Suppressing the effect of cullet composition on the formation and properties of foamed glass

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ABSTRACT

The process of foaming glass is very dependent on the chemical composition of the glass. In this study we used a foaming-agent/oxidizing-agent couple and a crystallization inhibitor to foam cullets of flat, container and CRT-panel glass. Foamed glass with a density of 110–120 kg m⁻³, a thermal conductivity of 50–52 mW m⁻¹ K⁻¹ and a homogenous pore structure was obtained from a mixture of panel glass, 0.33 wt% carbon and 4.45 wt% Fe₂O₃. We also showed that it is possible to fabricate foamed glass with the same density or pore structure as mentioned above by adding up to 50 wt% container cullet or 70 wt% flat glass to the mixture. In the foamed samples with a low content of panel glass, crystals form, resulting in an increased open porosity, density and inhomogeneous pore structure. The crystallization can, however, be inhibited by adding calcium phosphate, so enabling the preparation of high-quality foamed glass from flat glass or flat/container-glass mixture. The pore gas is predominantly CO₂ and the pressure inside the pores is 0.36–0.47 bar. The reduced effect of the composition on the foaming process suggests that there is a great potential for stabilizing the production of foamed glass and ensuring the product’s quality.

1. Introduction

Foamed glass is becoming increasingly common as an effective thermal insulation material. It is also recognized as being environmentally friendly because it is produced from waste materials and has a lifespan equal to that of construction materials, e.g., bricks and concrete [1–3]. This longevity is related to its inorganic composition and closed-pore structure, giving it high steam and frost-thaw cycle resistance. The limitation of foamed glass is its lower thermal insulation ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool. To expand the foamed-glass market’s potential, the production ability and its higher unit price compared to organic foams and mineral wool.

The high production costs of foamed glass are, among other factors, related to the need for a precise control of the glass’s composition, as compositional fluctuations are directly reflected in product quality [2]. Thus, adapting the waste glass composition by adding minerals and refining the melting process are used when producing high-quality foamed glass [4]. In contrast to this, the patent literature indicates that various kinds of glass(y) materials can be used in a process under similar conditions [5,6]. The foaming process is strongly dependent on the glass’s composition, since the glass is directly involved in the oxidation of carbonaceous foaming agents [2]. Thus, it would be a major advance to achieve a foaming process that would enable the production of a high-performance foamed glass under similar conditions from various cullets without the need to re-melt the glass and adjust its composition.

In order to decrease this dependence, the foaming reaction needs to be initiated only by the foaming additives and the glass must act as a largely inert matrix. A simple way to do this is to introduce metal carbonates, e.g., CaCO₃, into the raw-material batch [2,7–9]. At elevated temperatures, CaCO₃ decomposes and forms CO₂ in the viscous glass. However, the reaction of CaCO₃ with the glass is, again, dependent on the composition of the glass. Moreover, CaO, a solid residue of the decomposition, reacts with the glass, which can then trigger crystallization. Furthermore, the foaming with carbonates is difficult to control, as a rapid release of the gases results in rupturing of the pore walls and, thus, in an open pore structure [2,7–9].

Another option for decreasing the dependence of the foaming process on the glass’s composition is to use hydroxyl groups bounded on the surface of the glass [10–12]. At elevated temperatures these hydroxyl groups form water vapour, acting as a foaming gas or as a source...
of oxygen for carbon oxidation. To supply a sufficient amount of the bounded water, amorphous silica oxide, water glass and sodium hydroxide are added to the glass powder to prepare a thick suspension or paste [11,12]. After this, a lot of water vapour is released from room temperature to temperatures suitable for expanding the glass (i.e., 700–800 °C). The released water vapour can be used to oxidise a carbon-containing compound [12]. However, the combination of hydroxyl-saturated glasses with carbon results in the formation of a large amount of carbon monoxide and hydrogen gas during the foaming process [11]. These gases stay entrapped within the pores after cooling [13], thereby increasing the thermal conductivity of the foamed glass and increasing risks to health and problems with fire safety. CO2 is the most suitable gas if we take into account properties, price, health and sustainability.

The dependence of the foam’s properties on the cullet’s composition can also be suppressed by adding an oxidation agent to the powder batch, in addition to a carbonaceous foaming agent. The oxygen from the oxidizing agent is more readily available to oxidise the carbon than the oxygen from the glass. For example, the addition of manganese(IV) oxide (MnO2) improves the foaming effect of different foaming agents (carbon [14–16], SiC [15,16], Si3N4 [17] and AlN [18]). Also, other transition-metal oxides can be used to aid the foaming process [16,19–22]. However, it is important to select an oxidizing agent with a suitable oxidation state to achieve a superior foaming effect [23].

Crystallization is another factor that greatly affects the foaming process [2]. Most often, crystallization results from heterogeneous nucleation on the surface of a particle. Therefore, finely milled glass-powder mixtures are prone to nucleation, which can lead to extensive crystallization. To avoid crystallization, compositions with good glass stability have to be used. Alternatively, additives that inhibit the crystallization kinetics can be added to the powder batch. There are a number of potential additives that can be used for this purpose [16,24–27]. However, it is necessary to experimentally evaluate the effectiveness of an inhibitor on the foaming process and crystallization for the investigated composition of the glass. When using cullets with different glass compositions and stability, crystallization can appear in the less-stable glass compositions. In such cases a suitable crystallization inhibitor has to be used in order to allow the preparation of foamed glass from different cullets under similar process conditions.

Despite the observations of an improved foaming behaviour when foaming-agent/oxidizing-agent couples are used, there are no reports of using such couples to decrease the dependence of the foaming process on the composition of the glass. In this work we demonstrate the use of a foaming-agent/oxidizing-agent couple as well as a crystallization inhibitor to decrease the dependence of the foaming process on the composition of the glass. We used carbon as the foaming agent and iron (III) oxide (Fe2O3) as the oxidizing agent to foam cullets of flat glass, container glass and cathode-ray-tube (CRT) panel glass as well as their mixtures. These glasses possess similar viscosities (10^5.3–10^6.2 Pas) in the relevant temperature range (800–870 °C) [28], a pre-requisite for foaming at a similar temperature. We show that it is possible to foam these cullets under similar conditions and transform them into a high-quality foamed glass with a low density and thermal conductivity, which is necessary in the production of foamed-glass boards.

2. Experimental

Cullets of flat (Gerhardt, GmbH, Germany), container (Usioaines Oy, Finland) and CRT-panel glass (Averhoff A/S, Aarhus, Denmark) were supplied with a particle size below 100 µm. A second sample of flat glass was taken from a single obsolete window, hereafter referred to as window glass. The window glass was crushed, grinded and screened to below 100 µm to obtain a glass powder suitable for further processing. The chemical compositions of the cullets were analysed using X-ray fluorescence (PW2400, PANalytical, The Netherlands) and quantified using oxide standards (Wroxi, PANalytical). The compositions of the cullets are shown in Table 1. The compositions of the CRT-panel, container and window glass are in accordance with those of commercial glasses. The flat glass shows a higher alumina content than the typical flat glass’s composition. This indicates the presence of other glasses, most probably approximately 20 wt% of container glass. No diffraction peaks could be detected in the cullets with an X-ray powder diffraction (XRD) analysis. The glass powder was mixed with 0.33 wt% carbon (carbon black, acetylene, Alfa Aesar, Germany) and 3.01, 4.45, or 5.84 wt% iron(III) oxide (99%, Bie&Berntsen, Denmark). Additionally, 2 wt% of calcium phosphate (CaHPO4, 99%, Bie&Berntsen, Denmark) was added to the powder mixtures to suppress the crystallization tendency of the soda-lime-silicate compositions. The carbon/Fe2O3 mass ratio of 0.33/4.45 wt%/wt% (i.e., 1/1 mol/mol) is equal to half of the stoichiometric amount of Fe2O3 needed for Reaction 1.

$$\text{C(s) + 2Fe}_2\text{O}_3(s) \rightarrow \text{CO}_2(g) + 4\text{FeO(s)}$$

(1)

The powder mixtures were dry milled using an agate ball mill with 20-mm balls for 45 min to obtain particle sizes D50 and D90 in the ranges 5–6 µm and 15–18 µm, respectively. The ground powder mixtures were uniaxially pressed into pellets (40 MPa). These pellets (1 g, Ø = 13 mm) were used to study the influence of the foaming parameters on the properties of the foam. Larger samples of foamed glass (6 cm in diameter and 5 cm in height) were used to determine the thermal conductivity. The large samples were made from ~20 g of powder, which was pressed into pellets (Ø = 35 mm) with 30 MPa. The difference in the compaction pressure used for the small and the large samples has no impact on the foaming. The pellets were placed in an electrical laboratory tube furnace in a flow of argon (15–30 ml min^-1). To ensure a low oxygen content (estimated to < 0.5 vol%), the tube was tightly closed with flange and rubber seal, evacuated and flushed several times with argon. The samples were heated at 5 °C min^-1 to different temperatures (800–870 °C) for different periods of time (5–60 min). Subsequently, the small and large samples were cooled at, respectively, 12 and 7 K min^-1 to the glass-transition temperature (Tg) of 530 °C and then slowly cooled at 1–2 K min^-1 to room temperature. The temperature in the foaming zone was calibrated using an external thermocouple.

The apparent density (ρapp) of the small foam samples was determined using Archimedes’ principle in demineralized water. The reading was taken immediately after the sample was immersed in the water. Since the samples possess a hydrophobic surface and only small open pores were located on the surface, the amount of water absorbed was small, i.e., in the range of 0.1 g. The ρapp of the large foam samples was calculated from the sample masses and dimensions after cutting the samples to form a rectangular shape. The pycnometer density (ρpyc) of the foam samples was determined using a helium pycnometer (Ultrapyc 1200e, Quantachrome Instruments, US). The errors shown in the graphs and tables are the standard deviation of three foam samples or the estimated measuring error. The powder densities (ρpowder) of the cullets and the crushed foamed-glass samples with different compositions were
measured using the pycnometer. The total porosity ($\phi$) was calculated from the apparent density and powder density: $\phi = 1 - \frac{\rho_{app}}{\rho_{powder}}$.

The percentage of open pores (OPs) and closed pores (CPs) in the foam volume was calculated from the apparent, pycnometer and powder densities of the foam samples, as described elsewhere [7]. The open porosity is expressed as a percentage of the total volume of the foam ($V_{foam} = V_{glass} + V_{CP} + V_{OP}$).

Thermogravimetric (TG) analyses were performed using a Jupiter 449 simultaneous thermal analysis (STA) instrument coupled with a 403 C Aéoloss mass spectrometer (MS) (Netzsch, Selb, Germany). The measurements were made with a heating rate of 10 °C/min in argon. The CO$_2$ gas was ionized to several mass fragments, where CO$_2^+$ and CO$^+$ are the dominant species. The intensity ratio of the mass fragments 44 (CO$_2^+$) and 28 (CO$^+$) for pure CO$_2$ was 10–1 [23]. The higher intensity of mass fragment 28 indicates the presence of CO in the released gases. The powder mixture was compressed with 40 MPa and a small piece (30–40 mg) was placed in an alumina crucible for a TG–MS analysis. X-ray powder diffraction (XRD; Empyrean, PANalytical, The Netherlands) with a Cu-Ka radiation source and a voltage and amperage of 45 kV and 40 mA, respectively, was used to investigate the crystalline phases. Measurement range was 10–70° with a step size of 0.02°. For the XRD analysis, the samples were crushed and grinded using a pestle and a mortar. During this preparation, brittleness of the samples was qualitatively assessed, since some samples (partially crystallized) were rather brittle. The thermal conductivity was measured with a Hot Disk apparatus (TPS 2500 S, Hot Disk, Sweden) at 25 ± 2 °C using a kapton sensor with a radius of 9.6 mm. The repeatability of the measurements was better than ± 1%. The accuracy of the Hot Disk measurements was confirmed by comparing the thermal conductivity of commercial foamed glass samples measured using the Hot Disk with that measured using a guarded hot-plate apparatus (EP500, Lambda-Messtechnik, Germany). The comparison revealed good agreement between the methods (± 3%).

The CO$_2$ content and the pressure in the pores were assessed by crushing a sample in an evacuated, He-filled cylinder with a pressure gauge and subsequent gas analysis using gas chromatography. The CO$_2$ content was quantified by injecting triplicate 0.3-ml gas samples onto a Chrompack 9002 gas chromatograph with a TCD detector (Chrompak, NJ). The gases were separated on a PoraPlot Q column (0.53 mm × 30 m) using helium as the carrier gas (flow rate 1 ml min$^{-1}$). The oven temperature was 105 °C, the injector was 130 °C and the detector was 170 °C. The peak related to the CO$_2$ was fully separated from the other peaks and the sensitivity was of the order of 0.1 vol%.

The concentration of the CO$_2$ was quantified based on the injection of known standards. The standard curves were linear in the range 0.1–6.5 vol% CO$_2$. The volume of the foamed-glass samples was measured using the pycnometer. A foam sample of known volume was put into a stainless-steel cylinder with a known volume, together with a free-moving metal disk of known volume. The lid had a septum for taking gas samples from the cylinder and a connection to a pressure gauge. The cylinder was tightly closed, evacuated and then filled with He gas to 1 bar. The gas analysis was performed immediately after the gas inside the cylinder had been exchanged with He. First, a sample of the background atmosphere was injected into the GC (triplicate 0.3 ml). In all the experiments no CO$_2$ was detected in the background. The sample was then crushed by shaking the cell, and triplicate 0.3-ml gas samples from the cylinder were injected into the GC. Afterwards, the crushed glass was collected and the volume was measured with the pycnometer to calculate the released volume of gases. The content of CO$_2$ in the cylinder cell after crushing the samples was between 2 and 6 vol%. The obtained volume of CO$_2$ (under normal conditions) was compared to the total volume of gases released by crushing (under normal conditions) to calculate the content of CO$_2$ entrapped in the pores in vol%. The error of the measurement originating from the uncertainty in the measurement of the volumes and pressure was calculated to be ± 5%.

The pressure gauge, connected to the cylinder, was used to monitor the pressure in the cell at every stage. The pressure in the pores was calculated from the volume released by crushing, the free volume of the cell and the pressure change during crushing using Boyle’s law. The uncertainty of the measurement was calculated to be ± 2%.

3. Results

Fig. 1 shows the mass loss and gas evolution during the foaming process with the foaming-agent/oxidizing-agent couple in an oxygen-free atmosphere. The mass loss up to 570 °C is related to the release of gases (CO$_2$ and H$_2$O) adsorbed on the finely ground powders [23]. A small CO$_2$ peak (m/z = 44) is seen at 660 °C, which is related to the initial surface reaction between the glass and the additives. The surface reaction is initiated by the sintering process that starts at ~600 °C [7,29]. The sintering moves the particles closer to each other, thus enabling surface reactions between them. The sample sinters to closed porosity at ~680 °C ($T_{sint}$), where the intensity of the CO$_2$ signal (m/z = 44) drops to the background level [23,29]. Only when the pores are closed (above $T_{sint}$), the evolved gases can stay entrapped and foam the softened glass. A mass loss related to the foaming reaction starts at 705 °C ($T_{foam}$) and steadily continues to the maximum temperature (1000 °C). The initial mass loss in the temperature range 705–730 °C results in a significant gas release, which is likely related to the reaction on the surface of the sample and the bursting of many small closed pores. The bursting of the surface pores creates a thicker crust, preventing the second layer of gas bubbles from bursting into the surroundings. Hence, the gas evolution is less active in the range 760–850 °C. Above 850 °C the gas evolution is characterized by sharp spikes, caused by the bursting of large pores, releasing a large amount of gas.

The composition of the released gases changes from CO$_2$ to a mixture of CO$_2$ and CO at temperatures above 900 °C. Similar behaviour was observed in a previous study [23].

To find the optimum concentration of additives and the optimum heating conditions we prepared samples with panel glass and different amounts of carbon and Fe$_2$O$_3$, and heat treated them in different conditions. The optimum amount of carbon was found to be 0.33 wt%. Samples prepared with a smaller (0.2 wt%) or larger (0.5 wt%) amount of carbon exhibited a higher density or large pores with a higher proportion of open pores, respectively. The influence of Fe$_2$O$_3$ content and temperature on the density and open porosity is shown in Fig. 2. The optimum foam properties were obtained by adding 4.45 wt% Fe$_2$O$_3$ and...
employing a foaming temperature of 850 °C (15 min dwell time). Under these conditions the density is the lowest and the pores are closed. The pore structure of the samples is shown in Figs. 3a–c. The samples with 3.01 and 4.45 wt% Fe₂O₃ have a homogeneous pore size distribution, while in the sample with 5.84 wt% Fe₂O₃ some larger pores appear.

Based on the optimized temperature, time, Fe₂O₃ and carbon concentration, the CRT-panel glass was substituted with other glass cullets. Table 2 shows the effect of substitution on the apparent density, total porosity and open porosity. It is clear that at a 50% substitution with window (#5) or container glass (#6) and a 70% substitution with flat glass (#7), the properties of the foam remain, to a large extent, unchanged in comparison to the panel glass sample (#2). Substituting the panel glass completely with other glass types (#8–10), the density can be kept low when using flat or window glass, but the density increases steeply for bottle glass. Independently of the glass type, the complete substitution has a negative impact on the open porosity and the foams become more brittle.

According to the XRD analysis, the foam samples prepared from the CRT-panel cullet are amorphous, while several crystalline phases form in the samples containing a large fraction of flat or container glass (Fig. 4). The phases present in the samples produced from the flat glass (Fig. 4c), and also the sample from the window glass, are MgCaSi₂O₆ (diopside), Na₂Ca₃Si₆O₁₆ (devitrite) and SiO₂ (quartz and cristobalite). In the case of the foamed glasses prepared from container glass (Fig. 4e) the phases present are Na₂Ca₃Si₆O₁₆ (devitrite), CaFe₂O₄ (calcium iron oxide), SiO₂ (cristobalite and quartz), and Ca(Mg,Fe)Si₂O₆ (iron containing diopside). The addition of CRT-panel glass inhibits the crystallization, and thus the samples containing ≥ 50 wt% of panel glass are XRD amorphous. The sample with 70 wt% of flat glass contains a small amount of diopside (Fig. 4b), while the sample with 70 wt% of
container glass is a slightly higher (Figs. 4c and d). However, the positive effect of calcium phosphate is not as strong as in the sample with a large proportion of container glass (compare Fig. 4e and f). These samples remain partially crystalline as well as having open porosity. The crystallization causes breaking and cracking of the pore walls, leading to an increased content of open pores (Table 2). Moreover, the partially crystalline foam prepared from flat glass was found to be noticeably more brittle than the sample prepared from panel glass. An increased brittleness was not detected in the sample prepared from pure container glass, most probably due to a higher density.

The pore structure of the samples prepared from flat, window and container glass is shown in Figs. 3d–g. The samples exhibit a relatively homogeneous porosity, except for the sample prepared from container glass (Fig. 3g). In soda-lime-silica samples the pore size is smaller than in the sample prepared from CRT-panel glass (Fig. 3b).

The pressure in the pores of the amorphous samples varies between 0.36 and 0.39 bar (Table 2). The pressure in the pores is slightly higher (0.41–0.47 bar) in the partially crystallized samples prepared from flat or container glass (Table 2). A gas analysis of the pore gases revealed that the content of CO₂ in the samples containing panel glass is above 90 vol%. The results are comparable to those for commercial foamed glass prepared in a reducing atmosphere (CO₂ > 95 vol%, p = 0.35 bar) [3]. The CO₂ content is lower in the samples prepared from pure flat or container glass, which also exhibit a higher pressure in the pores.

The effect of the content of CRT-panel glass on the thermal conductivity was evaluated for the large samples. In order to obtain samples with different densities the foaming temperature and dwell time were changed in the range of 840–860 °C and 15–25 min, respectively. The density of the large samples prepared from the same batch and under the same conditions is significantly lower than the density of the small samples, while the open porosity for the partially crystallized samples is higher. These observations are related to a different temperature profile in the sample with increasing sample size. Hence, the cooling of the large samples is slower due to insulation of the core of the sample [14]. Moreover, in the case of large samples the thicker crust formed on the surface of the samples is cut away. The amorphous large samples have closed pores. The pore structures of the large samples are shown in Fig. 5. It is clear that the pore size of the sample with pure soda-lime-silica glass is smaller than in the samples containing panel glass. The pore size distribution of the sample prepared from pure soda-lime-silica glass is also narrower.

The thermal conductivity decreases with a decrease in the density of the samples (Fig. 6) as well as with an increasing content of the CRT-panel glass. The data points with the same content of soda-lime-silica glass can be fitted with a linear function, which indicates the equivalent thermal properties of the flat and container glass in the foamed glass product. At a density of around 110 kg m⁻³ the use of pure panel glass decreases the thermal conductivity by 9–12 mW m⁻¹ K⁻¹ in comparison to a pure soda-lime-silica glass composition. The lower conductivity of the foamed glasses prepared from the CRT-panel is attributed to the lower thermal conductivity of the panel glass (0.97 W m⁻¹ K⁻¹) in comparison to a soda-lime-silica glass (1.1 W m⁻¹ K⁻¹) [29,31,32]. The slope of the decrease in the thermal conductivity with the density also decreases with an increase in the content of panel glass.

Table 2

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<th>Window [wt%]</th>
<th>Container [wt%]</th>
<th>Fe₂O₃ [wt%]</th>
<th>CaHPO₄ [wt%]</th>
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XRD amorphous.

Partially crystalline.
4. Discussion

The TG–MS analyses revealed that the combination of carbon as a foaming agent and Fe$_2$O$_3$ as an oxidizing agent is suitable for foaming in an oxygen-free atmosphere. No important mass loss that could be related to the premature oxidation of carbon is observed below the sintering temperature (680 °C) [23]. The weight loss above 700 °C is moderate and continuous, equal to around 0.3 wt% per 100 °C. Additionally, CO$_2$ is the major constituent of the released gases up to 920 °C.

The optimum foaming-agent/oxidizing-agent ratio, i.e., 0.33 wt% carbon and 4.45 wt% Fe$_2$O$_3$ and different ratios of CRT-panel to soda-lime-silica glass. The data points with the same content of the panel glass are fitted with a linear function. The measurements were conducted at 25 ± 2 °C.

![Fig. 5. Pore structure of the large samples prepared with 0.33 wt% carbon, 4.45 wt% Fe$_2$O$_3$ and a) CRT-panel glass, b) 50 wt%/50 wt% flat/panel glass, c) 70 wt%/30 wt% flat/panel glass and d) 33 wt%/67 wt% container/flat glass with 2 wt% calcium phosphate addition.](image)

![Fig. 6. Thermal conductivity of the foamed glasses prepared with 0.33 wt% carbon, 4.45 wt% Fe$_2$O$_3$ and different ratios of CRT-panel to soda-lime-silica glass. The data points with the same content of the panel glass are fitted with a linear function. The measurements were conducted at 25 ± 2 °C.](image)
samples. It is anticipated that the content of CO in the closed pores would decrease by applying a slower cooling rate and annealing of the samples (at around $T_{\text{cs}}$), according to the Boudouard equilibrium. A slower cooling rate and annealing of the samples are required in industrial foamed-glass production to release the stresses in the foamed glass [3]. Thereafter we expect that in the case of industrial production the content of CO in the pores would be negligible.

In the case of a stable foam the forces working on a pore wall during the foaming process, i.e., viscosity, surface tension and furnace pressure, are in equilibrium with the pressure in the pores. For the estimation of the lower limit of the pressure in the pores, we assume a pressure of 1 bar (furnace pressure) in the closed pores at 850 °C, and the foamed glass is instantly cooled to room temperature. Thereafter, the pressure inside the foam at room temperature should be 0.27 bar [3], according to Gay-Lussac’s law. However, such a calculation does not take into account the change of the amount of gas molecules in the pores and the contraction of the pore volume. These changes occur due to the conversion of CO to CO$_2$ and the soft nature of the glass above the softening temperature ($T_{\text{soft}} \approx 700$ °C). Expectedly, the pressure in the pores, i.e., 0.36–0.39 bar in the amorphous samples (Table 2), is higher than the theoretical lower limit. In the partially crystalline foams the pressure is even higher. Several processes could influence the pressure in the pores in a partially crystalline sample: (i) the growth of crystals can increase the viscosity, thus a higher pore pressure is needed to obtain the same low density, (ii) the increased viscosity will also inhibit the shrinkage during cooling, leading to a lower pressure at room temperature, and (iii) large pores break while small pores remain closed (higher open porosity), leading to a higher pressure detected at room temperature (the pressure is related to the pore diameter [29]). The higher pressure in turn hinders the conversion of CO to CO$_2$ according to the Le Chatelier principle, which is in accordance with a lower content of CO$_2$ in the partially crystalline samples.

The large samples prepared for the thermal conductivity measurements exhibit a relatively homogeneous pore structure. The density of the large samples in comparison to the small samples is lower since the thicker surface layer, i.e., the crust, was not measured together with the core of the sample and also due to slower cooling of the interior of the sample. The open porosity in the partially crystalline samples reaches 85 vol%, which is much higher than in the small samples (e.g., 7 vol% for the container glass sample). Such a large increase in the open porosity in comparison to the small samples is generally observed, thus it is important to prepare larger samples for an evaluation of the application potential. The addition of calcium phosphate leads to a decrease in the open porosity, in accordance with the inhibition of the crystallization. The difference in the open porosity between the small and the large samples is most probably caused by a longer exposure to high temperatures and slower cooling of the large samples, which results in a more extensive crystallization. Crystallization inhibits the pore expansion and decreases the stability of the pore wall. Consequently, pressure in the pores increases until the pore wall breaks. This is in accordance with the higher content of open pores in the partially crystalline samples. The samples with open porosity are not suitable for thermal conductivity applications where the material would be exposed to humidity and frost [2].

The increased content of CRT-panel glass significantly decreases the thermal conductivity, which is in accordance with the lower thermal conductivity of the panel glass [29,31,32]. Interestingly, the slope of the thermal conductivity vs. density decreases with an increase in the panel glass content. The reasons for this could be the differences in the pore size, the foam structure and the gas composition; however, more detailed data about the foam structure need to be collected for an investigation of the slope in the graph of thermal conductivity vs. density. In comparison to the commercial samples [3,4,33], the thermal conductivity of the samples prepared in this study is higher (a correction of about –8% has to be applied to the results given in Fig. 6 to obtain the values at a standard measuring temperature of 10 °C). However, the results demonstrate that by using a foaming-agent/oxidizing-agent couple it is possible to prepare foamed glass from cullets with different compositions under similar conditions.

5. Conclusions
In this study we demonstrated the use of a foaming-agent/oxidizing-agent couple and a crystallization inhibitor for the preparation of foamed glass from different glass compositions. The results show that the couple of carbon and Fe$_2$O$_3$ (in concentrations 0.33 wt% and 4.45 wt%, respectively) is suitable for foaming in an oxygen-free atmosphere. The couple releases a moderate amount of predominantly CO$_2$ gas above the softening point of the glass, enabling the preparation of lightweight foams with a homogeneous pore structure from CRT-panel glass. Under the same foaming conditions it is possible to exchange panel glass with up to 70 wt% of flat glass or with up to 50 wt% of container glass without compromising the density or pore structure of the foamed glass. For a higher substitution of the panel glass, however, crystallization appears, which hinders the foaming process and results in a higher content of open pores, a higher density and an inhomogeneous pore structure. The identity of the formed crystalline phases depends on the chemical composition of the cullet. The crystallization in the samples with flat glass or a mixture of flat and container glass can be effectively inhibited by a small addition of calcium phosphate. The analysis of the gases in the pores shows a high content of CO$_2$ (> 90 vol%) and a pressure between 0.36 and 0.39 bar for the amorphous samples. In the partially crystalline samples, the content of CO$_2$ is smaller and the pressure higher than in the amorphous samples. The thermal conductivity of the samples decreases with an increasing content of CRT-panel glass, which is in accordance with its lower thermal conductivity in comparison to soda-lime-silica glass. The difference in the thermal conductivity between the samples prepared from the CRT-panel and soda-lime-silica glasses is 9–12 mW m$^{-1}$ K$^{-1}$ at a density of around 110 kg m$^{-3}$. The use of foaming-agent/oxidizing-agent couples and crystallization inhibitors represents a great potential for decreasing the effect of the glass composition on the formation and properties of the foam glass, thus stabilizing the production of foamed glass.

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Declarations of interest
None.

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