Effects of soda–lime–silica waste glass on mullite formation kinetics and micro-structures development in vitreous ceramics

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Abstract

The effects of soda–lime waste glass, from the recovery of bottle glass cullet, in partial replacement of Na-feldspar for sanitary-ware ceramic production are discussed. Attention is paid to the mullite growth kinetics and to the macroscopic properties of the final output, the latter ones depending on the developed micro-structures and vitrification grade. Measurements have been performed by in situ high temperature X-ray powder diffraction, scanning electron microscopy, thermal dilatometry, water absorption and mechanical testing. Glass substituting feldspar from 30 to 50 wt% allows one (i) to accelerate the mullite growth reaction kinetics, and (ii) to achieve macroscopic features of the ceramic output that comply with the latest technical requirements. The introduction of waste glass leads to (i) a general saving of fuel and reduction of the CO2 emissions during the firing stage, (ii) a preservation of mineral resources in terms of feldspars, and (iii) an efficient management of the bottle glass refuse by redressing a part of it in the sanitary-ware manufacturing.

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1. Introduction

Several papers on the use of different waste glasses in industrial products have been presented proving that such refuses can be an alternative to the traditional raw materials (Bernardo et al., 2010; Raimondo et al., 2007).

Among silica-rich wastes those from bottle banks have attracted much attention. Glass cullets (referred to as soda–lime or soda–lime–silica (SLS) glass) from urban waste consist mainly of silicon, sodium and calcium oxides. Thanks to its potential of low temperature viscous flow sintering, SLS glass can be considered as a good candidate for total, or partial, replacement of the natural fluxes (mainly Na-feldspar, NaAlSi3O8) in ceramic manufacturing. Souza et al., 2004 and Matteucci et al., 2002 proved the technical feasibility of replacing flux with SLS glass in ceramics. Tarvornpanich et al., 2005 and Youssef et al., 1998 claimed that SLS glasses can substitute feldspar-based fluxes up to 5 wt% without affecting the technological features of the output but reducing the sintering temperature. On this ground, new fluxes have been developed (Bragança and Bergmann, 2004; Romero et al., 1999) or are afoot, based on mixtures of feldspar and different amounts of SLS glass.

The use of SLS glass in the vitreous sanitary-ware ceramics provides an environmental safeguard by saving natural resources, and reducing the process energy consumption and CO2 emissions. However it is still a matter of debate how SLS-glass affects the basic ceramic reaction kinetics. Much attention has been paid to porcelain-type technology, but comparatively little has been spent for vitreous sanitary-wares, which result from high-temperature treatments (~1230 °C) of the system clay–kaolinite–feldspar–quartz.

In the present paper, we discuss the introduction of SLS glass into the vitreous sanitary-ware ceramic phase-system in partial replacement of the traditional flux agent (Na-feldspar) focussing the attention on two aspects:

(i) how SLS glass affects the sanitary-ware ceramic transformations at high temperature, in terms of mullite nucleation and growth;

(ii) how far SLS glass influences the micro-structures formation and, as a consequence, the technological properties of the output, as a function of the firing time (t f) and temperature (T f) (Martín-Marquéz et al., 2010; Tarvornpanich et al., 2008; 2008b, Stathis et al., 2004; Leonelli et al., 2001).
Such studies were carried out on samples with classical vitreous sanitary-ware compositions in which a fraction of feldspar is replaced by SLS glass. The mullite kinetics was investigated by isothermal runs using in situ High Temperature X-Ray Powder Diffraction (HT-XRPD) and Scanning Electron Microscopy (SEM). Samples fired over a $T_f$–$T_i$ grid to mimic a ceramic body were then studied by means of XRPD and technological testing to measure the properties relevant to vitreous sanitary-ware ceramic technology.

2. Experimental

2.1. Sampling

The system SLS glass–feldspar–quartz–kaolinite was explored in terms of Y wt% SLS glass, 22-Y wt% Na-feldspar, 28 wt% quartz and 50 wt% kaolinite, the latter mimicking the total clay + kaolinite content of a classical sanitary-ware mixture (Table 1a). Four batches ($G_0$, $Y = 0$; $G_{32}$, $Y = 7$, i.e. $Y/22 \times 100 = 32$; $G_{50}$, $Y = 11$, i.e. $Y/22 \times 100 = 50$; $G_{100}$, $Y = 22$, i.e. $Y/22 \times 100 = 100$) were prepared and hereafter labelled by the same notation used in earlier studies (i.e. Tarvornpanich et al., 2005).

### Table 1a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineralogical phases</th>
<th>Kaolin</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>SLS glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_0$</td>
<td>50</td>
<td>28</td>
<td>22</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>$G_{32}$</td>
<td>50</td>
<td>28</td>
<td>15</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>$G_{50}$</td>
<td>50</td>
<td>28</td>
<td>11</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>$G_{100}$</td>
<td>50</td>
<td>28</td>
<td>0</td>
<td>22</td>
<td></td>
</tr>
</tbody>
</table>

### Table 1b

<table>
<thead>
<tr>
<th>Oxides (wt%)</th>
<th>SLS glass</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>$G_0$</td>
<td>$G_{32}$</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>71.70</td>
<td>66.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>2.70</td>
<td>21.9</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.42</td>
<td>0.58</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.07</td>
<td>0.29</td>
</tr>
<tr>
<td>CaO</td>
<td>9.49</td>
<td>0.55</td>
</tr>
<tr>
<td>MgO</td>
<td>2.00</td>
<td>0.20</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.01</td>
<td>0.98</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>12.4</td>
<td>2.07</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>0.11</td>
<td>6.48</td>
</tr>
<tr>
<td>Sum</td>
<td>99.9</td>
<td>99.95</td>
</tr>
</tbody>
</table>

Fig. 1. Main crystalline phases that develop during the non-isothermal heating ramp. (a) sample $G_{32}$ and (b) sample $G_{100}$. 

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Na-feldspar, quartz and kaolinite are natural samples provided by Mineral Resources S.r.l., treated by magnetic separation to separate out impurities, accessory phases and contaminations. The particle size distributions of kaolinite, quartz and feldspar materials were measured by Laser-light-scattering, and yielded $d_{50}$-values of $\sim 7, 24$ and $17 \mu m$, respectively. The SLS glass exhibits a $d_{50}$ of $75 \mu m$. The whole chemical compositions of the blends and SLS glass are collated in Table 1b.

2.2. X-Ray Powder Diffraction (XRPD)

The samples were back-loaded on a flat sample-holder and measured by a Bragg-Brentano geometry PANalytical X'Pert Pro Diffractometer, using CuKα radiation (1.5417 Å, 40 kV and 40 mA) and a divergence slit of $1/2$. The XRPD patterns were collected over the 5–80° 2θ-range, with a counting time of 5 s/step and a 0.02° step. A XRPD qualitative analysis has first been performed by means...
of the PANalytical X’Pert HighScore software. The phase contents were determined from the XRPD patterns by the full profile Rietveld Method (Young, 1993) implemented in the GSAS software with EXPGUI as a graphical interface (Toby, 2001). Al2O3-NIST 67 was added as an internal standard to estimate the amorphous phase content (Gualtieri, 2000).

2.3. In situ high-temperature X-Ray Powder Diffraction (HT-XRPD)

The in situ HT-XRPD measurements were carried out by means of a Philips X’Pert diffractometer, in 0–0 Bragg–Brentano geometry, equipped with a furnace (AHT-PAP1600) operating at a maximum temperature of 1600 °C. The temperature homogeneity was ensured by two large alumina fibre blocks, heated by MoSi2 resistances (Dapiaggi et al., 2002).

Preliminary in situ HT-XRPD data collections were recorded from room temperature (RT) up to 1200 °C, passing from an isotherm to another with a heating rate of 30 °C/min. Such experiments were carried out using Cu-radiation to explore the 5–80° 2θ-angular range, with a 2θ-step of 0.02° and a counting time of 1 s/step.

Kinetic experiments were performed to study the mullite formation as a function of time under isothermal conditions (from 1060 to 1120 °C). The heating rate used to achieve the chosen temperatures was set at 25 °C/min for all the measurements. The data collections were restricted to the 40–45° 2θ-range, with a 2θ-step size of 0.03° and counting time of 1 s/step.

2.4. Scanning Electron Microscopy (SEM)

A Cambridge STEREOSCAN 360 SEM equipped with an energy-dispersive (EDS)-detector was used to investigate micro-morphology (secondary and backscattered electrons images) and to measure chemical compositions (detection threshold about 0.1 wt%; precision from 2 to 5%, from previous calibration), operating at 15 kV, beam size of ~100 nm and working distance of 11 mm. The image resolution is of 1024 × 730 pixels and 1 pixel corresponds to ~1.5 μm. High definition secondary electrons images to observe crystal habits were recorded from samples etched by a solution of 8 M fluoroboric acid for 10 min in order to remove the amorphous phase.

2.5. Physical–mechanical properties

We measured the technologically most relevant physical properties of the ceramic bodies obtained by firing the G-batches at Tr−Tf conditions, i.e. “firing conditions”. We focus on ceramic pieces produced with G50 and G32 compositions, as G100 apparently showed properties insufficient to fulfil the technical requirements. Note that the reproducibility of the results was verified by measuring the same observable four times on three different samples prepared with the same composition; here the average values are reported.

In particular we measured:

- water absorption (WA), i.e. the wt%-difference between a fired body and the same after water saturation by immersion in boiling water for 2 h (Bernasconi et al., 2011);
- linear shrinkage (LS), i.e. the %-shortening of a 10 cm long cylinder slip due to firing;
- modulus of rupture (M.o.R), i.e. M.o.R. = [(3 × Pb/9.8) × Ls]/(2 × b × S²) where Pb and Ls are the three points flexural

Figure 4. SEM-images: “primary” and “secondary” mullite crystals with different size and morphology after isothermal runs at the highest T in the samples (a) G0, (b) G32 and (c) G50, (d) G100 where only “primary” mullite crystals grow on glass matrix.
breaking load and the distance between the tension rods on which a sample bar of breadth (b) and thickness (s) is laid, respectively.
- linear thermal expansion (LTE), according to Bernasconi et al. (2011). A Netzsch Dilatometer 402 ED, previously calibrated on alumina, was used, setting a temperature increase rate of 5.5 °C/min from 20 to 820 °C and recording the sample length every 6th second.

2.6. Data treatment of kinetic data

The kinetics of mullite crystallisation was followed measuring the integrated intensities of the (121) Bragg peak and calculating the conversion \( \alpha \)-parameter, i.e. \( \alpha = (w(t) - w(0))/(w(\infty) - w(0)) \) where \( w(x) \) is the integrated intensity of (121) at a given x-time.

The isothermal kinetic analysis relies on the fundamental equation (Brown et al., 1980):

\[
\frac{da}{dt} = k f(\alpha)
\]

where \( k = A \exp(-E_a/RT) \); \( f \) depends on the physical nucleation-growth model that is being used. We tried out the most used models of literature (Table 1 of Khawam and Flanagan, 2006) and chose \( f(\alpha) \) on the basis of the logarithmic plot analysis. The first-order model (F1), i.e. \( f(\alpha) = (1 - \alpha) \), and the geometrical contraction model (A3), i.e. \( f(\alpha) = 3(1 - \alpha)^{2/3} \), turned out to be the most suited ones to describe the formation process of mullite. The fitting of our data was carried out using the logarithmic form of the integral of Equation (1), i.e.:

\[
\ln k + \ln t = \ln(-\ln(1 - \alpha))
\]

and

\[
\ln k + \ln t = \ln\left[(-\ln(1 - \alpha))^{1/3}\right]
\]

where (2) and (3) correspond to the F1 and A3 models, respectively.

From the Arrhenius plot, the apparent Activation Energies (\( E_a \)) values have been calculated. Although the activation energies values are not precise because of the unknown details of the complex microscopic diffusion processes (Sung, 2000 and references therein reported), the \( E_a \)s yet allow one to compare the grades of reactivity as a function of the SLS glass contents.

3. Results

3.1. In situ HT-XRPD analysis at equilibrium conditions

The observed mullite is of type 3:2, on the basis of the cell parameters (Schneider et al., 2008), and of 40 EDS-analysis points collected by SEM and yielding an average composition consistent with \( \textnormal{Al}_4.75\textnormal{Si}_1.5\textnormal{O}_8 \).

The equilibrium crystal phase evolution for G32 and G100 upon heating up to 1200 °C is displayed in Fig. 1a–b by way of example. All the samples bearing SLS glass exhibit formation of cristobalite, which crystallizes up to ~1100 °C. At higher Ts it shows a behaviour that depends on the SLS glass content: in particular, it dissolves in G32 whereas it keeps on crystallizing in G100. G100 at 1000 °C exhibits crystallisation of Ca–Na plagioclase (\( \textnormal{(Ca,Na)}_2\textnormal{AlSi}_2\textnormal{O}_8 \)), which, in turn, starts to dissolve in the glass matrix at higher \( T \) (Fig. 1b).

In general, after heating at 1200 °C (Fig. 2) one observes: (i) a slight increase of the amorphous phase in the blend with the highest SLS glass amount; (ii) the lowest mullite content in the sample where feldspar is absent.

3.2. Kinetic analysis

The \( \alpha \)-values measured at different Ts are plotted in Fig. 3 for all the investigated samples: after the induction time, a steadily linear kinetics is observed until approximately 95% of mullite has grown.

In the samples bearing SLS glass (G32, G50, G100) the mullite growth is well described by a linear reaction model (F1); conversely, in G0 a geometrical contraction model (A3) is suggested. The \( E_a \)-values are shown in Table 2. They show a monotonically decreasing dependence on the SLS glass content for samples G0, G32 and G50: the higher the replacement of the feldspar with glass, the lower the \( E_a \) for mullite crystallisation. This relationship can be parameterised by the linear regression \( y = -65(3)x + 1104(25) \), where \( x \) and \( y \) stand for the wt%-glass content and \( E_a \) (kJ/mol) values respectively.

\( t(\alpha = 0.5) \) is the time required to achieve an \( \alpha \) value of 0.5. In Table 2, at 1060 °C the samples G32 and G50 exhibit \( t(\alpha = 0.5) \% \)s of ~155 and ~90 min, respectively, thus indicating that the SLS glass

![Fig. 5. Phase content occurring upon heating as a function of \( t_1 \) and \( t_2 \).](image-url)
speeds up significantly the reaction of mullite formation. In the case of $G_0$, $T > 1060 \, ^\circ C$ is required to observe the mullite growth kinetics.

In the samples $G_0$, G32 and G50, after heating, small ($\sim 0.1 \, \mu m$) cubic-like mullite crystals appear ("primary mullite"), along with longer ($>1 \, \mu m$) needle-shaped mullite crystals ("secondary mullite"), the latter arranged in interlocking structures (Fig. 4a–c). In G100 no evidence of secondary mullite is revealed (Fig. 4d), in keeping with the absence of feldspar-phase.

3.3. Micro-structures and thermal–mechanical properties

XRPD measurements on the samples fired at $t_f$–$T_f$ conditions showed the occurrence of quartz, Na-feldspar, cristobalite, mullite and glass. In Fig. 5 the phase content evolution as a function of $t_f$ (0, 20, 40, 60 and 80 min) and $T_f$ (1140, 1170 and 1200 \, ^\circ C) for the samples G32 and G50 is displayed. For the sake of brevity the numerical values of the phase contents are not reported. In general, quartz and Na-feldspar dissolve upon heating leading to a larger content of the amorphous phase. On the other hand, the mullite content exhibits oscillations within one standard deviation of its mean value, and it is therefore quasi-constant over the whole explored range ($t_f$–$T_f$ range (Bernasconi et al., 2011). This means that mullite crystallisation achieves quasi-completion at the end of the heating ramp, on the timescale here employed.

A linear regression is sufficient to model the relationship between the firing $t_f$–$T_f$ parameters, and the phase contents. In Table 3 the slopes of the main phases' contents ($m_x$ where $x$ is quartz, mullite, Na-feldspar and glass, respectively) as a function of $t_f$, at given $T_f$ are reported. In particular, we have considered two different intervals (0–40 and 40–80 min respectively) over which the $m_x$ values were calculated. Table 3 shows that most reactions involving the dissolution of quartz and formation of glass take place during the first 40 min.

The changes of the most relevant physical–mechanical properties as a function of $t_f$ and $T_f$ are measured for G32 and G50, and displayed in Fig. 6. A marked decrease of the WA values as a function of $t_f$ and $T_f$ can be ascribed to a progressively vitrification process within the fired body, as proven by the monotonic increase of the glass phase amount during the first 40 min.

Table 3 shows the kinetic results of the samples undergone $t_f$–$T_f$ firing conditions prove that the introduction of waste glass does not remarkably change the final crystal phase contents with respect to the output of classical thermal treatment of a standard sanitary-ware blend (Martín-Marqués et al., 2009). In the bearing-glass mixtures we observe the crystallisation of cristobalite as a result of the SLS glass devitrification; plagioclase occurs in G100 and might be attributed to the reaction between SLS glass (yielding CaO) and meta-kaolinite (CaO + meta-kaolinite $\rightarrow$ Anorthite) (Knapp, 1965).

The kinetic results prove that the SLS glass influences the mechanism of mullite formation. In the glass bearing blends the mullite growth is well described by a first order reaction model (F1), whereas in $G_0$ a model corresponding to a random instant nucleation followed by a 3-dimensional crystal growth (A3) is required. The mullite kinetic parameters have been observed to depend on the SLS glass content: the higher the content of glass in the samples where both primary and secondary mullites appear, the lower the $E_x$. This does not apply to the case in which primary mullite only occurs (G100 sample). The inverse relationship between $t_f$ (at $a = 0.5$) and SLS glass content proves the latter speeds up the ceramic reactions.

Finally, the addition of glass influences the macroscopic properties in the fired bodies at the macroscopic scale. In particular, an appropriate use of SLS glass allows one to lower $T_f$ and shorten $t_f$ but preserving the technological features we have focussed on, as a result of an acceleration of the densification/sintering process. Firing temperature might be lowered by 70–100 \, ^\circ C with respect to a traditional process. As to $t_f$, for instance at 1170 \, ^\circ C, the glass bearing batches reach the optimal values for their mechanical properties.
features in 40–60 min, thus opening to a contraction of the usual firing time needed for a standard body (Martín-Marqués et al., 2010, 2009).

5. Conclusions

Soda–lime glass, added to a typical sanitary-ware raw-materials mixture, can partially replace the traditional fluxes. In particular, we conclude that:

(i) it intrinsically influences the mechanism of mullite growth and accelerates the sintering kinetics. Different kinetic models are required whether SLS-glass is introduced or not. $E_a$ of G50 decreases by 44 and 95% with respect to G32’s and G0’s, respectively. $t(\alpha = 0.5)$ passes from 155 to 90 min, in G32 and G50, respectively. An approximate relationship relating $E_a$ to SLS-glass content is proposed for samples wherein primary and secondary mullite is present: $E_a$(kJ/mol) = $-65 \times $ wt % (SLS-glass) + 1104;

(ii) it affects the slopes of the phase contents as a function of $t_f$, at a given $T_f$. This is apparent for quartz dissolution and glass-phase formation, whereas mullite nearly completes its nucleation-growth process at the end of the heating ramp. Most reactions take place in the first 40 min;

(iii) it accelerates the densification process, allowing one to tune $t_f$ and $T_f$ so as to preserve technologically acceptable values of open porosity, linear shrinkage and M.o.R. in comparison with those of a traditional vitreous sanitary-ware body.

The points above open new vistas on energy saving, by reducing the fuels required at the firing stage and, as a consequence, the CO$_2$ emissions. On the other hand, the replacement of a part of feldspar
implies a saving in terms of natural resources, a preservation of the landscape and an effective management of glass cullet waste.

Note that further studies are required to get insight into how the introduction of glass can change the rheologic features of the ceramic slip, thus affecting the slip casting stage of the sanitary-ware production processes.

References


