Preparation and characterization of glass-ceramic composites from South African coal fly ash

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Abstract. Though fly ash in South Africa has mainly been utilized in the construction industry, a large portion of it is still discarded. Production of glass-ceramic composites through fly ash devitrification has gradually become one of the applications being examined internationally. This study reports the investigation of producing glass-ceramic composites from fly ash and varying quantities of beverage waste glass and magnesium oxide as main raw materials. Glasses were obtained by melting fly ash and its additives using an arc furnace. Based on their behaviour when subjected to differential thermal analysis, the glasses were then crystallised through a double-staged thermal treatment to form glass-ceramic composites. The composition and behaviour of the glass-ceramic composites were investigated using X-ray diffraction, Scanning Electron Microscopy, mechanical and chemical assessments. The crystal content in the glass-ceramic composites increased as the magnesium oxide content was increased. The desired diopside phase decreased with an increased magnesium oxide content and ultimately resulted in the formation of forsterite and anorthite as the major and second major phases respectively. The glass-ceramic composites with lesser amounts of magnesium oxide were chemically and thermally resistant and they also demonstrated high cold compressive strength.

1. Introduction
South Africa has an abundance of coal deposits, and this has led to the country’s reliance on coal for energy generation. Eskom, the energy generation utility depends on the combustion of ±120 million tonnes of pulverised coal per annum for producing 90\% of its electricity and yielding 30 million tonnes of fly ash [1]. During the year 2014-15, Eskom reported that 34.4 million tonnes of ash were produced and only 7 volume\% of it was sold to the construction industry for cement and bricks manufacturing [2]. The remaining quantity was stored in ash dumps or dams which require: lining to prevent seepage of toxic elements contained in the ash into the groundwater, monitoring of groundwater and rehabilitation of the topsoil. These dumps are unsightly and environmentally undesirable resulting in an unprofitable use of land resources as well as a continued financial liability through their long term maintenance. The main commercial utilization of fly ash has been in the construction industry for cement manufacturing due to its cementitious properties. It has also been used as a raw material in brick manufacturing, though the success of new businesses has been a challenge due to its classification as a hazardous waste [2]. Whoever intends to use the fly ash is required by legislation to go through a lengthy process of applying for a Waste Management License, which also is costly. Consequently, the current rate of fly ash production far outweighs its consumption.
Besides its hazardousness, owing to the existence of the trace quantities of toxic heavy metals in its chemical composition, generally, fly ash has substantial amounts of oxides that are key in the ceramic industry. In its molten state, the oxides are categorised as the acidic component as well as the basic component [3]. Silicon dioxide (SiO₂), aluminium oxide (Al₂O₃) and titanium dioxide (TiO₂) form the acidic component and are considered to behave as receptors (network formers). The basic component is formed by calcium oxide (CaO), iron (III) oxide (Fe₂O₃), magnesium oxide (MgO), sodium oxide (Na₂O) and potassium oxide (K₂O). These basic oxides behave as oxygen donors (network modifiers). Additionally, fly ash is partially vitrified with few crystal phases [4] and it can be completely vitrified by melting it with other glass-forming oxides. Consequently, it has been explored as starting material in the production of glass-ceramics [4], [5], [6].

Glass-ceramics are finely structured and multi-crystalline materials (also referred to as advanced or technical ceramics), that are produced by the controlled crystallization (devitrification) of the parent glass. They are partially crystalline. Usually, the microstructure is 50-95 volume% crystalline, with the remainder being an amorphous content [7]. They present an option of combining superior properties of conventional sintered ceramics with the unique characteristics of glasses resulting in physical and mechanical properties such as: high bending strength and hardness, good corrosion as well as chemical, abrasion and high-temperature resistance. They've found use in electrical, magnetic, electronic and optical applications. They are appealing as construction and architectural material or for other specialised technical applications requiring integration of suitable biological and thermo-mechanical properties. Fly ash, if melted at high temperatures with the proper amount of glass additions results in relatively inert glass products. When these glasses are subjected to thermal treatments they are then converted to glass-ceramics with improved mechanical and thermal properties. Moreover, the process is said to yield fly ash reductions of a third to half of the original quantity [8].

Melting fly ash without any additives gave melts that were difficult to handle. Barbieri et al mentioned that melting fly ash with low a SiO₂/Al₂O₃ ratio without any additives have been found to yield glasses with high viscosities at melting temperatures [9]. High amounts of Al³⁺ ions in the ash, act as network formers by replacing the Si⁴⁺ ions and filling tetrahedrally matched spots with charge-balancing alkali or alkaline earth cations [10]. As a result, the degree of polymerization increases causing the viscosity to increase as well. Nevertheless, an increase of the basic oxides counteracts this behaviour by lowering the connectivity of the glassy network and the liquidus temperature. The weakening of the network results in low viscosity. Beverage waste glass was then added to the fly ash as a source of additional SiO₂ and basic oxides like Na₂O and CaO. Their presence increase the chemical and mechanical strength of the final glass-ceramic product. Additionally, dolomite (CaCO₃·MgCO₃) was also added to provide MgO, which facilitates crystallization and improves the thermal resistance of both the parent glasses and the glass-ceramic composites [10]. Moreover, the presence of MgO favours the formation of Diopside (CaMgSi₂O₆) as the major crystal phase [10], which have excellent thermal and mechanical properties [11].

This paper reports the conversion of South African fly ash to glass-ceramics. The effects of varying the quantities of beverage waste glass and analytically pure MgO on the microstructure and properties of the glass-ceramics were also studied.

2. Experimental
2.1. Preparation of materials
Fly ash from Kriel power station, beverage waste bottles and analytically pure MgO were used as raw materials. The chemical composition of fly ash and beverage waste glass were determined through inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectroscopy (AAS). Beverage waste bottles were added as a source of more SiO₂, Na₂O and CaO.
For the production of four parent glasses, the fly ash quantity was kept constant while the MgO and the beverage waste glass varied as indicated in Table 1. The glasses were labelled as per proportions listed in Table 1. The crushed beverage waste glass, fly ash and the MgO were mixed and milled in a laboratory ring pulverizer to increase homogeneity. The raw materials were then packed in alumina crucibles and melted in a large induction furnace at 1550°C for two hours. Thereafter melts were annealed at 550°C for two hours to relieve internal stresses that can potentially cause spontaneous breakage of the glass and subsequently cooled at room temperature.

| Table 1. Proportions of raw material used. |
|------------------------------------------|
| G1 | G2 | G3 | G4 |
|-----------------|--------------|------|------|
| Fly ash (wt %) | 60           | 60   | 60   | 60   |
| Beverage waste glass (wt %) | 40           | 30   | 20   | 10   |
| MgO (wt %)     | 0            | 10   | 20   | 30   |

In order to convert the parent glasses to glass-ceramic composites, the nucleation and crystallization temperature must be determined. Thus differential thermal analysis (DTA) was used and the glass samples were analysed with a Stanton Redcroft STA thermal analyser to 1000°C in the air with a heating rate of 10°C/minute. The glasses were milled to sub 75 microns, and 34 mg of each sample was lightly compacted in a platinum test crucible. Based on the DTA results, a two-staged thermal treatment was employed. The glasses were heated at a rate of 100°C/minute to a nucleation temperature of 750°C and held for 5 hours, thereafter heated to a crystallization temperature of 950°C at a rate of 150°C/minute and held for 20 minutes. Annealing of the samples was at a cooling rate of 450°C/minute to 600°C and the samples were held at the temperature for 2 hours and thereafter cooled to room temperature.

2.2. Characterization of the glass-ceramics

To determine the glass and the crystal content in the glass-ceramic composites, X-ray powder diffraction (XRD) was employed. The analysis was done using a Bruker D8 Advance powder diffractometer, with LynxEye detector and Co-Kα radiation from 3-80° (2θ) with a 0.02° step size. The observed peaks were matched to known minerals or compounds using DIFFRACplus EVA software. Only crystalline materials were detectable and the detection limit for this technique was approximately 3 mass percent. The method is dependent on the diffraction behaviour of the individual phases.

The microstructure of the final products was studied by Scanning Electron microscopy (SEM). A Zeiss EVO® MA15 SEM equipped with Bruker Energy Dispersive X-ray Spectrometer (EDS) and Quantax software were used. The analysis mainly focused on determining the chemical composition of both crystalline and non-crystalline materials by EDS elemental analysis. The backscattered electron (BSE) images were taken to illustrate the phases identified.

2.3. Properties

Numerous South African National Accreditation System (SANAS) accredited methods were used to assess the mechanical and physical characteristics of the glass-ceramic composites. The samples were subjected to a compressive load at room temperature to determine their cold crushing strength based on works procedure WP-308 (Rev 04). Thermal expansions were carried out according to works procedure WP-317 (Rev 02) to determine the fractional change in the size of the samples per degree change in temperature at a constant pressure. A low coefficient of thermal expansion at a high temperature is desired in this instance, which will imply a high thermal shock resistance for the glass-ceramic products. Bulk density by Archimedes was carried out according to works procedure WP-300 (Rev 04). The phase fraction of porosities was quantified using a DSX510 optical microscope. Chemical resistance tests were conducted by immersing unpolished glass-ceramic samples in 10% nitric acid (HNO₃) solution at 25°C for 1 week, 10% sodium hydroxide (NaOH) solution at 25°C for 48 hours and in the water at 25°C for 48 hours.
3. Results and discussions

3.1. Characterization of the glass-ceramics

Table 2 shows the chemical composition of fly ash and beverage waste glass. The elements found in fly ash are commonly reported in their oxide form because the oxide anion is superior in fly ash [3], hence the representation of the results below. The fly ash was classified as “class F” fly ash, with CaO less than 15 wt% and a combination of SiO$_2$+Al$_2$O$_3$+Fe$_2$O$_3$ greater than 70 wt%. A low SiO$_2$/Al$_2$O$_3$ ratio of 1.98 was obtained, which is said to result in melts that are too viscous to pour at the melting temperature [12]. Alkaline earth metal oxides, CaO and MgO were also detected in the fly ash at 7.62 wt% and 1.84 wt% respectively. The beverage waste glass had CaO at 11.87 wt% and MgO at 0.64 wt%. Having dual roles in silicate glasses, the metal oxides loosen the silica network by lengthening a bond between two silica tetrahedra and also breaking the Si-O bonds to reduce the viscosity caused by high polymerization [12]. The beverage waste glass had a significant amount of SiO$_2$, which was also necessary to increase the SiO$_2$/Al$_2$O$_3$ ratio and to ensure high mechanical strength of the glass-ceramic material.

Alkali metal oxides, Na$_2$O and K$_2$O, which break the Si-O bonds were at 12.96 wt% and 0.39 wt% respectively. Na$_2$O is the most effective in reducing the liquidus temperature. However, its addition decreases the chemical durability and the hardness of the obtained parent glass, while increasing the coefficient of thermal expansion [12]. To stabilize the glass melt, small quantities of Al$_2$O$_3$ (1–5 wt%) are required, thus improving the durability of the parent glass and the glass-ceramics [13].

Table 2. Chemical composition of fly ash and beverage waste glass.

| Composition (wt %) | SiO$_2$ | CaO | Al$_2$O$_3$ | MgO | Na$_2$O | K$_2$O | Fe$_2$O$_3$ | TiO$_2$ | Cr$_2$O$_3$ |
|-------------------|---------|-----|------------|-----|---------|--------|------------|---------|------------|
| Fly ash           | 55.95   | 7.62 | 28.40      | 1.84| -       | -      | 4.44       | 1.75    | -          |
| Beverage waste bottles | 71.41   | 11.87 | 1.59    | 0.64| 12.96   | 0.39   | 0.85       | -       | 0.29       |

Nucleating agents, Fe$_2$O$_3$ and TiO$_2$ were detected at 4.44 wt% and 1.75% respectively in the fly ash, whereas the beverage waste glass had Fe$_2$O$_3$ at 0.85 wt% and Cr$_2$O$_3$ at 0.29 wt%. These nucleating agents facilitate the development of small crystals within the bulk glass structure, which will result as nucleation sites for the main crystal phases in the glass-ceramic structure [14].

3.2. Thermal behaviour of the glasses

For effective control of nucleation and crystallization processes in glass-ceramics, the behaviour of the parent glasses under different temperatures must be determined. DTA is used to determine glass transition, crystallization, and melting temperatures of the glass as the temperature is gradually increased. During a physical change such as melting or dehydration of the sample, the temperature is absorbed. This will be denoted by an endothermic peak on the DTA curve. Contrarily when a chemical reaction occurs and the microstructure changes, heat will be released resulting in an exothermic peak on the DTA curve.

DTA results in figure 1 showed that G2 sample had a small endothermic event (shallow dip) at -740°C and a large exothermic event (sharp peak) at -930°C on heat up. G3 and G4 did not show the endothermic events but showed small exothermic events at -950°C on heat up. Due to the limited heating range of up to 1000°C, G1 sample had no endothermic or exothermic events during heat up, just a shallow hump at 900°C. The additional SiO$_2$ from the beverage waste glass made G1 to be stable under the heating range. All the glasses showed the same small endothermic event at -680°C on cooldown.
At 10 wt% MgO, the exothermic event of the G2 was sharp at 930°C but as the MgO content increased from G3 to G4, the peak became shallow and almost disappeared in glass sample 4. This can be attributed to the increased melting temperature of the samples by the addition of MgO. The thermal treatments for all the glasses were then conducted at a nucleation temperature of 750°C which was 10°C higher than the glass transition temperature for G2 and crystallization temperature of 950°C.

![Figure 1. DTA comparison of the glass samples.](image)

3.3. Characterization of the glass-ceramic

XRD analysis in table 3, indicated that after thermal treatments, the glass phase decreased as the MgO content increased. This can be attributed to the fact that increasing the addition of MgO content while decreasing the beverage waste glass content favoured crystallization. The silicate network was broken by MgO which facilitated the formation of crystalline phases. Initially, single silicate chain, pyroxene crystal phases were formed. Diopside (CaMgSi$_2$O$_6$) was formed from G1, composed of only fly ash and beverage waste glass. An introduction of MgO resulted in a slight decrease in diopside phase and a formation of another pyroxene crystal phase, augite ((Ca,Na)(Mg,Fe,Al)(Al, Si)$_2$O$_6$). The pyroxene phase was formed by the dissolution-precipitation process, wherein the dissolution of MgO in the viscous glassy phase initially occurred, and thereafter precipitated as pyroxene [15]. As the MgO content increased to 20 wt%, the diopside decreased with augite transforming to forsterite (Mg$_2$SiO$_4$), which is a mineral of the isolated silicate group called olivines.

At 30 wt% MgO content, the diopside quantity remained constant while forsterite dropped slightly and the glass phase having a notable decrease with the formation of very strong 3-dimensional framework silicates of the plagioclase feldspar group. The crystal phases formed were anorthite (CaAl$_2$Si$_2$O$_8$), dmisteinbergite (CaAl$_2$Si$_2$O$_8$) and bytownite ((Ca,Na)(Si,Al)$_2$O$_8$), indicating limited dissolution of MgO in the glass phase.
Table 3. Main phase compositions of the glass-ceramic composites with different MgO contents.

| Phases               | MgO content (wt %) |
|----------------------|--------------------|
|                      | 0                  | 10     | 20     | 30     |
| Glass phase          | 90                 | 77     | 55     | 24     |
| Pyroxene (diopside)  | 10                 | 8      | 5      | 5      |
| Pyroxene (Augite)    | -                  | 12     | -      | -      |
| Olivine (Forsterite) | -                  | -      | 39.6   | 31     |
| Anorthite            | -                  | -      | -      | 16     |
| Dmisteinbergite      | -                  | -      | -      | 9      |
| Bytownite            | -                  | -      | -      | 14     |

Figure 2 shows SEM images of the glass-ceramic components. By increasing the MgO content from 0-30 wt%, the crystal phases also increased. The phases progressed from the "worm-like" textures of Diopside phase at 40 wt % and 0 wt% of beverage waste glass and MgO respectively, to a dendritic pattern when 10 wt% MgO was introduced. As the MgO content increased to 20 wt%, spinitex texture of acicular olivine phenocrysts (dark grey lines) was observed in the glass groundmass. Ultimately at 30 wt% MgO and 10 wt% beverage waste glass, large euhedral crystals were formed. The plagioclase feldspar group minerals (light grey), anorthite, bytownite and dmisteinbergite were the major phases formed. Forsterite (dark grey) was also observed. As the MgO content was increased, the beverage waste glass content was reduced to make a total mixture of 100 wt %.

3.4. Properties

Figure 3 shows the correlation between the bulk density and the MgO content of the glass-ceramic samples. Addition of MgO increased the bulk density, which stabilized at 10 wt% MgO at 2.72 g/m³. More additions of the MgO resulted in a drop to 2.70 g/m³. As more crystals were formed due to the increased MgO and the reduced glass contents, porosity increased as well from 0.21% at 0 wt% MgO to 5.38% at 30 wt% MgO resulting in less compaction of the structure, hence the decline in the densities. This can be attributed to the decline in the glass-network interconnectivity due to increased crystallisation of more than 70%.
Figure 3. (a) Bulk density and (b) porosity as functions of MgO content.

The cold crushing strength (CCS) of the glass-ceramic in figure 4 increased to a maximum at 10 wt% MgO but dropped afterwards. This can be attributed to increased crystal content and porosity in the glass-ceramic composites that promoted cracking. The maximum CCS achieved was 118.4 Megapascal (Mpa) at 10 wt% MgO content.

Figure 4. Cold crushing strength as a function of MgO content.

The coefficient of thermal expansion (CTE) of the glass-ceramic composites in table 4 increased with the MgO content from 6.8 x 10⁻⁶/°C at 0 wt% MgO to 10.8 x 10⁻⁶/°C at 30 wt%. Increasing of the basic oxides, while reducing the silica content causes the CTE of the resulting glass to increase.

Table 4. Coefficient of thermal expansion (CTE) of the glass-ceramic composites.

| MgO wt% | Melting Temperature | CTE(°C)   |
|---------|---------------------|-----------|
| 0       | 724°C               | 6.8 x 10⁻⁶|
| 10      | 977°C               | 7.5 x 10⁻⁶|
| 20      | >999°C              | 8.9 x 10⁻⁶|
| 30      | >999°C              | 10.8 x 10⁻⁶|
The addition of oxides results in breakage of the connectivity of the glass network, which then softens the structure of glass. The increased CTE indicates that the glass-ceramic composites are less stable to temperatures above 999°C.

Figure 5. Glass-ceramic samples after soakage in distilled water.

After soakage in distilled water and being air-dried, there were no changes in all the glass-ceramic samples shown in figure 5. The traces of rust accumulation on glass-ceramic samples 3 and 4 were identified before its immersion.

Figure 6. Glass-ceramic samples after soakage in HNO₃ solution.

Figure 6 displays the glass-ceramic samples after soakage in an acidic solution. The glass-ceramic samples with 0-20 wt% MgO did not undergo any mass loss, but there were noticeable rust accumulations on the samples after they were air-dried. Glass ceramic sample with 20 wt% MgO had more accumulations than the others. At 30 wt% MgO, the glass-ceramic sample turned greyish and there was a 25% mass loss.

Figure 7. Glass-ceramic samples after soakage in NaOH solution.
In an alkali solution, all glass-ceramic samples were stable as shown in figure 7, except for the glass-ceramic sample with 30 wt% MgO which turned whitish with no mass loss though. The stability of glass-ceramic samples 1, 2 and 3 respectively can also be attributed to the glass phase content which was between 55-90 wt%. The glass network connectivity was stable enough to withstand the alkali attack. However, the glass network connectivity for glass-ceramic sample 4 was weaker due to increased crystallization.

4. Conclusion
The formation of glasses from South African fly ash with the addition of beverage waste glass and magnesium oxide was achieved by mixing and melting them at 1550°C. The parent glasses were easily crystallized through thermal treatment to form glass-ceramic composites with a diopside crystal phase. The conclusions are as follows:

- Addition of 10 wt% MgO seems ideal with less crystallinity and improved mechanical properties.
- The glass-ceramic sample with 10% MgO behaved excellently, displaying the best mechanical properties.
- Increasing the MgO content, while reducing the beverage waste glass resulted in a decline of the glass network connectivity leading to increased crystallization and poor mechanical properties of the glass-ceramic composites.
- The glass-ceramic composite with 10 wt% MgO had a cold crushing strength of 118.4 Mpa, which is comparable to the ones for bricks (50-140 Mpa) and stone (34-248 Mpa).
- The coefficient of thermal expansion at 10 wt% MgO was 7.5 x10-6°C at a melting temperature of 977°C which is comparable to the ones for granite (7.92 x10-6/°C) at melting temperatures 1215-1226°C.

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6. References
[1] Mashau S, Gitari W and Akinyemi A 2018. *Int. J. Environ. Res. Public Health* 15 (12) p 2841
[2] Reynolds-Clausen K and Singh N 2019. *CCGP Journal* 11 pp 10-7
[3] Xuan W, Zhang J and Xia D 2018. *Fuel* 222 pp 523-8
[4] Goodarzi F 2006. *Fuel* 85 (10-11) pp 1418-27
[5] Wang S, Zhang C and Chen J 2014. *J. Mater. Sci. Technol.* 30 (12) pp 1208-12
[6] Barbieri L, Lancellotti I, Manfredini T, Pellacani C, Rincón M and Romero M 2001. *J. Am. Ceram. Soc.* 84 (8) pp.1851-8
[7] Rawlings D, Wu P and Boccaccini R 2006. *J. Mater. Sci.* 41 (3) pp 733-61
[8] Ghouleh Z, Isac M, Guthrie R, Carabin P, and Kozinski J 2009. *8th Int. Conf. on Molten Slags, Fluxes, and Salts* pp 18-21
[9] Barbieri L, Manfredini T, Queralt I, Rincón M and Romero M 1997. *Glass Technol.* 38 (5) pp 165-70
[10] Xuan W, Whitty K, Guan Q, Bi D, Zhan Z and Zhang J 2015. *Fuel* 144 pp 103-10
[11] Park J and Heo J 2002. *Ceram. Int.* 28 (6) pp 689-94
[12] Vargas S, Frandsen F and Dam-Johansen K 2001. *PECS* 27 (3) pp 237-429
[13] Hülsenberg D, Harnisch A and Bismarck A 2008. *Microstructuring of glasses* Vol. 87 R Hull (Berlin: Springer) p 326
[14] Rezvani M, Eftekhar-Yekta B, Solati-Hashjin M and Marghussian V 2005. *Ceram. Int.* 31(1) pp 75-80
[15] Partyka J 2015. *Ceram. Int.* 41 (10) pp 14013-20
[16] Lu Z, Lu J, Li X and Shao G 2016. *Ceram. Int.* 42 (2) pp 3452-9