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Crystallization of Synthetic Wollastonite Prepared from Local Raw Materials

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Abstract Wollastonite ($CaSiO_3$) has been synthesized by the solid state reaction method at a temperature range of 1050-1250℃ from local raw materials, e.g. silica sand and limestone as well as pure chemicals in the form of carbonate and quartz with and without B_2O_3 adding as a mineralized. The resulting products are investigated employing XRD and SEM techniques. β-wollastonite was obtained at 1050℃ and transformed to pseudowollastonite (α- $CaSiO_3$) at 1150℃ due to the presence of B_2O_3. While the pure chemicals failed to give wollastonite at this range of temperature 1050-1150℃. As the temperature increased up to 1400℃, both experimental and standard samples have been melted.

Keywords Wollastonite, XRD, SEM

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1. Introduction

Wollastonite is a calcium metasilicate that has a chemical formula of $CaSiO_3$ with a theoretical composition of 48 wt.% CaO and 52 wt.% SiO_2 [1-2]. Wollastonite is rarely found in the pure state and it contains an insignificant amount of harmful impurities in the form of manganese, magnesium, iron, strontium and titanium oxides. It occurs predominately as a contact metamorphic deposit formed between limestones and igneous rocks, often associated with garnet, diopside, epidoite, calcite and quartz [3-4]. Wollastonite is a polymorphic substance that occurs in three polymorphic forms; low temperature triclinic form [1T], monoclinic form or the so called para-wollastonite [2M] and the high temperature form pseudo-wollastonite which occurs in the pseudo-hexagonal form which is found rarely in nature. The conversion of the low temperature form to the high temperature form takes place at 1125℃ [5-7].

Wollastonite is an extremely interesting but little studied material which has a combination of properties, such as lack of volatile constituents, fluxing characteristics, low dielectric constant, low dielectric loss, thermal stability, low thermal expansion and low thermal conductivity, hence is used in ceramic fabrication, medical material for artificial bones and dental roots, high frequency insulator, filler material in resins and plastics, paper, civil construction, metallurgy, paint and frictional products [8-15]. This situation has urged research workers to produce it synthetically [16].

Iraq has an abundance of limestone and silica sand resources with high purity contents of calcium oxide (CaO) and silicon dioxide (SiO_2). Till now, nobody has used Iraqi limestone and silica to produce wollastonite synthetically.

The present study aims to produce wollastonite at low sintering temperature from local raw materials e.g. silica sand and limestone which used as a source for CaO where they distributed abundantly in many regions of Iraq and compare it with those obtained from pure chemicals of $CaCO_3$ and quartz with and without addition of B_2O_3.

2. Materials and Methods

Table 1. Wet chemical analysis of silica sand and limestone

Constituting oxides	Silica Sand	Limestone
SiO_2	99.48	0.73
Al_2O_3	0.22	0.10
Fe_2O_3	0.03	0.09
MgO	0.02	0.88
CaO	0.13	54.78
Na_2O	0.04	0.06
K_2O	0.02	0.01
SO_3	-	0.07
*L.O.I	-	43.26

*L.O.I = Loss of ignition

Silica sand which is found abundantly in the western desert of Iraq with high content of (SiO_2) and large deposits of limestone are available in different regions of Iraq where it obtained from the quarry of Wadi Al-Ubaiyidh. These two raw materials were washed several times with distilled water to get rid of any accompanying dust and undesired materials,

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dried and mixed with and without the addition of 2.24 wt% B_2O_3 in the form of H_3BO_3 to produce experiment wollastonite (Exp.). While extra pure calcium carbonate 98-100% (Thomas Baker, made in India) and silica>99% (Sibelco, made in Belgium) were used to produce the so called "standard wollastonite" (St.). The chemical analysis of both raw materials, e.g. silica sand and limestone is depicted in Table 1.

For experimental wollastonite (Exp.) Fragments of limestone were primarily crushed to small particle size of 5 mm using electrical crusher, followed by grinding to a fine powder of 100 µm using an electric grinding machine that was done in Al-Noora factory. The fine powder was then washed with distilled water to remove the organic materials, dried at 100℃ for 24 hours and sieved through a 200 mesh to obtain powder less than 75 µm. The fine powder of limestone was calcined at 950℃ in an alumina crucible (Shangtao brand) for 5 hours in air atmosphere to obtain quicklime (CaO) according to the reaction:

$$CaCO_3 \xrightarrow{950^{\circ}C} CaO + CO_2$$

Fine powder of calcium oxide with off-white color was obtained**.** Calcium oxide (CaO) was mixed with SiO_2 in 1:1 molar ratio with the addition of 4 wt% boric acid (H_3BO_3) to provide about 2.24 wt% of boron oxide (B_2O_3) that act as a mineralizer during the sintering process. Stoichiometrically, the amount of these materials was weighed out using analytical electric balance (M254A) with weighing sensitivity of about ±0.0001 g to obtain a batch of 100 g as shown below:

Quicklime (CaO) = 47.22 g

Silica sand (SiO_2) = 50.54 g

Mineralizer (B_2O_3) = 2.24 g

The mixed powders with the addition of 300 ml of distilled water as a dispersive media and 2% PVA as a binder were wet milled by the planetary ball mill (SFM-1, QM-3SP2), which runs at 300 RPM for 15 hours to provide a homogenous fine mixture. The obtained mixture was oven dried for 24 hours at 80℃, then finely crushed using pestle and mortar. The aim of milling the mixture in water media is to hydrate the calcium oxide which reacts with water rapidly producing calcium hydroxide and heat, according to the following reaction:

$$CaO + nH_2O \xrightarrow{25^{\circ}C} Ca(OH)_2 + (n-1)H_2O + \Delta E$$

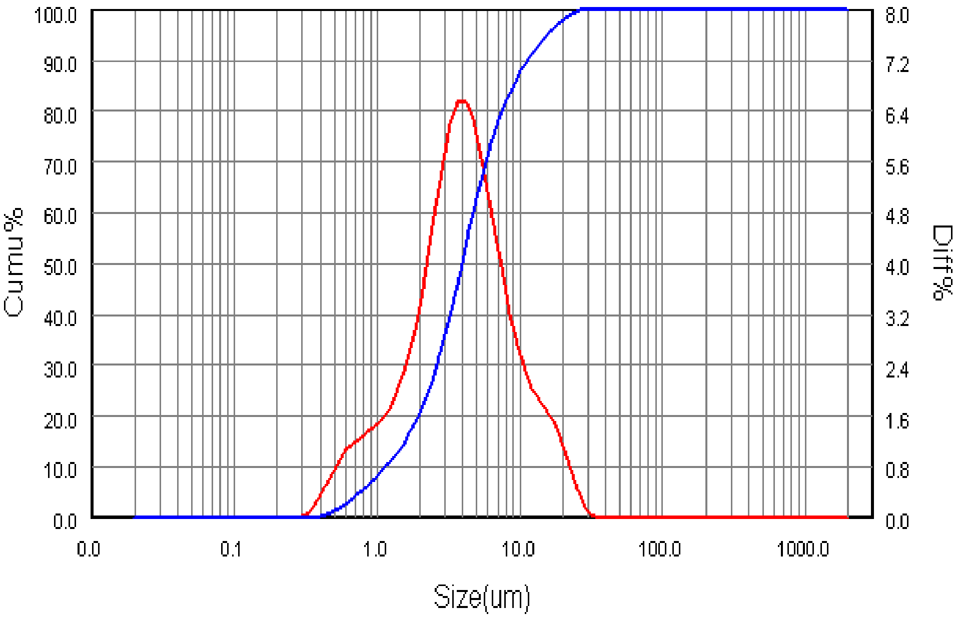
Excessive water was removed by drying process at 150℃ for 24 hours according to the following.

$$Ca(OH)_2 + (n-1)H_2O \xrightarrow{150^{\circ}C} Ca(OH)_2$$

The mixture of calcium hydroxide $Ca(OH)_2$, silica (SiO_2) and H_3BO_3 were calcined at 710℃ in an alumina crucible in air atmosphere for 3 hours, where calcium hydroxide start to decompose at temperatures above 580℃ to give calcium oxide while water is vaporized according to the following reaction:

$$Ca(OH)_2 \xrightarrow{710^{\circ}C} CaO + H_2O$$

At this temperature (710℃), boric acid (H_3BO_3) is decomposed to boron oxide (B_2O_3) which tend to lower the sintering temperature of the mixture. Particle size was measured using a laser particle size analyzer (Bettersize2000) to give an average particle size of about 5.47 µm According to D10, D50 and D90 as shown in Figure 1.

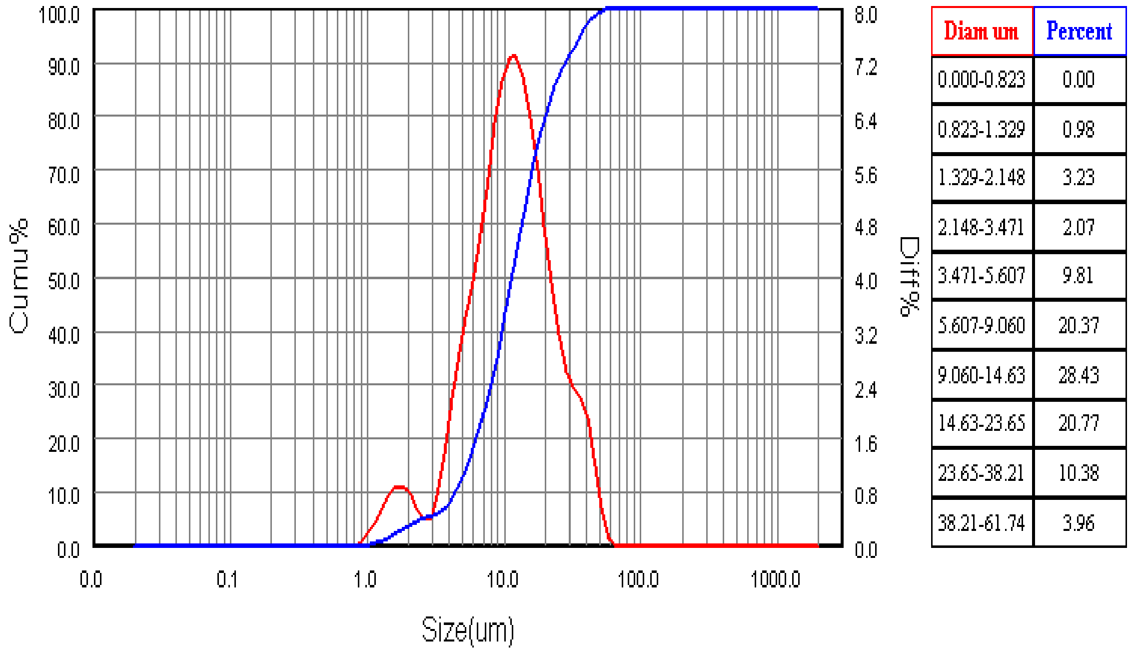


Diam um	Percent
0.000-0.279	0.00
0.279-0.475	1.01
0.475-0.810	4.61
0.810-1.381	6.95
1.381-2.355	13.18
2.355-4.014	25.59
4.014-6.843	25.31
6.843-11.66	13.85
11.66-19.88	7.47
19.88-33.89	2.03

Figure 1. Particle size analysis of the mixed experimental powder [6]

For standard wollastonite, carbonate and silica sand were bought from the local market with fine powder. 62.5 wt% of calcium carbonate and 37.5 wt% of silica sand are mixed to provide the exact molar ratio of SiO_2:CaO equal to one, and this mixture should produce wollastonite according the following reaction:

$$CaCO_3 + SiO_2 \xrightarrow{900℃} CO_2\uparrow + CaO + SiO_2 \xrightarrow{>1000℃} CaSiO_3$$



Diam um	Percent
0.000-0.823	0.00
0.823-1.329	0.98
1.329-2.148	3.23
2.148-3.471	2.07
3.471-5.607	9.81
5.607-9.060	20.37
9.060-14.63	28.43
14.63-23.65	20.77
23.65-38.21	10.38
38.21-61.74	3.96

Figure 2. Particle size analysis of the so called mixed "standard" powder

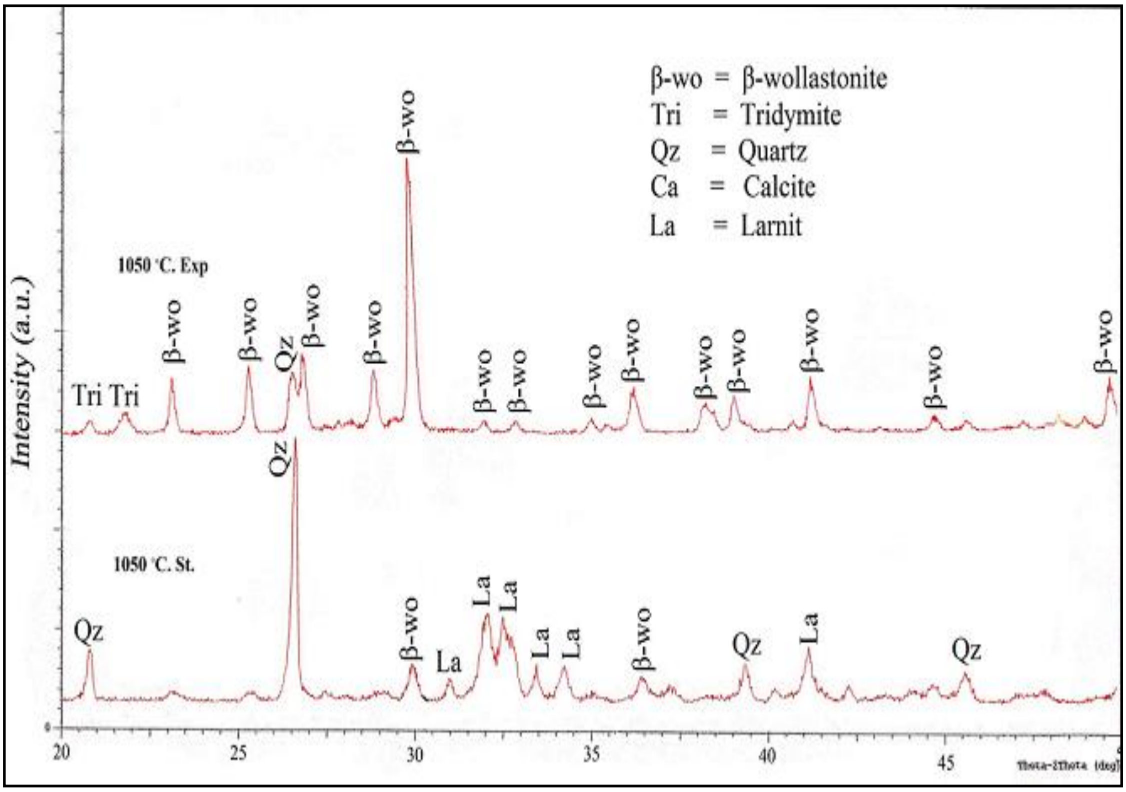


Figure 3. XRD patterns of the so called "standard" and experimental work at 1050℃

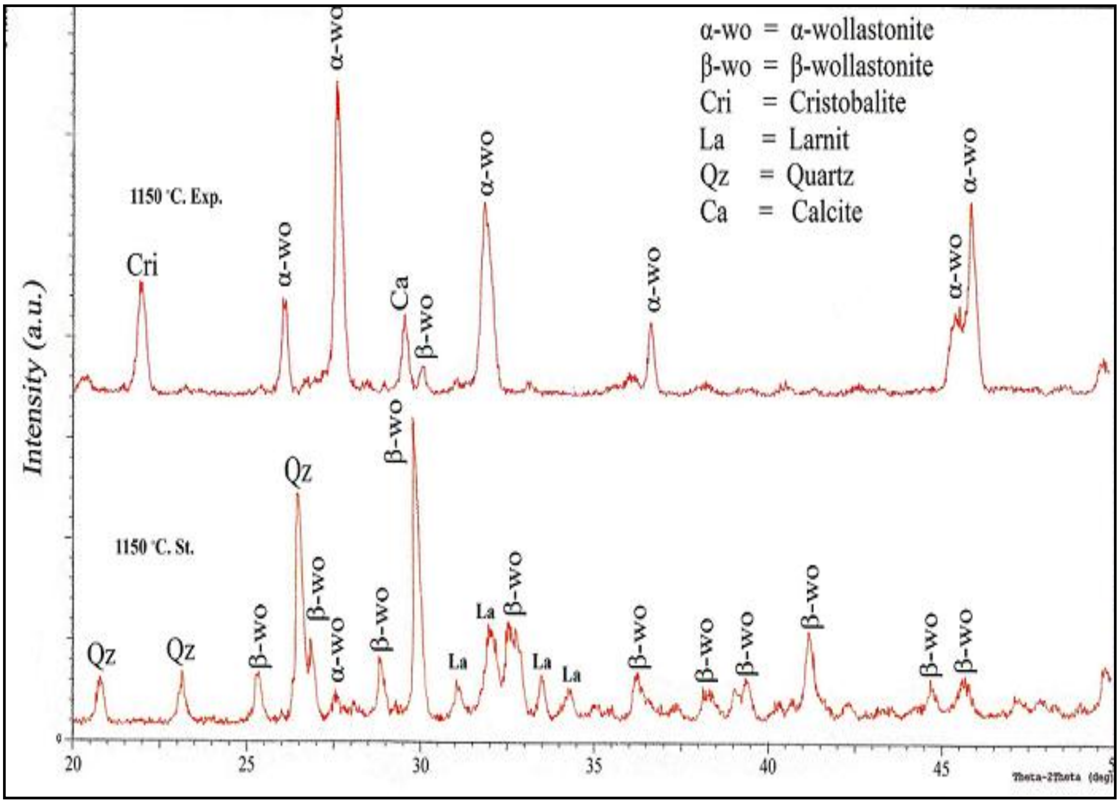


Figure 4. XRD patterns of the so called "standard" and experimental work at 1150℃

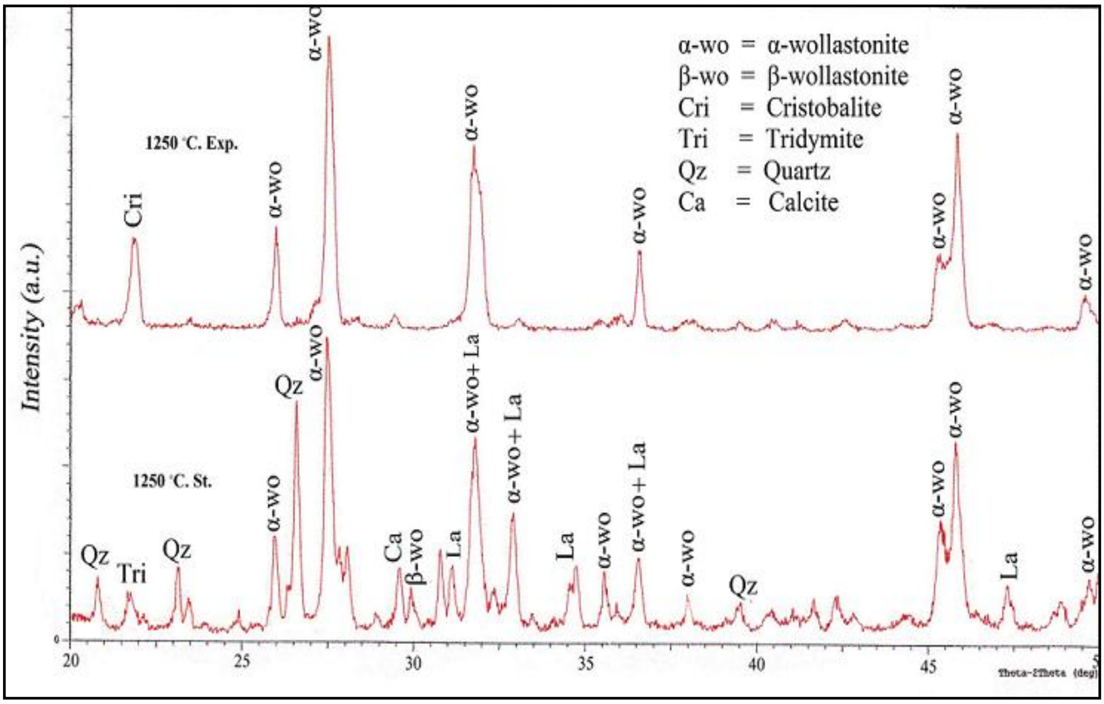


Figure 5. XRD patterns of the so called "standard" and experimental work at 1250℃

The mixed powders with the addition of 300 ml of ethanol as a dispersive media and 2% PVA as a binder were wet milled by the planetary ball mill (SFM-1, QM-3SP2), which runs at 300 RPM for 15 hours to provide a homogenous fine mixture. The wet mixture was oven dried at 100℃ for 24 hours to be sure that all moistures were removed. Particle size was measured using a laser particle size analyzer (Bettersize2000) to give an average particle size of 14.68 μm as shown in Figure 2.

Cylinders steel dies of 13 mm in diameter and 27 mm in height were processed under uniaxial pressure of 150 MPa using a uniaxial pressure device (CT340-CT440), dried at

100℃ for 24 h and fired in protherm electric furnace (PLF 160/15, made in Turkey) at different temperatures of 1050, 1150 and 1250℃ with an average heating rate of 7℃/min for both experimental and the so called "standard" work.

All samples obtained from the fired batches were finely grounded and scanned using x-ray diffractometer (Shimadzo, 6000) at room temperature using Cukα radiation ($\lambda = 1.5405$ Å), and a scanning speed of 5 °/min from 20 ° to 50 ° of 2Ө (Bragg angle) and 40 kV/30 mA as an applied power to estimate the crystallized phases. The microstructures were observed using the scanning electron microscope (VEGAII/TESCAN XMV). All samples were finely polished and then coated with a thin layer of gold by sputtering deposition technique (EMITECH, K450X, UK), prior to being scanned using the SEM instrument to produce images with a magnification of (X2000).

3. Results and Discussion

The crystallization behavior of both experimental and standard wollastonite is investigated by XRD at different temperatures. At 1050℃, it seems that almost all peaks are related to low temperature monoclinic wollastonite β-$CaSiO_3$ of a maximum relative intensity (100%) at a diffraction angle of 2Ө equal to 29.898 °(2.98 A °), with little amount of unreacted quartz. Meanwhile, some portion of SiO2 had been converted into its high temperature polymorph tridymite. This transformation was duly supported by the fact that quartz starts converting into tridymite at 867℃ [17]. While in the so called "standard work", unreacted quartz appears as a major phase at 2Ө equal to 26.566 °(3.35 A °). It can be noted that calcium oxide reacts with silica to give larnite (Ca_2SiO_4) and β-wollastonite with lower peak intensity as shown in Figure 3.

Figure4. represents XRD analysis of the so called "standard (St.)" and experimental (Exp.) work at a temperature of 1150℃ with a soaking time of 2 h. For experimental work, the peaks with maximum intensity at diffraction angles of 21.13 °, 27.638 °, 31.905 ° and 45.870 ° belong to triclinic α-wollastonite. It indicates that β-wollastonite obtained at 1050℃ is transformed to its high temperature polymorphic form α-CaSiO3. The former transformation is supported by the fact β-wollastonite starts converting to α-form above 1125℃ according to the phase diagram of CaO-SiO_2 system. β-wollastonite at 2Ө equal to 30.043 ° is appeared to be the lowest peak of a relative intensity of 8% and will disappear as the sintering temperature increased. It is notable that cristobalite at a diffraction angle of 2Ө equal to 21.939 ° (4.04 A °) which is the high temperature polymorphic form of silica starts to appear at this low temperature. The reason behind that B_2O_3 reacts with silica to form boronsilicate at low temperatures. Furthermore, XRD analysis reveals that calcite ($CaCO_3$) at 2Ө of 29.539◦ is present as unreacted material. On the other hand, in the standard work, the small proportion of monoclinic β-wollastonite which appeared at 1050℃ with a relative intensity of 13% is grown up to its maximum intensity at this temperature. It is also revealed that unreacted quartz has appeared as a major phase associated with β-wollastonite. It is notable that larnite (Ca_2SiO_4) appears at different diffraction angles which is almost associated with the synthesis of β-wollastonite and may require higher temperatures to be diminished. It is also observed that relative small peak at 2Ө equal to 27.566 ° belongs to pseudowollastonite (α-$CaSiO_3$) which starts to grow up and requires higher temperatures to be completely converted.

Figure 5. shows XRD pattern of the batches sintered at 1250℃. For experimental work with an addition of 2.24 wt% B_2O_3, the high temperature wollastonite α-CaSiO3 formation set in Figure 4. continued on a larger scale. The batch resulting in product showing only one peak of cristobalite at a diffraction angle equal to 21.909 ° (4.05 A °) with a lower intensity as compared with the former batch sintered at 1150℃. For the so called "standard work", α-wollastonite which appeared in Figure 4. with a lower peak intensity is grown up to its maximum intensity at a diffraction angle equal to 27.479 ° (3.24 A °) associated with unreacted quartz which appears as a major phase and requires higher temperatures to disappear. While a small proportion of it is transformed to tridymite at 2Ө equal to 21.694 ° (4.09 A °). Small peaks of larnite are overlapped with α-wollastonite at different diffraction angles. A lower peak belongs to β-wollastonite and calcite is also appeared as unreacted material.

The crystallization behavior of both experimental and the so called standard work is shown in **Figure 6** and **Figure 7** with respect to the sintering temperatures and the height of peaks measured in millimeters.

It seems that the addition little amount of B_2O_3 has a significant effect on the crystallization behavior of wollastonite at this low temperatures e.g., 1050 and 1150℃. As the temperature increased up to 1400 ℃, both experimental and standard samples have been melted.

A comparative study of the resulted microstructures for different samples sintered at 1050, 1150 and 1250℃.

Figure 8. Illustrates the SEM micrographs of the experimental and the so called "standard work" where there is a significant difference between their morphology. Picture (a) shows irregular particle shape where silicon dioxide and calcium oxide are not fused to promote enough grain growth, which indicates that the reaction is not yet accomplished as confirmed by XRD analysis Fig. 3. In contrast, picture (b) shows that the specimen is dense and has an obvious grain growth of granular particle shape due to the liquid phase resulted from the addition of B_2O_3.

Figure 9. Represents the SEM micrographs for samples with and without B_2O_3 addition sintered at 1150℃. Picture (c) exhibits a large number of small, irregular-shape grains and a rough morphological with a slight grain growth which related to the incomplete reaction. On the contrary, when B_2O_3 is added, the grains as shown in picture (d) become larger with a subspherical of interconnected pores and smoothing surface which appears more consolidate.

Figure 10. Demonstrates the SEM micrographs for batch

sintered at 1250℃ with a soaking time of 2 h. Picture (e) represents the so called "standard work" sintered at 1250℃ in which irregular agglomerate of grains of different size with a detectable grain growth. It is indicated that samples require higher temperatures to be densified. While picture (f) of experimental work shows a reasonable smooth surface with little amount of large isolated pores and voids distributed on it. The microstructure shows an appropriate grain growth of a large size without the precipitation of excessive secondary phases such as, CaB_2O_4 which appears denser than the batch sintered at 1150℃ as shown in **Figure 9 d**.

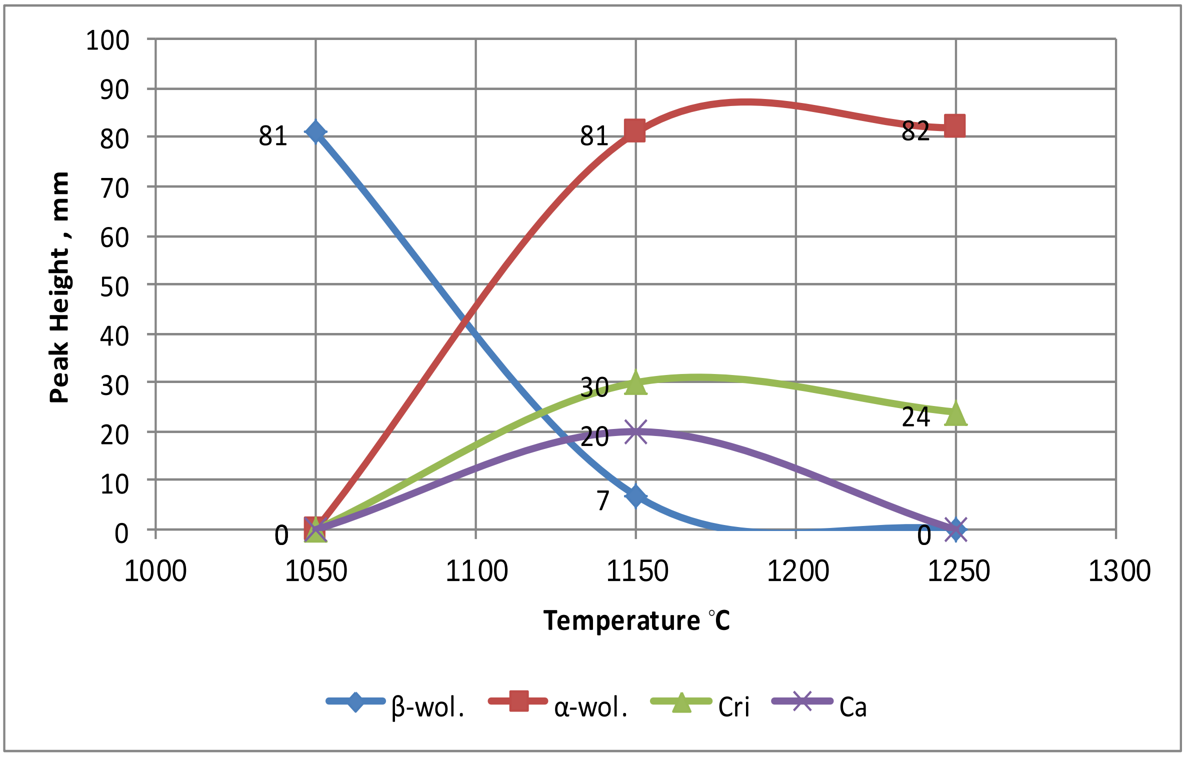


Figure 6. Crystallization behavior of experimental work with respect to the sintering temperatures

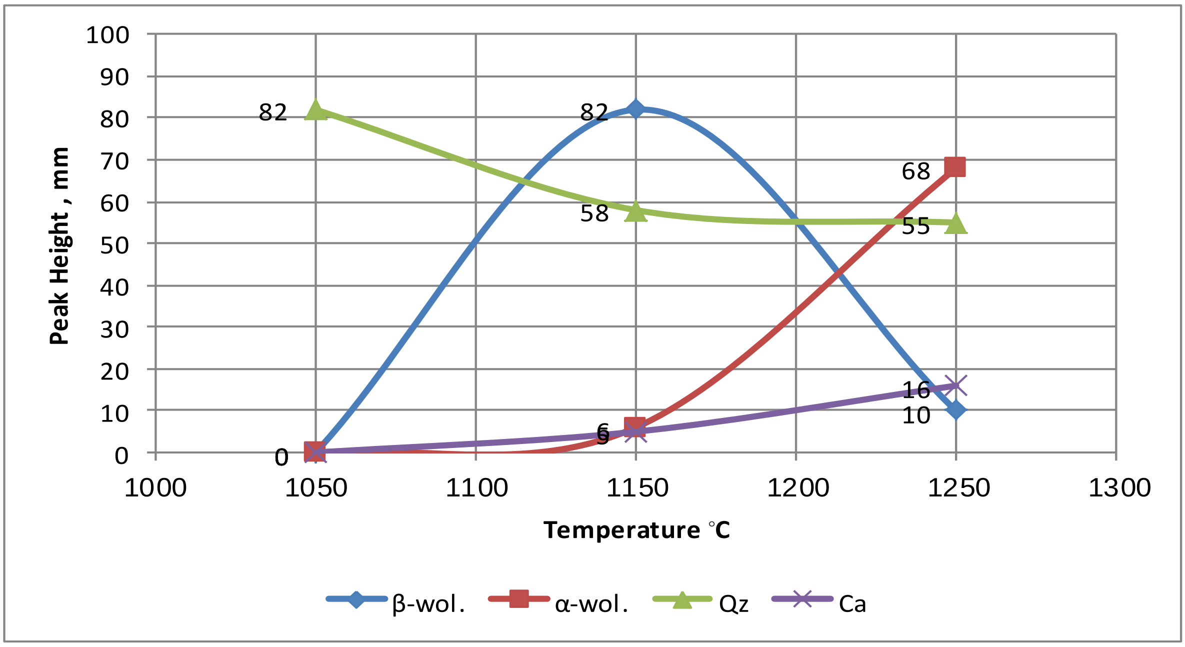


Figure 7. Crystallization behavior of the so called "standard work" with respect to the sintering temperature

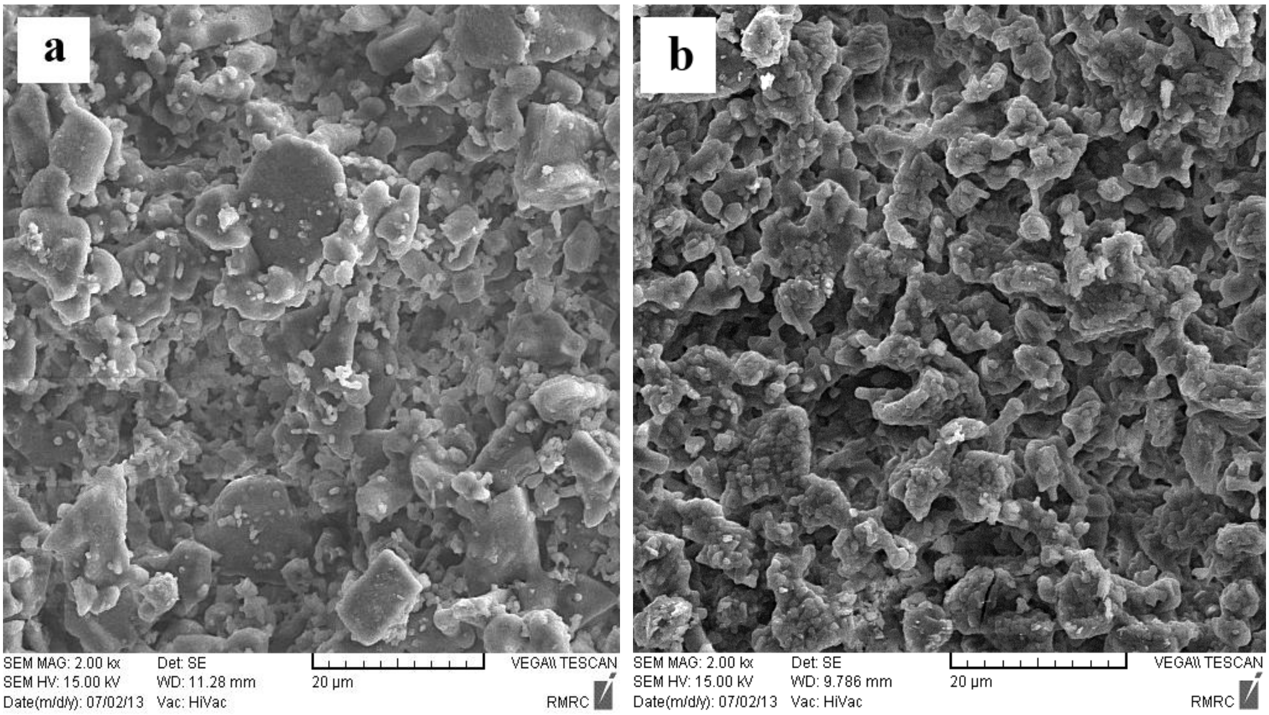


Figure 8. SEM micrographs for (a) the so called "standard" and (b) experimental work sintered at 1050℃ for 2 h [6]

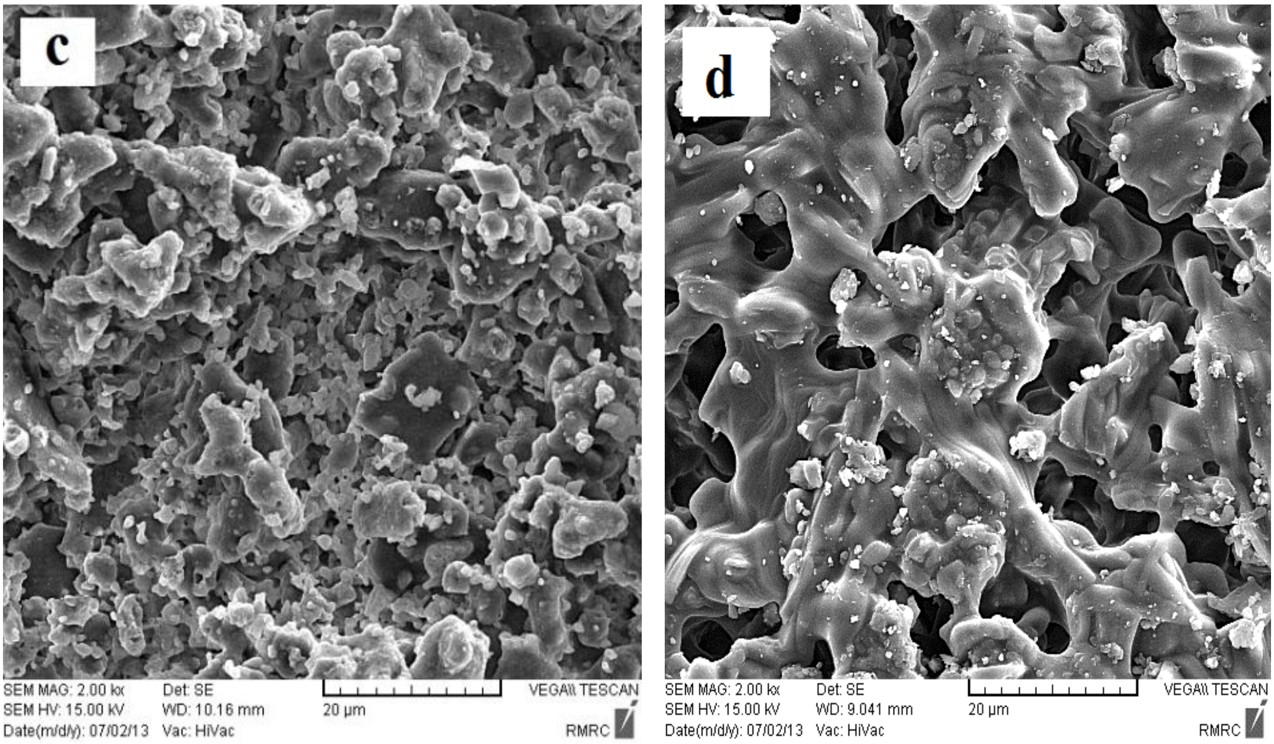


Figure 9. SEM micrographs for (c) the so called "standard" and (d) experimental work sintered at 1150℃ for 2 h [6]

This study was also compared with data previously reported by other researchers [18-19] who obtained the α-wollastonite at a temperature higher than 1150℃ as compared with the results obtained in this work, where energy is taken into consideration. Nizami [18] produced the same product from rice husk silica and limestone with the addition of 2% mineralizer at 1300℃ for 1 h with the formation of minor amount of tridymite. Grigorian et al., [19] also prepared α-wollastonite from Lithuanian gaze mineralized with 1.6% Na_2CO_3 or sodium metasilicate at 1200℃ for 2 h. While Nour et al., [20] and Endo et al., [21] are obtained β-wollastonite at 1150℃ with a soaking time of 2-3 h. It seems that B_2O_3 addition in this experiment lower the sintering temperature in the range of 100-150℃.

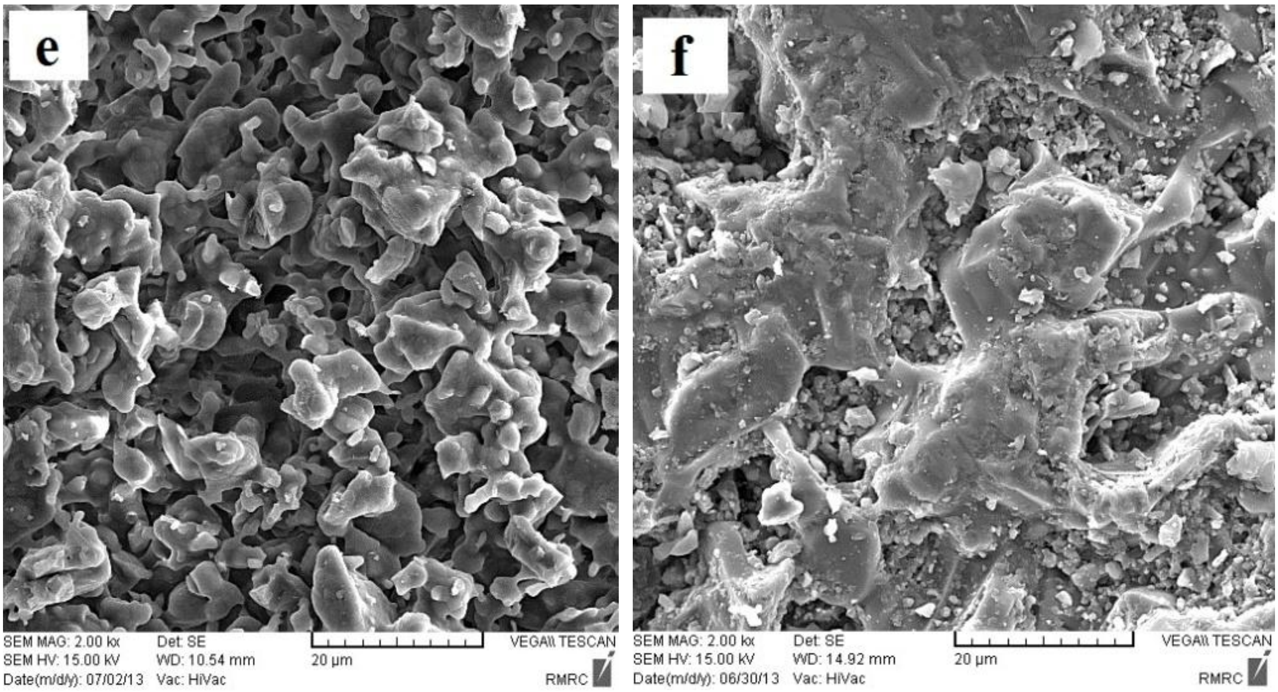


Figure 10. SEM micrographs for (e) the so called "standard" and (f) experimental work sintered at 1250℃ for 2 h [6]

4. Conclusions

Synthetic wollastonite was successfully prepared from limestone and silica sand with the addition of 2.24 wt. % B_2O_3 at low temperature of 1050℃ for β-wollastonite and of 1150℃ for α-wollastonite with relatively porous structure. Pure chemicals failed to give β- and α- forms at low temperature with highly porous structure as confirmed by XRD and SEM. Increasing in firing temperature to 1400℃ causes melting of both standard and experimental samples.

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