The mechanism of foaming and thermal conductivity of glasses foamed with MnO₂

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A B S T R A C T
We prepare foam glass from cathode ray tube (CRT) panels using MnO₂ as foaming agent at different temperatures for various durations. The reduction of MnO₂ to Mn₃O₄ leads to formation of O₂ gas, and hence, causes initial foaming. The Mn₃O₄ particles dissolve into the glass melt and subsequently reduce, causing further formation of O₂ gas and foaming of the glass melt. Increasing the treatment temperature and time enhances foam expansion, Mn₃O₄ dissolution, and lowers the closed porosity. Once the foam reaches a percolated stage, the foam continues to grow. This is caused by nucleation of new bubbles and subsequent growth. We discuss evolution of pore morphology in terms of pore number density, pore size and closed porosity. The thermal conductivity of the foam glasses is linearly dependent on density. The heat transfer mechanism is revealed by comparing the experimental data with structural data and analytical models. We show that the effect of pore size, presence of crystal inclusions and degree of closed porosity do not affect the overall thermal conductivity.

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1. Introduction

The production of foam glass is an effective method for low-cost recycling of waste glass. The foam glass is mainly used in the construction industry, where high compressive strength and thermal insulation are important. Therefore, many studies focus on understanding the relation between structural properties and mechanical and thermal properties. The compressive strength of foam glass is strongly dependent on foam density and pore morphology [1–3]. The thermal conductivity is also strongly related to the foam glass density; often in a linear fashion [2,4–7].

Both the mechanical strength and the thermal conductivity can be affected by the presence of crystals. For instance, the mechanical strength of glass is improved when it is partially crystallised, i.e. when it becomes glass-ceramic. However, if there exists a mismatch in the thermal expansion coefficients between the crystals and the glass matrix, cracking can occur during cooling, resulting in severe loss of mechanical strength. For the purpose of thermal insulation, the following consequences of crystal inclusions in foam glass should be considered. First, the crystals can be anisotropic. This makes the thermal conductivity dependent on the crystal orientation relative to the heat flow direction. However, the anisotropic effect should be averaged out if the crystals are random orientated. Second, the thermal conductivity of many silicate crystals [8] is higher than their amorphous counterparts: silicate glasses [9]. Third, the interfacial resistance between a crystal and a glass can decrease the effective solid conductivity [10–12].

The open/closed porosity is another important factor influencing the mechanical strength and thermal conductivity. Gasses entrapped in the glass melt outgasses when the pore wall breaks down during foam glass formation at high temperatures or when the solid foam glass is exposed to high mechanical stresses. This has a negative impact on the thermal conductivity, if the entrapped gas (e.g. CO₂) insulates better than the surrounding atmosphere. In addition, large open pores allow contribution from convective heat transfer to the overall thermal conductivity. As a result, the thermal insulation ability decreases with increasing degree of open porosity. The mechanical strength of cellular material with open pores is less resistant against mechanical stress compared to a cellular material with closed pores [13]. Open pores can also reduce the outdoor lifetime of a foam glass product since water can be absorbed through the pores. At low temperatures the water volume increases due to freezing and cracks will appear in the foam glass. Hence, the use of foam glasses with closed pores is an advantage in the construction industry. On the other hand, the catalyst industry prefers foam glasses with connected pores together with both high surface area and high mechanical strength [14,15]. High degree of open pores allows an overall faster reaction rate and high mechanical strength allows usage of a high flow rate.

Despite the importance of the open/closed pore structure, only few systematic studies demonstrate how control of open/closed porosity is attained during the foaming process [4,16,17]. In this work, we study the volume expansion kinetics and percolation kinetics of foam glass.
melts and the thermal conductivity of the derived foam glasses. We foam panel glass from cathode ray tubes (CRT) using MnO₂ as foaming agent. The CRT panel glass is a waste glass from television and computer monitors, which has, to our experience, excellent glass stability [4,18, 19]. This idealise the foaming mechanism, since crystallisation changes melt viscosity and affects the foam stability [20,21]. MnO₂ is often used in combination with other foaming agents (e.g. SiC, TiN, carbon) in the foam glass process [1,3,4,22–26]. We choose to foam only with MnO₂, since the resulting gas composition, O₂/air, has the same thermal conductivity (within three decimals) irrespective of O₂/air ratio at the measured temperature. This is ideal in sense of describing the thermal conductivity of the foam glasses obtained in this paper.

In this contribution, we show that the foam density decreases with time in an exponential fashion and that the time dependent transition from closed to open pores is fast and accelerates when temperature is increased. We discuss the thermal, redox and dissolution characteristics of manganese oxide and relate these to the foaming ability. Finally, we demonstrate that the thermal conductivity is linearly dependent on foam density and we describe this behaviour using the Schuetz–Glicksmann model.

2. Materials and methods

2.1. Characterisation of powder

The particle size distribution of the CRT panel glass powder and MnO₂ powder (99%, Merck) was determined with a LS 13320 laser granulometer (Beckman Coulter) using Mie theory and refractive index of the CRT panel glass (1.518) and MnO₂ (2.2). The D₅₀ values were 32 μm and 40 μm for the CRT panel glass and MnO₂, respectively. The chemical composition of the CRT panel glass was measured using X-ray fluorescence (PW2400, PANanalytical) with SuperQ software. Oxide standards (Wroxi, PANalytical) were used for quantification. The content of Sb₂O₃ was quantified separately. The composition shown in Table 1 are in accordance with the literature [27]. Thermal stability (i.e., the stability against thermal decomposition and redox reaction) of both MnO₂ powder and powder mixture was measured with thermogravimetry (STA Jupiter 449C, Netzsch) in a Pt crucible at 10 K/min in an air flow of 40 mL/min.

2.2. Preparation of foam glass

The CRT panel glass powder was mixed with 7 wt.% (~5.7 mol%) MnO₂ in a porcelain jar with Al₂O₃ spheres (Ø = 3 cm). The mixed powder was uniaxially compressed with a hydraulic press at 40 MPa under dry conditions. The green pellets had a diameter of 3.5 cm and a porosity of 44%. The pellets were then placed on a stainless-steel plate with a stainless-steel cylinder (Ø = 6 cm) surrounding the sample. To avoid sticking of the glass melt to the mould, the steel was coated with a kaolin suspension. The samples were then heated in air at 10 K/min to 1063 or 1083 K for different durations (5, 10, 20, 40, 80 and 160 min). The foams were cooled to 803 K (Tₓ) at 5 K/min and then to room temperature at ~1 K/min.

The foaming ability was measured in air with a custom made heating microscope (EM201x, Hesse Instruments) using image analysis software EM13.0.1a (Hesse Instruments). A dry pressed (40 MPa) cylindrical sample of 1 g was placed on alumina plate and heated to 873 K at 30 K/min and then at 10 K/min to 1150 K.

2.3. Characterisation of foam glass

The top and bottom parts of the foam glasses were plane polished to get regular cylinder shaped samples (Ø = 6 cm). The foams were then core drilled (height = 30–32 mm, Ø = 38 mm). The foam density (ρfoam) was determined from the diameter, height and mass of the core drilled foam cylinders. The powder density of the crushed foam glass (ρpow) was measured with a He-Pycnometer (Ultrapyc 1200e, Quantachrome). ρfoam was 2.82 ± 0.01 g/cm³. ρpow and ρfoam were used to calculate the porosity, ϕ, (Eq. (1)).

ϕ = \left(1 - \frac{\rho_{\text{pow}}}{\rho_{\text{foam}}}\right) \times 100\%

(1)

The skeletal density (ρskelet) was measured on the core drilled foam cylinders with a He-pycnometer. The skeletal density was used to calculate closed porosity, ϕcp, (Eq. (2)).

ϕ_{\text{cp}} = \left(\frac{\rho_{\text{skelet}} - 1}{\rho_{\text{pow}} - 1}\right) \times 100\%

(2)

The crystalline phases of the foam glasses were examined using powder X-ray diffraction (XRD). The XRD measurements were performed using an Empyrean diffractometer (PANalytical) with Cu Kα radiation. Voltage and working current were 45 kV and 40 mA, respectively. Measurement range of 2θ was 10 to 70° with a step size of 0.02°. The phase identification was carried out by comparing the peak positions and intensities with diffraction pattern in the Joint Committee on Powder Diffraction Standards (JCPDS) data files using Highscore software (PANanalytical). Scanning electron microscope (SEM) operating at 10 kV was used to characterise the pore structure of foam glass (EVO 60, Zeiss). The foam glasses were prepared by first cutting and then plane grinding with SIC paper using #120, #500, #1000, and #4000. For pore counting, foam glasses were mounted with Epofix epoxy resin (Struers A/S). The mounted samples were polished with 3 μm diamond DP-Suspension A (Struers A/S) on MD-DAC cloth (Struers A/S) using DP-blue (Struers A/S) as lubricant. The number of pores was counted from 50-times magnified SEM images (Fig. 1) by manually marking the pores and counting with Matlab software. The recorded images had a resolution of 1024 × 768 or 2048 × 1536. At least three SEM images were used for pore counting for each sample. All samples were gold coated prior SEM. Chemical composition was determined with the energy dispersive X-ray (EDX) spectroscopy (Thermo Electron Corporation).

The glass transition temperature (Tₓ) of foam glasses was determined using a differential scanning calorimetry (DSC) in argon atmosphere (STA Jupiter 449C, Netzsch). 43–49 mg of crushed foam glass was placed in Pt crucible. The samples were first heated slightly above Tₓ at 10 K/min in order to delete thermal history. Then the samples were cooled to room temperature at 10 K/min, only to subsequently perform a repeating heat-treatment again at 10 K/min. The glass transition was determined from the second measurement.

<table>
<thead>
<tr>
<th>Table 1</th>
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<td>Oxide</td>
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</tr>
<tr>
<td>SiO₂</td>
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<tr>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Na₂O</td>
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<td>MgO</td>
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<td>Fe₂O₃</td>
</tr>
<tr>
<td>ZnO</td>
</tr>
<tr>
<td>P₂O₅</td>
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<tr>
<td>Sb₂O₃</td>
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</tbody>
</table>
The thermal conductivity was measured on the top side of plane polished foam glasses (Ø = 6 cm, height = 4–6 cm) with an Isomet surface probe (2104, Applied Precision). The measurement was carried out at 283.7 ± 0.6 K in a temperature controlled chamber. Three repeating measurements varied within ±0.15 mW m⁻¹ K⁻¹ and the temperature of each sample varied by less than 0.1 K. The accuracy of the surface probe was checked with commercial materials of expanded polystyrene and foam glass. The measurements agreed very well with declared values. The reported error range of the surface probe is 3%.

3. Results and discussion

3.1. Thermal stability of MnO₂ and Mn₂O₃

3.1.1. Thermal characteristics of MnO₂ and Mn₂O₃

MnO₂ reduces to Mn₂O₃ at around 900 K (T_{\text{decomp,1}}) in air atmosphere when MnO₂ is heated at 10 K/min. This is observed by a distinct mass loss (Fig. 2). Increasing the temperature further, the sample mass becomes stable again at 990 K. This indicates that the reduction of MnO₂ to Mn₂O₃ is completed. Increasing the temperature even further (T ≈ 1173 K), Mn₂O₃ reduces to Mn₃O₄ [22,28,29].

3.1.2. Dissolution of Mn₂O₃

The MnO₂ mixed with CRT panel glass powder reduces at the same temperature as pure MnO₂, hence, no detectable interaction between CRT panel glass and MnO₂ occurs in the temperature range of 830 to 990 K. At elevated temperatures (T_{\text{decomp,2}}) the glass melt causes reduction of Mn₂O₃ as shown by distinct mass loss (Fig. 2). The glass melt destabilises Mn₂O₃, allowing reduction of Mn₂O₃ below 1173 K. Redox studies of Mn²⁺/Mn³⁺ in glass melts at high temperatures (T ≈ 1240–1550 K) show that Mn²⁺ is the dominating oxidation state [30]. Extrapolating to 1063 K results in Mn²⁺/Mn³⁺ ≈ 2. This indicates that Mn²⁺ is thermodynamically favourable in the CRT panel glass melt at treatment temperature.

The XRD results confirm that Mn₂O₃ crystals are gradually disappearing in the foam glass with increasing temperature and extending time (Fig. 3). This shows that Mn₂O₃ dissolves in the glass melt. After dissolution, the local redox potential causes reduction of Mn³⁺ to Mn²⁺ according to the equilibrium:

\[
2\text{Mn}^{3+}(\text{melt}) + \text{O}^{2-}(\text{melt}) \rightarrow 2\text{Mn}^{2+}(\text{melt}) + \frac{1}{2}\text{O}_2(\text{gas}) .
\]  

The diffusion of Mn²⁺ and O₂ away from the Mn₂O₃ particle enhances further reduction of Mn²⁺ according to the equilibrium (Eq. (3)). The dissolution of Mn₂O₃ particles is diffusion-limited and occurs faster at a higher temperature when melt viscosity decreases (compare Fig. 3a and b). Hence, the reduction of Mn³⁺ is coupled to the dissolution and diffusion kinetics.

![Fig. 1. SEM image of an epoxy mounted foam glass used for counting the number of pores per image area (N). The foam glass is prepared at 1063 K for 20 min.](image)

![Fig. 2. Mass loss of manganese oxide measured with TGA on pure β-MnO₂ and on CRT panel glass with 7 wt.% MnO₂ (left Y-axis). Densification and expansion curves of pure CRT panel glass (D_{90} = 32 μm) and of CRT panel glass with 7 wt.% MnO₂ (right Y-axis) were measured with heating microscope. TGA and heating microscope analysis were performed in air and at 10 K/min.](image)

![Fig. 3. XRD patterns of crushed foam glasses prepared at a) 1063 K and b) 1083 K at different treatment times (see legend). The spectra are shifted vertically for clarity. The JCPDS card number 01-089-2809 is used to identify Mn₂O₃.](image)
3.2. Foaming of glass melt

3.2.1. Foaming mechanism

Some glasses can foam at elevated temperature without foaming agents [17]. As shown in Fig. 2, CRT panel glass powder only densifies when heated but foams when MnO2 is added. The MnO2 decomposes in the temperature range, where the glass sinters (Fig. 2). Thus, a major part of the O2 generated from MnO2 reduction escapes the glass body. As shown in Fig. 2, the foaming begins at 950 K ($T_{\text{foam}}$) before the reduction of Mn2O3 is detected at 1100 K ($T_{\text{decomp}}$). This indicates that a small amount of O2 becomes entrapped in the sintered body. At elevated temperatures ($T > T_{\text{foam}}$) the O2 pressure in the pores increases and causes initial expansion.

In foam glass production, the foaming agent is often present as a solid particle. When Mn2O3 particles are located on the pore wall or partially immersed in the glass melt, O2 formed at the glass-Mn2O3 interface would not lead to any new pores but only increase of pressure in existing pores (Fig. 4a). With time, Mn2O3 particles become completely immersed in the glass melt. O2 formed at the surface of Mn2O3 particles can diffuse to the existing pores, increasing the pressure in pore (Fig. 4b). If the O2 formation is faster than the removal of O2 by diffusion, the glass melt becomes supersaturated. As a consequence, homogeneous or heterogeneous nucleation of closed pores (bubbles) can occur. Since Mn2O3 particles are present, bubble nucleation will preferably occur at the Mn2O3 surface. It is not possible to find any crystal particles located at the pore wall with SEM. However, high Mn concentrations combined with low Si concentrations are found as dark spots in the glass matrix (Fig. 5). This confirms that manganese oxide is immersed in the glass melt.

During the foaming process, the pores become open, allowing the exchange of O2 with air atmosphere. Since the reduction potential increases with decreasing oxygen pressure (Eq. (3)), a further reduction of dissolved Mn2+ can occur, resulting in nucleation and growth of new bubbles.

Based on valence state (Z) and ionic radii (r) of manganese with different coordination numbers (CN) from Shannon [31], the field strength ($FS = Z/r^2$) calculations indicate that Mn2+ should be classified as network modifier ($FS = 0.37–0.50$, CN = 4–8) and Mn3+ as an intermediate ($FS = 0.81$, CN = 5 or 6). The increased dissolution of Mn2+ could therefore lead to depolymerisation of the [$SiO4$] network. The depolymerisation of glasses is very often reflected in a decrease of the glass transition temperature. In our earlier work, we found that the $T_g$ of CRT panel glass decreases with the content of Na2O [18,32], which is a strong network modifier. Here, we have found that the effect of Mn2+/Mn3+ on $T_g$ to be much weaker than alkali oxides and no significant time dependent effect on $T_g$ is found (Table 2).

3.2.2. Foam growth

The time dependent heat-treatment shows that the foam density ($\rho_{\text{foam}}$) decreases exponentially with time at 1063 K and 1083 K (Fig. 6). The foam growth is caused by increasing O2 pressure. When the gas pressure exceeds the forces of surface tension and viscosity, the pore wall stretches, expanding the pore. The pressure in a spherical pore is inversely dependent on pore radius. Therefore, the pressure is lower in large pores than in small pores. As a consequence, the majority of O2 diffuses from the particles towards larger pores and they will grow faster than smaller pores. Since big pores have a larger surface area, they have greater accessibility to O2 diffusing from the glass melt. This contributes additionally to faster growth rate of the larger pores.

Initially the reaction (Eq. (3)) is far from equilibrium and the gas formation is fast. In addition, the dissolution rate is also expected to be faster in the beginning, since the total particle surface in contact with the glass melt is greater in the beginning if the particles are immersed. Since the amount of crystalline Mn2O3 decreases with treatment time, the total particle surface area decreases and, hence, the dissolution rate decreases. As dissolution rate decreases and Mn2+/Mn3+ ratio approaches equilibrium state, the gas formation rate diminishes with time.

![Fig. 4.](image)
(a) The Mn2O3 particle is partially immersed in the glass melt (short treatment times). The O2 formed from the reduction of Mn2+ diffuses to the existing bubble. (b) The Mn2O3 particle is completely immersed in the glass melt (long treatment times). The formed O2 diffuses to existing pores or nucleate new pores in the glass melt.

![Fig. 5.](image)
(a) SEM image and (b) EDX line scan of foam glass. The arrow shows the position and direction of the EDX line scan shown in b). The foam glass is prepared at 1063 K for 80 min.
At a higher treatment temperature the dissolution rate of Mn$_2$O$_3$ and the gas formation rate are higher, since the melt viscosity is lower. This results in a faster foam growth, due to accelerated pressure increase in the pores.

Foams often have a limited lifetime, as they are thermodynamically unstable [21]. Within our experimental time frame the foams do not cease to expand, since the high glass melt viscosity ($10^{5.5}$–$10^{5.2}$ Pa s [18]) ensures a long foam lifetime.

3.2.3. Formation of percolated foams

Simultaneously with pore growth, glass melt drains from the pore wall into the struts, resulting in thinner pore walls. At some critical thickness the pore wall ruptures and the pores sharing the pore wall merge together (coalesce). The thickness of vertical molten glass films [33–35] and walls of single bubbles [36,37] is measured as low as 86–200 nm. The critical thickness of rupture, however, is calculated to be in the range of 1–20 nm [37]. The critical thickness can be considered independent of viscosity [38]. Hence, the same range of critical thickness could possibly be found for pore walls in foam glasses. However, particles in foam suspension can destabilise pore walls [20] by increasing the critical thickness of rupture if the particle is partially or completely immersed into the glass melt [21]. Particles sticking to the pore wall might not promote rupture of the pore wall [21]. As shown in Fig. 5, Mn$_2$O$_3$ crystals are immersed in the glass melt. Additional particles identified in the glass matrix have high Si content and low content of other cations (Fig. 7). Cristobalite is a polymorph of SiO$_2$ formed at 1048–1373 K in float glass and borosilicate glass [39,40]. Since the foam glasses are prepared at 1063 and 1083 K, the Si rich particles are likely cristobalite. Both Mn$_2$O$_3$ and cristobalite can have a destabilising effect on the pore wall.

As discussed in a previous work [18] the foaming agent is heterogeneously incorporated into the glass melt. This is also the case for manganese oxide, observed by small concentration gradients of manganese found in the glass melt (Fig. 7c).

Initially after the coalescence of two pores, the new pore is irregularly shaped (Fig. 1). The new pore changes into a spherical shape again, since it has a lower surface energy. However, the shape transformation is kinetically dependent on the melt viscosity and since the viscosity is

### Table 2

<table>
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<tr>
<th>T</th>
<th>$t_H$</th>
<th>$T_a$</th>
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<td>1083</td>
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<td>800.5</td>
<td>16 ± 16</td>
<td>2.25 ± 0.07</td>
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Fig. 6. Foams density ($\rho_{\text{foam}}$) and porosity ($\phi$) of the foam glasses prepared at different treatment times ($t_H$) at two different temperatures (see legend). The lines are fitted exponential decay function. The error bars represent uncertainties of the foam volume determination. The inset shows the photographed foam glasses formed at 1083 K for different treatment times (5–80 min).

Fig. 7. a) SEM image of a strut. The arrows show the positions and directions of the EDX line scans: b) Scan #1 shows Si rich phase and c) Scan #2 shows inhomogeneous incorporation of Mn. The foam glass is prepared at 1083 K for 20 min. Notice the log scale on the Y-axis in (b).
high, the time required for the pore to return to spherical shape increases with pore size. Simultaneously, the coalescence rate is fast and the pore coalesces with near-by pores before gaining spherical shape. Thereby, the pores become increasingly irregular in shape with prolonged treatment (Fig. 8) and the number of connections with neighbouring pores increases (Fig. 8f).

The degree of connectivity is indirectly but clearly seen from the closed porosity ($\phi_{CP}$) trend with time (Fig. 9). Initially (0–10 min), the pores are closed and surrounding atmosphere cannot penetrate into the foam. Within short treatment time ($t_H > 20 \text{ min at } 1063 \text{ K}$) the foam becomes percolated ($\phi_{CP} < 20\%$). As the treatment temperature increases, the percolation time decreases. Two factors cause higher coalescence rate: First, increasing temperature accelerates the gas formation rate. Second, the pores will grow due to thermal expansion of the gas and the lower melt viscosity. In addition, Debregras et al. [41] show that for silicon oil ($10^{15} \text{ Pa s}$) the drainage rate increases with an increase of radius of film curvature. However, the viscosity of the foam glass melt is much higher ($10^{5.2} – 10^{5.5} \text{ Pa s}$). Therefore, drainage time scale is insignificant in comparison to our experimental time scale ($5–160 \text{ min}$) [42]. It is interesting to see that after a very long treatment time (e.g. $t_H > 80 \text{ min at } 1063 \text{ K}$), the closed porosity increases slightly again. This happens when new closed pores are nucleated in the struts or in the pore walls of larger pores.

The foam glasses develop a bimodal pore size distribution with increasing $t_H$ (Fig. 8c, d, f). Two possible mechanisms explain this. First, larger pores grow faster since they gain more oxygen due to their large surface area. Second, the pore size will increase due to coalescence and gas formation, meanwhile nucleation and growth of new pores will populate the lower part of the pore size distribution.

The percolation threshold ($\phi_{CP} < 50\%$) is reached when the foam reaches a density around $0.35–0.40 \text{ g/cm}^3$ (inset in Fig. 9). In comparison, the foaming of CRT panel glass with MnO$_2$/C using smaller particle size ($D_{90} = 14.8 \mu\text{m}$) can achieve lower density ($<0.20 \text{ g/cm}^3$) and a high degree of closed porosity [4]. In this study, we use larger particle size of MnO$_2$ ($D_{90} = 40 \mu\text{m}$). The larger particle size could promote faster coalescence.

Another important consequence of coalescence is a decreasing number of pores. The pore number density is shown in Table 2 and Fig. 10, where the bubble number density ($N_A$) is corrected for foam growth by multiplying the apparent bubble number density ($N_{ap}$) with the

![Fig. 8. SEM images of the foam glasses prepared from CRT panel glass and 7 wt.% MnO$_2$ foamed at a–c) 1063 K and d–f) 1083 K for different treatment times (see legends).](image_url)

![Fig. 9. The closed porosity ($\phi_{CP}$) of the foam glasses formed at different treatment times ($t_H$) and different temperatures (see legend). The volume of the samples is 34–36 cm$^3$. The closed porosity is calculated according to Eq. (2). The error bars represent combined standard deviations of $\rho_{foam}$, $\rho_{pore}$ and $\rho_{skel}$. The lines are sigmoidal Boltzmann curves. The inset shows $\phi_{CP}$ as a function of foam density ($\rho_{foam}$).](image_url)

![Fig. 10. The number of pores per image area ($N_A$) for samples prepared at different treatment times ($t_H$) and different temperatures (see legend). $N_A$ is obtained from at least three SEM images of the epoxy mounted foam glasses. The error bars represent the combined uncertainty of the pore counting ($N$) and the density ($\rho_{foam}$) measurement.](image_url)
3.3.1. Origin of heat transfer in foam glass

Radiative heat transfer is negligible at room temperature as the foam glass is dense. The foams in this study have open and relatively large pores with low pressure (large pores). Since the glass melt is saturated with O₂ formed from the Mn³⁺ reduction, there is a net diffusion of O₂ into every pore. Hence, Ostwald ripening cannot take place and coalescence is the main cause of the exponential decrease of \( N_A \). The pores coalesce at all times, the steady-state trend of \( N_A \) seems to reach a steady state or even a slight increase. Since the pores coalesce at all times, the steady-state trend of \( N_A \) must be influenced by the formation of new bubbles (nucleation). The SEM image (Fig. 8f) indicates that new pores are formed and grown in the struts and cell walls.

3.3.1. Origin of heat transfer in foam glass

Radiative heat transfer is negligible at room temperature as the foam glass is dense. The foams in this study have open and relatively large pores. Open pores permit exchange of foam gas (O₂) with exchanges with the surrounding atmosphere (air) and a contribution of convective heat transfer. The thermal conductivity of O₂ and air is similar around 283 K. Hence, the degree of closed porosity, in terms of different gas compositions, does not influence the overall thermal conductivity. The modelling results of Köse and Bayer [23,24] suggest that pore size (diameter = 1–5 mm) strongly influences the thermal conductivity of foam glass (\( \mu_{\text{foam}} = 0.2–0.4 \text{ g/cm}^2 \)). By comparing foam density (Fig. 6) and pore size (Fig. 8) with the overall thermal conductivity (\( \lambda_A \)) of our foam glasses (Fig. 11), we find that the pore size has no measurable effect on the thermal conductivity of foam glass with densities between 0.2 and 0.4 g/cm³ (\( \varphi = 86–92\% \)). Wu et al. [2] reported the similar observation for their glass-ceramic foams (\( \varphi = 85–94\% \)).

Contribution of convective heat transfer to the overall heat conductivity is important when pore size is above 4 mm [44]. In this work, the vast majority of the pores are below 4 mm in diameter. Hence, heat transfer through convection does not contribute significantly to the measured values. When pores are small (< 10 μm) [45,46], the effective thermal conductivity of the gas phase is reduced (known as the Knudsen’s effect). Decreasing the pore pressure reduces the thermal conductivity further [45,47]. The pressure in foam glass with closed pores is below 1 atm (0.3–0.8 atm), however, our foam glasses have only few pores smaller than 10 μm. Therefore, the combined effect of the low pressure and small pores should be insignificant for the foam glasses in this study.

Boundaries between solid inclusions and glass matrix can scatter the phonons [10–12], leading to a lower effective thermal conductivity of the solid part. As shown in Figs. 5 and 7, Mn₂O₃ and Si-rich inclusions are integrated in the glass matrix, nevertheless, they take up a minor part of the solid volume as indicated by the SEM (Figs. 5 and 7) and XRD results (Fig. 3), thus only few boundaries exist. Hence, the phonon scattering due to grain boundaries will not significantly influence the thermal conductivity. Therefore, only the solid and gas conduction need to be defined when predicting the thermal conductivity of foam glass.

3.3.2. Comparison between predicted and experimental values

We compare our experimental data to the existing models (Russell model, Landauer model and Schuetz–Glicksman model). Conduction through solid (\( \lambda_A \)) and gas (\( \lambda_g \)) is treated as decoupled in all the models. As discussed above, the gas conduction is constant (\( \lambda_g = 0.025 \text{ W m}^{-1} \text{ K}^{-1} \)), since it changes insignificantly with O₂/air ratio. The solid matrix is a complex mixture of inhomogeneous glass and crystalline phases. Since 96 vol.% (93 wt.%) of the solid part originates from glass powder, we treat the solid as an ideal phase consisting of only CRT panel glass. The \( \lambda_A \) of CRT panel glass at 298 K is estimated using empirical coefficients for each oxide component [48]. The thermal conductivity of several silicate glasses decreases on average 2.7% when temperature drops from 298 K to 283 K [49,50]. Corrected for temperature (2.7%), the resulting \( \lambda_A \) is determined to be 925 mW m⁻¹ K⁻¹. Many theoretical and semi-empirical models exist for predicting the thermal conductivity of porous materials (see the review by Collishaw & Evans [51]). The thermal conductivity of foam glass is calculated in several studies as function of foam density using analytical [2] and numerical models [2,5,24]. Russell [52] derived an analytical model from an array of gas-filled cubes (Eq. (4)):

\[
\lambda_f = \frac{\lambda_s [\lambda_g + \varphi^{2/3}(\lambda_g - \lambda_s)]}{\lambda_s + (\lambda_g - \lambda_s)[\varphi^{2/3} - \varphi]}
\]

where \( \lambda_s \) is the solid conductivity, \( \lambda_g \) is the gas conductivity and \( \lambda_f \) is the effective conductivity of the foam. Fig. 11 shows the calculated thermal conductivity using the Russell model. It appears that the model overestimates the thermal conductivity compared to the experimental data. Since 2/3 of the solid is parallel to the heat flow, solid conduction of low density foam glass is overestimated by the Russell model.

Landauer model [53] predicts thermal conductivity of two media randomly dispersed into each other (Eq. (5)). The thermal conductivity

![Figure 11](https://example.com/figure11.png)
of porous zirconia ($\varphi = 44\text{--}73\%$) agrees well with the Landauer model [46]:

$$\lambda_f = \frac{1}{4} \left[ \lambda_s(3\varphi - 1) + \lambda_t(3\varphi_s - 1) + \left( \lambda_s(3\varphi - 1) + \lambda_t(3\varphi_t - 1) \right)^{1/2} \right]$$

(5)

where $\varphi_t$ is the solidity $(1 - \varphi)$. It is seen that the thermal conductivity predicted by the Landauer model is lower than experimental values (Fig. 11). At high porosities the solid phase will be dispersed in a continuous gas phase and the conduction through the solid part will be broken by the gas phase. Hence, the Landauer model will underestimate the solid conduction of foam glass. Schuetz and Glicksman [54] developed a simplified expression for the Russell model at low densities (Eqs. (6) and (7)):

$$\lambda_f = \lambda_s + K(1 - \varphi)\lambda_t$$

(6)

$$K = \frac{\tau^2}{3 - \frac{f_s}{2}}$$

(7)

where $f_s$ denotes the amount of the solid located in the strut, $f_t = 0$ when the entire solid is located in pore wall and $f_s = 1$ when all the solid resides in the strut. The factor $(2/3 - f_s/3)$ represents the amount of the solid aligned parallel to the heat flow. The $\tau$ is a tortuosity factor. For staggered cubic cells, the solid conduction can reduce up to 20% ($\tau = 0.8$) due to the tortuous path of heat transfer through the solid matrix [54,55]. Eq. (6) can be used to estimate the lower limit of the thermal conductivity of a foam glass by assuming that all solid reside in the struts ($f_s = 1$) and the conduction through the solid is very tortuous ($\tau = 0.8$). The model predicts slightly lower thermal conductivity than the experimental data (Fig. 11). The SEM images show that cell walls are present. Therefore we can assume that $f_s < 1$. The $\tau$ value can be calculated from the mean pore wall thickness, average pore diameter and effective strut diameter by assuming ideal pore geometry [56,57]. However, such detailed structural information is not available for our foam glass. If we instead treat $K$ as a fitting parameter we obtain $K = 0.34$ and 66% reduction of the solid conduction ($\lambda_t$). The model shows a good agreement between model and experimental data (Fig. 11).

4. Conclusion

Addition of 7 wt.% MnO$_2$ to CRT panel glass powder enables the production of foam glasses with a density of 0.25–0.59 g/cm$^3$ (porosity of 79–92%) with different degrees of closed porosity (6–97%). The closed porosity decreases with increasing treatment temperature and time. Reduction of MnO$_2$ to Mn$_2$O$_3$ occurs simultaneously with the sintering of the glass particles. The main foaming is caused by the reduction of Mn$_2$O$_3$. The Mn$_3$O$_4$ dissolves in the glass melt and subsequently Mn$^{3+}$ is reduced to Mn$^{2+}$, leading to gas formation and foaming. Even when the pores become open and connected, the foams still continue to expand. This phenomenon can be attributed to enhanced nucleation and subsequent growth of new pores, due to an increase in the reduction potential when the entrapped O$_2$ outgases.

The XRD results confirm increasing dissolution of Mn$_3$O$_4$ particles with increasing temperature and time, while SEM uncovered additionally Si-rich inclusions.

The thermal conductivity of the foam glasses varies between 53.1 and 65.9 mW m$^{-1}$ K$^{-1}$ at 283 K and is linearly dependent on the foam density. The experimental data is described by a linear contribution from solid and gas conduction. The pore size (diameter between ~0.02 mm and 4 mm), crystal inclusions and degree of closed porosity (between 6% and 97%) are not the main factors influencing the thermal conductivity of the foam glasses studied in this work.

Nomenclature

- $\lambda_f$: thermal conductivity of foam
- $\lambda_t$: thermal conductivity of gas
- $\lambda_s$: thermal conductivity of solid
- $\varphi$: porosity of foam
- $\varphi_C$: closed porosity of foam
- $\phi$: solidity $(1 - \varphi)$
- $p_{\text{foam}}$: foam density
- $p_{\text{skel}}$: skeletal density (or pycnometric density)
- $p_{\text{pow}}$: density of powdered foam glass (solid density)
- $\tau$: tortuosity factor
- $f_s$: denotes the amount of the solid located in the strut
- $K$: fitting parameter
- $N$: number of pores per mm$^2$
- $N_A$: the bubble number density corrected for foam expansion
- $T_g$: glass transition temperature measured with DSC
- $V_0$: volume of foam produced at 1063 K for 5 min
- $V_i$: volume of ith foam

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