Thermally Tunable Glass Foams with Controllable Pore Size via Network Manipulation: A Melt-Casting and Float-Manufacturable Glass Foaming Method

Hongwei Guo, Congcong Zhao, Jian Xu, Yuxuan Gong, Mariano Velez, and Relva C. Buchanan

ABSTRACT: Glass foams are being widely used as constructional materials due to their unique properties in thermal insulation, fire retardation, and shockwave absorption. However, the cost of energy consumption and processes in a conventional glass foam production limited the use of glass foams as sustainable materials. In this study, for the very first time, thermally tunable CaO–SnO2–P2O5–SiO2 glass foams with controllable pore size were presented as a novel category of melt-casting and float-manufacturable glasses. It was found that the pore size and thermal properties become tunable by manipulating the glass network, i.e., connecting linear chained Sn—P network with [SiO4] units. In addition, the unique combination of thermal properties and porous structure of CaO–SnO2–P2O5–SiO2 glasses shows potential in float glass foam production, which can produce glass foams sheet-by-sheet with less complexity in manufacturing processes.

KEYWORDS: Glass foams, Network manipulation, Thermal properties, Pore size, Float-manufacturable

INTRODUCTION

Glass foam is a category of lightweight constructional materials that has been widely used in the exterior and interior walls of buildings due to its thermal and acoustic insulating properties. The porous structure, either being closed or open pores, of glass foam provides its unique properties in thermal insulation, fire retardation, and shockwave absorption. However, the unit price of glass foam limited its use in constructional needs, and tends to further restrict its use when the needs for energy-efficient buildings becomes more demanding.

The production cost of glass foams is associated with the investment of production equipment, large energy consumption, and sometimes cost of raw materials. During a typical production process, glass foams are being made by batching and melting of glasses with desired stoichiometry (batching and melting are not necessary when waste glasses are being used), grinding the as-melted glass or waste glasses (e.g., cathode-ray tube, window or bottle glass), mixing the glass particulates with foaming agents, foaming the mixture (in a mold) at elevated temperature, and annealing the as-prepared glass foam through a lehr. Finally, glass foams are cut or machined into desired size prior to being used in construction sites. Couple of approaches has been applied to lower the cost of glass foam production, among those include the use of waste glass cullets, novel foaming agent from municipal wastes (e.g., slag, fly ash, porcine bone, egg shell, and etc.), and fast sintering schedule. The use of waste glass cullets somehow allows a melting-free processing of producing glass foam, but also introduces accumulation of undesirable elements and fluctuations in batch-to-batch composition (i.e., inconsistency in batch-to-batch composition of glass cullets). Similarly, the use of novel foam agents from wastes only helps with the cost of raw materials. Methods of producing glass foams at lower energy consumption and higher production efficiency (or a much more automated production) have yet to be reported.
In addition, the foaming process and the final product were reportedly to be sensitive over glass composition as well as the chemistry of foaming agents.\textsuperscript{5,6,11} For example, a decomposition type foaming agent (e.g., carbonates, such as Na\textsubscript{2}CO\textsubscript{3}) usually forms open porosity in the glass foam; also, the ion exchange between sodium in the foaming agent and alkalis in the glass network has been reported to change the viscosity, surface tension, and final pore structure of glass foams.\textsuperscript{5,11} Similarly, a redox-type foaming agent like SiC will change the glass chemistry by introducing extra Si and reducing metallic cations in glass network (e.g., Zn, Pb, or Cu).\textsuperscript{6,5} Particularly, a study on the foaming agents shows that superior properties of glass foams can be achieved with the combination of Mn\textsubscript{2}O\textsubscript{3} and carbon as foaming agents.\textsuperscript{6,12} Therefore, the interaction between foaming agents and matrix glasses will greatly affect the properties of glass foams such as morphology of porosity, distribution of porosity, thermal and mechanical properties, and more importantly create problems in product consistency. With all these being said, is there a one-step and mold-free process of producing glass foam with controlled stoichiometry? Can the glass foam being produced just the way as float glasses, in other words a sheet-by-sheet production? Can such a process lower the cost of energy consumption, reduce the cost of labor, and increase the efficiency and consistency of production?

In this paper, we report, for the very first time, a melt-casting method of obtaining glass foam that satisfies the requirements for a float production process of glasses. Glass foams, at least in the Si–P glass family per our study, show potential in being produced sheet-by-sheet in a state-of-art one step process (i.e., float glass foam manufacturing). Also, the as-prepared glass foams showed controlled chemistry, distribution of porosity, pore size, and thermal property with good mechanical strength (>10 MPa). Moreover, the glass foams were found to be tunable in their thermal properties and pore size via the manipulation of glass network. It was found that the measured properties show a linear regression as a function of Si\textsuperscript{4+}/Ca\textsuperscript{2+}. More importantly, the cost-efficiency and potential impact of the shown method are discussed in detail.

\section*{MATERIALS AND METHODS}

\textbf{Processing.} Chemically pure ammonium diphosphate (Fisher Scientific, USA), tin(IV) oxide (Fisher Scientific, USA), calcium carbonate (Fisher Scientific, USA), silica (Fisher Scientific, USA) powders were weighed (see Table 1), mixed in a rotating roller for 12 h, placed into an alumina crucible, and melted at 1100 °C for 1 h. The composition of glasses was designed to vary the ratio of Si/Ca while not changing the amount of P\textsubscript{2}O\textsubscript{5} and SnO\textsubscript{2} (Sn/P less than 0.25), assuming that the pore size and thermal properties of foam glass changes as a function of Si-network connectivity (Si\textsuperscript{4+}/Ca\textsuperscript{2+}). The glass forming liquid was poured into a preheated (500 °C) and rectangular-shaped (~2 cm × 1 cm × 1 cm) graphite mold, annealed in a resistively heated oven for 1 h, and subsequently cooled overnight. The as-melted glasses show porous structure with entrapped gases from the decomposition of ammonium diphosphate and calcium carbonate. Therefore, the foaming process was achieved during the melting processes without the use of foaming agent or a further sintering process. The edges of the as-prepared glass foams were polished prior to the measurement of CTE. Triplicates were performed on the CTE measurement in order to generate standard deviations.

\section*{RESULTS AND DISCUSSION}

\textbf{Phase Identification and Analysis of Bulk Composition.} X-ray powder diffraction was performed on all pulverized glass samples with a Rigaku Dmax X-ray diffractometer. A Cu kα source, an emission current of 10 mA, and a voltage of 30 kV were used in all measurements. Data was collected from 10° to 70° 2θ with a step size of 0.01°. Bulk compositions as well as the chemical environments of the as-prepared glass foams were measured using a PHI VersaProbe X-ray photoelectron spectrometer. In order to obtain the bulk composition, the fracture surfaces (as fractured in the introduction chamber, pressure is ~10\textsuperscript{-6} Torr) were analyzed. The quantitative analyses were performed using high resolution scans of Si 2p, P 2p, Sn 3d\textsubscript{3/2} and Ca 2p peaks. Relative sensitivity factors for all elements (RSF\textsubscript{Si} 2p = 1, RSF\textsubscript{P} 2p = 0.60, RSF\textsubscript{Sn} 3d\textsubscript{3/2} = 4.32, RSF\textsubscript{Ca} = 9.32, and RSF\textsubscript{O} = 4.77) were derived from high resolution XPS scans of a vacuum-fractured Sn–P–Ca–Si oxide glass, assuming that the composition of glass fracture surface was identical to the bulk glass composition (obtained via ICP-OES and lithium metaborate digestion). Qualitative and quantitative analyses were performed with PHII MultiPak V8.0 software; peak positions of all scans were shifted/calibrated using adventitious alkyl C 1s peak located at 284.60 eV (the standard deviation of peak positions is less than 0.1 eV). The peak area value of each high resolution scan XPS peak was fitted by the Shirley-model after automated background subtraction. Details regarding XPS analyses on glasses are being reported elsewhere.\textsuperscript{21} The obtained elemental composition was then converted into oxide composition, as listed in Table 2. The measured standard deviation of Si is 0.2 mol %, P is 0.1 mol %, Sn is 0.4 mol %, Ca is 0.2 mol %, and O is 0.9 mol %.

\begin{table}[h]
\centering
\caption{Batched Composition of Glasses with Varying Amounts of Silica (mol %)}
\begin{tabular}{|c|c|c|c|c|}
\hline
Composition (mol %) & SiO\textsubscript{2} & P\textsubscript{2}O\textsubscript{5} & SnO\textsubscript{2} & CaO \\
\hline
Sn1 & 5.5 & 47 & 10 & 37.5 \\
Sn2 & 6.5 & 47 & 10 & 36.5 \\
Sn3 & 7.5 & 47 & 10 & 35.5 \\
Sn4 & 8.5 & 47 & 10 & 34.5 \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{X-ray Photoelectron Spectrometer Measured Composition of As-Prepared Glass Foams (mol %)}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Composition (mol %) & SiO\textsubscript{2} & P\textsubscript{2}O\textsubscript{5} & SnO\textsubscript{2} & CaO & Si\textsuperscript{4+}/Ca\textsuperscript{2+} \\
\hline
Sn1 & 5.7 & 47.2 & 9.4 & 37.7 & 0.15 \\
Sn2 & 6.5 & 46.7 & 9.3 & 37.5 & 0.17 \\
Sn3 & 7.4 & 46.3 & 9.2 & 37.1 & 0.2 \\
Sn4 & 8.3 & 45.9 & 9.1 & 36.7 & 0.23 \\
\hline
\end{tabular}
\end{table}

\textbf{Thermal Analysis, Characterization of Pores, and Mechanical Strength Test.} The DSC analyses were carried out using a NETZSCH Jupiter STA 409 thermal analyzer with a heating rate of 15 K/min. The CTE (coefficient of thermal expansion) values were measured from the casted glass foams using an Orton 1412 dilatometer (equipped with quartz sample tube and push rod), and a heating rate of 10 K/min was applied to all measurements with a high purity alumina as the standard. The microstructural image of the fractured glass foams was captured using a Zygo NewView optical profiler (a white laser interferometer), and the analysis of images was performed using ImageJ. For statistical significance, ten images from each sample were used for the microstructural analysis (pore size and rather than the requirements of ASTM standard.\textsuperscript{2} In addition, the flexural strength (four point bending test) was measured at a crosshead rate speed of 2 mm/min using an 8874 axial-torsion fatigue testing system (Instron, USA). The samples used for four point bending test were prepared using the method discussed elsewhere.\textsuperscript{2}

\section{DISCUSSION}

\textbf{Phase Identification.} Figure 1 shows the powder diffraction of all measured foam glass samples. All measured patterns did not show any diffraction peaks, which often can be found due to the crystallization of bulk glass as well as partial

\end{document}
decomposition of foaming agent. Therefore, the as-prepared glass foams were X-ray amorphous. It has been reported that a crystalline phase containing glass foam (so-called glass-ceramic foam) shows better mechanical performance comparing to its noncrystalline counterpart.\textsuperscript{2,4,5} The crystalline phase contained in a glass-ceramic foam hinders the propagation of cracks, and therefore reinforces the glass-ceramic foam.\textsuperscript{14} However, uncontrolled crystallization of glass foams can be challenging to product consistency, management of product performance, and engineering control of final product; also, further crystallization of these glasses may introduce additional manufacturing processes as well as energy consumption. Hence, it is believed that amorphous glass foams are desirable for the development of this new melt-casting and hence float-manufacturable (can be manufactured as float glass) method. The given CaO--SnO\textsubscript{2}--P\textsubscript{2}O\textsubscript{5}--SiO\textsubscript{2} glasses show minimum differences in stoichiometries between batched (see Table 1) and as-melted compositions (see Table 2). It can be challenging to study the chemistries of as-prepared glass foams if crystalline phases were present in the samples, i.e., the XPS will be detecting chemical information from the amorphous phase and crystalline phase simultaneously. Therefore, the absence of crystalline phases allows the study of correlations between glass network and physical properties of resultant glass foams.

**Microstructural and Thermal Characterization.** Figure 2 shows the optical profile image (both two- and three-dimensional images) of the fracture surface of Sn1, Sn2, Sn3, and Sn4 samples. The three-dimensional images were processed with third-order leveling in order to remove the tilt resulted from the fracture surface. Such leveling process does not change the accuracy of measurement related to pore size as well as its distribution.\textsuperscript{15} As shown in Figure 2, all imaged pores were homogeneously sized closed-pores with small pores occasionally being found in the walls between two adjacent pores. Pores were formed via the chemical reaction of ammonium diphosphate: negatively charged nitrogen ions were oxidized at elevated temperature to produce NO\textsubscript{x} gases, which then forms the porous structure found in this study. Generally, two types of porous structure were reported in glass foam studies:\textsuperscript{5} (1) open pores formed by the decomposition of carbonates, nitric acids, structural water, and sulfides; (2) close pores formed during a redox (mostly oxidation reactions) process of ammoniums, nitrides, carbides. Given the pores were closed-pores, it is postulated that the formation of pores in this study is primarily associated with the ammonium diphosphate (redox type foaming agent). Therefore, the relationship between close porosity and “foaming agent (ammonium diphosphate)” in our work agrees with results being reported elsewhere.\textsuperscript{5} It should be pointed out that the emission of NO\textsubscript{x} glass would be minimal since the pores were closed.

The average pore size (obtained from 10 images of each sample) of Sn1, Sn2, Sn3, and Sn4 is 99.9 ± 3.3, 88.9 ± 3.7, 78.5 ± 2.4, and 60.9 ± 2.2 μm, respectively. It was found that the average pore size of CaO--SnO\textsubscript{2}--P\textsubscript{2}O\textsubscript{5}--SiO\textsubscript{2} decreased with the addition of SiO\textsubscript{2}. The addition of SiO\textsubscript{2} (a glass network former) increased cross-linking of the glass network, increased the viscosity of the glass forming liquids at elevated temperature,\textsuperscript{16,17} and limited the motion of gas bubbles according to Stokes law (drag forces increase with increasing viscosity).\textsuperscript{18} Given that the motion of gas bubbles can be limited with higher viscosity, the forming of larger pores can be reduced because they are being formed by the merging of small gas bubbles. Therefore, the pore size of these melt-casted glass foams...
foams can be tuned via the addition of SiO\textsubscript{2}. A tunable pore size of glass foam will not only help tailoring the final product to different applications but also decrease the dimension of complexity during manufacturing processes.

The effect of SiO\textsubscript{2} addition on the network rigidity was evaluated using thermal properties including glass \( T_g \) (glass transition temperature) and CTE. As shown in Figure 3, \( T_g \) increased with the addition of SiO\textsubscript{2}; the \( T_g \) of Sn1, Sn2, Sn3, and Sn4 is 462.6, 469.1, 476.9, and 483.6 °C, respectively (see Table 3). \( T_g \) and CTE can be used as measures of glass network rigidity, and higher \( T_g \) and CTE values often represent a higher network rigidity as well as more developed cross-linking between network formers (Si and P in this study).\textsuperscript{19,20} The addition of SiO\textsubscript{2} increased the network rigidity of glass foams, and further decreased the average pore size by increasing the viscosity at elevated temperature. Similar results on CTEs were found (see Table 3), and lowered CTEs are beneficial to the thermal shock resistance of glass foams.\textsuperscript{21−24}

Table 3. Thermal Properties of As-Prepared Glass Foams

<table>
<thead>
<tr>
<th>Sample</th>
<th>CTE (10\textsuperscript{−7}/°C)</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn1</td>
<td>84.6 ± 1.1</td>
<td>462.6</td>
</tr>
<tr>
<td>Sn2</td>
<td>81.2 ± 0.8</td>
<td>469.1</td>
</tr>
<tr>
<td>Sn3</td>
<td>78.3 ± 0.6</td>
<td>476.9</td>
</tr>
<tr>
<td>Sn4</td>
<td>74.6 ± 1.3</td>
<td>483.6</td>
</tr>
</tbody>
</table>

The crystallizing events shown in Figure 3 were not studied given the fact that the crystallization temperature (above 700 °C) is much higher comparing to the annealing temperature (500 °C). During the processing of these glass foams, there were no crystallizing events as suggested by XRD results (see Figure 1).

Correlation between Glass Networks and Properties of Foam Glass. Aforementioned glass compositions were designed to have a Sn/P ratio less than 0.25, which can keep the Sn–P network as a linear chain network.\textsuperscript{25,26} A 4-fold \([PO_4] \) unit has one nonbridging oxygen termination and three bridging oxygen. Therefore, a Sn/P ratio less than the stoichiometry of linear chained Sn\textsubscript{(n+2)}/P\textsubscript{3}O\textsubscript{3n+1} kept the Sn–P network as linear chains, and further allows the addition of SiO\textsubscript{2} as a network former. Therefore, Si and P were acting as glass network formers in all prepared samples while Ca and Sn were acting as network modifiers. Because the Sn–P network was designed to be linear chains, the properties of as-prepared glass foams (e.g., network rigidity, network connectivity, thermal properties, and pore size) should hypothetically vary as a function of \( Si^{4+}/Ca^{2+} \) ratio (oxidation state of Ca ion was determined using XPS). In order to investigate the relationship between the glass network and thermal properties, the ratio of Si\textsuperscript{4+}/Ca\textsuperscript{2+} (addition to the Sn–P network) was quantitatively related to thermal properties.

Figure 4 is the plot of \( T_g \) as a function of \( Si^{4+}/Ca^{2+} \). \( T_g \) increased linearly (\( R^2 > 0.99 \)) with the increase of \( Si^{4+}/Ca^{2+} \), which increases the cross-linking between network forming units such as \([PO_4] \) and \([SiO_2] \). Because the Sn–P network is linearly chained, the addition of \([SiO_2] \) can connect the Sn–P chains via Ca\textsuperscript{2+}. Calcium ion, as a divalent ion, can be used to connect \([PO_4] \) chains (not fully charge compensated by Sn\textsuperscript{4+} because Sn/P ratio is less than 0.25) to \([SiO_2] \) units via the \(-O−Ca−O− \) bond. Therefore, the linear relationship between \( T_g \) and \( Si^{4+}/Ca^{2+} \) can be attributed to the cross-linking between \([PO_4] \) and \([SiO_4] \) units via divalent modifying ion Ca\textsuperscript{2+}.\textsuperscript{27,28} A similar linear relationship (\( R^2 > 0.99 \)) between CTE and \( Si^{4+}/Ca^{2+} \) was found as well, as shown in Figure 5.

It needs to be pointed that thermal properties, CTE and \( T_g \) in particular, are closely related to the network connectivity and rigidity of glasses. In addition to these two properties, viscosity of glass forming liquids can reflect the network properties as well. In this study, the viscosity of glass forming
The ratio of Si$^{4+}$/Ca$^{2+}$ increases. As discussed previously, the identical. Therefore, the change of glass chemistry (Si$^{4+}$/Ca$^{2+}$) only alters the average pore size by changing the thermal properties of the glass forming liquids. An R$^2$ better than 0.98 was reported for the shown linear regression.

As shown in Figure 6, the pore size decreases linearly when the ratio of Si$^{4+}$/Ca$^{2+}$ increases. As discussed previously, the increase of network connectivity or rigidity (e.g., Si$^{4+}$/Ca$^{2+}$) increases the viscosity of glass forming liquids. An increased viscosity or drag force limits the motion of small gas bubble (formed via redox of nitrogen in ammonium diphosphate) in the glass forming liquid, and therefore decreases the apparent pore size by limiting the merge of small gas bubbles. However, the area percentage porosity of the glass foams does not change (within statistical error) as a function of Si$^{4+}$/Ca$^{2+}$, as shown in Figure 7.

Within statistical error (STD is around 2%), the area percentage porosity does not change as a function of Si$^{4+}$/Ca$^{2+}$. Therefore, the change of glass chemistry (Si$^{4+}$/Ca$^{2+}$) only alters the average pore size by changing the thermal properties of the glass forming liquids. On the other hand, the area percentage porosity is related to the amount of foaming agent added instead of being dependent on the glass chemistry.

In addition to the linear relationship between glass network and thermal properties or pore size, the flexural strengths (a.k.a. modulus of rupture, MOR) were found to be linearly related to the ratio of Si$^{4+}$/Ca$^{2+}$ (see Figure 7) because the network rigidity is also related to strength of glasses. We conclude that the ratio of Si$^{4+}$/Ca$^{2+}$ determines the glass network properties of this particular glass system and changes the thermal properties of as-prepared glass foams. Therefore, the tunability of CaO–SnO$_2$–P$_2$O$_5$–SiO$_2$ glass foam in thermal properties, pore size, and mechanical strength was achieved via the manipulation of glass network.

**PERSPECTIVES OF COST-EFFICIENCY AND POTENTIAL IMPACT**

This paper presents a series of novel glass foam that can be produced in a sheet-by-sheet manner similar to float glass. Conventional methods of manufacturing glass foams often involve melting and grinding of glass frits, molding of glass foams, and sintering of final products. The relative complicated processes of conventional glass foams as well as the high energy consumption during those processes limited a cleaner and more efficient manufacturing of glass foams. In contrast, the method shown in this study presents melt-casted glass foams (mold-free and nonsintering) that are suitable to be produced in a highly automated glass float line in just one step. However, mechanical tools related to this melt-casting and float-manufacturable glass foams have yet to be studied and the trade-offs between cost of tin oxide and reduced processing temperature or complexity of processes need to be further studied.

Apart from the manufacturing side of these CaO–SnO$_2$–P$_2$O$_5$–SiO$_2$ glasses, the unique combination of thermally tunable properties with controllable pore size made these glasses desirable for manufacturing processes. In addition, it was reported that Sn–M–P (M = alkaline earth, Mg, Zn, Ca, Sr, and Ba) glass system has lower viscosity and higher chemical durability than other low melting glass systems such as bismuth borosilicate, borates, tellurides, and lead-containing glasses. A lowered viscosity helps the reduction of energy required for the melting and annealing processes of manufacturing foam glass since the liquidus temperature (or so-called melting temperature) and $T_g$ (glass transition temperature) are lowered. Thus, the advantages of CaO–SnO$_2$–P$_2$O$_5$–SiO$_2$ glass foams presented in this study are summarized as follows:

1. thermal properties and pore size can be tuned via the manipulation of glass network, i.e., connecting the linearly chained Sn–P network with [SiO$_4$] units using Ca$^{2+}$;
2. the glass foams show potential to be manufactured in a sheet-by-sheet float glass line because it is a melt-casted glass foam;
3. the network of these glasses make themselves suitable as constructional materials with good thermal shock resistance (low CTE), insulation properties (close porosity), and chemical durability.

**CONCLUSIONS**

Float-manufacturable CaO–SnO$_2$–P$_2$O$_5$–SiO$_2$ glasses were prepared using a one-step melt-casting method. The closed porosity was created by the redox reaction of negatively charged nitrogen in ammonium diphosphate. The linearly
chained Sn–P network was connected with [SiO₄] units by Ca²⁺, and such increase in cross-linking increased the viscosity of glass forming liquids. Therefore, the NOₓ gas bubbles were retained in the melt to form porous structure. In addition, the manipulation of network via alkaline earth and silica makes the as-prepared glass foams tunable in their thermal properties, mechanical strengths, and pore sizes. Glass foams in the present study are promising in reducing the cost-efficiency of glass foam production, and revolutionize the processes in glass foam production by introducing a float-manufacturable process.

■ AUTHOR INFORMATION

Corresponding Authors
*Dr. Yuxuan Gong. Tel.: +1-513-539-5300. Fax: +1-513-539-5177. E-mail: gongyuan8@gmail.com.
*Dr. Jian Xu. Tel.: +86-391-3987811. E-mail: xujian@hpu.edu.cn.

ORCID
Yuxuan Gong: 0000-0001-5735-6508

Author Contributions
Y.G., J.X., and R.C.B. conceived the research. H.G., C.Z., M.V., and Y.G. performed the experimental work. H.G. performed the thermal analysis. Y.G. and J.X. performed the XPS and other characterization work. C.Z. performed the four point bending test. Y.G. and J.X. researched into the industry impact of this work. All authors discussed and analyzed the data. Y.G. wrote the paper. All authors discussed and commented on the paper.

Notes
The authors declare no competing financial interest.

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