Development of a new glass–ceramic by means of controlled vitrification and crystallisation of inorganic wastes from urban incineration

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Abstract

This paper reports the results of a study of the feasibility of recycling the solid residues from domiciliary waste incineration by producing a glass-ceramic. The major components of the raw material (TIRME F+L), which was from a Spanish domiciliary incinerator, were CaO, SiO₂ and Al₂O₃ but nucleating agents, such as TiO₂, P₂O₅, and Fe₂O₃ were also present in reasonable amounts. It was found that a relatively stable glass with suitable viscosity could be obtained by mixing 65 wt% TIRME F+L with 35 wt% glass cullet. The heat treatment required to crystallise the glass produced from this mixture, designated TIR65, was nucleation at 560°C for 35 min followed by crystal growth at 100°C for 120 min. The resulting glass-ceramic contained a number of crystalline phases, the most stable being clinoenstatite (MgSiO₃), or perhaps a pyroxenic phase which incorporates Ca, Mg and Al in its composition, and åkermanite (Ca₂MgSi₂O₇). The microstructure contained both fibre-like and dendritic crystals. The mechanical properties were acceptable for applications such as tiles for the building industry.

Keywords: incinerator waste products; microstructure-final; mechanical properties; glass; glass ceramics.

1. Introduction

A major problem in developed countries is the large quantity of domiciliary solid waste (DSW) that is generated and which has to be disposed. For example, in Spain each inhabitant is estimated to produce 1.036 kg⁻¹ day of DSW and the total for that country is about 15×10⁻⁶ tons year [1]. A number of methods are used for disposal of DSW including dumping in the sea and in land-fill sites (63.74%), treatment to produce fertilizer (13.99%) and incineration

(4-67%)[2]. Although dumping is currently the most common disposal method, it is now considered to be environmentally unacceptable and a better strategy is the recycling of DSW. However recycling, which involves selection and classification of the waste materials, is only suitable for 47% of DSW and hence recycling alone cannot solve the disposal problem. The complementary, and growing option in Europe, for the disposal of the non-recyclable fraction (53%) is incineration with energy recovery.

Unfortunately incineration is not without its difficulties. The incineration of DSW leaves large amounts of solid residues, such as bottom ashes, fly ashes and slag, which are produced in the proportion of 20–25 (wt%) of the DSW incinerated. A single large European plant may produce fly ashes at a rate of 10,000 tons year⁻¹. These residues may be toxic due to concentration of heavy metals as well as organic pollutants and consequently they are classified in several European countries as a hazardous waste. Most residues are buried in land-fills, which is a costly and environmentally unsatisfactory procedure. The increasing tendency for waste incineration, together with the rising economic and environmental costs of land-fill disposal, make it essential to search for new options for recovery or recycling of the solid residues from waste incineration.

Glass-ceramic materials, prepared by controlled devitrification of glasses, are used for technological applications ranging from biomedical implants to radomes. Controlled devitrification is only possible for certain glass compositions and usually involves a two stage heat treatment, namely a nucleation stage and a crystallisation stage. In the nucleation stage small nuclei are formed within the parent glass. After formation of stable nuclei, crystallisation proceeds by growth of a new crystalline phase [3]. Knowledge of nucleation and crystallisation parameters is important in the preparation of glass-ceramics with desired microstructures and properties.

Recent papers have reported on the use of vitrification and crystallisation processes to recycle different wastes such as red muds from zinc hydrometallurgy [4], coal fly ash [5, 6], iron blast-furnace slags [7], and even filter dust from waste incinerators[8] but, to the authors' knowledge, no attempt has been made to determine the nucleation and crystallisation parameters of glasses produced from wastes from domiciliary incinerators.

This paper reports the results of a study to characterise the fly ash from a Spanish domiciliary incinerator and to assess the feasibility of producing a glass-ceramic from this fly ash. In particular, the temperature range over which nucleation occurs, the temperature where the nucleation rate is a maximum, and the crystallisation kinetics have been determined together with a preliminary assessment of properties.

2. Materials and Methods

2.1. Raw material

A mixture of the residue from a gas purification reactor, which is formed from an excess of Ca(OH)_2 and calcium salts in purification of the acid gases, and fly ash from an incinerator in Mallorca (Spain) was supplied by Tirme, S.A. The mixture, designated TIRME F+L, was a grey colour and appeared to be homogeneous.

The mixture was characterised by means of particle size analysis (Malvern Laser Sizer with water as the transport medium), chemical analysis using an inductively coupled plasma method, phase constitution by X-ray diffraction (CuK_α radiation in a Philips PW1710 diffractometer) and thermal stability by differential thermal analysis (Stanton Redcroft thermal analyser, STA-780 Series, using Pt crucibles with calcined alumina as reference in flowing air at $65 \text{ cm}^3 \text{ min}^{-1}$ and a heating rate of $25^\circ\text{C min}^{-1}$).

2.2. Crystallisation

The first stage in glass-ceramic production is to produce a melt of suitable viscosity at a reasonable temperature ($\leq 1500^\circ\text{C}$) from which a glass may be formed. The glass forming tendencies of TIRME F+L, with and without additions of ground Spanish waste glass, was investigated by holding the various mixtures at 1500°C , observing the pouring characteristics and monitoring the final product by X-ray diffraction (XRD).

Glass was prepared from a suitable glass forming TIRME F+L-waste glass mixture by melting in a platinum crucible at 1500°C for 30 min. Usually the melt ($\sim 50 \text{ g}$) was poured onto a preheated metal plate to produce a glass, annealed at 600°C for 2 h and slowly cooled to room temperature. In a few cases, in order to study the effect of cooling rate on crystallisation, a small amount of melt ($\sim 5 \text{ g}$) was quenched by pouring into water.

To ascertain whether there were differences in the crystallisation behaviour of annealed and quenched glasses, differential thermal analysis (DTA) measurements were performed on both bulk and powder (<100 and $300\text{--}500 \mu\text{m}$) samples. The DTA tests were carried out as previously described for the study of TIRME F+L. The DTA curves were normalised with respect to the sample weight, which was in the range 12–15 mg. DTA was also used to determine the optimum nucleation temperature and time from measurements on $300\text{--}500 \mu\text{m}$ size particles ground and screened from the annealed glass. For the determination of the nucleation temperature, the glass particles were heated in the DTA apparatus at 15 K min^{-1} to different nucleation temperatures in the range 400 to 730°C inclusive, and held at the

nucleation temperature for 30 min. After the nucleation treatments the samples were heated, without removal from the DTA apparatus, at 15 K min^{-1} until crystallisation was complete, i.e. the temperature exceeded the finish temperature of the exothermic crystallisation peak. The plot of the height of the exothermic crystallisation peak, δT_p , versus the nucleation temperature allowed the specification of the optimum nucleation temperature from the maximum of the curve.

To determine the optimum nucleation time, DTA was performed using the same conditions as those for nucleation temperature determination except that the glass powder was held at the specified optimum nucleation temperature for different nucleation times (10–90 min inclusive) and then heated until crystallisation was completed. Typically a plot of δT_p versus nucleation time reaches a plateau, the onset of which corresponds to the optimum nucleation time.

The value for the activation energy for crystallisation, E , was calculated from DTA data. E was calculated from the heating rate dependence of the temperature, T_p , corresponding to the maximum of the exothermic peak. The glass powder was heated at 15 K min^{-1} until the optimum nucleation temperature and held at that temperature for the optimum nucleation time. The nucleated samples were then crystallised at seven heating rates, ϕ , namely 5, 10, 15, 20, 25, 30, 40 K min^{-1} , and the data analysed using the equation proposed by Kissinger [9]:

$$\ln \frac{\phi}{T_p^2} = -\frac{E}{RT_p} + \text{cte} \quad (1)$$

where *cte* is a constant and R is the gas constant.

The Avrami exponent, n , in the Johnson–Mehl–Avrami equation were also calculated. The Johnson–Mehl–Avrami model was developed to describe nucleation-growth processes in isothermal conditions:

$$V_f = 1 - \exp(-gIU^nT^{n+1}) \quad (2)$$

V_f is the volume fraction, g is a shape factor, U is the growth rate, I is the nucleation rate and n is the Avrami parameter, which is related to the directionality of crystal growth and the time dependence of nucleation. The parameter n was determined from the dimensions of the crystallisation exotherm using the equation:

$$n = \frac{2.5}{\Delta T} \times \frac{RT_p^2}{E} \quad (3)$$

where ΔT is the width of the exotherm at half maximum.

The optimum crystallisation temperature and time were estimated from X-ray diffraction (XRD) data from specimens ($10 \times 5 \times 5 \text{ mm}^3$) of the annealed glass that were given different heat treatments. After heat treatment the samples were ground and sieved to a particle size $< 70 \mu\text{m}$ and XRD data obtained using CuK_α radiation. A plot of the ratio of the intensity of the maximum XRD intensity peak to the total peak intensity (I_n/I_{total}) versus the crystallisation temperature was employed to determine the temperature giving the maximum crystallisation rate and the minimum time required for crystallisation at the optimum crystallisation temperature.

2.3. Glass-ceramic production and characterisation

Bulk glass-ceramics samples were prepared following a two-stage crystallisation process. The bulk glass was heated at 5 K min^{-1} up to the optimum nucleation temperature and held for the optimum nucleation time. The nucleated glass was then heated at 5 K min^{-1} up to optimum crystallisation temperature and held for the optimum crystallisation time.

Scanning electron microscopy (SEM) of polished and etched samples (2% HF for 1 min) was used to examine the microstructure of the glass-ceramics produced by various heat treatments. The density of the glass and glass-ceramics was determined by Archimedes' method.

The thermal and mechanical properties of the glass and glass-ceramics have been assessed. Dilatometric measurements were performed in a Netzsch dilatometer between room temperature and 950°C on bars ($25 \times 5 \times 5 \text{ mm}^3$) in order to determine the average coefficient of thermal expansion over the experimental temperature range. Vickers indentation was used to characterise the hardness (H_v) using loads of 300 g. In addition the fracture toughness, K_{IC} , was estimated from the length of the cracks arising at the corners of the Vickers indent using the equation [10].

$$K_{IC} = 0.048 \left(\frac{c}{a} \right)^{-1.32} \left(\frac{E}{H_v} \right)^{0.4} H_v \sqrt{a} \quad (4)$$

where E is the Young's modulus, which was determined by means of a resonance frequency technique.

Erosion tests were carried out using sand carried in a stream of air and impacting on the sample at an angle of 90° . The sand feed rate and average velocity were 210 g min^{-1} and 15.1 m s^{-1} , respectively. Mass loss from the sample was measured after every 150 g of sand and then converted into volume loss using the density. Erosion rate was obtained from the slope of the plot of volume loss versus mass of sand. The machinability was assessed by cutting with a hard-metal high speed tool.

3. Result and Discussion

Fig. 1 shows that the fly ash-residue mixture (TIRME F+L) has a wide particle size range from about 1 to $700 \mu\text{m}$ with mean particle size (D_{50}) of $40.7 \mu\text{m}$. The results of sieving experiments to give the volume of particles in the ranges <53 , $53\text{--}100$, $100\text{--}150$, $150\text{--}300$, $>300 \mu\text{m}$ were in good agreement with the Laser Sizer data.

Fig. 1. Density of distribution (—) and particle size distribution, % (---) for fly ash-residue mixture (TIRME F+L).

Table 1 shows the chemical analysis by ICP of TIRME F+L, the major components are CaO , Na_2O , SiO_2 and Al_2O_3 and there is significant loss of ignition (LOI), which is probably due to the loss of volatiles associated with the decomposition of the different calcium compounds. The sum of oxides plus LOI is in all cases near to 90%, the remaining 10% could correspond to elements such as Cl and S that cannot be determined by ICP method. It is important to note that species known to be nucleating agents, such as TiO_2 , P_2O_5 , and Fe_2O_3 , are present in reasonable amounts. The chemical composition of the Spanish waste glass used to adjust the batch composition is also shown in Table 1.

Table 1. Chemical analysis (wt%) of TIRME F+L fly ash and Spanish waste glass as determined by ICP method

	TIRME (F+L)	Spanish waste glass
CaO	44.0	10.89
SiO₂	5.5	72.47
Al₂O₃	3.4	1.77
Fe₂O₃	0.7	1.19
MgO	1.5	1.30
Na₂O	3.7	12.38
K₂O	2.9	0.84
P₂O₅	0.8	0.02
TiO₂	0.5	0.08
ZnO	0.65	0.01
LOI	29.3	-----

The X-ray diffractogram for TIRME F+L is given in Fig. 2. Ca(OH)_2 is the major phase but $\gamma\text{-CaSO}_4$, $\text{CaCl}_2\cdot\text{Ca(OH)}_2\cdot\text{H}_2\text{O}$ and CaCl_2 are also present. Fig. 2 also shows the differences in the proportions of the phases present in the five particle size ranges obtained by sieving. It can be seen that there is a decrease of the major phase Ca(OH)_2 and the phases $\text{CaCl}_2\cdot\text{Ca(OH)}_2\cdot\text{H}_2\text{O}$ and $\gamma\text{-CaSO}_4$, as the particle sizes increase. In contrast, the CaCl_2 percentage increases with increasing particle size. Some fractions are enriched in SiO_2 (<53 μm fraction) and quartz (53–100 μm fraction); these phases could be not detected in the unsieved, as-received mixture.

Table 2 demonstrates that the optimum composition to maximise use of the raw material, while producing a melt with an acceptable viscosity as well as forming a relatively stable glass, is 65 wt% TIRME F+L + 35 wt% glass waste (designated TIR65). Greater proportions of raw material resulted in either unstable glasses that crystallised on cooling or batches that were not completely molten at 1500°C. The process schedule described in Section 2.1 produced homogeneous, transparent, green glass from TIR65; XRD analysis confirmed its glassy nature.

Fig. 2. X-ray diffractogram for as-received TIRME F+L mixture and for the different particle size fractions.

Table 2. Melting and casting observations from different mixtures TIRME F+L and Spanish glass waste and TIRME (F+L)

TIRME F+L (wt %)	GLASS WASTE (wt %)	RESULT
50	50	Molten at 1500 $^{\circ}C$ with acceptable viscosity. Glass formed
60	40	Molten at 1500 $^{\circ}C$ with acceptable viscosity. Glass formed
65	35	Molten at 1500 $^{\circ}C$ with acceptable viscosity. Glass formed (TIR65)
68	32	Molten at 1500 $^{\circ}C$ with acceptable viscosity. Crystal growth during cooling
70	30	Molten at 1500 $^{\circ}C$ but high viscosity. Does not pour
>70	<30	Not molten at 1500 $^{\circ}C$

The DTA curves for powder and bulk (annealed and quenches) samples from TIR65 glass show a glass transition at 750°C, followed by two exothermic crystallisation peaks and finally an endothermic reaction indicating formation of a liquid phase (Fig. 3). The differences in the crystallisation temperatures for annealed and quenched samples is typically only 5 K and for all practical purposes may be considered negligible, thus the crystallisation of TIR65 glass does not depend on the rate of cooling of the melt. In contrast the crystallisation temperatures are lower for the fine (<100 µm) powder sample, e.g. for the first crystallisation peak $\approx 1030^\circ\text{C}$ for bulk and $\approx 920^\circ\text{C}$ for fine powder sample, and this indicates that surface crystallisation plays a major role in the crystallisation of the fine powder. The peak temperatures shift to higher temperatures the larger the particle size; the temperatures of the peaks of the coarse powder with particles of 300–500 µm, which was used in the nucleation test, are 1015 and 1120°C for the first and second crystallisation peaks, respectively, and these temperatures are close to those for bulk samples.

Fig. 3. DTA curves for different TIR65 glass samples.

The plot of crystallisation peak height versus nucleation temperature (Fig. 4) demonstrates that the maximum nucleation rate is about 560°C for TIR65 glass. Fig. 5 is a plot of crystallisation peak height versus nucleation time in samples nucleated at 560°C; both crystallisation peak heights have been plotted. The first peak curve is unusual in that instead of reaching a plateau after a certain time it exhibits a maximum at around 34 min. The reduction in the effective nuclei number for the first crystallisation peak is attributed to the onset of the second crystallisation reaction. It appears that the latter, at least partly, involves the same nuclei as the

first crystallisation process, hence the reduction in the number of nuclei available for the first crystallisation peak. It should be noted that the curve for the second crystallisation peak shows the normal characteristics in that a plateau is reached.[11] The time to the plateau is about the same as that to the maximum in the curve for the first crystallisation peak.

Fig. 4. Identification of the nucleation temperature of $\approx 560^\circ\text{C}$ from the plot of the crystallisation peak height versus nucleation temperature for TIR65 glass.

Fig. 5. Plot of crystallisation peak height versus nucleation time at 660°C for TIR65 glass.

A linear relationship was obtained between $\ln(\phi/T_p^2)$ versus $1/T_p$ in accordance with the Kissinger equation [Eq. 1] for both crystallisation peaks (Fig. 6). The values of E determined from the slopes of these plots are 379 and 319 kJ mol^{-1} for TIR65 first and second crystallisation peaks.

Fig. 6. Determination of the activation energy for crystallisation from the slope of $\ln (\varphi/T_p^2)$ versus $1/T_p$ [see Eq. 1].

The Avrami parameters calculated from Eq. 2 are 1.1 and 3.1 for the first and second crystallisation peaks, respectively. A value of n close to 1 denotes surface crystallisation while a value of 3 implies bulk crystallisation.

To investigate the effect of crystallisation temperature on microstructure, bulk glass samples that had received a nucleation treatment of 35 min at 560°C were held at different temperatures in the range 900–1075°C for 2 h. The changes resulting from the heat treatments as observed by the naked eye on cross-sections are summarised in Table 3. The changes start at 925°C with the formation of a thin crystallised layer on the glass surface; this is in agreement with the value of 1.1 for the Avrami exponent for the first crystallisation peak. At 950°C there is evidence of both surface and bulk crystallisation, the latter being consistent with $n \approx 3$ obtained for the second crystallisation peak. At 1000°C the sample is fully crystallised. The fact that bulk nucleation occurs demonstrates that there is sufficient quantity of nucleating agents, e.g. TiO_2 , P_2O_5 and Fe_2O_3 , in the raw material.

Table 3. Effect of heat treatment temperature (heat treatment time 2 h) on crystallisation and colour of TIR65

TEMPERATURE (°C)	CRYSTALLISATION
900	No evidence of crystallisation. Dark green
925	Surface crystallisation layer. Green
950	Surface + bulk crystallisation. Green
1000	Full crystallisation. Light green
1025	Full crystallisation. Light green
1050	Full crystallisation. Brown
1075	Full crystallisation. Brown

Fig. 7 shows the X-ray spectra for TIR65 glass after heat treatment at different temperatures for 2 h. Crystallisation starts at 925°C and the crystalline phases identified are clinoenstatite (MgSiO_3) åkermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and γ -calcium silicate ($\gamma\text{-CaSiO}_4$) together with some unidentified peaks. The relative proportions of the phases as a function of temperature were estimated from the ratio I_n/I_{total} where I_n is the intensity of a chosen X-ray peak for each phase and I_{total} is the sum of the intensities of all of the peaks. Due to the overlap of some X-ray peaks for the different crystalline phases it is not possible to use the maximum X-ray intensity peak for each phase. The peaks used for the I_n/I_{total} calculation were 2.98 Å (MgSiO_3), 3.07 Å ($\text{Ca}_2\text{MgSi}_2\text{O}_7$), 2.72 Å ($\gamma\text{-CaSiO}_4$) and 2.60 Å (unidentified phase).

Figure 7. X-ray diffractogram for TIR65 glass after heat treatment for 2 hours at temperatures in the range 900°C to 1075°C inclusive (□ Ca₂MgSi₂O₇; ○ MgSiO₃; Δ γ-CaSiO₄; ☆ unidentified phase).

The plot of I_n/I_{total} versus crystallisation temperature for TIR65 glass shows that four crystalline phases are present from early stages of crystallisation (Fig. 8). All the crystalline phases, with the exception of Ca₂MgSi₂O₇, are present at the lowest crystallisation temperature of 925°C and Ca₂MgSi₂O₇ appears by 950°C. When the temperature increases from 925 to 1000°C the relative proportion of γ-CaSiO₄ and the unidentified phase are reduced and those of MgSiO₃ and Ca₂MgSi₂O₇ are increased. Above 1000°C there are only small changes in the relative proportion of the phases. In order to investigate the effect of crystallisation time, heat treatments were carried out at 1000°C for times up to 160 min. The plot of I_n/I_{total} versus crystallisation time of Fig. 9 demonstrates that the proportions of γ-CaSiO₄, and unidentified phase are reduced whereas the relative proportion of MgSiO₃ and Ca₂MgSi₂O₇ increases with increasing time up to 2 h. The changes associated with longer (> 120 min) heat treatments are within experimental error.

The data of Fig. 8 and Fig. 9 indicate that MgSiO₃ and Ca₂MgSi₂O₇ are the more stable crystalline phases, i.e. the relative proportions of these phases initially increase with time. Also from these figures it may be concluded that a crystallisation treatment at 1000°C for 2 h is the most appropriate treatment to produce a glass-ceramic from TIR65 glass as increasing either the time or temperature of heat treatment has a negligible effect on the degree of crystallisation.

Fig. 8. Plot of I_n/I_{total} versus crystallisation temperature for TIR65 glass (heat treatment time is 2 h)

Fig. 9. Plot of I_n/I_{total} versus crystallisation time at 1000°C for TIR65 glass.

The microstructures of the heat treated TIR65 samples described in Table 3 are shown in the scanning electron micrographs of Fig. 10. At 925°C/2 h [Fig. 10(a) and Fig. 10(b)] a crystalline layer, consisting of branching leaf-like arms, grows perpendicular to the surface of the sample. Similar surface microstructures can also be seen in the TIR65 samples heat treated at higher temperatures. At 925°C/2 h there are no significant differences between the compositions, as

determined by SEM/EDX, of the crystalline and glassy phases (Table 4). Thus, surface crystallisation does not involve large compositional changes between the crystalline phase and the parent glass. The EDX and XRD analyses indicate that the crystalline phase associated with surface crystallisation is γ - Ca_2SiO_4 .

Fig. 10. SEM micrographs of TIR65 samples heat treated at different growth temperatures for 2 h: (a) and (b) 925°C, (c) and (d) 950°C, (e) 1000°C, (f) 1050°C.

Table 4. EDX analyses (wt%) of the glassy and crystalline phases of TIR65 heat treated at different temperatures

HEAT TREATMENT	PHASE	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	SiO ₂ /CaO
925°C/2h	Glassy matrix	1.14	1.82	3.95	45.84	47.25	0.97
	Crystalline layer	1.43	1.97	5.01	44.58	47.01	0.95
950°C/2h	Glassy matrix	3.15	4.81	7.34	45.88	38.82	1.18
	Fibrillar crystal	0.07	0.90	2.16	45.11	51.76	0.87
	Dendritic crystal	0.35	1.27	1.85	44.62	51.91	0.86
1000°C/2h	Fibrillar crystal	0.08	0.77	0.85	43.51	54.79	0.79
	Dendritic crystal	0.14	0.48	1.28	42.95	55.15	0.77

When TIR65 glass is heat treated at 950°C/2 h, surface and bulk crystallisation take place simultaneously. The microstructure of the interior where bulk crystallisation occurs is

composed of fibre-like crystals, whose width is in the range 2–7 μm and whose length is variable up to about 200 μm [Fig. 10(c) and Fig. 10(d)]. In some areas there is a well defined dendritic structure. EDX analyses collected in spots on fibrillar crystals, dendritic crystals and the surrounding glassy matrix (Table 4) show that bulk crystallisation involves large compositional changes. At 950°C/2 h the glassy matrix is enriched in Na_2O , MgO and Al_2O_3 with respect to the crystalline phase whereas the crystalline phase is enriched in CaO . The SiO_2 content is similar in the residual glass and in the crystalline phases, thus the compositional changes produced when bulk crystallisation takes place affect the SiO_2/CaO ratio; the SiO_2/CaO ratio in the crystalline phase decreases from 0.95 to approximately 0.87 when the temperature of the thermal treatment increases from 925 to 950°C whereas in the glassy matrix the ratio increases from 0.97 to 1.18 over the same interval of temperature. The SiO_2/CaO ratio is approximately the same for fibrillar and dendritic crystals (0.87 and 0.86, respectively), the Na_2O , MgO and Al_2O_3 contents being the major difference between the two types of crystals; the fibrillar crystals are enriched in Al_2O_3 while the Na_2O and MgO content is greater in dendritic crystals. In spite of XRD analyses identifying MgSiO_3 , as one of the crystalline phases formed on heat treatment, the EDX results do not confirm the presence of this calcium-free phase. It is possible that the phase identified as MgSiO_3 by XRD is not 'pure MgSiO_3 ' but a pyroxenic phase, such as augite ($\text{CaMg}(\text{SiO}_3)_2+(\text{Mg,Fe})(\text{Al,Fe})_2\text{SiO}_3$), which incorporates Ca, Mg and Al in its composition.

At 1000°C/2 h the sample is fully crystallized with the main crystal morphologies being fibre-like and dendritic [Fig. 10(e)]. Comparison of the microstructures shown in Fig. 10(e) and Fig. 10(c) indicates changes in the number and length of the fibrillar crystals as the crystallisation temperature increases from 950 to 1000°C. At 1000°C there are more crystals but with an average length of only 25 μm , which is smaller than that corresponding to treatment at 950°C. The microstructure of TIR65 heat treated at temperatures greater than 1000°C is similar to that at 1000°C but the fibrillar crystallisation is predominant and the average length is 200 μm [Fig. 10(f)].

The physical and mechanical properties of TIR65 glass and glass-ceramic are presented in Table 5. The mechanical properties, including erosion resistance, of the glass-ceramic are better than those of the parent glass and are comparable with those of the cast Silceram glass-ceramics,[12, 13, 14] Overall the properties are acceptable for applications such as tiles for the building industry. Both the glass and the glass-ceramic performed well in the cutting test with hard-metal high-speed tools.

Table 5. Physical and mechanical properties of TIR65 glass and glass-ceramic

PROPERTY	GLASS	GLASS-CERAMIC 1000°C/2 hours
Density (Mg/m ³)	2.96	2.95
Hardness (GPa)	5.5	5.9
Young's modulus (GPa)	121.5	134.4
Thermal expansion coef.(10 ⁻⁶ °C ⁻¹)	10	9
Fracture toughness, K _{IC} (MPa m ^{1/2})	1.1	1.5
Erosion coefficient (10 ⁻⁵ cm ³ /g)	8.65	1.63
Machinability	Good	Good

4. Conclusions

The possibility of fabricating vitreous and glass-ceramic materials from solids residues from domiciliary waste incineration was shown. The major components of the solid residue (TIRME F+L) were CaO, SiO₂ and Al₂O₃ but nucleating agents, such as TiO₂, P₂O₅, and Fe₂O₃ were also present in reasonable amounts. The optimum composition to maximise the use of fly ashes from urban incinerator as raw material and to produce a relatively stable glass with suitable viscosity proved to be 65 wt% TIRME F+L plus 35 wt% glass cullet (designated TIR65).

DTA scans for TIR65 glass exhibited two exothermic crystallisation peaks. The crystallisation behaviour did not depend on the cooling process whereas the crystallisation temperature shifted to higher temperatures the greater the particle size (from 920°C for powder samples to 1030°C for bulk samples). This behaviour suggested that surface crystallisation was playing a major role in the crystallisation of the fine powder. The Avrami parameter n was 1.1 and 3.1 for the first and second crystallisation peaks, respectively. These values indicated that both surface (first peak) and bulk (second peak) crystallisation processes were operative. The activation energy E was 379 and 319 kJ mol⁻¹ for the first and second peak respectively.

The optimum nucleation temperature and time for TIR65 were determined as 560°C and 35 min. Crystal growth commenced at 925°C but the most appropriate crystallisation treatment was 1000°C for 2 h.

The crystalline phases identified by X-ray diffraction were clinoenstatite (MgSiO₃), akermanite (Ca₂MgSiO₇) and gamma-calcium silicate (γ -CaSiO₄); there was also a small amount of an unidentified phase. The proportions of MgSiO₃ and Ca₂MgSi₂O₇ increased with increasing heat treatment time and temperature. There is some evidence from EDX that MgSiO₃ may not be

present but instead a piroxenic phase which incorporates Ca, Mg and Al in its composition. The crystals in the bulk of the glass-ceramic had fibre-like and dendritic morphologies.

The mechanical properties of the glass-ceramics were better than those of the parent glass, e.g. fracture toughness was 1.5 and 1.1 MPa m^{1/2}, respectively.

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