Microwave synthesis of wollastonite powder from eggshells

S. Vichaphund, M. Kitiwan, D. Atong, P. Thavorniti *

National Metal and Materials Technology Center, 114 Thailand Science Park, Pathumthani 12120, Thailand

Available online 31 March 2011

Abstract

Wollastonite powder was synthesized by microwave assisted solid-state reaction in a 2.45 GHz microwave furnace with a maximum power output of 2.4 kW. Bio-solid waste eggshell and SiO_2 were used as starting materials for the synthesis. α-Wollastonite formation started at 800 °C. The single phase was obtained after 10 min heating at 1100 °C. The use of microwave heating lowered the processing temperature and time for wollastonite synthesis.

© 2011 Elsevier Ltd. All rights reserved.

Keywords: Eggshell; SiO_2; Microwave process; Powders-solid state reaction; Sintering

1. Introduction

Wollastonite has attracted a lot of attention since it can be used in many industries such as ceramics, glasses, cements, paints, paper and plastics.[1–3] Moreover, it has been recently focused on as a bioactive material in medical applications for artificial bone, dental root and use in order to enhance the mechanical properties of biopolymers because of its good bioactivity, biocompatibility and degradability.[4–9] Generally, wollastonite powders are synthesized by solid-state reaction in conventional furnace. This conventional synthesis is the simplest method for the industrial manufacturing.[10] However, this method requires high temperatures (over 1200 °C) and long reaction time.[7] Thus, the use of new and highly efficient heating technique for solid-state synthesis is of interest.

Microwave has been extensively utilized for heating materials due to the fact that microwave processing promotes many interesting advantages over the conventional process. Microwave is an electromagnetic wave which can couple dielectric materials and consequently generate volumetric heating. A unique characteristic of microwave processing is rapid heating because materials are heated directly through the interaction with microwave energy which is opposite to the slow heating by convection heating in a conventional furnace. The higher heating rate brings about the reduction of energy consumption as well as manufacturing time and cost. Moreover, the volumetric

heating yields a uniformity of product. By microwave processing, materials are heated differently depending on their dielectric property. This condition allows selective heating and possibly achievement of new materials. Many of research studies have demonstrated the viability of microwave applications on ceramic materials such as synthesizing, calcination and sintering.[11–14]

Most of the ceramic materials cannot absorb microwave because they have a low dielectric loss factor. However the dielectric loss factor can increase with temperature; then the materials can absorb microwave more efficiently. Application of a microwave susceptor as the secondary heat source is one of the most effective ways to accelerate the heating process. SiC has been widely used as a susceptor for microwave heating of ceramic materials because of its excellent loss factor. The technique in which microwave energy is applied to a sample accompanied by heat radiation from susceptor is called "microwave hybrid heating". In addition, susceptors are always placed symmetrically surrounding the sample in order to generate the homogeneous heating.[15,16]

In this paper, microwave synthesis of wollastonite powder using bio-waste, eggshell, as a Ca source and the sinterability of the synthesized powder are reported.

2. Materials and methods

2.1. Raw materials and characterization

Eggshell wastes collected from household kitchens were washed with water and then dried at 100 °C in an oven for 24 h. After drying, the dried eggshells were crushed and sieved

---

* Corresponding author. Tel.: +66 25646500; fax: +66 25646447.
E-mail address: parjaret@mtec.or.th (P. Thavorniti).

through 100 mesh. The particle size of eggshell powder was equal to or less than 150 μm. Chemical and mineralogical characterizations of the ground eggshell have been reported elsewhere.[17] The thermal behaviour of eggshell was examined by a thermogravimetric analyzer and a differential thermal analyzer at heating of 20 °C/min in air atmosphere (Simultaneous Thermal Analyzer, STA449C Jupiter, NETZSCH).

2.2. Preparation of powder

The eggshell powder was mixed with silica (commercial grade, 98% SiO_2, supplied by AjaxFinechem) in a conventional ball mill for 5 h. The mixing molar ratios of $CaO:SiO_2$ were in the range of 1:1 to 1:0.8. After milling, the slurries were dried at 100 °C for 24 h and sieved through 100 mesh (150 μm). Next, the mixtures were put in a boron nitride (BN) crucible and placed into the SiC susceptor which was located at the center of microwave chamber and then heated at temperatures range from 700 to 1100 °C for 10 min. The microwave furnace used in this study consisted of three 2.45 GHz magnetrons with maximum power of 2.4 kW (MHDT-1800-2.4 kW, Linn high term GMBH, Germany). The microwave chamber was insulated by transparent alumina fibre board and the cavity dimension was 13.5 cm × 13.5 cm × 13.5 cm. The temperature measurement was carried out by infrared pyrometer (Pyroskop217-LWL, Kleiber). Fig. 1 is the schematic of microwave furnace used.

The synthesized products were characterized using X-ray diffraction technique (XRD, JEOL JDX-3530) with a CuK$_\alpha$ radiation. The morphology of the powders was examined by scanning electron microscope (SEM; JEOL, JSM-5410).

2.3. Sintering and characterization

The obtained $CaSiO_3$ powder was ground and milled with 5 wt% polyvinyl alcohol (PVA) as a binder in conventional ball mill for 24 h. After drying and sieving through 100 mesh, the powders were uniaxially pressed into bars (3 mm × 4 mm × 34 mm) under a pressure of 49 MPa. The sintering was done in a conventional electric furnace for 2 h and the sintering temperature varied between 1100 °C and 1250 °C.

The density and porosity of sintered wollastonite materials were determined by using the Archimedes' method according to ASTM C373-88. The room temperature bending strength was measured with a universal testing machine (Instron model, 55R4502) using four-point bending test method with a constant crosshead speed of 0.5 mm/min. The microstructure of sintered
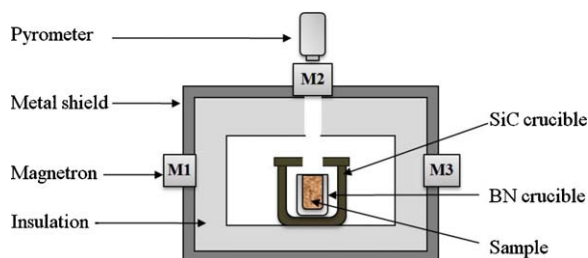
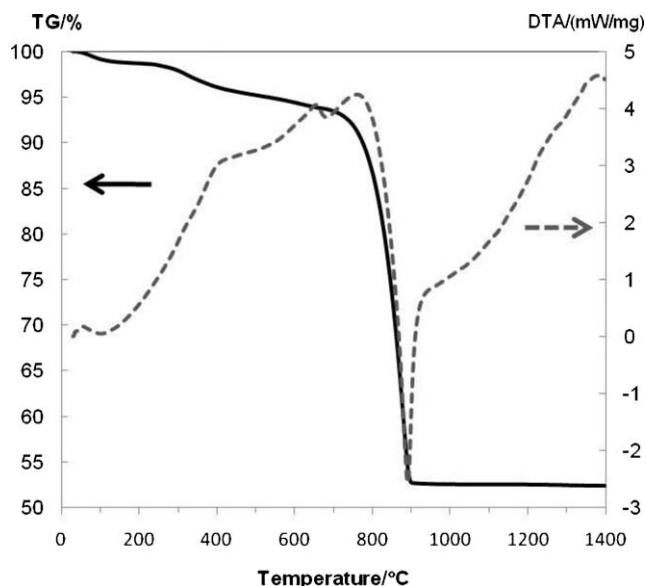Fig. 1. Schematic diagram of microwave furnace.

Fig. 2. TG–DTA curve of the eggshell.

materials was observed by scanning electron microscope (SEM; JEOL, JSM-5410).

3. Results and discussion

3.1. Raw material characterization

The eggshell was mainly composed of calcium carbonate ($CaCO_3$).[18–20] In order to use $CaCO_3$ as a Ca-source for synthesis, its thermal behaviour was investigated. The result of TG-DTA analysis is given in Fig. 2. The thermogravimetric curve exhibited a slight weight loss in the temperature range from 100 °C to 700 °C and a weight loss of about 36% at temperatures between 700 °C and 900 °C. The total weight loss of the eggshell up to 1000 °C was 44%. The first weight loss was due to the removal of water and some organic compounds in the eggshell. The second progressive loss corresponded to an endothermic peak at 900 °C in DTA curve and was associated with the decomposition of $CaCO_3$. This finding was confirmed by the XRD pattern in Fig. 3 which shows that $CaCO_3$ was completely decarbonized and turned to CaO after the eggshell calcined at 900 °C.

3.2. Powder synthesis and characterization

Initially, eggshell was mixed with silica in the stiochiometric composition, i.e., the molar ratio of $CaO:SiO_2$ is 1:1 and the mixture was heated in the microwave at 1000 °C. Fig. 4(a) shows the XRD pattern of the obtained powder. α-Wollastonite ($CaSiO_3$; JCPDS file no.: 74-0874) and larnite ($CaSiO_4$; JCPDS file no.: 33-0302) were found together with un-reacted silica. All peaks of this un-reacted silica were indexed as cristobalite (JCPDS file no.: 39-1425). This result suggests that the mixing ratio of 1:1 was not appropriate. Therefore, a decreasing in the proportion of silica in the mixture was performed in order to find the needed amount.
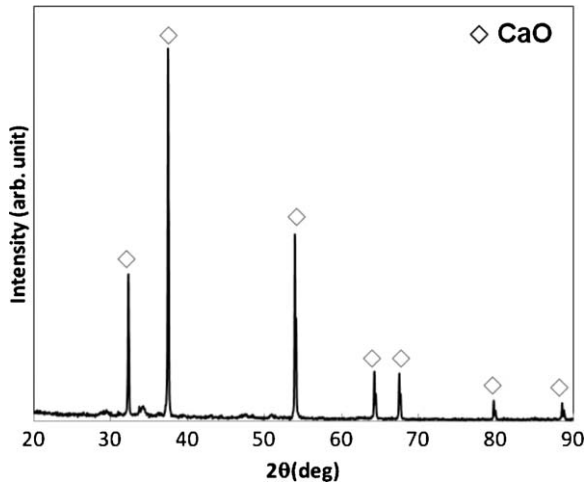
Fig. 3. XRD pattern of the eggshell calcined at 900 °C.

Fig. 5. XRD patterns of the wollastonite powders with the mixing ratio of 1:0.8 heated at different temperatures for 10 min.

The XRD patterns of the mixtures with lower amount of silica are shown in Fig. 4(b) and (c). Similar to the mixing ratio of 1:1, α-wollastonite, larnite and cristobalite were observed in the mixing ratio of 1:0.9 but the peak intensity of the excess silica in this mixing ratio was lower than that of the ratio of 1:1. After further decreasing the amount of silica to the ratio of 1:0.8, no un-reacted silica was detected. The major crystalline phase was α-wollastonite. Only a trace amount of larnite was found. This result indicates that the mixing ratios had an effect on the synthesis of wollastonite.

From the above result, the mixture with the ratio of 1:0.8 was selected for use in further experiments.

In order to examine the effect of the temperature on the wollastonite formation, the mixed powders were heated at different temperatures for 10 min in a microwave furnace. The XRD anal-
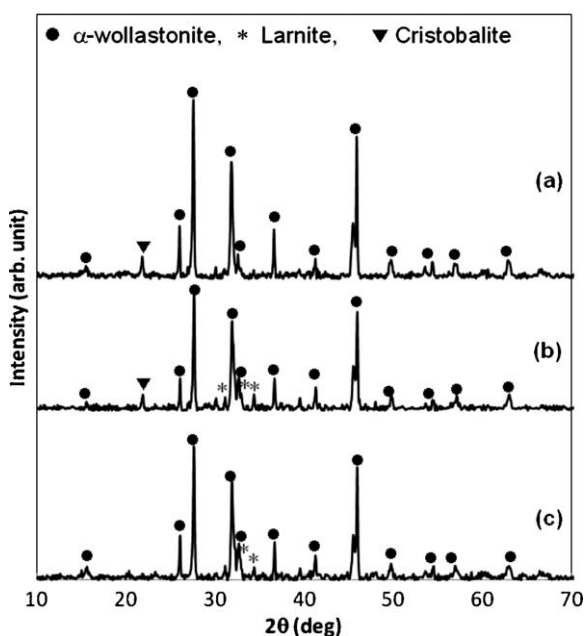
ysis results of the obtained powders are shown in Fig. 5. It can be seen that the formation of α-wollastonite started at 800 °C. On heating, the peak of CaO disappeared and α-wollastonite, larnite and small amount of cristobalite was observed at 900 °C. The presence of α-wollastonite as the major phase was found accompanied by a trace amount of larnite when the temperature increased to 1000 °C. For obtaining the single phase, the powder was heated at higher temperature. Fig. 6(a) exhibits that the single phase of α-wollastonite was obtained after heated at 1100 °C for 10 min. In contrast with the powder synthesized at the same condition by conventional solid state reaction (Fig. 6(b)), low temperature phase wollastonite (β-wollastonite)

Fig. 4. XRD patterns of the mixture of eggshell and SiO₂ with the mixing ratio of (a) 1:1, (b) 1:0.9, (c) 1:0.8 heated at 1000 °C.
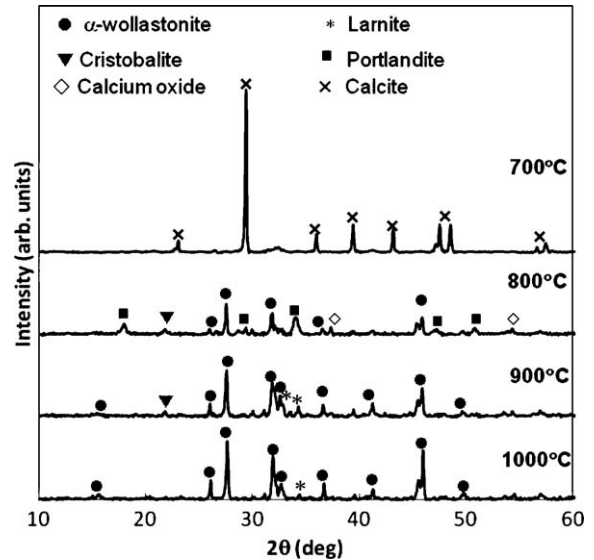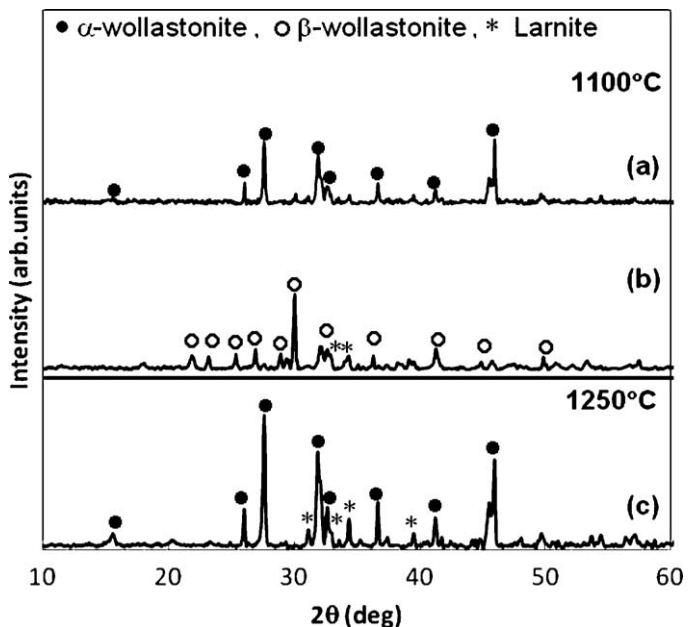

Fig. 6. XRD patterns of the wollatonite powders with the mixing ratio of 1:0.8 heated (a) at 1100 °C for 10 min in microwave furnace, (b) at 1100 °C for 10 min and (c) at 1250 °C for 1 h in conventional furnace.

Table 1
Bending strength of sintered wollastonite.

	Sintering temperature (°C)	Synthesis method	Conditions and soaking time	Bending strength (MPa)
This work	1100	Solid-state	2 h	27.06
	1150			48.88
	1200			48.78
	1250			52.95
Lin et al.[4]	1100	Precipitation	CIP, 3 h	58.02
			CIP, 2 h	65.89
	1200		CIP, 3 h	53.48

and larnite were observed. α-Wollastonite formation in conventional synthesis occurred at higher temperature. As shown in Fig. 6(c), α-wollastonite was found as the main phase after calcined at 1250 °C for 1 h. This indicates that the formation of α-wollastonite took place more easily in the powder prepared by microwave synthesis than the powder prepared by conventional synthesis. Also, it is worth noting that α-wollastonite could be obtained by microwave synthesis in a short period of time. The microwave heating contributed to the solid state synthesis of wollastonite powder in terms of providing lower the temperature and shorter the period of soaking time.
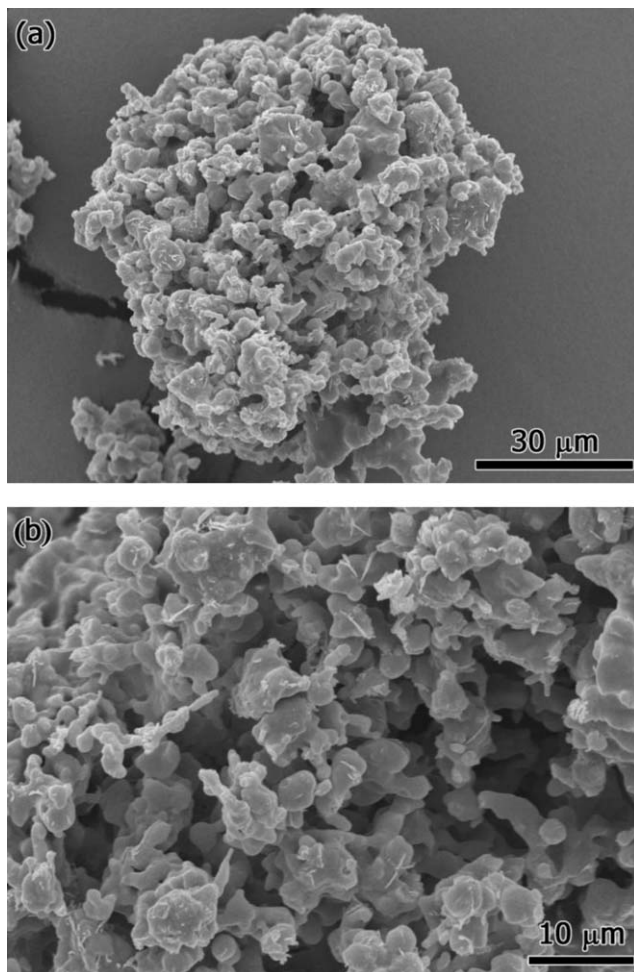
The SEM micrographs of the powder prepared by microwave synthesis at 1100 °C for 10 min are shown in Fig. 7. The particles were agglomerated and the magnified image indicates that the agglomerates consisted of small particles with the size of less than 5 μm.

It has been reported that the transformation of β-wollastonite to α-wollastonite generally begins at temperature above 1125 °C.[21] On the contrary, it can be noticed from the present results that after being heated at a temperature between 800 °C and 1000 °C, no transition phase such as β-wollastonite was detected before α-wollastonite formation. The enhancement in the transformation may be due to the high microwave heating rate and the good dielectric property of β-wollastonite.[8,22]

3.3. Properties of sintered wollastonite

Fig. 8 shows the relative density and porosity of sintered wollastonite materials. As can be seen from this figure, the relative density of wollastonite increased rapidly as the sintering temperature increased from 1100 °C to 1150 °C and changed slightly with an increase in the sintering temperature. The porosity decreased significantly from 29% for the wollastonite materials sintered at 1100 °C to 0.64% for those sintered at 1250 °C. This corresponded to the microstructure in Fig. 9. The wollastonite materials sintered at 1100 °C was porous and the amount of
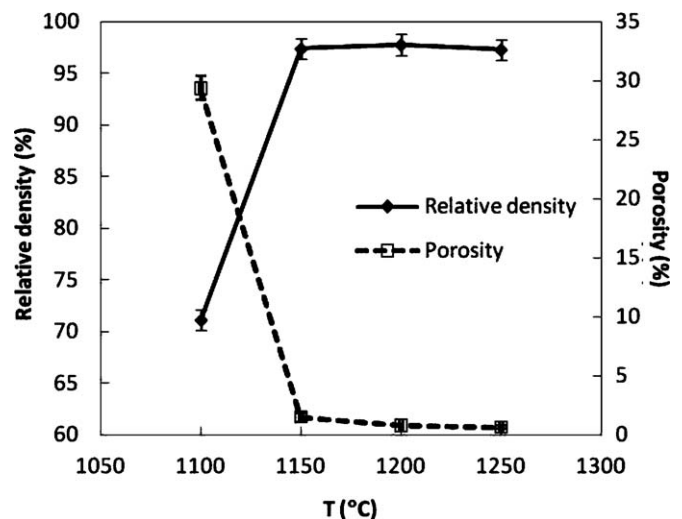

Fig. 7. SEM micrographs of the wollastonite powder heated at 1100 °C for 10 min. (b) is a high magnification of (a).

Fig. 8. Relative density and porosity of sintered wollastonite (the theoretical density of wollastonite is 2.91 g/cm^3).[22]
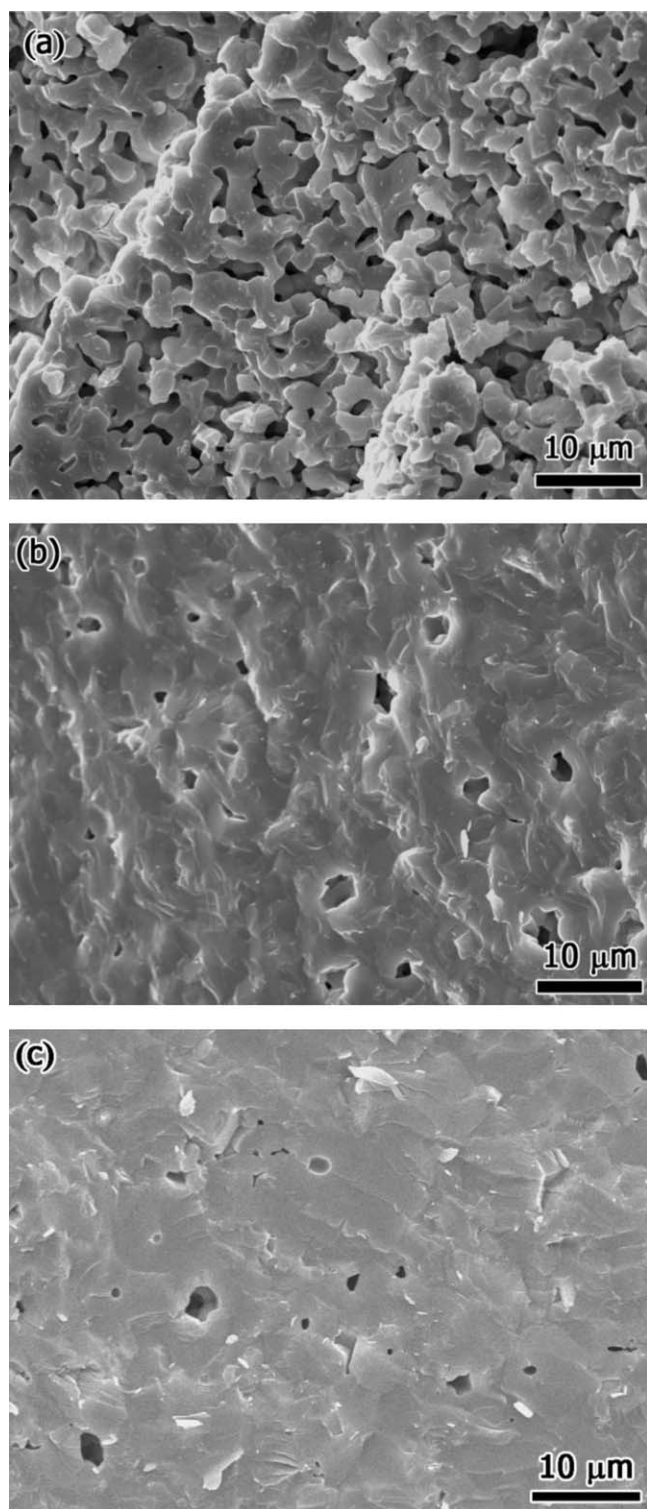
Fig. 9. SEM micrographs of fracture surfaces of wollastonite sintered at different temperatures: (a) 1100 °C, (b) 1150 °C and (c) 1200 °C for 2 h.

pore decreased with sintering temperature which resulted from the removal of open pores after sintering at high temperature.

The bending strength of sintered wollastonite materials is given in Table 1. The bending strength of wollastonite materials sintered at 1100 °C was 27 MPa and the maximum value of 53 MPa was attained in the wollastonite materials sintered at

1250 °C. The bending strength of sintered wollastonite in this study was comparable to that reported for wollastonite prepared by precipitation method.[4]

4. Conclusion

Wollastonite was successfully synthesized from the mixture of eggshell and silica by microwave assisted solid-state reaction. The results showed that the mixing ratios had an effect on the synthesis and the appropriate molar ratio of CaO and SiO_2 was 1:0.8. The single phase α-wollastonite was obtained after 10 min heating at relative lower temperature (1100 °C) that required for conventional synthesis. The use of microwave could reduce both the processing temperature and time needed to form α-wollastonite. The microwave method found to be simple and fast for wollastonite synthesis.

Acknowledgements

References

1. Yun Y-H, Yun S-D, Park H-R, Lee Y-K, Youn Y-N. Preparation of β-wollastonite glass–ceramics. *J Mater Synth Process* 2002;**10**: 205–9.
2. Nour WMN, Mostafa AA, Ibrahim DM. Recycled wastes as precursor for synthesizing wollastonite. *Ceram Int* 2008;**34**:101–5.
3. Lin K, Chang J, Lu J. Synthesis of wollastonite nanowire via hydrothermal microemulsion methods. *Mater Lett* 2006;**60**:3007–10.
4. Lin K, Zhai W, Ni S, Chang J, Zeng Y, Qian W. Study of the mechanical property and in vitro biocompatibility of $CaSiO_3$ ceramics. *Ceram Int* 2005;**31**:323–6.
5. Sreekanth Chakradhar RP, Nagabhushana BM, Chandrappa GT, Ramesh KP, Rao JL. Solution combustion derived nanocrystalline macroporous wollastonite ceramics. *Mater Chem Phys* 2006;**95**:169–75.
6. Carrodeguas RG, De Aza AH, De Aza PN, Baudín Jiménez J, López-Bravo A, Pena P, et al. Assessment of natural and synthetic wollastonite as source for bioceramics preparation. *J Biomed Mater Res* 2007;**83A**:484–95.
7. Lin K, Chang J, Chen G, Ruan M, Ning C. A simple method to synthesize single-crystalline β-wollastonite nanowires. *J Cryst Growth* 2007;**300**:267–71.
8. Wang H, Zhang Q, Yang H, Sun H. Synthesis and microwave dielectric properties of $CaSiO_3$ nanopowder by the sol–gel process. *Ceram Int* 2008;**34**:1405–8.
9. Long L, Zhang F, Chen L, Chen L, Chang J. Preparation and properties of β-$CaSiO_3$/ZrO_2 (3Y) nanocomposites. *J Eur Ceram Soc* 2008;**28**:2883–7.
10. Ibanēz A, Pena JMG, Sandoval F. Solid-state reaction for producing β-wollastonite. *Ceram Bull* 1990;**69**:374–8.
11. Clark DE, Folz DC, Folgar EC, Mahmoud MM. *Microwave solution of ceramic engineering*. Massachusetts: The American Ceramic Society; 2005.
12. Atong D, Clark DE. Ignition behavior and characteristic of microwave—combustion synthesized Al_2O_3–TiC powders. *Ceram Int* 2004;**30**:1909–12.
13. Atong D, Clark DE. Microwave-induced combustion synthesis of TiC–Al_2O_3 composites. *Ceram Eng Sci Proc* 1999;**20**:111–8.
14. Atong D, Clark DE. Synthesis of TiC–Al_2O_3 composites using microwave-induced self propagating high temperature synthesis (SHS). *Ceram Eng Sci Proc* 1998;**19**:415–21.

15. Zhao C, Vleugels J, Groffils C, Luypaert PJ, Van der bliest O. Hybrid sintering with a tubular susceptor in a cylindrical single-mode microwave furnace. *Acta Mater* 2000;**48**:3795–801.

16. Ramesh PD, David B, Schachter L. Use of partially oxidized SiC particle bed for microwave sintering of low loss ceramics. *Mater Sci Eng A* 1999;**266**:211–20.

17. Vichaphund S, Thavorniti P. Synthesis wollastonite from eggshell waste. Patent Application No. 1001000306, Thailand, 2010.

18. Rivera EM, Araiza M, Brostow W, Castano VM, Díaz-Estrada Hernández R, Rodríguez JR. Synthesis of hydroxyapatite from eggshells. *Mater Lett* 1999;**41**:128–34.

19. Tai WT, Yang JM, Lai CW, Cheng YH, Lin CC, Yeh CW. Characterization and adsorption properties of eggshells and eggshell membrane. *Bioresour Technol* 2006;**97**:488–93.

20. Chojnacka K. Biosorption of Cr(III) ions by eggshells. *J Hazard Mater B* 2005;**121**:167–73.

21. Kotsis I, Balogh A. Synthesis of wollastonite. *Ceram Int* 1989;**15**: 79–85.

22. Wang H-P, Xu S-Q, Lu S-Q, Zhao S-L, Wang B-L. Dielectric properties and microstructures of $CaSiO_3$ ceramics with B_2O_3 addition. *Ceram Int* 2009;**35**:2715–8.