

Synthesis and characterization of wollastonite from egg shell and diatomite by the hydrothermal method

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Wollastonite was synthesized using calcium oxide from egg shells and silica from diatomite by being calcined at 800 °C. The calcium oxide and silica was synthesized in a molar ratio of 1 : 1 using the hydrothermal method at 100, 150, and 200 °C for 24 hours and then calcined at 1,000 °C for 24 hours. The morphology of wollastonite which was characterized by SEM indicated that the particles were an agglomerate consisting of small particles with sizes less than 1 µm. The FTIR spectra showed that the carbonate band at 1459 cm⁻¹ was absent from calcination product and that was further confirmed by a thermogravimetric analysis. The ν(Si(OSi)₃O-Ca wollastonite band presented as a band at 930 cm⁻¹. The XRD results clearly show the structural formation of wollastonite. This method used to synthesize wollastonite is simple and able to function using cheap starting materials.

Key words: Wollastonite, Egg shell, Diatomite, Hydrothermal Method, Calcination.

Introduction

Wollastonite or CaSiO₃ has been the focus of study because it has been used in ceramics as a sanitary ware and also table ware. More recently, wollastonite has been used in electrical applications as a high voltage insulator [1]. Nowadays, researchers have worked to improve the properties of wollastonite as a material for bioceramics and biomaterials such as artificial bond [2], antibacterial growth [3], and as a platform for the regeneration of hard tissue [4]. The conventional synthesis of wollastonite done through a solid-state reaction since this is a simple method to produce this material for industrial applications especially ceramics. However, long reaction times and calcination at high temperatures are required for this method and the resulting wollastonite products tend to have large grain sizes [5]. The microwave synthesis of wollastonite has also been reported although high purity starting materials are required to prepare nano size samples of wollastonite [6]. The hydrothermal method can use low temperatures with high pressure and can yield high purity nano sized wollastonite [7]. Intermediate phases can be limited to reduced the duration of the synthesis experiment [8].

The conventional starting materials used to synthesize crystalline wollastonite are calcium oxide and silica. The normal sources of calcium oxide are Ca(NO₃)₂

[5, 7], CaO [9], and egg shells [10]. The sources of silica are commercial silica [11], tetraethylorthosilica [12] and Na₂SiO₃ [5]. Since some of these starting chemicals are expensive we examined the use of egg shells to replace other sources of calcium oxide. Egg shells can be found as waste products from restaurants and fresh markets in the Chiang Mai province, Thailand since egg is a popular food with high protein and low cost. The chemical composition of eggshell is calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%), and organic matter (4%) by weight [13]. Also, diatomite is naturally abundant in the Lampang basin and contains highly levels of silica. The purpose of this work was to synthesize wollastonite from calcium oxide and silica obtained from egg shell and diatomite, respectively under hydrothermal conditions at different temperatures (100, 150, and 200 °C) and testing the effect calcination on the SEM morphology (particle shape and dimension) and FTIR spectroscopy. The synthesized wollastonite samples were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The main advantage of synthesizing wollastonite using this methodology is that it is a simple method which uses cheap starting materials. One additional benefit of this wollastonite product is that it yields nanosize scaled products.

Experimental

The waste egg shells collected from restaurants were

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rinsed with tap water several times and then dried in air. The dried egg shells were then crushed and calcined in the muffle furnace at 800 °C for 2 hrs. The silica extraction was modified from Kalapathy's work [14]. Diatomite (68% wt% SiO₂) was dissolved using 1 M NaOH in a ratio of 1 : 6 weight by volume and filtered with adjusted pH equal to 8 by 1M HCl. The gel product was washed with hot water, filtered, and dried at 80 °C until a silica powder was obtained.

CaO and SiO₂ at a molar ratio of 1 : 1 was synthesized by the hydrothermal method at 100, 150, and 200 °C for 24 hrs and calcined at 1,000 °C for 24 hr.

The morphology of the synthesized products was investigated using a scanning electron microscope (JSM-5410LV, JEOL, Japan). The formation of wollastonite was analyzed by Fourier transform infrared spectroscopy (Spectrum RXI, Perkin Elmer, United State), and X-ray diffractometry (X'Pert, Philips, England). The thermogravimetry analysis was performed by STA 409 EP (NETZSCH, Germany). The samples were prepared at a heating rate of 10 °C/min under air atmosphere.

Results and Discussion

The morphology of the wollastonite prepared by CaO from eggshell and SiO₂ from diatomite using the hydrothermal method with and without calcination at 800 °C is shown in Fig. 1 and Fig. 2, respectively. The SEM results indicate that the particles of wollastonite agglomerated into small particles sized more than 1 µm when they were not calcined. In contrast, they had a clear shape when calcined with the size of 0.3 µm (width) × 2 µm (length) obtained under hydrothermal method at 100 °C (Fig. 2(a)). The size of the particle

increases as the temperature of reaction increased to 150 and 200 °C (Fig. 2(b) and 2(c)). At high temperatures, the shape more clearly resembled a size of 1 µm (width) × 2-4 µm (length). The size of wollastonite produced in this work after being calcinated at high temperature, was found to be smaller than wollastonite prepared using microwave and sintered at 1,100 °C for 2 hr [11]. However, this size was larger than the wollastonite prepared using the sol-gel process and calcined at 1000 °C for 1 hr [15]. It should be noted that the different methods to synthesize wollastonite provide different product sizes. The needle-like morphology of commercial wollastonite with a size of ~10-15 µm (width) is demonstrated in Fig. 3. The synthetically produced wollastonite has a distinctly different morphology from commercial wollastonite.

The FTIR spectrum of calcium oxide from egg shell in Fig. 4(a) exhibited a band at 1410-1490 and 875 cm⁻¹ assigned to the CO₃²⁻ including the band at 1630 cm⁻¹ and a weak band at 750 cm⁻¹ assigned to CaO [16]. This indicates that the carbonate existed in the CaO

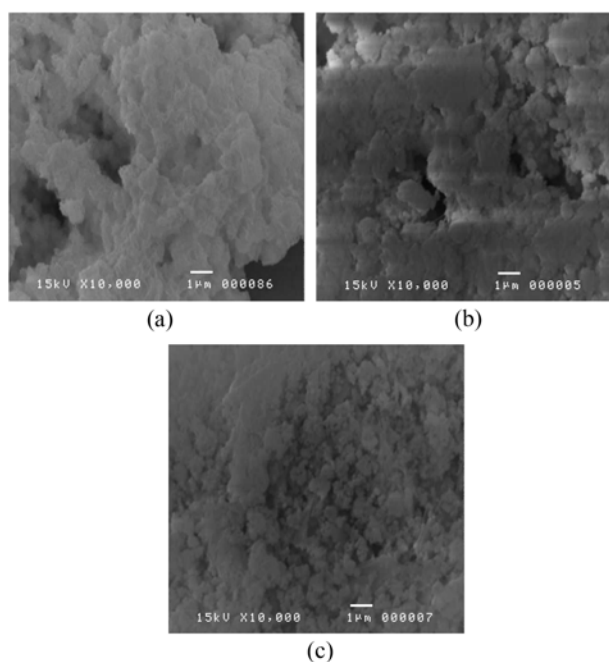


Fig. 1. SEM of wollastonite at (a) 100 (b) 150 and (c) 200 °C.

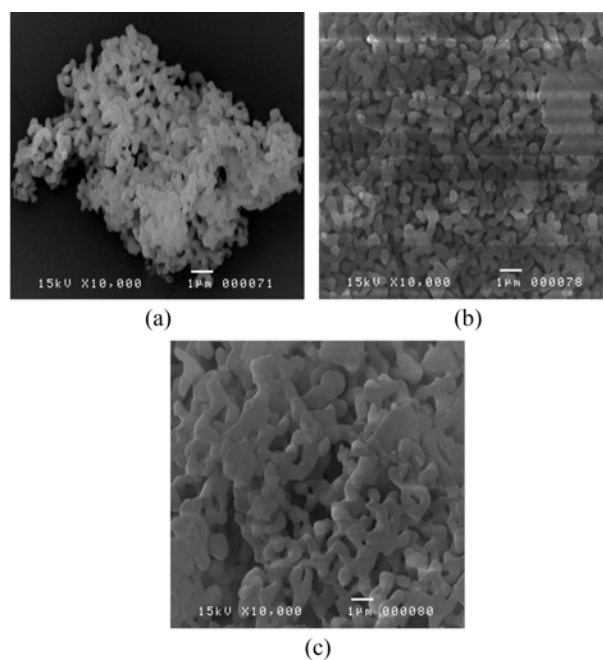


Fig. 2. SEM of wollastonite at (a) 100 (b) 150 and (c) 200 °C with calcination.

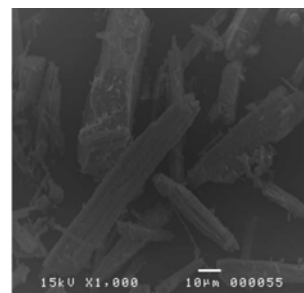


Fig. 3. SEM of commercial wollastonite.

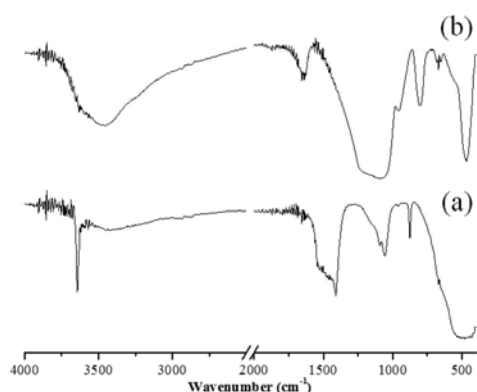


Fig. 4. FTIR spectra of (a) calcium oxide from egg shell and (b) silica from diatomite.

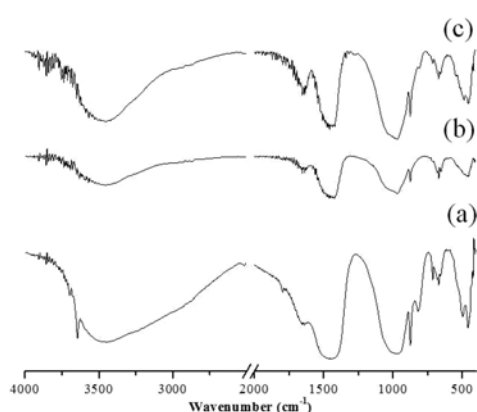


Fig. 5. FTIR spectra of wollastonite at (a) 100 (b) 150 and (c) 200 °C.

product without calcination. The FTIR spectrum of silica from diatomite in Fig. 4(b) showed similar results to Kalapathy's report [14]. The broad band between 3400 and 3570 cm^{-1} corresponds to silinol OH groups and adsorbed water on the surface of the silica. The

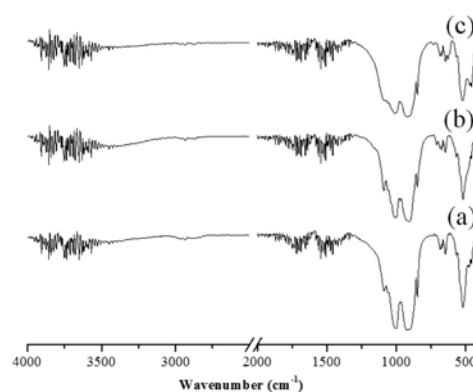


Fig. 6. FTIR spectra of wollastonite at (a) 100 (b) 150 and (c) 200 °C with calcination.

predominant band at 1300-1200 cm^{-1} was that of a siloxane bond (Si-O-Si). The bands between 803 and 468 cm^{-1} were vibrational modes of the gel network. Fig. 5 and Fig. 6 show the FTIR spectra of wollastonite using the hydrothermal method at 100, 150 and 200 °C with and without calcination at 1,000 °C for 2 hr, respectively. After calcination, the bands between the 3,400 and the 3,570 cm^{-1} silinol OH groups including 1,631-1,638 and 875 cm^{-1} which were due to CaO disappeared. Also the bands at 1,440-1,450 cm^{-1} assigned to carbonate disappeared. The broad band at 960-969 cm^{-1} in Fig. 5 split to ~1,010 and 870 cm^{-1} in Fig. 6 and was assigned to the characteristic peaks of the amorphous SiO_2 [$\nu(\text{Si-O-Si})$] and Si-O-Ca, respectively [10, 17]. The FTIR spectra showed the occurrence of wollastonite and provided a similar FTIR pattern to that of natural wollastonite [18].

The result of the thermal analysis and differential thermal analysis of wollastonite at 100, 150, and 200 °C with calcination are shown in Table 1 and 2, respectively. The temperature range 100 °C to 1,200 °C

Table 1. The thermal analysis of wollastonite at 100, 150, and 200 °C with calcination.

Wollastonite at 100 °C		Wollastonite at 150 °C		Wollastonite at 150 °C	
Temperature range (°C)	% Weight loss	Temperature range (°C)	% Weight loss	Temperature range (°C)	% Weight loss
81.5 - 436.2	0.6	70.5 - 429.1	0.2	64.6 - 426.3	0.6
436.2 - 494.2	1.1	429.1 - 492.2	1.7	426.3 - 490.7	2.6
494.2 - 651.4	0.6	492.2 - 734.5	0.9	490.7 - 664.1	0.6
651.4 - 730.7	1.3	734.5 - 1,205.3	0.4	664.1 - 738.6	1.5
730.7 - 1,205.3	0.9	-	-	738.6 - 1,205.3	0.7
Total % weight loss	3.9	Total % weight loss	3.1	Total % weight loss	5.6

Table 2. The differential thermal analysis of wollastonite at 100, 150, and 200 °C with calcination.

Wollastonite at 100 °C		Wollastonite at 150 °C		Wollastonite at 150 °C	
Type of reaction	Temperature of reaction (°C)	Type of reaction	Temperature of reaction (°C)	Type of reaction	Temperature of reaction (°C)
endothermic	489.3	endothermic	488.6	endothermic	480.9
	724.0		722.6		728.2

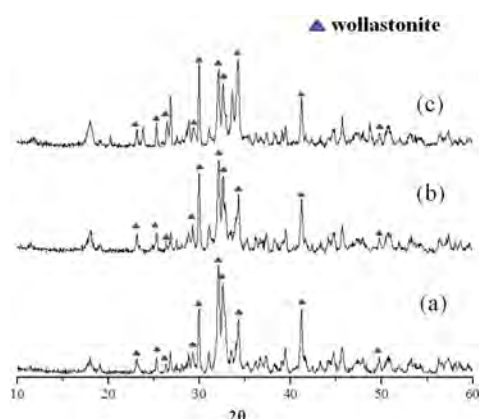


Fig. 7. XRD pattern of at (a) 100 (b) 150 and (c) 200 °C with calcination.

shows a slight weight loss. The total weight loss of wollastonite up to 1200 °C was 3.9, 3.1 and 5.1 at 100, 150, and 200 °C, respectively in Table 1. The differential thermal analysis at 480 °C displayed an endothermic reaction due to the water and some organic compounds which were removed. At 730 °C there was an endothermic reaction due to decomposition of CaCO_3 in Table 2. [11] This corresponded to the FTIR results with the bands of carbonate which disappeared after calcination.

Fig. 7 shows the X-ray diffraction of wollastonite prepared using the hydrothermal method at 100, 150, and 200 °C and being calcined at 1,000 °C for 2 hr. The XRD peaks pattern of wollastonite were characterized as wollastonite (JCPDS no. 01-073-1110) with mixed phases of $\beta\text{-CaSiO}_3$ and $\alpha\text{-CaSiO}_3$ [11]. Vichuphun *et al.* [11] synthesized wollastonite from egg shell powder and commercial silica (98%) using a microwave assisted solid-state reaction. The XRD pattern of wollastonite sintered at 1,100 °C for 10 min in a microwave furnace generated $\alpha\text{-CaSiO}_3$. This result was compared to the XRD patterns of wollastonite sintered at 1,100 °C for 10 min and 1,250 °C for 1 hr in conventional furnace which yielded $\beta\text{-CaSiO}_3$ and $\alpha\text{-CaSiO}_3$, respectively. Tongboriboon *et al.* [10] synthesized calcium silicate with calcium oxide from egg shells and fume silica using the sol-gel method sintered at 900 °C. These XRD results yielded a small amount of wollastonite ($\text{Ca}_3\text{Si}_3\text{O}_9$; JCPDS no. 01-073-1110) and suolunite (orthorhombic, $\text{Ca}(\text{SiO}_3)(\text{H}_2\text{O})$; JCPDS no. 01-089-7639). The XRD patterns of calcium silicate sintered at 1,000 and 1,200 °C are $\beta\text{-CaSiO}_3$ and $\alpha\text{-CaSiO}_3$, respectively. This indicates that the calcination of wollastonite at higher than 900 °C might lead to higher yields of $\beta\text{-CaSiO}_3$ and/or $\alpha\text{-CaSiO}_3$. The purity of silica could also affect the mixed phase of wollastonite.

Conclusions

Wollastonite can be synthesized using calcium oxide

from eggshells and silica from diatomite from the hydrothermal method with and without calcination. The temperature and calcination levels influence the particle size and FTIR results of wollastonite. The hydrothermal method at 100 °C with calcination provides the size of wollastonite less than 1 μm . The silinol OH group, carbonate and calcium oxide bands disappeared after calcination. This method used to synthesize wollastonite is simple and has the addition benefit of using cheap starting materials.

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References

1. N.S. Negmatov and Zh.Z. Abdullaev, *Glass Cerm.* 58 (2001) 396-397.
2. H. Teramoto, A. Kawai, S. Sugihara, A. Yoshida and H. Inoue, *Acta Med. Okayama* 59 (2005) 201-207.
3. W. Ortega-Lara, D.A. Cortés-Hernández, S. Best, R. Brooks and A. Hernández-Ramrez, *Ceram. Int.* 36 (2010) 513-519.
4. M. Magallanes-Perdomo, Z.B. Luklinska, A.H. De Aza, R.G. Carrodeguas, S. De Aza and P. Pena, *J. Eur. Ceram. Soc.* 31 (2011) 1549-1561.
5. K. Lin, J. Chang, G. Chen, M. Ruan and C. Ning, *J. Cryst. Growth* 300 (2007) 267-271.
6. J. Wu, Y. Zhu, G. Cheng and Y. Huang, *Materials Research Bulletin* 45 (2010) 509-512.
7. K. Lin, J. Chang and J. Lu, *Mater. Lett.* 60 (2006) 3007-3010.
8. K.G. Grigoryan, G.A. Arutunyan, L.G. Baginova and G.O. Grigoryan, *Theor. Found. Chem. Eng.* 42 (2008) 583-585.
9. S.H. Javed, S. Naveed, S. Tajwar, M. Shafaq, M. Kazmi and N. Feroze, *J. Agric. Res.* 47 (2009) 319-327.
10. N. Tangboriboon, T. Khongnakhon, S. Kittikul, R. Kunanuraksapong and A. Sirivat, *J. Sol-Gel Sci. Technol.* 58 (2011) 33-41.
11. S. Vichaphund, M. Kitiwan, D. Atong and P. Thavorniti, *J. Eur. Ceram. Soc.* 31 (2011) 2435-2440.
12. H. Wang, Q. Zhang, H. Yang and H. Sun, *Ceram. Int.* 34 (2008) 1405-1408.
13. Z. Wei, C. Xu and B. Li, *Bioresour. Technol.* 100 (2009) 2883-2885.
14. U. Kalapathy, A. Proctor and J. Shultz, *Bioresour. Technol.* 73 (2000) 257-262.
15. H. Wang, Q. Zhang, H. Yang and H. Sun, *Ceram. Int.* 34 (2008) 1405-1408.
16. M. Manso, M. Langlet, C. Jiménez and J.M. Martínez-Duart, *Int. J. Inorg. Mater.* 3 (2001) 1153-1155.
17. A. Meissterics, L. Rosta, H. Peterlik, J. Rohonczy, S. Kubuki, P. Henits and K. Sink, *J. Phys. Chem. A* 114 (2010) 10403-10411.
18. T.V. Vakalova, N.P. Karionova, V.M. Pogrebenkov, V.I. Vereshchagin and V.V. Gorbatenko, *Refract. Ind. Ceram.* 51 (2010) 295-301.