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# SYNTHESIS AND CHARACTERIZATION OF WOLLASTONITE GLASS-CERAMICS FROM EGGSHELL AND WASTE GLASS

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## ABSTRACT

*Abundance of waste products disposed by communities has huge environmental impacts which lead to serious problems. Some waste products such as eggshells (ES) and soda lime silica (SLS) glass waste can be used as CaO and SiO2 resources to bring on new potentially $CaSiO_3$, wollastonite glass ceramics (WGC) materials. Three samples labelled as S1, S2 and S3 with different compositions, each with of ES (15, 20, 25 weight%) and SLS glass (85, 80, 75 weight%) respectively, were prepared via solid state reaction method. All the samples were sintered at 800°C, 900°C and 1000°C. The elemental analysis of the raw materials and the WGC samples has been determined using the X-Ray Fluorescence (XRF) system where the experimental results show that the samples were mainly contained of CaO and $SiO_2$. The density of the WGC samples increase linearly with the sintering temperatures. The XRD results reveal that the optimum crystalline phase of the WGC samples was at around 900°C.*

Waste, depending on the type of material, is defined as an unwanted or undesired material that may consists of the leftover from the manufacturing process or from community and family activities. Most food waste contains valuable minerals that could function as raw materials for the production of glass, ceramic and glass-ceramic [1]. $SiO_2$, CaO, $K_2O$, $Na_2O$, MgO, $Al_2O_3$, $P_2O_5$ are the examples of minerals present in the common food wastes. The eggshell contains of 94% of $CaCO_3$, 1% of $MgCO_3$, 1% $Ca_3(PO_4)_2$ and 4% of organic matter [2-3]. While soda lime silicate (SLS) glass is the most common type of glass usually used for windowpanes and food containers. Common glasses are primarily composed of silica in the range of 70.9 to 80.0 weight % and other oxide elements such CaO, $Na_2O$, $K_2O$, and $Al_2O_3$, which influence the properties of glass [4]. Hence the household wastes such as eggshells (ES) and soda lime silica (SLS) glass waste can be used as the prime source of calcium oxide (CaO) and $SiO_2$ respectively in order to form new product such as wollastonite glass ceramics (WGC) [5-6]. In this work, waste soda lime silica, SLS glass bottles and waste hen eggshells had been used as the based materials in order to form WGC via solid state reaction. The objectives of the research are to produce wollastonite glass-ceramic (WGC) from the ES waste and SLS glass bottle and also to study the effect of heat treatment on the physical properties of WGC.

The ES waste and the SLS glass bottles collected from the kitchen were washed thoroughly with water to remove the contaminants present and then were left dried at room temperature for 72 hours. The cleaned and dried ES then, were being crushed by using plunger and hammer then were ground into powder by using mortar and pestle. The ES powder had undergo two heat treatments (calcination) by using the electric furnace. The first heat treatment was at 500°C for 3 hours in order to remove the unwanted elements presents in the ES powder and the second heat treatment was at 900°C for 6 hours in order to gain the elements needed to produce wollastonite. Thermal analysis during the first heat treatment process may remove the $H_2O$, $CO_2$ and $NO_2$ in the ES while the second heat treatment will produce the mineral desired for glass ceramic batching materials [1, 3]. The main substances exist in ES is $CaCO_3$, which will be converted into CaO through the calcination process. The raw ES powder were calcined (heat treatment) in order to eliminate the impurities present [1]. When the ES were calcined, the color of EG turned to dark black and then white after a few hours of calcination process. The color changed showed that most of the organic materials were burnt out [7]. The result of the calcination showed that the $CaCO_3$ turned into CaO. The percentage of CaO present was 99.14%. The second heat treatment was done at 900°C for 6 hours. The amount of CaO observed was comparable from before but it still remained as the highest element that existed in the ES powder. Referring to Cornejo *et al.* [1], the second heat treatment was needed to produce mineral desired for the glass batching. The heated ES powder had been screened manually through a sieve to obtain an ideal size which is 63 µm. The cleaned SLS glass bottles were also crushed by using plunger and hammer and then were ground by using mortar and pestle. The SLS poweders were also sieved to obtain 63 µm grain size. The ES powder was mixed with the SLS glass powder. In order to get the homogeneous powder mixture, the mixture that consist of 15 wt%, 20 wt% and 25 wt% of CaO obtained from EG and 85 wt%, 80 wt % and 75 wt% of SLS glass powder, respectively, were mixed in the rotary ball mill for 24 hours. The powder mixture was blended with the organic binder polyvinyl alcohol (PVA) and was pressed into pellets. The pellets formed were in 13 mm diameter then undergoes a sintering process at three different temperatures, which were 800°C, 900°C and 1000°C for 2 hours each. One pellet from each composition would be left at room temperature as a marker. Each batch glass-ceramic samples S1 contains 15 weight percent of ES powder and 85% SLS glass, whereas sample S2 and S3 contain 20 wt%, 25wt% of ES powder and 80wt% and 75wt% of SLS glass powder respectively. Table 1 shows the percentage of ES and SLS added in each batch or green WGC sample that will be undergone heat treatment. The density of each the WGC pellet was determined according to the Archimedes principle, while the XRF measurement was performed by using an Energy Dispersive X-ray Spectrometer of model EDX-270 Shimadzu [8]. The X-ray Phillips (Model PW 1830) was used to identify the structure of each WGC samples. The results obtained were then extracted by using X'Pert Highscore software [9]. Table 1 and the Figure 1 depict the densities of the S1, S2 and S3 at different sintering temperatures. It can be clearly seen that as the sintering temperature increased, the densities of all WGC samples increased. At room temperature, 27°C, the samples have densities around 2.5 g/cm$^3$ which are closer to the density of SLS glass. As the WGC samples had been sintered at higher temperatures, starting from 800°C until 1000°C, the densities of S1, S2 and S3 samples kept rising in the range of 2.7 g/cm$^3$ at 800°C, 2.9 g/cm$^3$ (900°C) and reached around 3.0 g/cm$^3$ at 1000°C.

**Table 1.** Densities of the WGC samples at different temperatures

| Sample code | ES (wt%) | SLS (wt%) | Density (g/cm$^3$)at different temperature ($\pm$0.01 °C) | | | | Data analysis | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 27 | 800 | 900 | 1000 | Gradient, *a* | y-intercept, c | Percentage change, Δ ρ (%) |
| S1 | 15 | 85 | 2.50 | 2.70 | 2.86 | 3.01 | 0.15 | 2.54 | 20.25 |
| S2 | 20 | 80 | 2.52 | 2.75 | 2.90 | 3.07 | 0.16 | 2.58 | 21.77 |
| S3 | 25 | 75 | 2.53 | 2.79 | 2.92 | 3.10 | 0.15 | 2.627 | 22.675 |

The WGC solid samples have well-developed structure will become more dense as the porosity decrease. As the sintering temperature increases, the size of the internal pores decreases, and the value of packing degree increases, which resulting higher density [5]. The analytical data from the linear trend lines of the graphs are also shown in Figure 1. All of the $R^2$ values for all WC samples are in the range of 0.99, which indicates a good fit of the line to the data. The c value which represents the y-intercept and *a* value which indicates the gradient of the graph showed the linear trend. Such high density of WGC samples around 3.0-3.1 g cm$^{-3}$ are closely reaching the bulk density of wollastonite which is around 2.8 to 3.09 g/cm$^3$ [10].

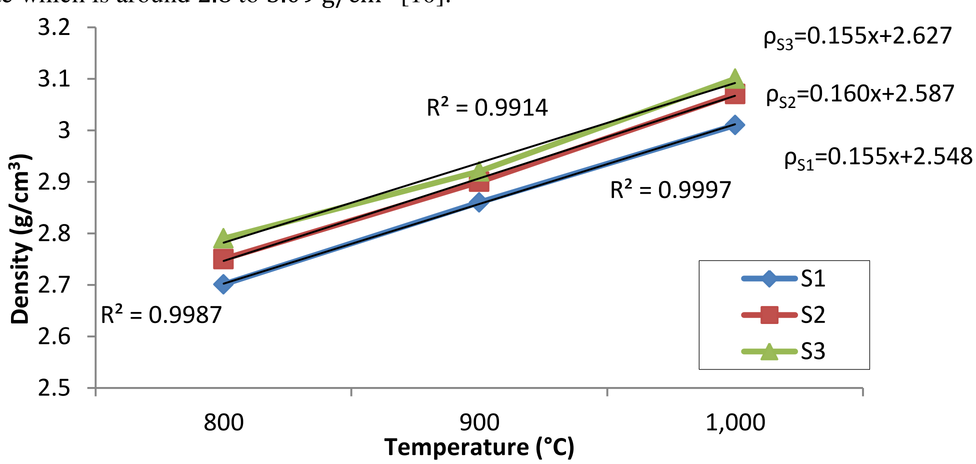


**Figure 1.** Density of the WGC samples at three different temperatures.

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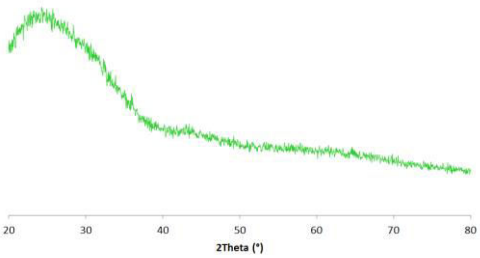
Table 2 presents the percentage of main element contained in the ES at different conditions determined by the XRF measurement. It can be seen obviously that 99.017% of $CaCO_3$ present in the raw ES powder [2]. SLS glass waste contains mainly 61.773 % of $SiO_2$, 20.344 % of CaO and 12.897 % of $Na_2O$. The current finding was agreed with the result presented by Shelby [11] and Bateni *et al.* [4] .

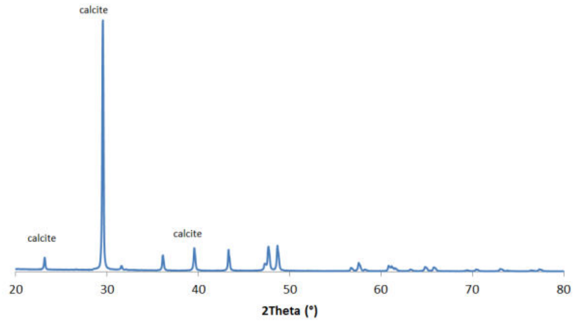
**Table 2.** Percentage of main oxides in each WGC samples at different temperatures.

| Samples | Main oxides | Percentage of oxide at different temperatures (%) | | | |
|---|---|---|---|---|---|
| | | 27°C | 800°C | 900°C | 1000°C |
| S1 | CaO | 65.518 | 59.413 | 53.561 | 57.211 |
| S2 | | 68.617 | 64.347 | 62.613 | 57.769 |
| S3 | | 70.989 | 68.355 | 63.827 | 46.483 |
| S1 | $SiO_2$ | 31.455 | 48.328 | 44.134 | 41.231 |
| S2 | | 28.039 | 33.782 | 35.831 | 38.714 |
| S3 | | 26.986 | 29.811 | 34.113 | 38.552 |

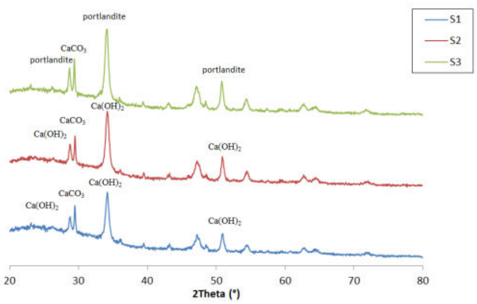
Table 2 shows the percentage of main substances that contained in each sample at room temperature as well as at three different sintering temperatures which were 800°C, 900°C and 1000°C. After being sintered at three different temperatures, it still can be observed that the CaO and $SiO_2$ were still monopolized the samples by being the major oxides existed within the samples. Although the amounts of the cap are slightly higher than $SiO_2$ in each WGC sample, it is believed that the wollastonite ($CaSiO_3$) can still be formed in the glass ceramic phase. This finding is supported through the XRD pattern obtained. Figure 2(a) also presents the XRD pattern of the SLS glass bottle. The XRD pattern shown a widely spread scattering at low angle in range of 20°- 30°, which indicates amorphous of glass sample. This finding was consistent with the finding obtained by Bateni *et al*. [4] where SLS glass possessed short range order and random arrangement of atom. Figure 2(b) illustrates the XRD pattern of the crystallization behavior of raw ES. The pattern shown that the raw ES was in the crystalline phase since the calcite peaks exist within the raw ES. The highest calcite ($CaCO_3$) peak was observed at angle $\theta$=30° and this result was synchronized with the earlier findings by Saeed *et al*. [12] and Arpášová *et al.* [2].



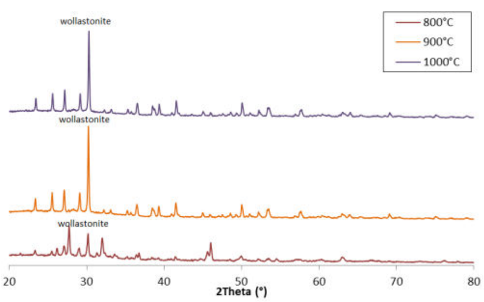

(a) SLS Glass



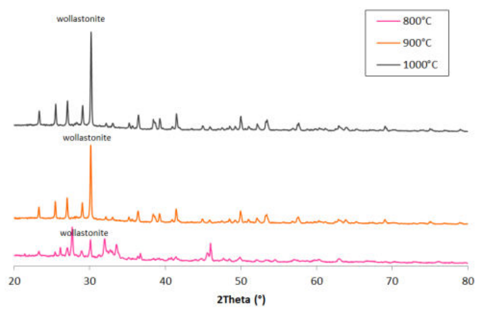

(b) Raw Eggshell (ES)



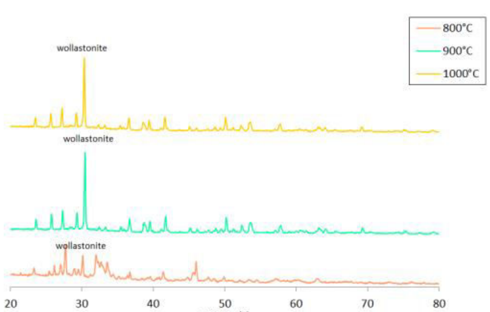

(c) Batch WGC Samples (27$^{o}$C).



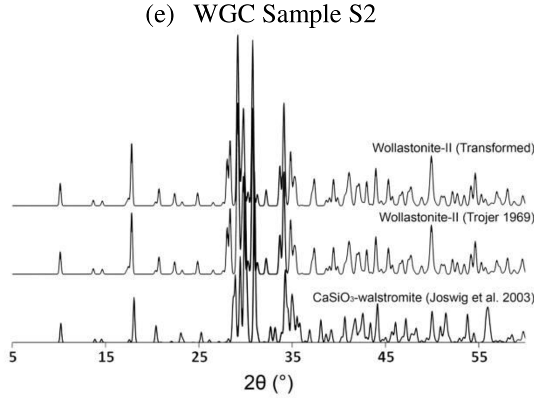

(d) WGC Sample S1




(e) WGC Sample S2




(f) WGC Sample S3




(g)Wollastonite sample taken from Refs: http://ammin.geoscienceworld.org/content/96/5-6/797/F3.large.jpg

**Figure 2.** The XRD patterns of raw ES, SLS and WGC samples at three different temperatures.

Figure 2 (c) also shows the XRD pattern of the ES and SLS batch mixture at room temperature where it can be observed that few peaks corresponding to calcium hydroxide ($Ca(OH)_2$), calcium carbonate or calcite ($CaCO_3$) and portlandite. Portlandite is a rare oxide mineral which naturally occurring form of calcium hydroxide. The XRD patterns of S1, S2, and S3 after sintered at three different temperatures were shown in Figure 2(d) -2(f). It can be noticed that at a higher sintering temperature (more than 900$^{o}$C) the crystalline phases occurred at $\theta$=30° where these peaks are associated with the wollastonite which are comprable to those peak in Figure 2(g).

WGC has been synthesized successfully from ES as the CaO sources and SLS glass bottle as the $SiO_2$ source by using solid state reaction method. The XRF measurement of each WGC samples before and after the sintering process had been analyzed in order to know the percentage of the main elements, CaO and $SiO_2$ that existed within the samples. At temperature beyond 900$^{o}$C, the XRD result of WGC samples revealed the pattern of crystalline phase of wollastonite. As the sintering temperature increased, the density of the WGC samples increased. This was due to the size of the internal pores decreased and hence cause the packing degree increased.

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