

Low temperature production of wollastonite from limestone and silica sand through solid-state reaction

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ABSTRACT

Wollastonite was produced using solid-state reaction from limestone and silica sand. Limestone containing a high percentage of CaO (55.10%) and silica sand with 99% SiO₂ were used as starting materials. The ratios of limestone/sand used were 1:1, 2:1 and 3:1 with various firing temperatures, namely 1100, 1200, 1300, 1400 and 1450 °C. The raw materials and fired products were characterised for mineral phases, chemical composition of content such as CaO, SiO₂ and loss on ignition (LOI), density and microstructure. CaSiO₃ with an α-phase was detected at firing temperatures as low as 1300 °C, together with olivine and quartz phases, obtained from a 1:1 ratio. No α-CaSiO₃ was detected for 2:1 and 3:1 ratios; only olivine and larnite phases were present. The density of the product was 2.93 g cm⁻³, which is close to the theoretical value, with a specific surface area of 3.23 m² g⁻¹. This study shows that the Malaysian limestone and silica sand can produce good properties of wollastonite materials.

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1. Introduction

Calcium silicate is an industrial material that has many uses in industries, but the most important applications are in building materials such as glass, cement, bricks and tiles for roofs, fireproof ceilings and building board. Calcium silicate consists of four types of compound, i.e. monocalcium silicate (CaSiO₃), dicalcium silicate (Ca₂SiO₄), tricalcium silicate (Ca₃SiO₅) and tricalcium disilicon heptaoxide (Ca₃Si₂O₇), all of which are obtained by reacting various molar ratios of calcium oxide (CaO)/silicon dioxide (SiO₂), namely 1:1, 2:1, 3:1 and 3:2. The transformation of mineral phases of the calcium silicate material varies according to the molar ratio, which depends upon the melting point of limestone (825 °C) and silica sand (1650 °C) [1–3].

Wollastonite, also known as monocalcium silicate (CaSiO₃), has been synthesised using a few techniques such as precipitation,

sol-gel, solid-state reaction, etc. Precipitation is the most frequently used technique, with sintering temperature between 900 and 1250 °C, which produce the amorphous β-phase of wollastonite [4–8]. Production of β-wollastonite using solid-state reaction has been reported by several researchers [4,9]. They used reagent grade limestone and natural silica sand as raw materials with a sintering temperature of 1400 °C for 2 h. De la Casa-Lillo et al. [10] used the sol-gel technique to produce wollastonite and obtained a stable phase of α-wollastonite (pseudowollastonite) at 1400 °C.

Malaysia has an abundance of limestone and silica sand resources. To the best of our knowledge, nobody has used Malaysian limestone and silica sand to produce wollastonite materials. Malaysian limestone is used mainly in construction and the agricultural industry, while Malaysian silica sand is widely used in the glass industry. Therefore, it is essential to diversify the potential usage of Malaysian limestone and Malaysian silica sand into various applications as a source for implantable biomaterial, as reported by Caruta [11] and Kaifi et al. [12]. According to previous studies, calcium silicate materials produced from a mixture of limestone and silica sand are found to possess bioactive properties in a simulated body fluid solution environment, especially the silicate mineral chains wollastonite (CaSiO₃) and diopside (CaMgSi₂O₆) [4,13].

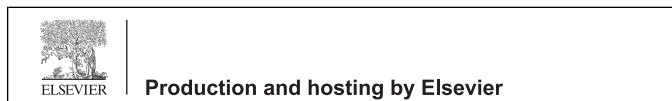
In the present study, we attempted to produce wollastonite material using limestone and silica sand as they are easily obtained and cheap sources of starting materials that can be applied in the biomedical field at a later date. A solid-state technique with various limestone/silica sand ratios and different firing temperatures was employed for producing the wollastonite materials at a low temperature. The phases present and microstructures of the final fired materials are reported.

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2. Materials and methods

Limestone and silica sand were obtained from Malaysia with as-received particle sizes of 10 mm and 600 μm , respectively. Both the raw materials were sampled and ground separately using a ball mill to obtain a finer particle size, i.e. of 100% passage through a $\sim 70\text{-}\mu\text{m}$ sieve.

Calcium silicate material was prepared from a mixture of limestone (CaCO_3) and silica sand (SiO_2) via the solid-state route according to the following equation:



Limestone/sand molar ratios of 1:1, 2:1 and 3:1 and firing temperatures of 1100 $^\circ\text{C}$, 1200 $^\circ\text{C}$, 1300 $^\circ\text{C}$, 1400 $^\circ\text{C}$ and 1450 $^\circ\text{C}$ were used in this study. The mixed powders were placed in a box furnace (MODUTEMP) and heated at a ramping rate of 5 $^\circ\text{C min}^{-1}$ for up to 4 h. The heated powders were then cooled to room temperature and ground for 30 min using a ball mill to obtain a finer powder.

The raw materials and final products were characterised for particle size distribution using a laser particle sizer (FRITSCH), phase identification using X-ray diffractometry (XRD) (BRUKER D8 Advanced) with $\text{CuK}\alpha$ radiation, analysis of CaO content using a titrimetric method with a standard solution of ethylenediaminetetra-acetic acid disodium salt (EDTA) and gravimetric method for SiO_2 and loss on ignition (LOI) content through the dissolution process and wet loss, respectively. Density was measured using pycnometer (Ultrapycnometer 1000) and morphology was examined using a scanning electron microscope (FESEM, Supra 40). The impurity contents were carried out by using inductively coupled plasma spectroscopy (Perkin-Elmer Optima 5300 AES).

3. Results and discussion

3.1. Characteristics of raw materials

Limestone granules and silica sand were ground for different periods to obtain a particle size that could completely pass the $\sim 70\text{-}\mu\text{m}$ sieve. Limestone had to be ground for an hour to get a median size (d_{50}) of 11.57 μm , while silica sand had a median size (d_{50}) of 12.28 μm after 2 h of grinding. By performing the grinding process separately, a uniform degree of liberation was achieved which involved the reduction of a similar particle size and resulted in isolation of minerals of the limestone and silica sand [14]. Table 1 shows the particle size distribution of the raw materials.

Fig. 1 shows the XRD patterns of the raw material, and consists of calcite from limestone and quartz from silica sand; both of these have a hexagonal structure. The results of CaO, SiO_2 , LOI, density and specific surface area analyses are tabulated in Table 2. The obtained CaO (55.10%) and SiO_2 (99%) contents show that the limestone and silica sand used in this study were from high-grade material [15]. The LOI content of the limestone of 43.3% and silica sand of 0.24% revealed the decomposition of carbonates from limestone and also showed that elimination of volatile matter, such as water hydration and organic materials, had occurred [15]. The obtained limestone had a density of 2.73 g cm^{-3} and silica sand of 2.65 g cm^{-3} , which are close to their typical densities of 2.71 g cm^{-3} and 2.65 g cm^{-3} , respectively [1,3]. The acquired specific surface

Table 1

Particle size distribution of the raw materials.

Particle size (μm)	Cumulative (%)	
	Limestone	Silica sand
1	4.76	3.13
2	13.23	11.53
5	28.95	27.9
10	45.83	44.19
20	69.09	67.65
30	86.53	86.41
50	99.34	99.61
70	100	100
100	100	100
150	100	100
200	100	100

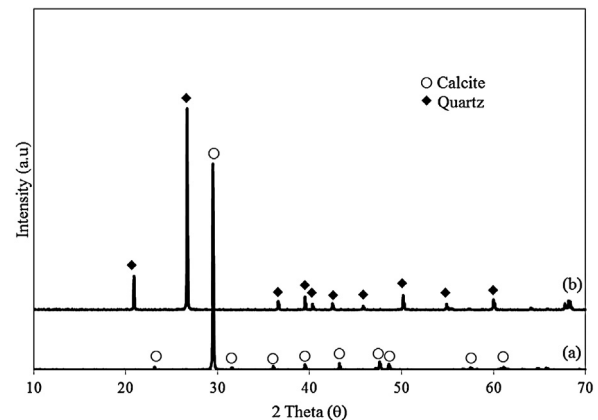


Fig. 1. XRD patterns of the raw materials: (a) limestone and (b) silica sand.

area was not very different for the raw materials: 0.99 $\text{m}^2 \text{g}^{-1}$ for limestone and 0.83 $\text{m}^2 \text{g}^{-1}$ for silica sand; this was because both the raw materials were ground and passed through a $\sim 70\text{-}\mu\text{m}$ sieve. Therefore, it can be concluded that the specific surface area was affected by the particle size obtained.

Fig. 2 presents the SEM micrographs of raw materials, limestone and silica sand after the grinding process. It can be seen that neither of the starting materials had a particular shape or size. EDX analysis confirms the presence of Ca, O and C peaks as the main elements in limestone, and Si and O in silica sand (Fig. 2).

3.2. Characteristics of fired products

X-ray diffraction analysis of mixed limestone and silica sand at different molar ratios, fired in the range of 1100–1450 $^\circ\text{C}$, is shown in Fig. 3. It is noted that after the firing process, X-ray patterns showed that all of the final products were in the crystalline phase. The calcite phase no longer existed at any firing temperatures, while quartz was still detected at 1100 $^\circ\text{C}$ and 1300 $^\circ\text{C}$ at a $\text{CaCO}_3/\text{SiO}_2$ molar ratio of 1:1. This is because SiO_2 has a high melting temperature of around 1600–1725 $^\circ\text{C}$. From the XRD results, no SiO_2 was detected at 1450 $^\circ\text{C}$; therefore, we can conclude that it had completely melted at 1450 $^\circ\text{C}$ with the assistance of limestone that served as a flux material and further lowered the melting point of silica sand [1,3].

Table 2

CaO, SiO_2 , LOI, density and specific surface area of the raw materials.

Material	CaO (%)	SiO_2 (%)	LOI (%)	Density (g cm^{-3})	Specific surface area ($\text{m}^2 \text{g}^{-1}$)
Limestone	55.10	–	43.30	2.73	0.99
Silica sand	–	99.00	0.24	2.65	0.83

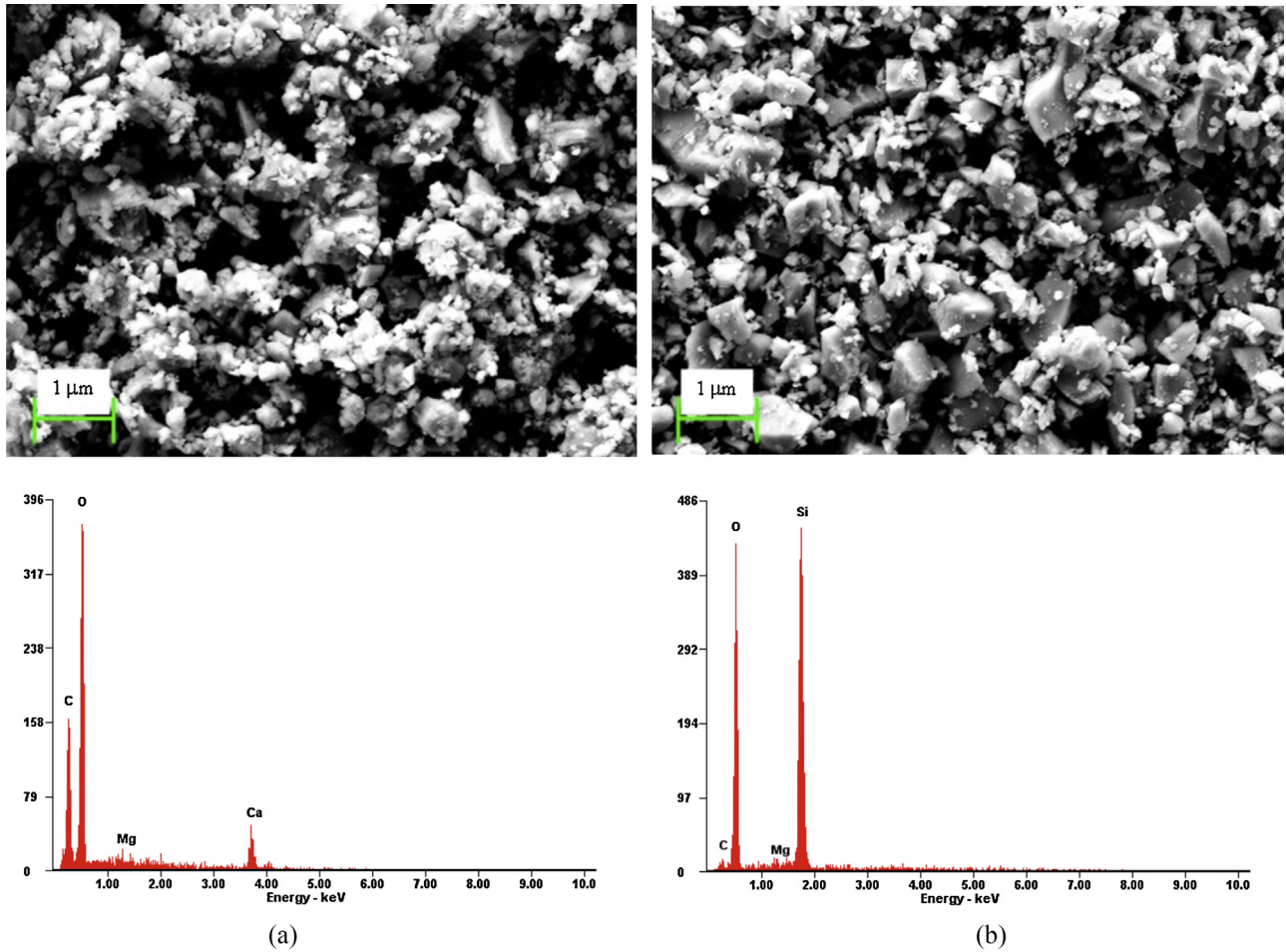
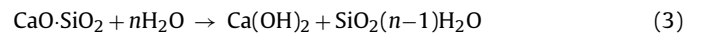


Fig. 2. SEM micrographs and EDX spectrums of the raw materials: (a) limestone and (b) silica sand.

At a low firing temperature (1100 °C), reaction between limestone and silica sand was not fully complete, and mineral phases such as portlandite, quartz and olivine were obtained. As the firing temperature increased, all of these mineral phases transformed to

other stable phases, such as pseudowollastonite at 1450 °C [2]. In this study, the pseudowollastonite phase was observed as early as 1300 °C for the stoichiometric mixture of limestone and silica sand of 1:1 proportion.

A few new mineral crystalline phases, such as portlandite [Ca(OH)₂], larnite (Ca₂SiO₄) and olivine [Ca₂(SiO₄)], can be obtained at particular firing temperatures. According to Lea [2], portlandite and larnite minerals are usually found at low firing temperature through the following reactions:



Larnite was phase-detected at molar ratios of 2:1 and 3:1 at 1450 °C together with the olivine phase. Neither larnite nor olivine phases were observed at a CaCO₃/SiO₂ molar ratio of 1:1 at any firing temperature. The formation of larnite and olivine is in agreement with the work done by Chen et al. [16], and Wesselsky & Jensen [17] reported that the phases exist at higher molar ratios of limestone/silica sand, i.e. 2:1 and 3:1. No α-wollastonite phase was detected at the molar ratio of 2:1 and 3:1. Pure calcium silicate material in the crystallite mineral phase of wollastonite, larnite and allite were not found in Malaysia [18].

The main components obtained from the fired products at a molar ratio of 1:1 were CaO, SiO₂ and LOI, and are displayed in Figs. 4 and 5. The CaO and SiO₂ contents increased as the firing

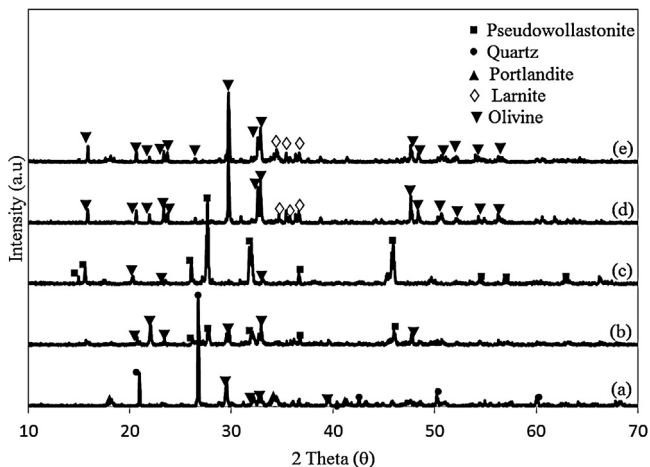


Fig. 3. XRD patterns of CaCO₃/SiO₂ final products at different molar ratios and firing temperatures: (a) 1:1, 1100 °C; (b) 1:1, 1300 °C; (c) 1:1, 1450 °C; (d) 2:1, 1450 °C and (e) 3:1, 1450 °C.

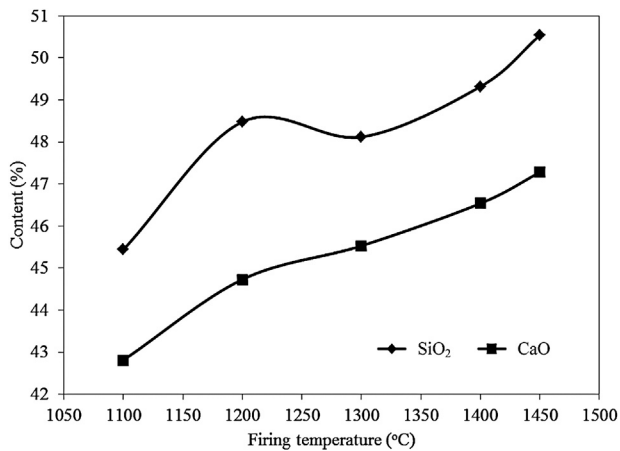


Fig. 4. CaO and SiO₂ content of the final products after firing at different temperatures at a molar ratio of 1:1.

temperatures increased, while LOI decreased with the increasing temperature. Consequently, the purity of the calcium silicate produced was influenced by the chemical reaction between limestone and silica sand that occurred at each firing temperature. Nevertheless, the LOI content was more affected by the decomposition of limestone and the removal of volatile materials produced from the firing process [15]. At 1450 °C, a complete chemical reaction between limestone and silica sand was obtained, with CaO, SiO₂ and LOI contents finally reaching values close to commercial grade in the range of 43.0 to 47.7%, 49.5 to 53.0% and 0.5 to 2.1%, respectively [19].

Density of the fired products at a molar ratio of 1:1 increased with temperature (Fig. 6) and was highly influenced by the sintering temperature and purity of the raw materials, limestone and silica sand [20]. At 1450 °C, α-wollastonite was produced with a density approaching its typical density of 2.86–3.09 g cm⁻³ [21]. Morphology of the obtained α-wollastonite was a needle-like structure (Fig. 7a) and the existence of Ca, Si and O elements in the EDX spectrum confirmed the formation of wollastonite (Fig. 7b).

The impurity of the obtained α-wollastonite (Table 3) indicated that the main heavy metal ions arsenic (As), cadmium (Cd) and lead (Pb) had fulfilled the requirement of ASTM F1538-03 standard

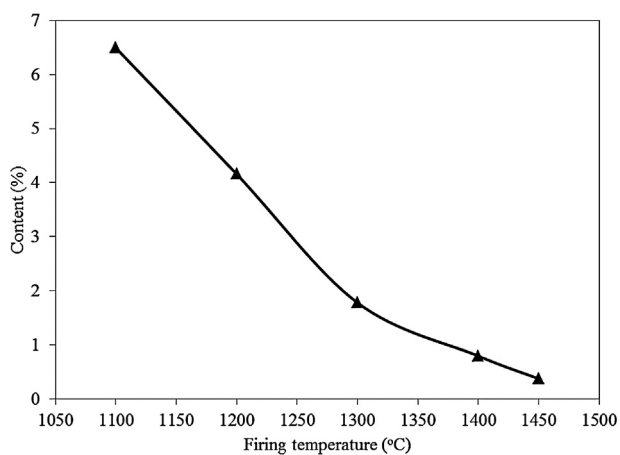


Fig. 5. LOI content of the final products after firing at different temperatures for molar ratio 1:1.

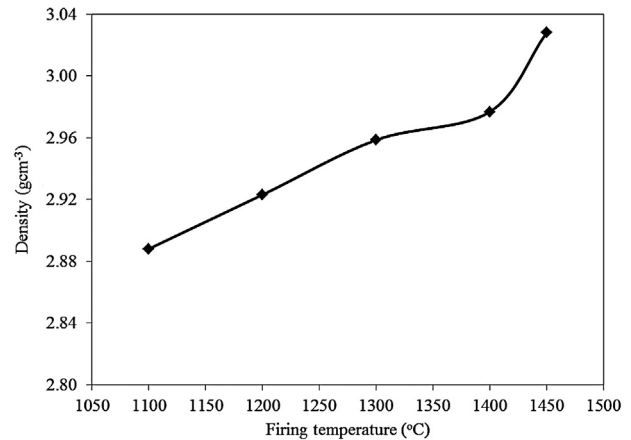
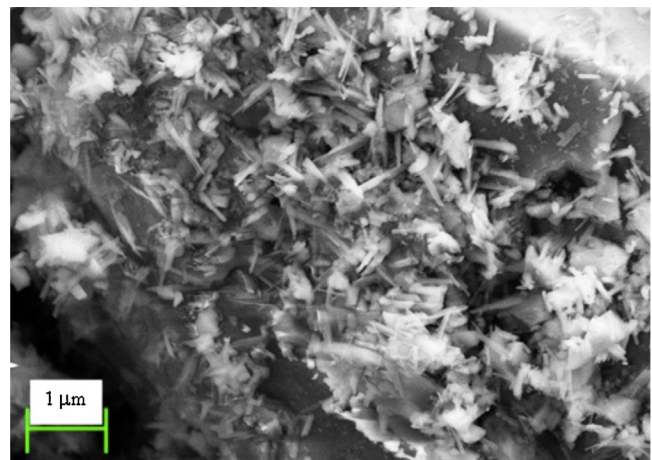
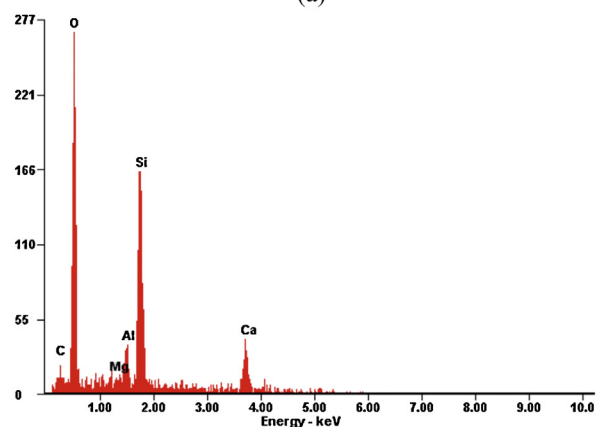


Fig. 6. Density of final products after firing at different temperatures for molar ratio 1:1.

specification [22] to be used as a biomaterial. No mercury (Hg) was detected in the obtained α-wollastonite. According to the standard specification, the permissible levels of As, Cd, Hg and Pb in the biomaterial field should not exceed 3, 5, 5 and 30 ppm, respectively [23,24]. The other elements present in the obtained α-wollastonite also confirmed that the raw materials used in this study naturally exist in low-grade impurity contents [23,24].



(a)



(b)

Fig. 7. (a) SEM micrograph and (b) EDX spectra of α-wollastonite produced.

Table 3The impurity contents of α -wollastonite produced at 1450 °C at molar ratio 1:1.

Element	Content (ppm)
Ag	1.441
Al	3845
As	1.793
B	6348
Ba	2.514
Cd	0.067
Ce	1.706
Co	0.023
Cr	219.7
Cu	3.593
Fe	290.2
K	1671
Lu	0.070
Mg	4199
Mn	36.12
Ni	80.29
P	57.71
Pb	0.047
Sn	0.564
Ti	142.4

4. Conclusion

Calcium silicate material was successfully synthesised from local limestone and silica sand using a solid-state reaction. The α -wollastonite phase was fully obtained at a limestone/silica sand molar ratio of 1:1, sintered at 1450 °C for 4 h, with a dense microstructure and olivine as a minor phase. Purity of the raw materials, molar ratio of limestone/silica sand and firing temperature all had an influence on the final product of calcium silicate materials. Higher molar ratios of 2:1 and 3:1 produced calcium silicate materials consisting of olivine and larnite phases. The study shows that the melting point of the silica sand was successfully reduced by the limestone, which acted as a flux and formed α -wollastonite at low temperatures.

Acknowledgements

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