

Preparation of Synthetic β -Wollastonite Produced from Amorphous SiO_2 Bamboo Leaf Ash and *Meretix Meretix* Shell

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Abstract. The objective of this study is to produce β -wollastonite from amorphous SiO_2 obtained from bamboo leaf ash (BLA) and CaO derived from *meretix meretix* shell (MMS) using solid state reaction. Amorphous SiO_2 utilization in this work obtained by precipitation of BLA and calcined at 700 °C for 3 h, whereas CaO MMS was generated by calcination of MMS at 1000 °C for 5 h. High purity amorphous SiO_2 obtained was 99.325 wt % and CaO purity obtained was 97.531 wt %. Single phase of β -wollastonite found in this study as confirmed by XRD results. The vibrations at 933.42, 904.49, and 890.99 cm^{-1} were caused by the Si-O-Ca bond, which shows the bonding of β -wollastonite obtained from the FTIR. The acicular morphology of β -wollastonite with average grains size of 0.28, 0.33 and 0.71 μm was obtained for the samples calcined at 900, 1000, and 1100 °C respectively.

Introduction

In the previous twenty years wollastonite (CaSiO_3) has received a lot of attention attributable to its extraordinary properties and wide applications in industry. Owing to its high strength, low shrinkage, less volatile constituents as well as its fluxing properties, wollastonite has been used in cements manufacturing [1] and ceramics industry [2]. In the biomedical field wollastonite is used for artificial bone [3-4], tooth roots [5] and cell growth [6-7]. In addition, wollastonite is also utilized in the plastic industry [8], and electronics [9].

Many methods have been used in the preparation of wollastonite, including the solid reaction method [10-12], sol gel method [13], microwave methods [14] and hydrothermal methods [14-16]. The conventional method used in the preparation of wollastonite is the solid state reaction method. Although this method requires a long reaction time and high calcination temperature and produces samples with large grain sizes [17], the solids state reaction method is the simplest method for obtaining wollastonite material in the ceramic industry.

Recently many efforts have been conducted to develop synthetic wollastonite by solid state reaction using bio waste as raw materials. For example, Phutthawong et al [18] found that wollastonite is formed along with an increase in grinding time from 5-8 hours, and the optimum time for the formation of wollastonite is 7 hours grinding time with a calcination temperature of 1000 °C for 2 hours which is synthesized using silica rice husk ash and snail shells (*Pomacea canaliculata*) with 1: 1 molar ratio. The same method was also used by Rashid et al. [11] through synthesizing silica sand (99.56 wt%) and CaO from limestone to produce β - CaSiO_3 phase at 1050 °C sintering and changing the phase to α - CaSiO_3 at 1150 °C sintering temperature. With calcium nitrate and fumed silica as raw materials synthesized by the solid method, single-phase

β -CaSiO₃ and α -CaSiO₃ were obtained by sintering at 950 °C and 1200 °C with an average particle size of 29-50 nm [19]. Meanwhile, in a study conducted by Nizami [20], the wollastonite crystals formed at 1100 °C are β -CaSiO₃ and at 1300 °C are α -CaSiO₃. In addition, the solids reaction method obtained wollastonite crystals at a sintering temperature of 1250 °C with a density of 1.98 gr/cm³ [21]. Eventhough, many studies have been conducted to synthesis wollastonite by using bio waste materials, however to our knowledge, no report have been published preparing wollastonite using SiO₂ derived from bamboo leave ash and meretix meretix shells. In this paper, for the first time preliminary study of the solid state reaction of SiO₂ derived from bamboo leave ash and meretix meretix shells to produce single phase of β -wollastonite been reported.

Experimental Method

Preparation of Raw Materials and its Characterization

Raw materials used in the preparation of wollastonite were bamboo leaves (BL) as a source of amorphous SiO₂ and *meretix meretix* shells (MMS) as a source of CaCO₃. BL were obtained from East Lampung Regency, Indonesia, whereas MMS were collected from seafood restaurant around Bandar Lampung city Indonesia. To extract amorphous SiO₂ from BL, at first BL washed thoroughly with tap water to remove the adhering soil and dust, then dried under sunlight for 24 h and followed by oven dried at 100 °C for 10 h. The dried BL then was grinded by using laboratory blender for 20 minutes to become fine powder. 30 g BL powder was citric acid leached at 80 °C for 60 minutes, filtered and washed using deionized water and then dried in oven at 100 °C for 10 h. The dried citric acid leached BL then calcined at 700 °C for 6 h with heating rate 5 °C/minutes to obtain bamboo leaf ash (BLA) powder. Following this BLA washed with 250 ml deionized water and refluxed with 6 N HCL for 2h at 100 °C, then filtered and washed with 250 ml hot deionized water to make it acid free. It was then stirred in 2.5 N NaOH at 80 °C for 2 h and then filtered to obtain Na₂SiO₃ solution. The concentrated H₂SO₄ was then added drop wise to the solution in order to lower the pH of the solution to 2. The precipitated silica was then washed repeatedly with boiling deionized water until the filtrate became alkali free, dried in oven at 100 °C for 24 h, then calcined at 700 °C for 6 h with heating rate 5 °C/minutes.

The Synthesis of calcium carbonate powders were prepared from the meretix meretix shells according to the route described by Asmi and Zulfia [22]. CaCO₃ from MMS was prepared by washing MMS with tap water to remove meat leftover and the dirt then dry in oven at 100 °C for 10 h. Dried MMS then ground using mortar and pestle and grinded by using laboratory blender for 20 minutes to become fine powder and sieved through 200 mesh. The powder obtained then calcined at 1000 °C for 5 h. The amorphous SiO₂ precipitated BLA powder and calcined MMS powder obtained then ground using agate mortar and sieved through 200 mesh. The chemical compositions of raw materials then were analysis using X-ray Fluourescence (XRF-PAN analytical). The amorphous SiO₂ BLA obtained were characterized using diffractometer (PW3040/60 Xpert Pro) using CuK α radiation, 40 kV and 30 mA in 2 theta range of 5-80 degrees and thermal behavior of decomposition of CaCO₃ to CaO were investigated using a thermogravimetric analyzer and a differential thermal analyzer with heating rate 10°C/min in nitrogen atmosphere (Simultaneous Thermal Analyzer, STA449C Jupiter, NETZSCH).

Preparation of β -Wolastonite Powder and its Characterization

To synthesise β -wollastonite, the amorphous SiO₂ precipitated BLA powder was mixed with calcined MMS powder with molar ratio 1:1 and ball mill for 10 h in medium ethanol. The slurry then dried, grounded and sieved through 200 mesh. The mixed dried powder then heat treated at 900 °C, 1000 °C and 1100 °C for 3 h with the heating rate of 5°C/min. The crystal structure, compositional of functional group, and morphology of samples were monitored by using x-ray diffractometer (PW3040/60 Xpert Pro), FTIR spectrophotometer (Perkin Elmer Optima 100), and

scanning electron microscopy (SEM JEOL 5610LV). Thermal behavior of precursor β -wollastonite examined using Simultaneous Thermal Analyzer, STA449C Jupiter, NETZSCH in temperature range from room temperature to 1200 °C with heating rate 5 °C/min.

Results and Discussion

Characterization of Raw Materials

The chemical compositions of raw materials by XRF analysis is shown in Table 1. The precipitated BLA powder obtained from XRF analysis results shows high purity amorphous SiO_2 of 99.325 wt% with impurities of 0.001 % MgO , 0.137 % Al_2O_3 , 0.342 % P_2O_5 , 0.035 % K_2O , 0.088 % CaO , 0.003 % TiO_2 , 0.006 % MnO , 0.032 % Fe_2O_3 , 0.003 % CuO , 0.001 % ZnO , 0.024 % Ag_2O , and 0.003 % Cl . The XRD spectra of this sample also proved that the high purity of SiO_2 obtained was amorphous as depicted in Figure 1. The abundant CaO content in calcined MMS obtained is 97.531 wt % with minorities compound of 0.093 % SiO_2 , 0.354 % MgO , 0.741 % Al_2O_3 , 0.232 % P_2O_5 , 0.024 % K_2O , 0.05 % MnO , 0.203 % SrO , and 0.112 % Cl respectively.

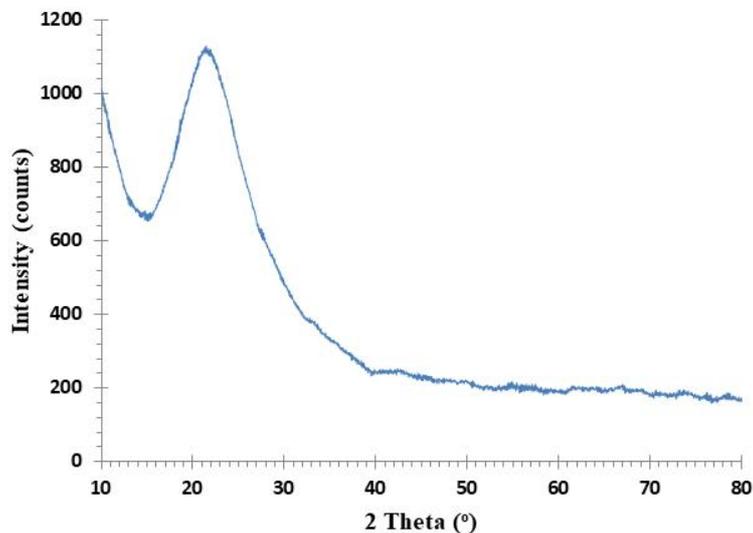


Figure 1. XRD pattern of amorphous SiO_2 precipitated bamboo leave ash.

Simultaneous of TGA and DTA curves β -wollastonite depicted in Fig. 2. There are three distinctive steps thermal decompositions take places in TGA curve. To begin with weight loss of 17 % below 200 °C was due to the thermal events of evaporation water, which is related in DTA curves as small endothermic peak around 128 °C. The following step of weight loss of 22 % happened at extend roughly of 210 – 585 °C in TGA curve related with exothermic hump within the DTA curves, which is credited to the low temperature decarbonitation. The final weight loss of 23 % begin at 585 °C and closes at 800 °C corresponding to high decarbonitation temperature and to dehydration of silanol groups. In the DTA curve high exothermic peak at 825 °C and small exothermic peak at 1125 °C indicated the crystallization temperature of β -wollastonite and the evolution of β -wollastonite to α -wollastonite respectively [20].

The XRD pattern of β -wollastonite samples calcined at different temperature shown in Figure 3. XRD pattern shows a single phase of β -wollastonite (JCPDS # 043-1460) and no other secondary phases or unreacted starting materials were observed in samples calcined at 900 °C and 1000 °C. However calcined sample at 1100 °C, small crystalline peak at 2 theta 41.721° was observed and belong to α -wollastonite (JCPDS # 01-074-0874).

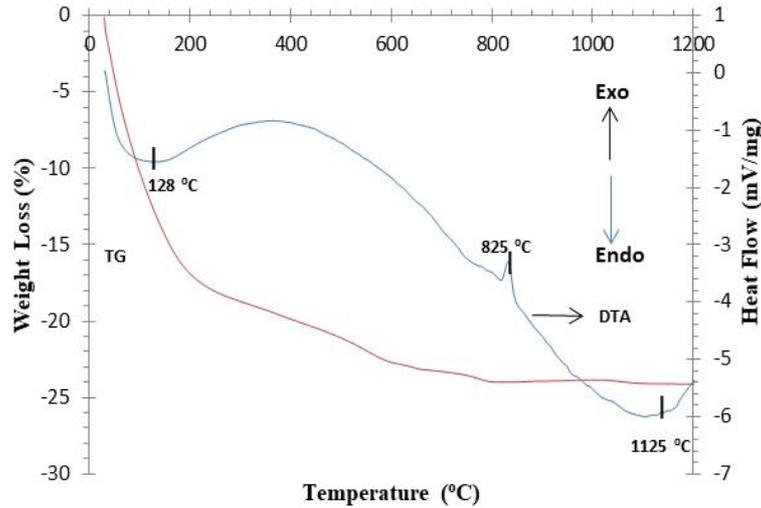


Figure 2. Thermal analysis (TGA and DTA pattern) of β -wollastonite.

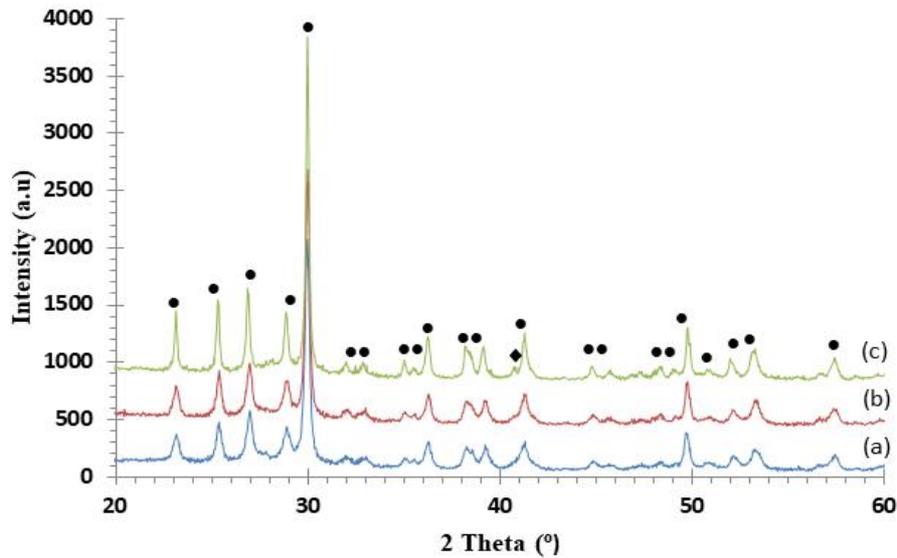


Figure 3. X-ray diffraction (XRD) spectra of β -wollastonite samples calcined at 900 °C (a), 1000 °C (b), and 1100 °C (c) for 3 h. • = β -wollastonite and ◆ = α -wollastonite.

FTIR spectra of β -wollastonite calcined 900 °C (a), 1000 °C (b), and 1100 °C (c) shown in Fig.4. Spectral result in all samples shows the broad band absorption peaks at 3454.05 cm^{-1} , and small absorption peaks at 2335.49 cm^{-1} and 1631.56 cm^{-1} due to vibration of the OH bond, which is caused by absorption moisture from the air. In the spectrum, it can be seen that the intensity of the absorption peak in the range of 3400 cm^{-1} to 1600 cm^{-1} is decrease as the calcination temperature increases. The absorption peaks at 1056.85 cm^{-1} and 1023.7 cm^{-1} were associated with O-Si-O bond [19]. The vibrations at 933.42 cm^{-1} , 904.49 cm^{-1} , and 890.99 cm^{-1} were caused by the Si-O-Ca bond, which shows the bonding of β -wollastonite [23]. Vibrations at 728.99 cm^{-1} , 678.85 cm^{-1} and 640.28 cm^{-1} occurred due to bending vibrations of the Si-O-Si bonds [24] and absorption peaks that occurred at 539.99 cm^{-1} , 520.71 cm^{-1} , and 478.28 cm^{-1} were due to bending vibrations from Si-O [19].

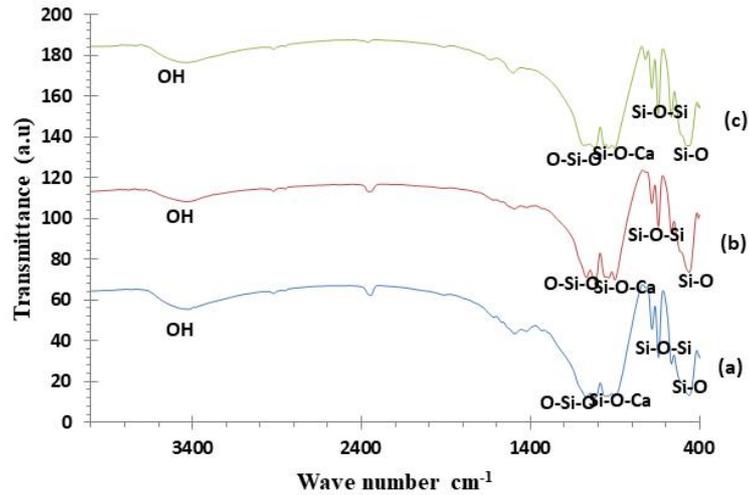
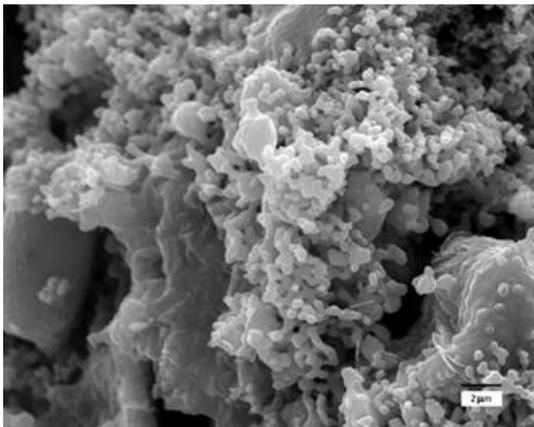
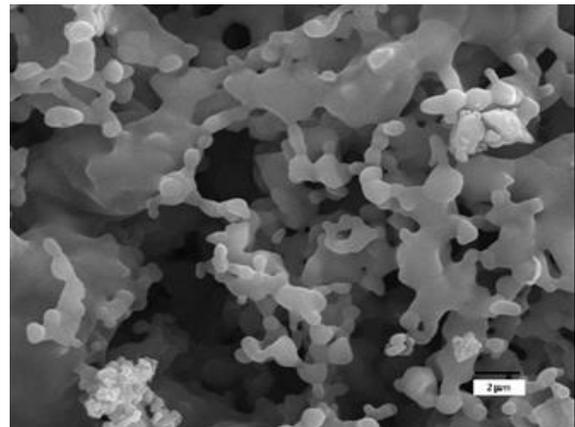


Figure 4. FTIR spectra β -wolastonite calcined at 900 °C (a), 1000 °C (b), and 1100 °C (c).

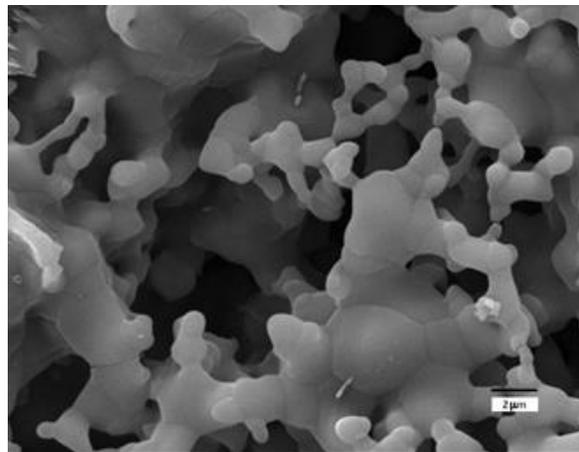
The SEM micrographs of the sample calcined at 900 °C (a), 1000 °C (b), and 1100 °C (c) for 3 h are shown in Figure 5. The morphology observed in the sample calcined at 900 °C (Fig. 5a) is acicular shape with the average grains size of 0.28 μm [25-27]. Increased calcined temperature from 1000 °C (Fig. 5b) to 1100 °C (Fig. 5c), the grain growth was observed and the grain size of the sample is 0.33 and 0.71 μm , respectively.



(a)



(b)



(c)

Figure 5. SEM of β -wolastonite calcined at 900 °C (a), 1000 °C (b), and 1100 °C.

Conclusions

Synthetic pure β -wollastonite has been successfully produced from bio waste materials (bamboo leave ash and meretix meretix shells). In this study found that the high purity amorphous silica derived from precipitated bamboo leave ash is 99.325 %, whereas the CaO content in calcined meretic meretic shells obtained is 97.521 %. Single phase of β -wollastonite found in this study and also confirmed by XRD and FTIR results obtained. The acicular morphology of β -wollastonite calcined at 900, 1000, and 1100 °C with average grains size of 0.28 μm , 0.33 μm and 0.71 μm respectively was obtained from the SEM results. Based on the test results that have been carried out, therefore amorphous SiO_2 derived from bamboo leaves ash and CaO from meretix meretix shells is potentially be used as an alternative source raw material to produce β -wollastonite which simple route.

Acknowledgments

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