

EFFECT OF HEAT TREATMENT ON GLASSES MADE FROM TWO THAI BOTTOM ASHES

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Abstract

Silicate-rich industrial wastes such as bottom ash are attractive for the production of glass products used in construction and other industrial areas. The properties of these glasses can often be improved by converting them to glass-ceramics using controlled heat treatments. The effect of heat treatment on the properties of glasses made from two different bottom ashes was investigated. A lignite bottom ash from Lampang (BL) and a municipal solid waste bottom ash from Phuket (BP) were melted at 1300 to 1500°C to produce opaque, black glasses, which were then heat treated at 600 or 900°C. For 600°C it was found that BL and BP glasses remained amorphous but phase separated and saw limited changes to the density, refractive index and Vickers hardness. For 900°C, the BP glass remained amorphous and was heavily deformed, while the BL glass was found to contain augite crystals with a submicron particle size. The melting temperature of the starting BL glass appeared to influence the augite crystallization and resulting properties. The average density (3.18 vs 2.88 g/cm³), refractive index (1.69 vs. 1.64) and Vickers hardness (8.95 vs. 6.29 GPa) of the BL glass-ceramic were significantly increased compared to the BL glass. These findings show the viability of producing glass-ceramics from domestic waste bottom ashes.

Keywords: Coal Bottom Ash; MSW Bottom Ash; Glass; Glass-Ceramic

Introduction

Glass-ceramics are a composite ceramic material produced from the partial crystallization of an amorphous glass host. They combine the ease of glass processing with the improved properties of polycrystalline ceramics. A benefit of glass-ceramics is the wide range of tailorable properties that are available, often in different combinations (Vogel, 1994, Höland and Beall, 2020). Like glasses,

glass-ceramics can be optically transparent to opaque and come in a variety of colors. Mechanically, glass-ceramics are typically stronger, harder, tougher and more abrasion resistant than glasses. Thermally, glass-ceramics can be refractory and have zero thermal expansion, which makes them very thermally shock resistant. Lastly, just like many glasses and ceramics, glass-ceramics can be

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chemically inert and offer good corrosion resistance to various chemicals (Zanotto, 2010; Pinckney, 2013; Comte, 2021).

The common method of producing glass-ceramics is from the melt, like ordinary glasses. The host glass is batched using ordinary glass making materials, with the addition of nucleating agents, such as TiO_2 or ZrO_2 (Vogel, 1994), though they are not a strict requirement. The nucleating agent produces bulk, internal nucleation of a crystal phase. The batch materials are melted and may be shaped using standard glass forming techniques, such as casting and molding. After forming, one of several thermal treatment methods is used to produce the crystal phase (Rawlings *et al.*, 2006). In the traditional ceraming method, the cooled glass is reheated and undergoes a two-step heat treatment. The first, low temperature step, induces nucleation and the second, high temperature step, produces crystal growth. Ceraming can also be done in a single step if nucleation and growth temperatures are similar, or using slow cooling after glass melting, called the petrurgic method.

Like glasses, the potential number of glass-ceramic compositions is very large. In commercial practice though, only a small number of glass-ceramic systems are used, based primarily on the silicates (SiO_2), but aluminosilicates (Al_2O_3 and SiO_2) and several others are also used (Beall, 1992, Höland and Beall, 2020). This is due to the desirable combinations of crystal phases, microstructures and properties that result. Commercial glass-ceramics are produced from typical glass making materials, including mined minerals such as sand and feldspar, and synthetic materials such as soda ash. These materials are selected for reasons including cost, availability, and purity (Wilhauk and Harikantha, 2005; Di Pierro, 2021).

In recent years, some industries have become more environmentally conscience and have sought to minimize their impact on the environment. One way of achieving this goal is to use recycled or waste materials as an alternative to mined and synthetic materials. Glass-ceramics have been produced from many different silicate-rich industrial wastes. These include blast and steel furnace slags, hydrometallurgy sludge, as well as various fly and bottom ashes from coal and municipal waste incineration (Rawlings *et al.*, 2006; Chinnam *et al.*, 2013; Jayaranjan *et al.*, 2014). Fly and bottom ashes are a waste byproduct resulting from the combustion of coal, such as by electric power plants or from the incineration of solid wastes, such as food scraps and household trash. Ashes generated from the combustion of coal, are largely composed of inert multicomponent oxides, the exact composition dependent of the local

geology of the coal deposit. Ashes generated from the incineration of municipal solid waste (MSW) are a mix of inert materials, such as sand, stone, glass, porcelain, metals and ashes from the burnt materials (Heuss-Aßbichler *et al.*, 2021). The composition of the ashes varies by location, based on the components of the solid waste stream.

It is estimated that the global output of coal ash is 600 to 800 million tons per year, of which only 30% is utilized in some way (Jayaranjan *et al.*, 2014). The remaining ash is stored or landfilled, and can leach toxic elements into the environment. Coal ash can be divided into fly ash and bottom ash, of which fly ash makes up 70 to 80%. Fly ash has found use as a cement substitute in concrete due to its pozzolanic activity. Bottom ash has a much larger particle size and is much less reactive, so it is not utilized in concrete (Chindaprasirt *et al.*, 2009). Other uses for coal ash are as backfill in building and road construction, though these types of applications add very little value to the waste. There are approximately 1200 million tons of MSW produced annually across the globe. Much of it is incinerated, which reduces the mass by ~70%, leaving several hundred million tons of MSW ash (Al-Ghouti *et al.*, 2021). As opposed to coal ash, MSW ash is ~80% bottom ash and 20% fly ash. MSW ashes can have similar uses as the coal ashes, although they can have more contamination from heavy and toxic metals, which must be considered (Heuss-Aßbichler *et al.*, 2021).

Several researchers have investigated the use of various coal and MSW ashes to produce both glasses and glass-ceramics. A homogeneous black colored glass was obtained by melting of MSW bottom ash at 1400°C for 2 hours (Monteiro *et al.*, 2006; 2008). The resulting glass had good chemical resistance and mechanical properties. Glass-ceramics from fly ash mixed with up to 70 wt.% MSW bottom ash were successfully produced by melting at 1500°C followed by a two-step ceraming process at 730 and 880°C . Diopside ($\text{MgCaSi}_2\text{O}_6$), a member of the pyroxene group, was identified as the main crystal phase (Qian *et al.*, 2006). Glass-ceramics have also been produced from 100% MSW bottom ash (Barbieri *et al.*, 2000), and several crystal phases were identified, which included wollastonite (CaSiO_3), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and two pyroxenes, diopside and augite ($\text{Ca}(\text{Mg,Fe})(\text{Al,Si})_2\text{O}_6$) both of which can have several elemental substitutions. Finally, with mixtures of coal ash and soda lime glass melted at 1500°C , glass-ceramics were made using the petrurgic method containing multiple different crystal phases, including the mixed feldspar plagioclase ($\text{NaAlSi}_3\text{O}_8$ - $\text{CaAl}_2\text{Si}_2\text{O}_8$) and augite (Francis *et al.*, 2002).

Many commercial glass-ceramics typically only have one main crystal phase. For example, the calcium aluminosilicate system produces the wollastonite crystal phase with the resulting glass-ceramic being strong and durable. It is sold commercially under the name Neopariés by NEG of Japan as an imitation stone material for building cladding (Höland and Beall, 2020). Other examples include crystals of β -quartz (SiO_2) and β -spodumene ($\text{LiAlSi}_2\text{O}_6$) solid solutions produced in the lithium aluminosilicate system. These two phases create glass-ceramics with near zero coefficients of thermal expansion, which makes them ideal for applications where thermal shock resistance is required, such as induction stovetops and cookware (Zanotto, 2010).

In contrast, the crystal phases found in glass-ceramics derived from silicate-rich wastes can be assemblages of different crystal phases, some of which are uncommon in commercial glass-ceramics, as previously mentioned above (Barbieri *et al.*, 2000; Francis *et al.*, 2002; Qian *et al.*, 2006). The wide chemical variability of such wastes also makes it difficult to predict and control which crystal phases may be produced.

When iron-rich silicate wastes are used, several different iron crystal phases have been reported, including magnetite (Fe_3O_4), hematite (Fe_2O_3), olivine ($\text{Mg,Fe}_2\text{SiO}_4$) and various pyroxene phases, including augite and esseneite (CaFeAlSiO_6), which are iron aluminosilicates (Rawlings *et al.*, 2006; Chinnam *et al.*, 2013). The chemical composition of the silicate wastes, as well as the thermal processing, are important factors for determining the crystal phases that are produced. For glass-ceramics produced with iron-rich coal ash and additions of soda lime glass using the peturgic method, the crystal phase assemblage changed as a function of glass content. Simple oxides, such as SiO_2 and Fe_2O_3 , were reported for the pure ash, while for a 60% glass addition, a major plagioclase and a minor augite phase were found, when the cooling rate was $1^\circ\text{C}/\text{min}$. (Francis *et al.*, 2002). Their results showed that the addition of sodium and calcium favored the creation of the plagioclase and augite phases.

When the same ash and glass compositions were cooled at $10^\circ\text{C}/\text{min}$, the resulting glass-ceramics were more amorphous, with the pure ash again producing simple oxide crystal phases, as well as anorthite. With a 60% glass addition, there was little crystallization, with only small peaks for magnetite and $\text{Ca(Al,Fe)}_{12}\text{O}_{19}$. It was pointed out

that the more rapid cooling rate prevented the previously observed plagioclase and augite crystal phases from being formed (Francis *et al.*, 2002).

The typical crystal phases found in waste-derived glass-ceramics have been reported to often have beneficial aesthetic, chemical and mechanical properties, with potential application in construction materials, such as building tiles (Rawlings *et al.*, 2006). When an iron-rich glass-ceramic is found to contain magnetite or other magnetic phases, the potential for exists for electrical and magnetic applications (Chinnam *et al.*, 2013).

While many of the aforementioned research papers have explored glasses and glass-ceramics made from ashes amended with other wastes, such as glass cullet, this research used glasses made from 100% bottom ash. One bottom ash produced from the combustion of lignite coal at the Mae Moh electric plant in Lampang, Thailand and the other from a municipal solid waste incinerator in Phuket, Thailand. Bottom ashes are less desirable than other wastes, due to their characteristics such as large particle size and varied morphology. However, they can still be a significant source of raw materials useful for glass and glass-ceramics. This research sought to determine the effect of heat treatment on bottom ash glasses for glass-ceramic forming, which could provide another potential use for what are otherwise waste materials. We have previously shown the glass forming ability of these two bottom ashes (McCuiston *et al.*, 2024), but to our knowledge, there has been no research on the glass-ceramic forming ability of these bottom ash powders.

Materials and Methods

Materials and Glass Preparation

The bottom ashes for this study were obtained from two different sources. The first bottom ash was from a municipal solid waste incinerator in Phuket, Thailand, referred to here as BP. The second bottom ash was from the lignite coal fired Mae Moh electric power plant, Lampang, Thailand, referred to here as BL. The BP powder was light gray in color with an average particle size of $70.56\text{ }\mu\text{m}$ ($D_{4,3}$), while the BL powder was light black in color with an average particle size of $91.10\text{ }\mu\text{m}$ ($D_{4,3}$) as determined by laser diffraction particle size analysis (Malvern Mastersizer S). Images of the as-received BP and BL ash powders are shown in Figure 1(a) and (b), respectively.

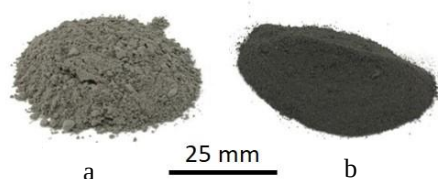


Figure 1. Images of the as-received (a) BP and (b) BL ash powders

To improve melting and homogenization of the glass, the as-received BP and BL bottom ash powders were ball milled and sieved to obtain a fine powder with a maximum particle size of 45 μm . Glass samples were prepared directly from the milled BP and BL powders without any additions. For each glass sample, 100 g of milled powder was melted in an open alumina crucible at a temperature of 1300, 1350, 1400, 1450, or 1500°C for 2 hours, using a heating rate of 10°C/min. The glass melts were cast into a rectangular brass mold (25 x 75 mm) that was pre-heated to 450°C and allowed to solidify for approximately 1 minute before removal. The still hot glass was then placed into a 500°C annealing furnace for 2 hours, and then cooled to room temperature inside the furnace.

To study the effect of heat treatment and glass-ceramic forming ability, segments of the BL and BP glasses were heated at 600 or 900°C for 2 hours in an electric furnace. The heating and cooling rate used was 5°C/min. The heat-treated glass samples are referred to as BPH or BLH, denoting a Phuket or a Lampang glass, respectively, with the addition of 600 or 900 referring to the heat treatment temperature. For example, BPH600 would be the BP glass heat treated at 600°C.

Characterization and Testing

For the various sample characterizations, the samples were sectioned using a low speed saw (Buehler IsoMet) with a diamond blade and mounted in epoxy resin. The cut samples were polished using silicon carbide paper in the order of 150, 200, 600, 1000 and 1200 grit, and then mirror finished using 1 μm colloidal alumina powder. For microscopy, samples were etched using hydrofluoric acid for ~10 seconds.

The microstructure of the polished and etched samples was examined using a scanning electron microscope (SEM) (JEOL JEM-6335F) with an electron accelerating voltage of 15 kV and imaged with the secondary electron detector.

The chemical composition and phase analysis were done using an X-ray fluorescence (XRF) spectrometer (Bruker AXS S4 Pioneer) and an X-ray diffractometer (XRD) (Bruker AXS D8 Discover). For the XRD, samples were analyzed from 20 to 80° with a step size of 0.02° using Cu K α radiation with a wavelength of 1.541 Å.

Differential thermal analysis (DTA) was performed using a differential thermal analyzer (Stanton-Redcroft DTA 673-4) equipped with a high temperature adaptor. Samples were heated from room temperature to 1200°C, with a heating rate of 10°C/min. Alumina sample cups were used with an alumina powder as a reference material. The glass transition behavior of the glasses was characterized using a dilatometer (NETZSCH DIL 402 PC) in the temperature range of 25 to 800°C. A cylindrical glass specimen 5 cm long with a 5 mm diameter was used.

The refractive index was measured using a refractometer (GIA Duplex II). A 5 mm thick polished sample was coupled to the refractometer using refractive index liquid. A standard monochromatic yellow light ($\lambda \sim 589.3 \mu\text{m}$) was used, corresponding to the refractive index n_D of the sodium D line.

The density was measured using the Archimedes method (A&D Weighing AD-1653). A cut and polished sample was weighed in air and then weighed again while submerged under distilled water, to an accuracy of 0.0001 g. The density of the sample ρ_s was calculated according to Equation (1).

$$\rho_s = \frac{W_1}{W_1 - W_2} \times \rho_L \quad (1)$$

Where W_1 is the sample mass in air, W_2 is the sample mass submerged under water and ρ_L is the density of the water for a given temperature.

The Vickers indentation hardness was measured using a micro hardness tester (SHIMADZU HMV2 TDA), according to ASTM C1327 (ASTM, 2015). A cut and polished sample was indented with a load of 980.7 mN ($Hv0.1 = 100\text{g}$) for an indentation time of 10 seconds. Five indents were made per sample. The diagonal lengths of the indents were measured using an optical microscope and the hardness Hv calculated according to Equation (2).

$$Hv = 1.8544 \frac{P}{d^2} \quad (2)$$

Where P is the load in kg and d is the average length of the indent diagonals in mm.

Results and Discussion

Chemistry, Phase Analysis and Microstructure

The chemical compositions in weight percent (wt.%) as determined by XRF for the BP and BL glasses melted at 1350 and 1450°C are shown in Table 1. The results are reported as stoichiometric oxides. The BP and BL glasses had similar major chemical components, being composed of SiO₂, CaO, Al₂O₃ and Fe₂O₃, with lesser amounts of MgO, Na₂O and K₂O. All of these are common glass making components, with the exception of Fe₂O₃ which is typically only used in very small amounts (< 0.1 wt.%) as a colorant (Shelby, 2005). There are some differences in the trace elements contained in the “other” row. The BP glass also contained traces (< 0.2 wt.%) of CuO, MnO, PbO, SrO, BaO, SnO₂, ZrO₂, NiO and the BL glass contained traces of MnO, SrO, BaO, ZrO₂. Of note is that both glasses contained small amounts of Ti and Zr. While TiO₂ and ZrO₂ are commonly used as glass-ceramic nucleating agents, it is unknown how the Ti and Zr are incorporated into the BP and BL glasses. Neither of those pure oxides was detected in XRD patterns of the starting powders (McCuiston *et al.*, 2024).

It is seen in Table 1, that the BP glass contained more of the glass network former SiO₂, a similar amount of CaO and lesser amounts of Al₂O₃ and Fe₂O₃ than the BL glass. The BP glass also had more total network modifier content (Na₂O and K₂O). Due to these compositional differences, the BL glass was found to have a higher density, was slightly more refractory, as well as mechanically harder than the BP glass (McCuiston *et al.*, 2024). The melting temperature of the glasses from 1300 to 1500°C was found to slightly alter the composition and properties of the glasses, particularly at 1500°C. The expected volatiles, such as sulfur (SO₃), were reduced, as well as oxides prone to volatilization in open crucible glass melting, such as Na₂O and K₂O (Shelby, 2005).

The DTA results of BL and BP glasses melted at 1450°C are shown in Figure 2. The glass transition temperatures, labeled T_g, of the BL and BP glasses were determined to be ~645 and ~650°C, respectively. However, the confidence in the T_g values was not high as the endotherms were not well defined. The BL glass exhibited a crystallization exotherm at ~900°C, label T_c, which is favorable for the formation of a glass-ceramic. The BP did not exhibit any apparent crystallization exotherms, indicating a low chance of it spontaneously crystallizing during heat treatment.

The reported T_g and dilatometric softening temperature T_d of the BL and BP glasses melted at 1300 and 1500°C, as determined by dilatometry, are shown in Table 2. The average T_g of the BP glass was ~659°C and ~693°C for the BL glass. The average dilatometric softening temperature of the BP glass was ~729°C and ~758°C for the BL glass. These values are in line with what we previously reported as the T_g and dilatometric softening temperatures as determined by fiber elongation viscometry (McCuiston *et al.*, 2024).

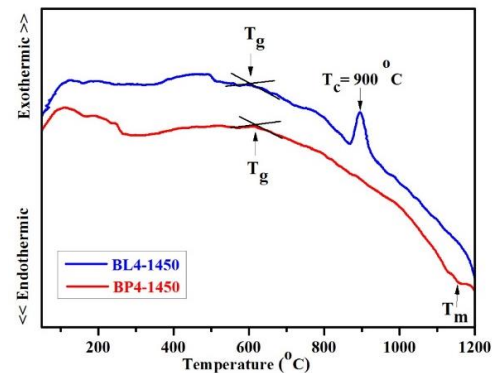


Figure 2. DTA curves of BL and BP glasses melted at 1450°C. The BL glasses exhibits a crystallization peak at 900°C

Table 1. XRF chemical composition of BP and BL glasses melted at 1350 and 1450°C. The results are reported as stoichiometric oxides

Chemical Composition	BP1350 (wt.%)	BP1450 (wt.%)	BL1350 (wt.%)	BL1450 (wt.%)
SiO ₂	47.19	43.76	31.63	33.14
CaO	25.03	27.64	25.23	24.27
Fe ₂ O ₃	11.12	10.73	19.19	17.57
Al ₂ O ₃	6.51	7.96	17.17	17.96
Na ₂ O	3.29	3.03	0.84	1.30
K ₂ O	1.12	1.02	2.37	2.24
MgO	1.24	1.28	2.04	2.02
P ₂ O ₅	2.16	2.22	0.19	0.32
TiO ₂	0.76	0.81	0.60	0.57
ZnO	0.65	0.64	-	-
SO ₃	0.09	0.08	0.23	0.08
Other	0.79	0.77	0.49	0.45
Total	99.95	99.94	99.98	99.92

Table 2. Measured glass transition T_g and dilatometric softening T_d temperatures of BL and BP glasses melted at 1300 and 1500°C

	BP 1300	BP 1500	BL 1300	BL 1500
T_g (°C)	654.7	664.0	686.4	699.9
T_d (°C)	724.4	734.2	743.4	772.7

The glass transition temperature T_g represents the transition of a glass from a solid elastic behavior to a more viscoelastic behavior (Shelby, 2005; Vogel, 1994). At or above the T_g glasses can quickly rearrange their atomic structure towards an equilibrium state, while sufficiently below T_g glasses lack the thermal energy for much structural rearrangement. The selection of 600°C as the first heat treatment temperature considered the glass transition temperature. It should be high enough to promote some structural change, without risk of sample deformation, while the selection of 900°C was based on the observed crystallization exotherm of the BL glass and it was hoped to act as a single step ceraming process.

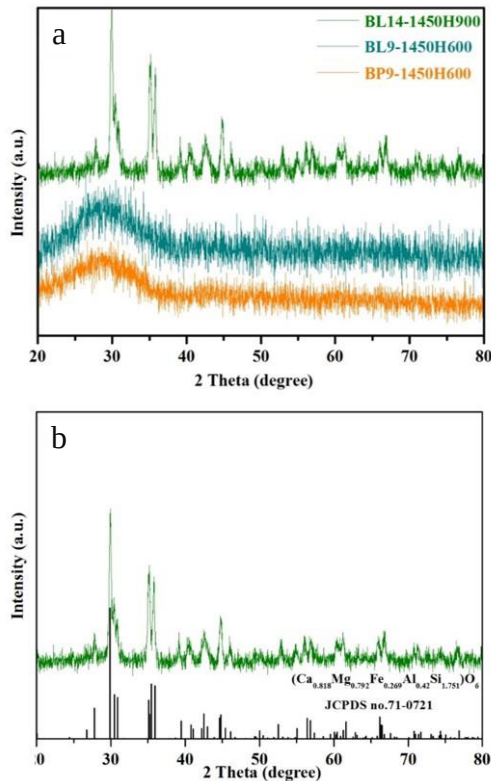


Figure 3. (a) XRD patterns of the BPH600, BLH600 and BLH900 glasses melted at 1450°C. (b) Identification of augite phase in the BLH900

Figure 3(a) shows XRD patterns of the BPH600, BLH600 and BLH900 glasses that were melted at 1450°C. It is seen for the BLH600 and BPH600 glasses that they both remained amorphous after heat treatment at 600°C, as indicated by the amorphous hump at $\sim 29^\circ$. Any nucleation that occurred would likely not be detectable by XRD. The pattern for the BLH900 glass, heat treated at 900°C, showed several sharp peaks, indicating the presence of one or more crystalline phases. In Figure 3(b), the crystalline phase was matched with augite (JCPDS 71-0721) having a listed composition of $(Ca_{0.818}Mg_{0.792}Fe_{0.269}Al_{0.42}Si_{1.751})O_6$. Augite is a calcium clinopyroxene with the general form $Ca(Mg,Fe)(Al,Si)_2O_6$ with many different possible atomic substitutions based on atomic size and valence (Nesse, 2017). Augite has a monoclinic crystal structure and is found in nature as stubby, black or green colored crystals in rocks of volcanic origin. Several researchers have also reported augite in glass-ceramics made from bottom ashes and other materials such as basalt (El-Shennawi *et al.*, 1999; Francis *et al.*, 2002; de Lima *et al.*, 2022).

Images of BPH600 and BPH900 as well as BLH600 and BLH900 glasses melted at 1450°C are shown in Figures 4 and 5, respectively. The original BP and BL glasses had a smooth, glossy surface with a deep black color (McCuiston *et al.*, 2024). After heat treatment at 600°C, the glossy black appearance was retained for both BPH600 and BLH600 glasses, along with the starting sample geometry, i.e. no deformation was observed. However, heat treatment of the BP and BL glasses at 900°C produced noticeable changes. Both BPH900 and BLH900 samples had a dull surface finish with a green-tinted black color. While the BLH900 sample retained its starting geometry (Figure 5(b)), the BPH900 sample became very deformed (Figure 4(b)), with the starting geometry unrecognizable. The BPH and BLH samples produced at the other glass melting temperatures of 1300, 1350, 1400 and 1500°C had the same outcome with heat treatments at 600 and 900°C.

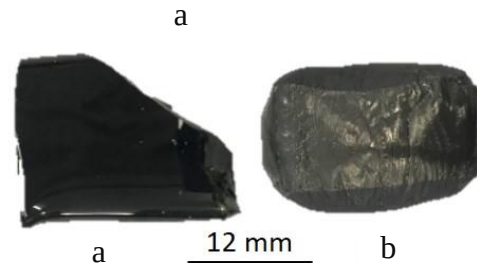


Figure 4. Images of (a) BPH600 and (b) BPH900 melted at 1450°C

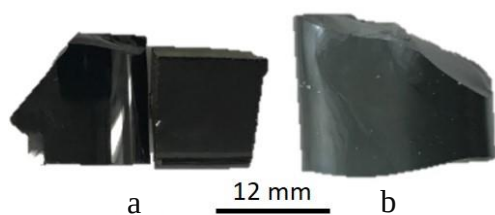


Figure 5. Images of (a) BLH600 and (b) BLH900 melted at 1450°C

For the BPH and BLH glasses heat treated at 600°C, the absence of visual change was not surprising as it was essentially just another anneal. When glasses are annealed, it is not expected to significantly impact their shape or appearance. For the heat treatment at 900°C the significant change of geometry of the BPH900 samples was due to it being above the softening temperature of ~814°C, which allowed the BPH glasses to deform under their own weight. For this reason, further characterization of the BPH900 glasses was not conducted. The BLH glasses did not deform at 900°C because they were crystallized sufficiently to support themselves. As we have pointed out (McCouston *et al.*, 2024), the compositions of the BP and BL glasses resembled those of rockwools, which are discontinuous glass fibers made from volcanic rocks such as basalt and rhyolite. The finding that the BL glass is capable of crystallization is beneficial in a rockwool application because it provides high temperature mechanical stability to the fibers, preventing them from collapsing (Yue *et al.*, 2021).

The reason for the slight color change from black to a green-tinted black is not known. Both the BPH900 and BLH900 displayed the same color change, so crystallization was likely not the reason. The only significant colorant in the BP and BL glasses was iron, which can produce a green color in the Fe^{2+} valence. However, that valence is more typical of reduced glasses melted in an oxygen deficient condition, which these glasses were not.

SEM images of the microstructures of the BPH600 and BLH600 glasses melted at 1450°C and 1500°C are shown in Figure 6(a-d). It is seen that the microstructure of the BPH600 and BLH600 glasses were very similar. The images were not smooth and featureless, which is typical of ordinary glasses, but appeared to show two continuous networks, one of glass and one of porosity, which was presumably from a selectively HF etched phase.

The microstructures suggested that continuous phase separation occurred in both the BPH600 and BLH600 glasses. Phase separation has been shown to occur in iron-rich silicate glasses (Höland and Beall, 2020), where one of the phases is iron-rich and the other phase is silicate-rich. Upon further heat treatment, the iron-rich phase would typically be the one to crystallize. An identical microstructure was observed (Klein *et al.*, 2019) in basalt glasses with similar heat treatment at 600°C, also HF etched, however the authors attributed the appearance to microcracking upon cooling.

The increased melting temperature from 1450 to 1500°C appeared to further define the phase separation. The difference was readily apparent in the BPH600 samples in Figure 6(A) melted at 1450°C and Figure 6(B) melted at 1500°C. It is less apparent in the BLH600 samples, seen in Figure 6(C) melted at 1450°C and Figure 6(D) melted at 1500°C. The continuous phase separation observed suggested that spinodal decomposition was the phase separation mechanism. At lower temperatures it is often less well defined and is improved with further increases in temperature or time due to improved atomic diffusion (Shelby, 2005). While the pair of samples for BPH600 and BLH600 were both heat treated at 600°C for 2 hours, they had different melting temperatures. That may be a contributing factor to the phase separation.

SEM images of the microstructures of BLH900 glasses melted at 1450 and 1500°C are shown in Figure 7(A) and (B), respectively. These samples contain the crystalline augite phase. The appearance is similar to what was seen in Figure 6. There was observed to be a continuous crystalline phase and a continuous porous network, which again was presumably created by the HF etch. It is likely that the HF has etched the silicate-rich amorphous phase rather than the iron-rich crystalline phase. The observed augite crystals had a stubby morphology. From the SEM images, the estimated crystal size is ~100 nm for the glass melted at 1450°C and ~50 nm for the glass melted at 1500°C. As the monoclinic crystal structure of augite is relatively equiaxed, having lattice parameters of $a \sim 9.7\text{\AA}$, $b \sim 8.8\text{\AA}$, and $c \sim 5.3\text{\AA}$ (Nesse, 2017), the crystal size was estimated as the thickness between the etched gaps. This was with the assumption that only one crystal spans the width. The reason for the reduced crystal size with increased melting temperature is unknown, but it could be due to increased nucleation. The amount of crystallization appeared significant, likely greater than 60%.

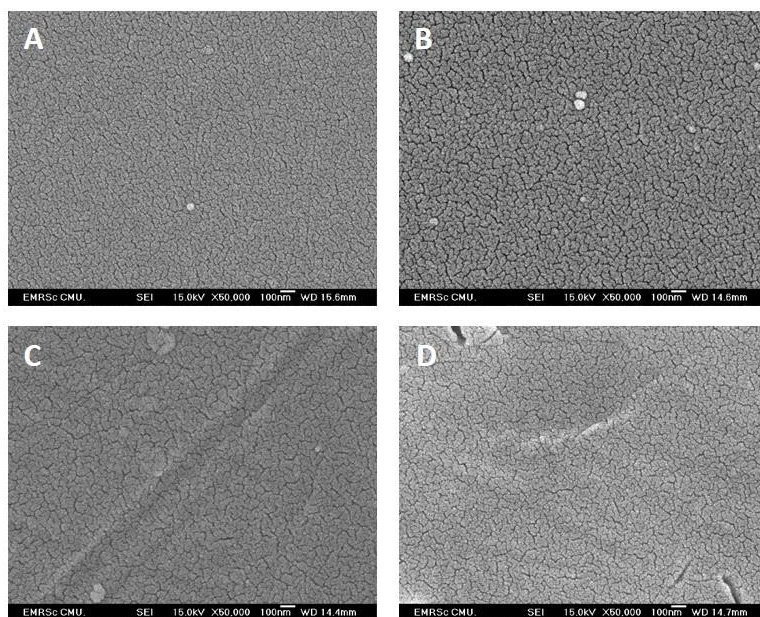


Figure 6. SEM images of BPH600 melted at (a) 1450°C and (b) 1500°C as well as BLH600 glasses melted at (c) 1450°C and (d) 1500°C

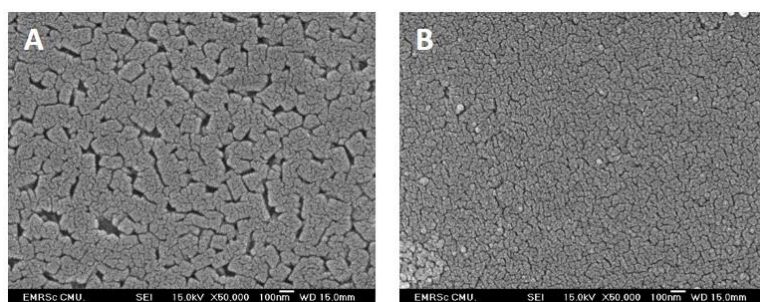


Figure 7. SEM images of BLH900 glasses melted at (a) 1450°C and (b) 1500°C

Properties of Heat Treated Glasses

The bulk density of the BPH600, BLH600 and BLH900 glasses are shown in Figure 8. The average bulk density for all melting temperatures of the BL and BP glasses were previously measured as 2.88 and 2.74 g/cm³, respectively (McCuiston *et al.*, 2024). The heat treatment of the glass at 600°C did not significantly change the average density of the BLH600 glass, while it slightly increased the density of the BPH600 glass to 2.75 g/cm³. Both bulk density curves were relatively flat with changes in glass melting temperature. The occurrence of phase separation in the BPH600 and BLH600 would not be expected to influence the bulk density (Shelby, 2005). As the density of the BLH600 and

BPH600 glasses did not change much with the additional heat treatment at 600°C, it is likely that the original annealing at 500°C was sufficient to reach an equilibrium state.

The bulk density of the BLH900 glasses were significantly higher, with an average density for all melting temperatures of 3.18 g/cm³. The increase in bulk density was likely due to the presence of the augite crystals, which is reported to have an average density of ~3.37 g/cm³ (Nesse, 2017). The bulk density curve of BLH900 had a slight upward trend with glass melting temperature, perhaps due to increasing augite content.

The refractive index n_D of BPH600, BLH600 and BLH900 glasses are shown in Figure 9. The average refractive indices for all melting temperatures of the BL and BP glasses were previously measure as 1.64 and 1.59, respectively (McCuiston *et al.*, 2024). The heat treatment at 600°C did not change the average refractive index of the BLH600 glass, while it slightly increased the average refractive index of the BPH600 glass to 1.60. The refractive index curves for the BLH600 glass showed a slight downward trend, while the curve for the BPH600 glass remained relatively flat. It should be noted that the refractive index measurement technique that was used does not have high precision, such that the curves may not be able to clearly show a trend due to the glass melting temperature.

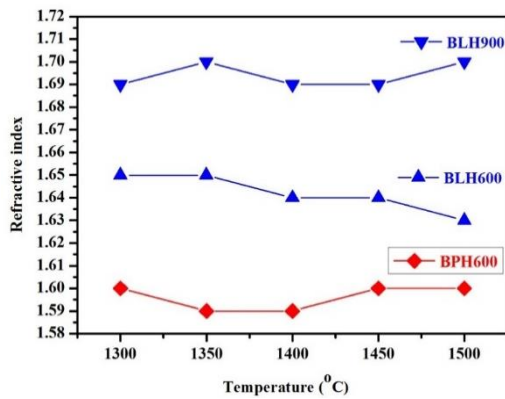


Figure 9. Refractive index of BPH600, BLH600 and BLH900 glasses as a function of melting temperature

The refractive index of the BLH900 glasses were noticeably higher at compared to the BLH600 glasses, with an average for all melting temperatures of 1.69. The BLH900 glasses contained the augite crystal phase, which has a greater refractive index, in the range of 1.67 to 1.74, with increasing iron content seen to increase the refractive index. (Nesse, 2017). The refractive index curve BLH900 was relatively flat as a function of glass melting temperature.

The Vickers indentation hardness of BPH600, BLH600 and BLH900 glasses are shown in Figure 10. The average hardness for all melting temperatures of the BL and BP glasses were previously reported were 6.29 and 6.06 GPa, respectively (McCuiston *et al.*, 2024). The heat treatment of the glass at 600°C increased the average hardness of the BLH600 and BPH600 glasses to 6.61 and 6.17 GPa, respectively. Both

BLH600 and BPH600 glasses showed a slight upward trend of hardness with increased melting temperature. The same trend was previously observed (McCuiston *et al.*, 2024) in the BL and BP glasses annealed at 500°C and it was speculated that it was due to an observed increase in density, possibly as the result of a slower cooling rate from higher melting temperature. However, the density of the BLH600 and BPH600 glasses did not change much with melting temperature. However, there was the apparent relationship between melting temperature and phase separation characteristics seen in Figure 6 that may be impacting the hardness.

At a heat treatment temperature of 900°C, the hardness of the BLH900 glasses was increased significantly to an average of 8.95 GPa. Similar hardness values have been observed in glass-ceramics derived from basalt, a rock with similar composition (Klein *et al.*, 2019; de Lima *et al.*, 2022). There was also observed a rather strong upwards trend of the BLH900 hardness with increased melting temperature. The large increase in hardness was very likely due to the presence of the augite crystal phase. The upward trend could be explained due to an increased augite content as postulated by the increased density shown in Figure 8, or by the effect of reduced crystal size seen in Figure 7.

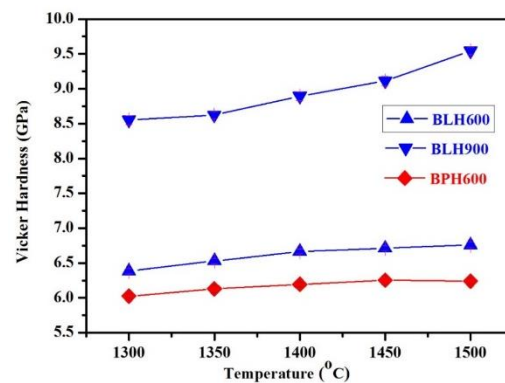


Figure 10. Vickers hardness of BPH600, BLH600 and BLH900 glasses as a function of melting temperature

In Figures 8-10, it was observed that the BLH600 glasses for all melting temperatures had a greater density, refractive index and hardness, over that of the BPH600 glasses. This is due to a combination of compositional and structural differences due to the composition. The BL glasses had a slightly greater amount of network former (SiO_2) and property modifiers (CaO , Al_2O_3 and

Fe₂O₃) than the BP glasses, seen in Table 1. The BL glasses also have slightly less total network modifiers (Na₂O and K₂O) than the BP glasses. This resulted in the BL glasses having greater density and refractive index, due to the increased iron content, and higher hardness and increased thermal properties, due to the stronger network structure (Shelby, 2005; Zawada, 2020).

Conclusions

Glasses were produced from 100% bottom ash, one a lignite bottom ash (BL) from Lampang and the other a municipal solid waste bottom ash (BP) from Phuket, Thailand. They were melted at 1300 to 1500°C and annealed at 500°C. The glasses were then heat treated at 600 or 900°C to study the effect on properties and the potential to form glass-ceramics. The heat treatment at 600°C did not significantly change the density or the refractive index, but did slightly increase the Vickers hardness, possibly related to an observed phase separation. The BL glasses had slightly better properties than the BP glasses, due to compositional and structural differences. With DTA and XRD it was found that at 900°C the BL glasses crystallized and produced an augite crystal phase. The BP glasses did not crystallize at 900°C, though it is likely possible using another ceraming schedule or the addition of a nucleating agent. The BLH900 glass-ceramic had increased average density (3.18 vs 2.88 g/cm³), refractive index (1.69 vs. 1.64) and Vickers hardness (8.95 vs 6.29 GPa) over the BLH600 glass. This was due to the augite crystal phase. The BLH900 glass-ceramic melted at 1500°C attained the highest hardness and smallest observed crystal size, which would imply that it has the best potential for use in a mechanical application, such as a building tile. The similarity of these materials to basalt glass-ceramics also suggest the production of fibers could be another potential application. The significant improvement to the properties from thermal treatment suggests that further research on the ceraming of these domestic bottom ash glasses is warranted.

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