Preparation of Sintered Glass-Ceramic from CRT Glass and Red Gypsum Wastes for Tiling Application

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Abstract. This study aims to prepare sintered glass-ceramic (SGC) from a combination of cathode ray tube glass and red gypsum wastes specifically for tiling application. Bentonite clay which acted as a binder was also added to the prepared formulation. The starting materials were milled individually, mixed and compacted into button shape by using a uniaxial hydraulic press machine. The effects of sintering temperature and red gypsum content on the physical-mechanical properties and crystallization behaviour were investigated. The test results revealed that the glass-ceramic sintered at 850 ºC with 20 wt.% of red gypsum gave the best combination of physical-mechanical properties. Modulus of rupture and linear shrinkage were measured at 33.75 MPa and 6.47 %, respectively. Water absorption was low enough and recorded at 0.4759 % while the density was measured at 2.6638 g/cm³. The results also discovered that increasing red gypsum content by 10 wt.% and sintered at similar temperature deteriorate the quality of the glass-ceramic. Therefore, this particular sintered glass-ceramic has the potential to be used as outdoor walkway tile or brick owing to the high physical-mechanical properties, colour suitability as well as low production cost.

1. Introduction
Recycling is important in reducing wastes that cause negative impacts on the environment. Recycling conserves our natural resources and energy, saves landfill space, reduces water and air pollution, and greenhouse gas emissions that cause global warming. In the past 20 years, numerous researches have been conducted to utilize glass and industrial waste to form sintered glass-ceramic for building applications and others. Many have agreed that glass-ceramics manufacturing has been considered as a very effective method for recycling and utilizing many types of industrial waste especially by the sinter-crystallization method. Based on this method (sinter-crystallization), by optimizing the processing parameter and minimizing the powder particles size (enhanced specific surface areas) can cause the densification and crystallization process to complete in a very limited time and at relatively low temperatures. Hence, reducing the cost of waste treatment. Besides processing advantages, the sintering approach may lead to the formation of unusual crystal phases and resulted in glass-ceramic with remarkable mechanical properties. For example, E. Bernardo and his colleagues [1-5] have done a great effort for the last 10 years in demonstrating how various industrial wastes can be recycled to form glass-ceramic via the sinter-crystallization process. They have proved that glass waste (e.g. soda-lime glass and cathode ray tube glass), mining residue, low grade feldspar and lime waste from flume abatement system of the glass industry can be mixed together and recycled to form glass-ceramic with excellent physical-mechanical properties. Their studies show that some of the glass-ceramic samples exhibiting a surface hardness of over 6 GPa and modulus of rupture (MOR) of more than 100 MPa which are higher.
than conventional porcelain stoneware tile or the commercial Neoparies® glass-ceramic tile’s properties. Similar research also was conducted by Maschio and his team [6] using paper mill sludge, glass cullet and natural red clay as main components in a body formulation to produce glass-ceramic via fast firing sintering treatment at 1040-1140 °C. The results suggested that the mixture of powder containing 42 wt.% paper mill sludge, 28 wt.% glass cullet and 30 wt.% natural red clay resulted in the glass-ceramic having good hardness and strength. They recommended that some of the produced glass- ceramics could be used in the construction industry particularly for tiling purposes.

On the other hand, Zhang et al. [7-8] had tried a different approach by adopting a reactive crystallization route to produce glass-ceramic from glass waste. They used a series of combination of kaolin, talc and chemical reagent to synthesize the crystallization promoters and incorporated them into the glass-ceramic body formulation. They managed to fabricate diopside-albite and wollastonite glass-ceramic from soda-lime glass (known for its lower tendency to crystallize) with the aid of crystallization promoter at a temperature of below 950 °C. However, the mechanical properties of the produced glass-ceramic were not as high as that being reported by E. Bernardo and his colleagues. It was also reported recently that a good quality of glass-ceramic had been produced using rice husk ash (RHA) as a silica precursor [9]. Boron oxide/sodium oxide and aluminium oxide/magnesium oxide had been added in the batch formulation to facilitate the melting process and to increase the tendency of forsterite crystal precipitation, respectively. The results obtained showed that it is possible to use RHA to produce glass-ceramic by a sinter-crystallization process obtaining nepheline (Na₂O·Al₂O₃·SiO₂) as the main crystalline phase and forsterite (2MgO·SiO₂) at a temperature as low as 900 °C. The sintered material also showed higher bending strength values and Mohs hardness with respect to commercial glass-ceramics such as Neoparies®. In the Malaysian context, Juoi et al. [10] managed to produce glass composite material (GCM) from incinerated scheduled waste bottom slag (BS) and soda lime silicate waste glass. The effect of BS waste loading on the GCM and the microstructural properties was studied and the results revealed that higher BS waste loading produces GCM with higher porosity, higher water absorption and lower bulk density. In contrast, the Vickers microhardness value and modulus of rupture (MOR) were decreased. In their study, MOR as high as ~70 MPa with a density around 1.9 g/cm³ was achieved with 30 % BS waste loading.

Based on concerns for increasing trend of environmental pollution at the present time, the Mineral Research Centre (MRC) being the only research centre in the field of minerals is taking the opportunity to initiate a repurposing project involving utilization of cathode ray tube (CRT) glass and red gypsum waste by turning them into sintered glass-ceramic which can be applied in construction industry. CRT glass is a glass that primarily found in old television and monitor and it contains up to 25% of lead which make them even harder to recycle owing to the toxic nature of lead. However, the sinter-crystallization method applied in this study is a very effective method to immobilize this hazardous waste by turning it into sintered glass-ceramic which make them fairly stable physically and chemically. Meanwhile, red gypsum (RG) is a waste product during the extraction of titanium (IV) oxide from the ilmenite ores and it comes in the formed of reddish brown semi-solid mud. Therefore, the objectives of this study are: (1) to develop sintered glass-ceramic for tiling application by using recycled cathode ray tube (CRT) glass and red gypsum waste and (2) to examine the effects of sintering temperature and red gypsum content on physical-mechanical properties as well as crystallization behaviour of produced glass-ceramic.

2. Experimental Method

2.1. Materials
The cathode ray tube glass (CRT) and red gypsum (RG) wastes were used in this study (shown in Figure 1). They were sources from PUM Cullet Sdn. Bhd. (Pasir Gudang, Johor) and Tioxide (Malaysia) Sdn. Bhd. (Kemaman, Terengganu), respectively. Both materials were ground to the size of ~75 µm by using mortar grinder. Bentonite clay which is act as a binder was also added to the formulation to bind the powder particles together and aiding in improving the green strength of unfired samples. The chemical composition of the CRT glass, red gypsum and bentonite clay were determined by using Shimadzu XRF-1700 X-ray fluorescence spectrometer and the results are shown in Table 1. XRD analysis for bentonite, CRT glass and red gypsum wastes also been carried out as depicted in Figure 2. As expected, CRT glass
is completely amorphous while red gypsum consists of gypsum as a major mineral phase and ilmenite as a minor phase. On the other hand, bentonite clay consists of quartz, cristobalite and montmorillonite as major mineral phases. In this study, two formulations were prepared as presented in Table 2.

![Figure 1. Starting materials used in this study, (a) CRT glass waste, (b) red gypsum waste and (c) bentonite clay.](image)

| Oxide       | SiO₂ | Na₂O | CaO | MgO | Al₂O₃ | K₂O | SO₃ | Fe₂O₃ | F   | PbO | TiO₂ | Etc. |
|-------------|------|------|-----|-----|-------|-----|-----|-------|-----|-----|------|------|
| CRT Glass (%) | 62.72 | 7.25 | 3.27 | 2.76 | 4.51  | 7.62 | -   | 0.51  | 2.07 | 5.6 | -    | 3.69 |
| Red Gypsum (%) | 3.12 | -    | 32.09 | 1.26 | 0.76  | -   | 30.01 | 24.71 | 0.69 | -   | 6.61 | 1.37 |
| Bentonite (%) | 71.32 | 0.59 | 3.05 | 4.58 | 15.65 | 0.39 | -   | 4.0   | -   | -   | 0.33 | 0.09 |

![Figure 2. XRD diffractogram of starting raw materials.](image)

2.2. Sample Preparation
All materials as shown in Table 2 were dry-mixed in the rotary mixer for at least 5 hours. Approximately 6 - 8 wt. % of water was added to the mixture to aid in the forming process. The samples in button shape were prepared by using a uniaxial hydraulic press machine at a pressing weight of 20 tons. The diameter and thickness of the buttons were approximately 35.5 mm and 10 mm, respectively. The green strength of the unfired buttons was not measured. However, it is essential to note that these buttons were strong enough to be handled, carried and moved.
2.3. Sintering Process
The dry unfired buttons (SGC 1) had undergone a sintering process where the heat was gradually applied to the samples to bind the compacted powder particles. The sintering temperature was set at four different levels namely 750, 800, 850, and 900 °C. In order to investigate the effect of red gypsum content on the properties of glass-ceramic, additional samples (SGC 2) was also prepared and sintered at the same temperature. Sintering time and heating rate were set constant at 30 minutes and 5 °C/min, respectively throughout the experiment. During heating, the temperature was held for 30 minutes at 450 °C to remove the remaining water moisture and organic matters that might present in samples. After the sintering process, samples were let to cool down to room temperature naturally in the furnace. Finally, the sintered glass-ceramic samples were ready to be tested.

2.4. Sample Characterization
The sintered glass-ceramic were characterized in terms of their density, water absorption, linear shrinkage, modulus of rupture (MOR) as well as phases evolution. The density and water absorption of the samples were measured by adopting Archimedes principles and performed according to ASTM C373-88 [11]. Modulus of rupture was determined by using the universal testing machine (Instron 3367). For this purpose, the samples were cut to 30 mm (L) x 15 mm (W) in dimension. The test was carried out by using 20 mm span and 0.5 mm/min crosshead speed [12]. Linear shrinkage was determined by comparing the diameter of the samples before and after the sintering process, while the phase analysis was examined by using X-ray diffraction analyser (Bruker XRD D8 Advance) with step size and analysing range (2θ) of 0.009° and 10° – 70°, respectively. Each quantitative data presented here is an average measurement of at least 5 different samples.

3. Results and Discussion
The prepared SGC 1 (20 wt.% RG) and SGC 2 (30 wt.% RG) are shown in Figure 3. In terms of colouration, it is observed that for both SGC 1 and SGC 2, the intensity of the reddish colour becoming slightly brighter when the sintering temperature was increased from 750 to 900 °C. It is also observed that increasing red gypsum from 20 wt.% to 30 wt.% did not affect much on the colouration of the samples as the reddish colour remains almost similar for every level of temperature. It is believed that the resulting reddish colour of the products was because of the significant presence of iron oxide in the formulation.

### Table 2. Formulation of glass powder to prepare glass-ceramic materials.

| Sample | CRT Glass (wt. %) | Red Gypsum (RG) (wt. %) | Bentonite Clay (wt. %) |
|--------|------------------|-------------------------|----------------------|
| SGC 1  | 65               | 20                      | 15                   |
| SGC 2  | 55               | 30                      | 15                   |

3.1. Physical-mechanical properties
Densification of glass-ceramic is controlled by the viscous flow of the glassy phase and it is greatly related to the amount of glassy phase in the body and its viscosity [13]. In addition, the rate of densification process in the body will slow down when the crystalline phase starts to occur because it reduces the amount of glassy phase and increases the viscosity of the glassy phase, which in turn increases the resistance of viscous flow thus, prevent further densification.
Figure 3. SGC 1 and SGC 2 sintered from 750 to 900 °C.

As shown in Figure 4, for SGC 1, increasing sintering temperature from 750 °C to 800 °C has witnessed a sharp increase of density from 2.3634 g/cm³ to 2.6249 g/cm³. A significant improvement of modulus of rupture (MOR) from 18.93 MPa to 32.60 MPa was also observed. This is mostly attributed to the lower viscous flow resistance of the glassy phase at high temperature and lead to higher densification degree of a body. In addition, the formation of crystal structure would also act as reinforcement to the glassy matrix [7]. Thus, improving the strength of glass-ceramic. Further increase the temperature to 850 °C and subsequently to 900 °C, density was slightly increased to 2.6638 g/cm³ and 2.6837 g/cm³, respectively. At 850 °C, the values of MOR reached its peak at 33.75 MPa before deteriorated to 27.16 MPa at 900 °C. The decline in modulus of rupture is most likely because of the growth of crystalline phases at a higher temperature which in turn enhance the viscosity of the glassy phase and inhibits further densification process as a consequence [14-15]. The microstructure also would
become coarser and more porous owing to the lack of densification and enhanced crystallinity [16]. A similar trend was also observed for SGC 2 whereas the densities were improving as the temperature increased and measured at 2.2340 g/cm$^3$, 2.4247 g/cm$^3$, 2.5305 g/cm$^3$ and 2.6418 g/cm$^3$. The MOR was also increased from 13.72 MPa to 19.70 MPa and subsequently to 20.70 MPa as sintering temperature increased from 750 °C to 850 °C. Though, contrary to SGC 1, instead of slightly falling down, the MOR kept improving to 21.10 MPa at 900 °C indicating that the temperature might be not high enough to encourage crystallization that potentially prevents densification of glass-ceramic body.

As can be seen in Figure 5, the linear shrinkages of the samples were inversely proportional to water absorption as sintering temperature increased from 750 – 900 °C. For SGC 1, the lowest water absorption was measured at 900 °C which is 0.1747 %, improving tremendously from 3.6960 % where it was measured at 750 °C. Upon heating up to 750 °C, the viscous flow of the glassy phase just began and densification was starting to take place at this point. Once the temperatures were increased to 800 °C and subsequently to 850 °C, the viscosity of glassy phase was low enough for the densification to occur at a greater rate and in turn reducing the formation of open pores and lowering its open porosity. As a result, water absorption was improved to 0.6569 % and 0.4759 %, respectively. The linear shrinkage was also enhanced from 3.13 % at 750 °C to 5.98 % at 800 °C and later to 6.47 % at 850 °C. The highest value was measured at 900 °C which is 6.61 %, thus indicated that the degree of densification is maximum at this point and contributed to the lowest value of water absorption as well as the highest linear shrinkage. On the other hand, SGC 2 which contained 30 wt.% of red gypsum also experienced similar results. The water absorptions were improving from 6.3024% at 750 °C to 2.59 % at 800 °C and later to 0.5543 % at 850 °C. The highest value was recorded at 900 °C which is 0.5531 %. The improvement of water absorption is most likely because of the lack of open pores on the surface of the samples due to more rapid densification at higher temperature. Increasing temperature from 750 – 900 °C also resulted in ascending pattern of linear shrinkage where it was measured at 2.43 %, 4.83 %, 5.93 % and 6.97 %, respectively. Comparing SGC 1 and SGC 2, in general, the densities, MOR, water absorption and linear shrinkage for SGC 1 were significantly better than SGC 2 which indicate that the sintering temperature for SGC 2 was not high enough to accelerate densification process due to the presence of the higher amount of red gypsum in SGC 2.
3.2. Crystallization Evolution

Figure 6 shows the phase diffractogram of SGC 1 and SGC 2 during thermal treatment from 750 °C to 900 °C. For both samples, upon heating up to 750 °C, no new crystalline phases were formed except quartz, cristobalite, montmorillonite and gypsum phases that originated from bentonite and red gypsum. Heating further up to 800 °C, new peaks starting to emerge which belong to crystalline phases of diopside, augite and lead oxide. When the temperature was increased to 850 °C, the peaks intensity is becoming stronger and reach its maximum at 900 °C. At 850 °C, new peaks that belong to titanian andradite was formed for both samples. However, it was observed that at 900 °C, the titanian andradite’s peaks intensity for SGC 2 was more noticeable than SGC 1 possibly because of the higher content of red gypsum in SGC 2 as red gypsum contains a fairly significant amount of calcium, ferum and titanium. The formation of lead oxide in crystalline form also means that it is more stable chemically and will hardly leach out over time unlike in amorphous form. It is also believed that the formation of diopside crystal improved the mechanical strength of the glass ceramic as reported by Zhu et al and Hasheminia et al [17-18].

![Phase Diffractogram of SGC 1 and SGC 2](image)

**Figure 6.** Phases evolution of SGC 1 and SCG 2 with increasing sintering temperature from 750 °C to 900 °C

4. Conclusions

In the present research, cathode ray tube (CRT) glass and red gypsum wastes mixed with bentonite clay were converted into sintered glass-ceramic by a simple sinter-crystallization process. Two formulations with a variation of red gypsum content were prepared, pressed into a button shape and sintered at various sintering temperature. The produced glass-ceramic features obtained can be summarized as follows:

- for both SGC 1 and SGC 2, increasing the sintering temperature from 750 °C to 900 °C, the modulus of rupture, density, water absorption and linear shrinkage were improved except MOR at 900 °C for SGC 1 where a slight deterioration was observed
- in general, the modulus of rupture, density, water absorption and linear shrinkage for SGC 2 were noticeably inferior than SGC 1 which could be attributed to the higher content of red gypsum in SGC 2
- sintering a mixture of CRT glass, red gypsum and bentonite leading to the formation of new multi-crystalline phases such as diopside, augite, lead oxide and titanian andradite at a moderate temperature of 800 – 900 °C
- the developed product (particularly SGC 1) has a potential to be used as outdoor walkway tile or brick owing to the high physical-mechanical properties, colour suitability as well as low production cost (waste utilization and low sintering temperature)
5. References

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