. The anomalous behavior could appear in most of the borate properties such as transition temperature (Tg), viscosity, coefficient of thermal expansion (CTE). In the present studied material, there is no result can be obtained from Tg and CTE. This is because the material contains fructose and carbonate which can be elaborated by thermal energy. Therefore the boron anomaly in this study can be extracted from results of NMR and Raman spectroscopy, since the N_4 fraction shown a nonlinear behavior which is depending on both the type and the fraction of the added modifier [16,17]. Then the boron anomaly is represented by the nonlinear changes in some of the structural factors with increasing modifier content [15-17]. This effect is related to the initial transformation of the boroxol B_3O_3 and planner BO_3 to BO_4. At extremely high modifier concentrations, the well-formed BO_4 goes back to asymmetric BO_3.

Now, let's discuss how the change of the boron coordination can play the main role in changing the properties of the borate structure in an anomalous manner [18]. The anomaly behavior could be noticed in oxide which can withstand the high temperate of annealing or preparation. In such cases, T_g increases with increasing modifier content up to ≈26 mol% then it starts to decrease with further M_2O addition. And the CTE shows the opposite behavior, it decreases up to 20 mol% of modifier and then increases. The increase and decrease in these properties are considered due to the increase or decrease of bridging oxygen (BO) or non-bridging oxygen (NBO) in BO_4 groups.

Not only the concentration of BO or NBO effects but also the crosslinking capability has also the main influences [19,20]. For instance, divalent barium oxide as a modifier in BaO-B_2O_3 matrix and monovalent sodium oxide in the NaO-B_2O_3 binary borate network has approximately the same N_4 fraction. But there is the main difference in some of the studied physical properties. For instance, the BaO-B_2O_3 system has Tg higher than that of Na-modified glass. This difference is attributed to the higher oxygen coordination and higher crosslinking of M^{2+} ions compared to the M^+ alkali ions. It was suggested previously that, the change of the boron coordination is not the only parameter that affects the glass properties but also the cation crosslinking capability [18].

The same considerations have been considered in the B_2O_3 structure containing ZnO, or CaO [21]. The mechanism of Ca^{2+} in the modification of the borate matrix differs from that of Zn^{2+} although the two types have the same charges. The Zn has two states divalent and tetrahedron but Ca^{2+} has no valences which can possess different properties. All the above-given information is considered to be useful in understanding the data obtained on Ca and Zn fructoborate systems.

Raman spectroscopy of borate glasses offers insight into which peaks correspond to which superstructural units in borate glasses can be resolved. The spectrum is significantly harder to interpret in terms of N_4 fraction than an NMR spectrum [22,23]. Therefore a primary aim of this study is to correlate the N_4 fraction given by NMR spectroscopy to the structural changes caused by the addition of $CaCO_3$ and $ZnCO_3$ to fructoborate glasses. NMR spectroscopy is very useful in the study of fructoborate composition as it can clearly distinguish between the two chemically distinct BO_3 and BO_4 sites and quantify the proportion of each.

3.3. ^{11}B NMR Spectroscopy

The coupling processes between boron and oxygen contain positive and negative components which cancel out each other so that a singlet is observed for ^{11}B NMR spectra of H_3BO_3 Figure **5**.

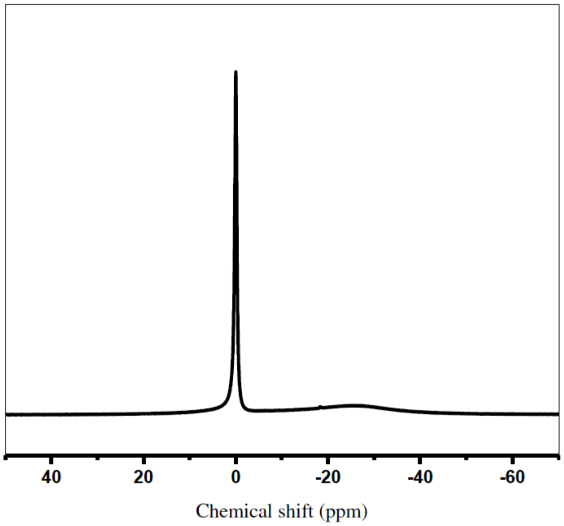

Figure 5: ^{11}B NMR spectra of boron atoms in H_3BO_3.

But there are great differences between the coupling processes between boron and oxygen in the modified $CaCO_3$ fructoborate units (CaFB) which cannot cancel out each other so that several resonance lines are observed for ^{11}B NMR spectra of CaFB Figure **6**.

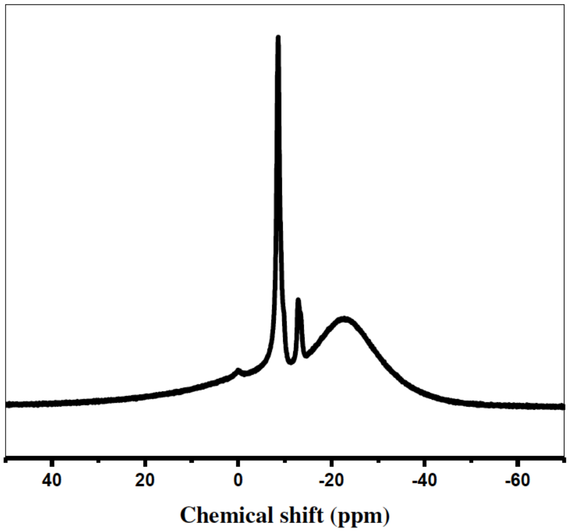

Figure 6: ^{11}B NMR spectra of a boron atom in CaFB compounds.

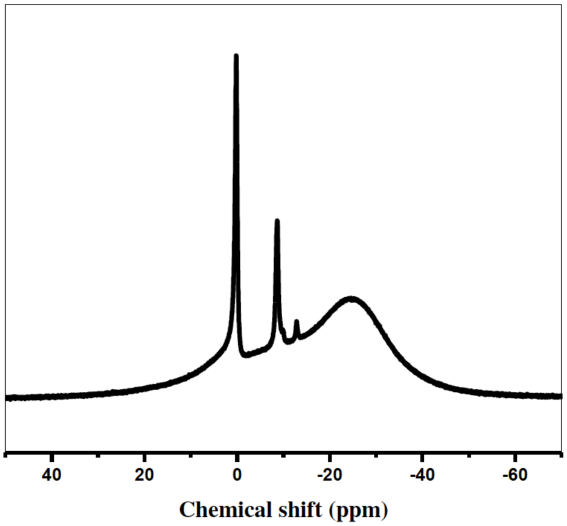

Figure 7: ^{11}B NMR spectra of a boron atom in ZnFB compounds.

It can be seen from Figures **6** and **7** that the sharp resonance peak on the experimental spectrum of H_3BO_3 (at 0 ppm in Figure **5**) is absent in Figure **6**. This leads that both the fructose and calcium carbonate as modifier species played the role of the transformation of the free boric acid (0 ppm) into additional derivatives, such as BO_3. BOC_2, BOH, and BO_4 units. These considerations are confirmed for the presence of resonance lines at -8.5 ppm, -12.8 ppm, and abroad one at -22.5 ppm (Figure **6**). Figure **8** presents the change of fraction of tetrahedral boron with increasing $ZnCO_3$ at expense of $CaCO_3$. It can be observed from Figure **8** that N_4 is maximum at 0 $ZnCO_3$ then decreased with increasing $ZnCO_3$.

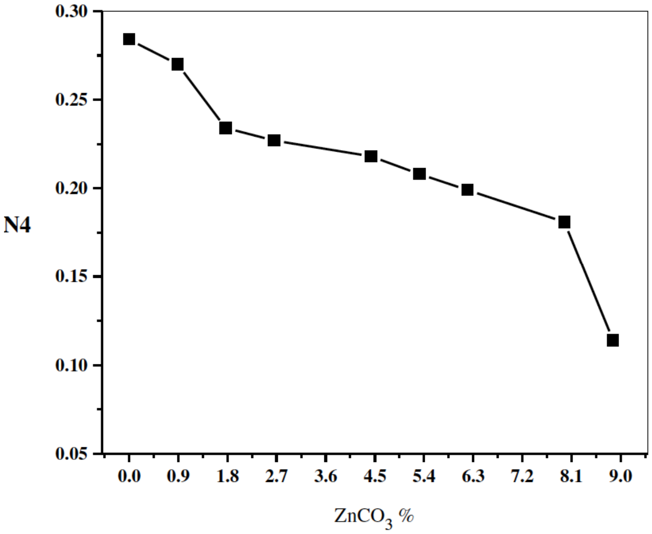

Figure 8: The change of N_4 with increasing of $ZnCO_3$ at expense of $CaCO_3$.

4. CONCLUSION

The as-prepared borate compound is investigated by XRD spectroscopy. The amorphous structure of the fructoborate compound is the dominant feature upon modification with $ZnCO_3$ or $CaCO_3$. ^{11}B NMR solids and solution and Raman spectroscopy were developed to determine different types and the amount of borate derivative present in products. The four coordinated units can be produced due to modification by $CaCO_3$ molecules. Raman spectra of pure B_2O_3 confirm the presence of the boroxol borate ring as the main structural units. Different borate units can be formed upon modification by calcium carbonate and fructose. Modification by $ZnCO_3$ had a few effects on boron transformation. Both ^{11}B NMR solid and solution have confirmed the formation of bio-derivatives units from borate esters.

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