Crystallisation of nepheline-based glass frits through fast-firing process

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Abstract

The aim of this research was to study the feasibility of producing sintered nepheline glass-ceramic through a fast firing route. The thermal behaviour of the original glass was analyzed by mean of differential scanning calorimetry (DSC) and X-ray diffractometry (XRD). The microstructural analysis of glass-ceramic materials was carried out by field-emission scanning electron microscopy (FE-SEM). The results showed that the studied wastes are able to produce a glass and glass-ceramic materials through a sinter-crystallization process, 100 μm being the critical glass particle size. Glass-ceramics are composed of residual glassy phase and crystalline phases such as nepheline ($\text{NaAlSi}_3\text{O}_8$), augite $(\text{Ca}, \text{Na})(\text{Mg}, \text{Fe}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$ and a solid solution belonging to the melilite group $(\text{Ca}, \text{Na})(\text{Al}, \text{Mg}, \text{Fe})(\text{Si}, \text{Al})_2\text{O}_7$. In a first evaluation, water absorption (0.02%) and bending strength (71MPa) of glass-ceramic achieved after thermal treatment at 1100°C/5min suggest that sintered glass-ceramics can be easily produced from coal fly ash and metallurgical slag wastes by a fast-firing cycle and they are extremely serviceable for outdoor flooring and wall cladding.

Keywords: Sintering; coal fly ash; nepheline; augite; melilite; ceramic tile

1. Introduction

Glass-ceramics are multi-phases materials composed by at least one glassy phase acting as matrix and a finely dispersed crystalline phase uniformly embedded in the matrix. Glass-ceramics are

developed through controlled devitrification (nucleation and crystal growth) of a parent glass. This parent glass is melted and subsequently it undergoes a thermal process aiming to precipitate one or more crystalline phases. By controlling internal crystallization, efficient nucleation step conducts to the development of randomly oriented fine crystals and glass-ceramics materials free of defect like micro-cracks or porosity. In most of cases, nucleating agents are added to the parent glass for improving the nucleation process [1]. However, glass-ceramic materials could be also prepared by sintering-crystallization process [2]. In this case, crystallization takes place on interfaces between glass particles. The major advantage of this process is the absence of nucleating agents since particles boundaries act as nucleating sites but its disadvantage is the final residual porosity. Generally, glass-ceramics present so many benefits in relation to parent glasses such as higher strength, wear resistance, thermo-physical properties, etc, which make them attractive materials for structural applications.

In the design of glass-ceramics, the two most important factors are composition and microstructure [1] since their properties fundamentally depend on the type and appearance of the crystalline phase. The major crystalline components of glass-ceramics are silicates. Among this, nepheline-based glass-ceramics are characterised by high chemical and mechanical strength and impact resistance. In the last decades glass-ceramics containing nepheline as crystalline phase had been developed for several applications, such as microwave ovens [3] and dental applications [4,5].

Nepheline glass-ceramics are usually prepared from bulk glasses of the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system and the addition of different nucleating agents, such as TiO_2 , Cr_2O_3 , ZrO_2 or LiF is mandatory to promote crystallisation [6,7]. Recently, Martín et al. [8,9] and Andreola et al [10] reported on the viability of the production of a wide variety of forsterite–nepheline glass-ceramics by a sinter-crystallisation process from a $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{MgO}-\text{Na}_2\text{O}$ base glass. Tiling and cladding was suggested as potential applications for these materials given that sintered nepheline materials showed similar bending strength values than the commercial glass-ceramics tile Neoparies® and water absorption $<0.5\%$, which allowed to classify these materials into the Group BIa characteristic of high sintered ceramic tiles according to European Standard rule.

In last years, fine-grained nepheline glass-ceramics were also produced by vitrification of coal fly ashes and subsequent controlled heat treatment of the parent glasses. The results showed that glass ceramics exhibit attractive mechanical properties if compared with building ceramic tiles [11-13]. Nevertheless, in these investigations glass-ceramics were prepared from bulk glass samples and

devitrification was normally carried out at slow heating rate and long dwell times (120 min) at the crystallization temperature. Such conditions unfit the fast-firing thermal cycle used in the manufacture of ceramic tiles (60-90 min cold-to-cold and temperature rates up to 60°C/min) result in glass-ceramic materials from fly ashes that are economically unviable due to high energy costs associated with processing.

The present manuscript studies the feasibility of producing sintered nepheline glass-ceramic through a fast firing route, so that they can be easily adapted to the cycle used in the manufacture of ceramic tiles and therefore, to obtain a new marketable product to be used as material for the construction industry.

2. Experimental procedure

2.1 Raw materials

Fly ash and metallurgical slag were used as raw materials to obtain a glass formulation; moreover, Na_2CO_3 was added to the glass composition to assist the melting process.

The fly ash used in this investigation was originated from Petacalco coal-fired power plant, located in La Unión, Guerrero State, Mexico. The ash was used as-received without any prior conditioning stage. The metallurgical slag proceeds from ArcelorMittal steelmaking plant located in Lázaro Cárdenas, Michoacán State, México. In this case, prior to its use, the slag was grinded by high energy milling and sieved to a particle size $< 100 \mu\text{m}$.

2.2 Materials preparation

A glass (hereafter designated CEC glass) in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-Na}_2\text{O}$ base system was formulated by using the fly ash as silica source and the metallurgical slag as alkali oxides supplier. A previous vitrification study evidenced that the optimum composition to maximise the use of fly ash and slag, while producing a melt with an acceptable viscosity was 58.5 wt% fly ash + 31.5 wt% Arcelor Mittal metallurgical slag + 10.0 wt% Na_2O [14]. The batch components were mixed for 15 minutes in a blender (TURBULA) to get a homogeneous mixture. The batch was placed in an aluminosilicate crucible and heated at 15°C/min in an electric furnace up to 1450°C. After a holding time of 60 minutes at the melting temperature, the melt was quenched by pouring into water producing a glass frit. For performing the crystallization study, the original glass was sieved to a particle size $< 100 \mu\text{m}$ and the glass powders were moistened by spraying with distilled water (5 wt

%) and pressed into 15x15x8mm compacts by using a laboratory uniaxial hydraulic press (Mignon-S Nanetti) at a pressure of 40 MPa. Moreover, test pieces of 50x15x5mm were prepared for bending strength measurements. The green compacts were sintered at 750–1130°C and soaked for 5 to 30 min at the sintering temperature. The samples were placed in a furnace at the temperature required for the heat treatment and removed as soon as the exposure time had expired.

2.3 Materials characterization

The chemical composition of the CEC glass was determined by X-ray fluorescence (XRF) (Bruker model S8 Tiger equipped with the software package SPECTRA^{Plus}). To evaluate the thermal behaviour of CEC glass, differential scanning calorimetry (DSC) was performed using a Setaram (Labsys) TG-DTA/DSC unit in air atmosphere. The analyses were carried out at a heating rate of 50°C/min, in platinum crucibles and calcined alumina as reference. DSC curves were recorded on samples with particle sizes ranging from 63µm to 1mm. The temperature precision given by the equipment is ± 0.1 °C. Each measurement was reproduced three times in order to estimate experimental errors. The activation energy (E) can be estimated using Ozawa [15] and Kissinger [16] analyses, according to equations 1 and 2 respectively:

$$\ln \varphi = -\frac{E}{RT_x} + cte \quad (1)$$

$$\ln \frac{\varphi}{T_c^2} = -\frac{E}{RT_c} + cte \quad (2)$$

where φ is the heating rate, T_x is the onset crystallisation temperature, T_c is the peak temperature of crystallisation peak, cte is a constant and R is the gas constant. The evaluation of E was carried out from the DSC scans on CEC glass with particle size <100µm recorded at different heating rates (10, 20, 30, 40 and 50°C/min).

The evaluation of the amorphous nature of CEC glass after melting, and the mineralogical study of the crystalline phases devitrified after thermal treatment was performed by X-ray diffraction (XRD) (Bruker model D8 Advance) with Ni-filtered Cu K α radiation operating at 30 mA and 40 kV. Data were recorded in the 5-60° 2 θ range (step size 0.019732° and 0.5 s counting time for each step). The microstructural analysis of glass-ceramic materials was performed by field emission scanning electron microscopy (FE-SEM) (Hitachi model S-4800) using an accelerate voltage of 20kV. Semi-quantitative analysis of different phases were obtained by energy dispersive X-ray spectroscopy

(EDS) (Bruker model QUANTAX Esprit 1.9) provided by a beryllium (Be) window. SEM observation were performed on different samples; viz., fresh, fracture; polished specimens using 6, 3 and 1 μm diamond pastes after grinding with silicon carbide paper and water; and polished surfaces etched in 5% HF solution, washed ultrasonically with distilled water and ethylic alcohol. All the samples were Au-Pd coated in a sputter (Balzers SCD 050).

The density of selected glass-ceramic materials was measured using Archimedes' principle with distilled water as an immersion liquid. The error in this method has been determined based on repetitive measurements. The errors in density were found to be about 0.1%. Water absorption and bending strength of a selected glass-ceramic material was measure according to ASTM C329-88 and UNE-EN 841-1, respectively. Bending strength tests were performed in an electronic universal tester (Servosis, ME402101 model) by a three point loading test with a span of 36 mm and a crosshead speed of 1 mm/min. The tests were carried out on 6 test pieces of 50x15x5 mm. The errors in bending strength were found to be about 0.3%.

3. Results

Table 1 summarizes the chemical composition of the original CEC glass, determined by XRF.

Table 1. Chemical composition (wt. %) of the original CEC glass. The errors in the experimental composition are approximately ± 0.2 wt%.

Oxide	Percentage	Oxide	Percentage
SiO ₂	42.88	SO ₃	0.28
Al ₂ O ₃	18.10	P ₂ O ₅	0.23
CaO	14.12	Rb ₂ O	0.06
Na ₂ O	11.60	Cr ₂ O ₃	0.06
Fe ₂ O ₃	4.98	ZrO ₂	0.05
MgO	4.94	SrO	0.05
TiO ₂	0.97	PdO	0.03
MnO	0.84	NiO	0.01
K ₂ O	0.83	ZnO	0.01

Figure 1 shows the DSC curves recorded on both bulk (~3x3x4 mm) and fine (powder without granulometric control) CEC glass samples. The DSC curve of the powder sample exhibits clearly the glass transition temperature (T_g) at 663°C. After T_g , an exothermic peak at 868°C (T_m) indicates the formation of crystalline phases and finally an endothermic peak at 1148°C points out the formation of a liquid phase. Regarding the bulk sample, it exhibits T_g and T_m at the same temperatures than the powder sample. In order to determine the most effective particle size for conducting the crystallisation study of CEC glass, DSC curves were recorded on samples with particle sizes ranging from 63 μ m to 1mm (Figure 2).

Figure 1. DSC curves for powder and bulk samples of CEC glass at a heating rate of 50 °C·min⁻¹.

Figure 2. DSC curves of powdered CEC glass samples at different particle size distribution at a heating rate of $50\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

Figure 3 depicts the Ozawa and Kissinger plots.

Figure 3. Plot for determination of the activation energy according with Kissinger and Ozawa methods.

To know the behaviour of the original glass towards crystallisation, the time-temperature-transformation (TTT) diagram was drawn through examination of the XRD patterns of glass samples after heat treatment at different (T^a ,t) pairs. The heat treated glass was considered to be “amorphous” when no peaks corresponding to crystalline phases were observed in the XRD pattern, “crystallisation onset” when small peaks appear above the background of the pattern and “total crystallisation” when these peaks were intense and there was no evidence at low angles of scattering from a glassy phase. Figure 4 shows the TTT diagram.

Figure 4. TTT diagram of CEC glass. (○) amorphous; (◆) onset of the crystallisation; (●) crystallised.

For a better discussion of nepheline devitrification from CEC glass, the glass composition has been located in the phase diagrams of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ and $\text{SiO}_2\text{-MgO-CaO}$ systems (Figure 5).

Figure 5. Location of the CEC glass composition in the phase diagrams (wt%, T in °C) of the a) SiO₂-Al₂O₃-Na₂O system, b) SiO₂-Al₂O₃-CaO system and c) SiO₂-MgO-CaO system

The variation of the different crystalline phases with temperature and time were estimated by XRD from the ratio $(I_{\text{relative}})_{T,t} = (I_n)_{T,t} / I_{\text{max}}$. For each of the crystalline phases, I_n is the XRD intensity of a selected diffraction peak and I_{max} is the intensity of the peak in the XRD pattern corresponding to the heat treatment (T,t) resulting in higher development of this phase. The peaks used for I_n calculations were 2.86 Å (melilite), 3.84 Å (nepheline) and 2.96 Å (augite). Figure 6 depicts the plots of I_{relative} versus time at different crystallisation temperatures.

Figure 7 shows the microstructure observed at the surface of glass particles heat treated for 5 or 10 min at different temperatures in the interval from 750 to 1050°C. The XRD patterns of the resulting materials are also collected in Fig. 7.

Figure 6. Variation of the different crystalline phases with time at different heat treatment temperatures as estimated by XRD from the ratio $(I_{rel})_{T,t} = (I_n)_{T,t} / I_{max}$.

Figure 7. SEM images, X-ray diffraction patterns and nepheline EDS analysis for CEC samples heated for 5 or 10 min at different temperatures in the interval from 750 to 1050 °C.

Figure 8 shows the mineralogical and microstructural characterization of materials resulted after treatment at 1050°C for 5 min. The combined secondary electron and back scattering electron image makes easier the location of different phases. Melilite (Mel) appears as brighter regions because its composition includes higher content of elements with higher atomic number (Fe, Ti and Mn).

Figure 8. Mineralogical and microstructural characterization of material resulted after treatment of CEC glass at 1050°C for 5 min.

Figure 9 displays micrographs collected after etching a CEC glass sample heat treated at 1050°C for 5 min. Partial removal of the remaining glassy phase by acid leaching results in more accurate analyses of crystalline phases.

Figure 9. SEM images of material resulted after treatment of CEC glass at 1050°C for 5 min. a) augite and nepheline crystals; b) detail of augite crystals; c) EDS analysis of augite phase.

4. Discussion

SiO₂, Al₂O₃, CaO and Na₂O are the main components in CEC glass (Table 1). The glass composition also contains nucleating oxides, such as TiO₂, Cr₂O₃, ZrO₂ or MnO, which are expected to promote the glass devitrification in sodium aluminosilicate glasses [17,18].

The main difference between the DSC curves recorded on bulk and fine CEC glass samples (Fig. 1) is the lack of an exothermic crystallisation peak in the DSC curve of the bulk sample. This result indicates that the crystallisation process of CEC glass in a subsequent thermal treatment will occur preferably through a surface mechanism in which devitrification is initiated at low energy surface sites [1]. Accordingly, it will be necessary a sinter-crystallisation process to transforming the original glass into a glass-ceramic material.

The DSC curves recorded on different particle size fractions of CEC glass confirm the high dependency in the degree of crystallisation and the particle size of the glass sample. Glass fractions with smaller particle size (<63–250 μm) show high intensity and well defined crystallisation peak.

However, in fraction with larger particle size (250-1000 μm) the peak intensity decreases and becomes a crystallisation band in which several crystallisation effects overlap. In view of these results, a glass sample with particle size $< 100 \mu\text{m}$ was selected for the study of crystallisation of CEC glass.

Both Ozawa and Kissinger plots (Fig. 3) indicate a linear relationship with a linear correlation factor within the range 0.9271-0.9754. From the slope of the plot, the Kissinger model results in an activation energy value of $E = 324 \text{ KJ/mol}$; on the other hand, using the Ozawa approach the value is $E=377 \text{ kJ/mol}$. Both values are similar; however, the linear correlation coefficient is closer to unity for Kissinger plot, which is indicating that Kissinger approach is more suitable. As explained below, devitrification of CEC glass begins with the development of nepheline crystals. The values of activation energy values calculated from both Ozawa and Kissinger plots are slightly lower than those reported in others studies on nepheline devitrification [8]. This variation can be due to slight differences in the glasses viscosity caused by dissimilar chemical compositions. In fact, compared with the glass composition studied in [9] CEC glass contains higher CaO and lower MgO and Na_2O contents.

The TTT curve of CEC glass (Fig. 4) shows a high tendency to devitrify on heating, as the first sign of crystallisation is observed at 750°C for a dwell time of 20 minutes. By increasing the temperature of the heat treatment, the holding time necessary for the development of crystalline phases decreases so that at 800°C a holding time of 10 min is required, while above 850°C only 5 min are necessary to promote crystallisation of the glass. The incorporation of TiO_2 in the base glass composition is known to be an effective nucleating agent, which favours early devitrification in such glasses. Accordingly, CEC glass can be easily adapted to the industrial fast-firing cycle used in the manufacture of ceramic tiles, in which the tiles are inside the furnace no longer than 60-90 min, with a dwell time of 7-10 minutes at the maximum temperature.

The crystalline phases identified by XRD were nepheline ($\text{NaAlSi}_3\text{O}_8$; JCPDS-85-1487), which is the single crystalline phase formed in the onset of crystallisation (thermal treatment at 800°C for 5 min and 750°C for 20 and 30 min). Moreover, melilite solid solution $((\text{Ca},\text{Na})(\text{Al},\text{Mg},\text{Fe})(\text{Si},\text{Al})_2\text{O}_7$; JCPDS-79-2423) and augite $((\text{Ca},\text{Na})(\text{Mg},\text{Fe},\text{Al})(\text{Si},\text{Al})_2\text{O}_6$; JCPDS-24-0203) are also precipitated in high crystallised samples.

The favoured devitrification of nepheline from the parent glass upon heat treatment may be explained by the following reasons:

a) Nepheline formation is consistent with the location of the glass composition in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-Na}_2\text{O}$ ternary diagram (Figure 5a), within the primary phase field of nepheline crystallisation.

b) Nepheline precipitation is in accord with the “nepheline discriminator” (ND) proposed originally by Li et al. [18] as a means to recognize glass compositions that might be more susceptible to nepheline precipitation. The ND indicates the level of SiO_2 above which nepheline formation is not predicted, and is given by

$$N_{Si} = \frac{g_{SiO_2}}{g_{Al_2O_3} + g_{Na_2O} + g_{SiO_2}} \geq 0.62 \quad (1)$$

where N_{Si} is the normalized silica concentration, and g_i is the i th component mass fraction in glass. Glasses with $N_{Si} > 0.62$ are predicted to be free of nepheline. In the case of CEC glass, its chemical composition leads to $N_{Si} = 0.59$, which predicts nepheline formation in a subsequent heat treatment [19].

c) Nepheline devitrification is also in agreement with the concept of optical basicity (OB). It is hypothesized that more basic cations are more likely to cause aluminosilicates to precipitate as they readily donate valence electrons and thus become removed from the covalent glass network [20]. In general, the theoretical OB can be computed for any given glass (A_{glass}) from the OB of constituents as:

$$A_{glass} = \frac{\sum_i x_i q_i A_i}{\sum_i x_i q_i} \quad (2)$$

where q_i is the number of oxygen atoms in the i th component oxide, x_i is the i th component oxide mole fraction, and A_i is the i th oxide molar basicity. Nepheline devitrification is expected at high basicities ($OB > 0.55\text{--}0.57$) [21]. Regarding CEC glass, its OB calculated from the constituent oxides is $A=0.64$, which also envisages the precipitation of nepheline.

On the other hand, the devitrification of nepheline is consistent with the prevalent surface crystallisation mechanism previously determined by DSC. Indeed, several studies have shown that the devitrification of nepheline in glasses begins with the formation of crystalline nuclei at the surface of the glass particles and therefore, a sinter-crystallisation process is the most suitable route to prepare glass-ceramic materials from such glasses [7-9,22]

Because of the location of CEC glass composition in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ (Fig. 5b) and $\text{SiO}_2\text{-MgO-CaO}$ (Fig. 5c) systems, the development of anortite and tridymite in the derived glass-ceramics was also expected. However, the mineralogical study showed that these phases are not formed and instead, a solid solution of the melilite group crystallises. Nepheline is the first phase devitrified from CEC glass at low temperatures and short holding time. Its formation consumes Al_2O_3 and SiO_2 , which eventually causes a deficit of silica and alumina in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ system; whereby, the composition of the residual glass shifts to the bottom right corner of this system. Thus, the residual glass would be located in the region of formation of gehlenite phase, which is a silicate belonging to the melilite group. Concerning to augite (pyroxene group) devitrification, several studies have shown that the incorporation of TiO_2 in the base glass not only facilitates early devitrification but it also enhances the development of crystalline phases belonging to the pyroxene group [17]. Both melilite and augite are common crystalline phases in glass ceramics prepared from wastes vitrification [23-26] and basalt glasses [27] and they lead to glass-ceramics with potential application in the building material industry [28].

Fig. 6 shows that nepheline is the only crystalline phase present at 750°C , whereas gehlenite and augite appears by 800°C . It can be seen that the different phases precipitate from the glass with high crystallisation rate; so that, once the development of a crystal phase begins, a slight variation in temperature results in a considerable increase of the amount of crystalline phase formed. It can be clearly appreciated analyzing the treatments carried out with a dwell time of 10 min. Thus, heat treatments at 750°C resulted in amorphous materials; however a slight increase in temperature up to 800°C promotes the growth of gehlenite, nepheline and augite with high crystallisation rate, which leads to glass-ceramic materials showing an important crystallisation degree ($I_{\text{rel}} > 60\%$). The high crystallisation rate also results in the short time required to achieve the maximum degree of crystallisation of the glass under the experimental conditions studied in this research. Therefore, the relative intensity of crystallisation increases during the first 10 minutes of heat treatment; but as of this time, the degree of crystallisation is stabilized and longer treatment does not result in the further development of crystalline phases. Concerning the evolution of the different crystalline phases with temperature, nepheline is the first to crystallise and reaches the maximal development in the glass-ceramic resulted after treatment at 800°C ; above it, a temperature increase results in decreasing I_{rel} values. Conversely, the intensity of melilite and augite increases in the overall temperature range studied.

After treatment at 750°C, the glass particles retain their amorphous character as evidenced by the absence of diffraction peaks in the corresponding pattern (Fig. 7) and the characteristic microstructure of glass particles in which three distinct regions (mirror, mist and hackle zones) [29-31] can be differentiated on the fracture surface. However, a small peak at $2\theta=21.28^\circ$ would indicate the occurrence of crystallisation in lesser extent. Higher magnification observation reveals the development of nanocrystals on the surface of the glass particles, which should correspond to nepheline phase since as shown in Fig. 5, nepheline is the first crystalline phase to appear during devitrification of the CEC glass. As the temperature increases, nepheline crystals increase in size, which results in a decrease of the population density (number of crystals per unit volume) from ~ 130 crystals/ μm^2 to 30 crystal/ μm^2 in samples treated at 750°C/10min and 1000°C/5min, respectively. Above 1000°C, nepheline crystals cannot be distinguished on the surface of the glass particles because the high degree of sintering, which causes the particles to join together and form a solid mass. However, in such cases hexagonal prism of nepheline can be detected within the glass particles, and their size allows them to be analyzed by EDS. The analysis (average from ten analyses) reveals a high percentage of CaO and low percentage of K₂O with respect to the stoichiometric composition of nepheline (41.13% SiO₂, 34.90% Al₂O₃, 15.91% Na₂O, 8.06% K₂O). Therefore, it is a solid solution of Na₂Al₂Si₂O₈ - CaAl₂Si₂O₈ system since nepheline can take up to 35 mol% anorthite (44.40% SiO₂, 35.84% Al₂O₃, 19.20% CaO, 0.56 Na₂O) into solid solution [32].

Clusters of melilite and augite crystals could be clearly seen in the FESEM observations on polished cross sections of glass samples heat treated at 1050°C or above. The compactness of glass particles in treatments at lower temperature was insufficient to allow polishing of samples. Augite (Aug) develops with a dendritic habit with a typical multi-branching tree-like form whereas the darker grey regions correspond to the remaining glassy phase (Fig. 8). The EDS analyses collected from the different regions indicate that the composition of melilite is compatible with an intermediate constituent of the solid solution between the Al-rich end-member gehlenite (Ca₂Al(Al,Si)O₈) and the Mg-rich end-member akermanite (CaMgSi₂O₇) [33]. Regarding the EDS analysis of augite phase, it collects a high amount of Al₂O₃ and Na₂O₃ with respect the composition of stoichiometric augite. The small size of augite crystals (<1 μm), which are below the analysis area of the SEM equipment, together with the intermingle between augite crystals and the glassy phase cause that the analyses of augite crystals are also collecting X-rays generated by glassy phase.

Augite (Aug) and nepheline (Neph) crystalline phases are visible in Fig. 9a but melilite crystals are not detected in the SE images. Augite crystals appear distributed within a dendritic microstructure.

The high magnification observation of augite (Fig. 9b) reveals stubby crystals with a flattened lightly pyramidal termination, whose chemical composition analyzed by EDS is closer to the stoichiometric composition of augite (Fig. 9c).

For a first assessment of the technological properties of glass-ceramics materials prepared from CEC glass, the glass-ceramics obtained after thermal treatment at different temperatures in the interval from 1050° to 1110°C for 5 min were tested in order to determine the values of density and bending strength, which are collected in Table 2. In all cases, the glass-ceramics show density values higher than that corresponding to the parent CEC glass (2.657 g/cm³), which can be explained by the occurrence of crystalline phases with higher density. However, the most noticeable of Table 2 is the increment in bending strength as thermal treatment temperature increases, reaching values higher than those showed by materials traditionally used as building tiles, such as natural stone (12-14 MPa), porcelain stoneware (35-40 MPa) or Neoparies® (40 MPa). These findings suggest that they should be extremely serviceable for flooring and wall cladding.

Table 2. Density and bending strength of glass-ceramics prepared after thermal treatment of CEC glass. The errors in density values are approximately ± 0.002 .

Temperature	Density (g/cm ³)	Bending strength (MPa)
CEC1050-5	2.684	14.27 $\pm$ 0.04
CEC1080-5	2.689	34.60 $\pm$ 0.10
CEC1100-5	2.751	43.95 $\pm$ 0.13
CEC1105-5	2.757	65.64 $\pm$ 0.20
CEC1110-5	2.762	71.28 $\pm$ 0.21

Conclusion

This study investigates the preparation of sintered glass-ceramics materials from a base glass (designated as CEC) synthesized from a mixture of 58.5 wt % coal fly ash fly ash, 31.5 wt % metallurgical slag, and 10% Na₂CO₃. The following conclusions are drawn:

- The crystallisation process of CEC glass in a subsequent thermal treatment occurs through a surface mechanism in which devitrification is initiated at low energy surface sites.

- A glass particle size below 100µm has been found as the most effective for preparing glass-ceramics by a sinter-crystallisation process.
- CEC glass shows a high tendency to devitrify on heating and can be easily adapted to the industrial fast-firing cycle used in the manufacture of ceramic tiles.
- Thermal treatments leads to glass-ceramics composed of nepheline (NaAlSiO_4), melilite solid solution $((\text{Ca},\text{Na})(\text{Al},\text{Mg},\text{Fe})(\text{Si},\text{Al})_2\text{O}_7)$ and augite $((\text{Ca},\text{Na})(\text{Mg},\text{Fe},\text{Al})(\text{Si},\text{Al})_2\text{O}_6)$.
- First evaluation of technological properties indicated that glass-ceramic materials show high technological properties for industrial use in construction (tiling and cladding applications).

Acknowledgements

The authors thank Mrs. P. Díaz and Mrs. E. Sánchez for their technical assistance. H. R. Guzmán-Carrillo wants to thank CONACyT for scholarship and to Dr. J. Rincón from the IETcc-CSIC for his valuable advice.

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