Porous glass-ceramics made from microwave vitrified municipal solid waste incinerator bottom ash

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Abstract

Global warming and depletion of resources have fueled research towards innovative building materials of low environmental impact and high performance engineering properties. Porous glass-ceramics were synthesized using municipal solid waste incinerator (MSWI) bottom ash (BA) as a starting material. BA was initially milled and then vitrified, as a purification step, by direct microwave heating, characterized by a high glass yield. Highly porous glass-ceramics were produced by intensive mechanical stirring of vitrified bottom ash (VBA) aqueous suspensions under weak alkali activation (1M NaOH and 2.5M NaOH) and sinter-crystallization at 800 °C or 900 °C. The obtained glass ceramics, with up to 70 vol% porosity, exhibited compressive strength well above 1 MPa, being comparable to lightweight construction materials, such as aerated concrete. High relative permittivity was measured for the 10 wt% soda-lime glass doped porous VBA material sintered at 800 °C, paving the way for its use as a potential semiconductor catalyst.

Keywords: MSWI bottom ash; vitrification; microwave heating; porous glass-ceramics; alkali activation

1. Introduction

In view of preventing the disposal of waste in landfill sites, additional and improved waste management policies have already been established in Europe [1]. Incineration of municipal solid waste is considered as an appealing waste strategy route as the process generates heat, which can be recovered and converted into electricity. Although the incineration process leads to the decomposition of pollutants and minimization of the waste volume, it also produces municipal solid waste incinerator (MSWI) bottom ash (BA), accounting for 25-30 wt% or 10 vol% of the initial waste [2,3].

BA is currently used as a structural material in landfill foundations, as an embankment filler or as aggregate in road construction or concrete [4]. However, the major issue that inhibits the direct use of BA as a secondary raw material emanates from the high content of heavy metals, which requires beneficiation techniques to upgrade its quality. Up to now, the industrially applied treatment methods are metal extraction, washing and ageing. Vitrification is considered a cost-intensive technique [2] and has attracted research interest for heavy metals immobilization, organics destruction and waste volume reduction [5].

Significant efforts have been pursued to mitigate the high cost of the vitrification process by introducing alternative heating technologies such as microwave heating [6]. The high heating rates of electromagnetic heating result in time savings depending on the material under treatment and the process equipment. Microwave vitrification of BA was recently demonstrated in a single-mode microwave cavity, resulting in enhanced glass yield with modest energy input [6].

The glassy end product, namely the vitrified BA (VBA), has higher chemical stability compared to the untreated ash, rendering the use of VBA as a raw material in products for the building industry a key valorization solution [7]. VBA has already found application in bituminous mixtures for road construction, highlighting its appropriateness to replace filler and aggregates in concrete [8]. In addition, the high silica content of VBA allowed its use as a fluxing agent to facilitate sintering of porcelain stoneware [9] or as an additive in a ceramic glazing process [10].

Glass-ceramics are considered as attractive building materials and several waste-derived glasses have been already valorized as such [11]. In particular, porous glass-ceramics are interesting in delivering thermal and acoustic insulation properties and can be used as panels or as aggregates for concrete [11]. Recent studies have demonstrated the feasibility of producing an inorganic polymer porous material as an alternative to cellular concrete [12] and the feasibility of cellular glasses production through the consolidation of ‘green’ porous materials. In the latter, the authors activated the glass powders by low molarity (2.5M) alkaline solution, causing progressive gelation (‘inorganic gel casting’) [13] which were subsequently subjected to intensive mechanical stirring and sintering. The process enabled a reduction of the sintering temperature and consequently of the cost of the process, as no foaming reaction e.g. oxidation of C or SiC additives [11], needed to take place. In addition, the flexibility of the above-described process has favored its implementation in glasses with various chemical compositions, including silicate or carbonate hydrated compounds [13–15].

The work herein strives to assess the feasibility of valorizing BA, vitrified by microwave process, for the manufacturing of porous glass-ceramics by inorganic gel-casting. The influence of the molarity of the activating solution as well as the addition of recycled soda-lime glass (SLG) on the physical and mechanical properties were investigated. Electrical conductivity and relative permittivity measurements were performed to assess the potential use of the porous glass-ceramics beyond thermal and acoustic insulation applications, as in electro-catalytic applications.

2. Material and Methods

2.1 Characterization of vitrified bottom ash

The vitrification process of BA was realized by microwave irradiation. BA has been found to be susceptible to microwave energy absorption above 320°C when the pyrolysis of organic matter and char production initiate dielectric heating [16]. VBA was produced using a 2.45 GHz single-mode microwave furnace, operated at 800W for 6 min. These operational conditions [Flesoura G, unpublished data], formed a compromise between moderate energy consumption (8578 kJ/kg) and high glass yield (86 wt%). Similar data on the microwave process has been reported elsewhere [6].

VBA was ground in a vibratory ring mill (Retsch RS200) to a particle size < 100 µm. The particle size distribution (PSD) of VBA and SLG was determined by laser diffraction using a Malvern Mastersizer Micro Plus analyzer and a refractive index of 1.8. The d_{10} , d_{50} , and d_{90} values are intercepts for 10%, 50%, and 90% of the cumulative mass of each powder. The specific surface area of the milled VBA and SLG powders was measured according to the Blaine method (EN 196-6).

Recycled soda-lime glass was provided by SASIL SpA (Biella, Italy), in the form of fine powders, as a fraction of non-usable container glass resulting after colored glass separation and metallic and polymeric residue removal [13].

The chemical composition of VBA and SLG was measured using a Bruker S8 TIGER 4 kW sequential WD-XRF spectrometer with rhodium anode and Quant Express software. The mineralogy of powder VBA was analyzed by X-ray Diffraction, using a Bruker D8 Advance, in the 10°-70° 2θ range using CuK_α radiation (0.15418 nm), at 40 kV and 40 mA, with a step size of 0.05°. Qualitative phase identification of the as received VBA was performed using EVA V.3.1 (Bruker AXS) software and the quantitative analysis was carried out by Topas-Academic V.5 [17], based on the Rietveld method and the structural data were taken from the ICSD database [18].

2.2 Preparation of VBA-based porous glass-ceramics

Fine glass powders (100 wt% VBA or 90% VBA-10 % SLG) were activated by an alkaline solution (1 M or 2.5 M NaOH) in a liquid/solid ratio of 0.43. Addition of SLG was tested in order to enhance the densification during sintering. The suspensions were subjected to low speed mechanical stirring (400 rpm, ARGOLab AM20-D), for 3h, before casting in closed polystyrene molds (60 mm diameter) and cured in an oven (Valentini Orlando Thermostabil PN4) at 75°C for 1-3h to promote the alkali activation.

Subsequently, 4 wt% triton X-100 (non-ionic surfactant, polyoxyethyleneoctylphenyl ether, (C₁₄H₂₂)(C₂H₄O)_n with n = 9-10, Sigma Aldrich, Gillingham, UK) was added to the suspensions and foamed by intense mechanical mixing (2000 rpm, AM 20-D ARGOLab overhead stirrer). Foamed structures were kept in an oven (Valentini Orlando Thermostabil PN4) at 40 °C for 48 h, in order to enhance the alkali activation reaction and drying. Finally, VBA-based porous ‘green’ specimens (i.e. after alkali-activation, pre-curing, stirring with surfactant addition and curing) were subjected to a sintering treatment at 800 °C or 900 °C in a muffle furnace (Elite Thermal Systems Limited, Tersid) in static air at a heating rate of 10 °C/min and holding time of 1 h [13]. The processing conditions are summarized in Table 1.

Table 1: Processing conditions for porous VBA-based glass-ceramics.

Group of samples	VBA	SLG	Alkaline solution	75 °C curing time	Sintering temperature
	(wt%)	(wt%)	(NaOH)	(h)	(°C)
2.5M/800	100	0	2.5M	1	800
2.5M/900	100	0	2.5M	1	900
1M/800	100	0	1M	3	800
1M/900	100	0	1M	3	900
1M/SLG/800	90	10	1M	1.5	800
1M/SLG/900	90	10	1M	1.5	900

2.3 Characterization of VBA-based porous glass-ceramics

The 1M/green porous VBA-based ceramic was used as a reference to measure the heat flow and mass loss during thermal cycling, which was monitored by simultaneous differential scanning calorimetry-thermogravimetric analysis (DSC-TGA) using an SDT Q600 (TA instruments). For the SDT experiments, 200 mg of porous material in the form of fine powder was heated in an alumina sample holder at a heating rate of 10 °C/min, under atmospheric conditions from 25 °C to 1000 °C. The dimensional changes for the 1M/green porous material were recorded with a dilatometer (TMA Q400 V7.4). The measurement was performed on 3 mm × 3 mm × 3 mm cubic sample by applying a 0.05 N force, at 10 °C/min heating rate, under atmospheric conditions from 25 °C to 900 °C.

Fourier-transformed infrared spectroscopy (FTIR model 2000, Perkin Elmer Waltham, MA) was applied on VBA and on both green and sintered powdered materials, operating in the absorbance mode with a resolution of 4 cm⁻¹, for 32 accumulated scans in the 4500 to 550 cm⁻¹ range to assess the lattice and functional group vibrations.

The crystallographic analysis on green and sintered porous VBA was investigated by X-Ray Diffraction (XRD) on powdered samples. The diffraction patterns were recorded in the 10°-70° 2 θ range using CuK α radiation (0.15418 nm), at 40 kV and 40 mA, with a step size of 0.05°. Qualitative XRD spectra analysis was performed through EVA V.3.1 (Bruker AXS) software.

The physical and mechanical properties of the sintered porous materials were evaluated on 10 mm × 10 mm × 10 mm cubic samples. The geometric density (ρ_{geom}) of sintered materials was evaluated considering the mass to volume ratio. The apparent (ρ_{apparent}) and true (ρ_{true}) densities were measured by helium pycnometry (Micromeritics AccuPyc 1330, Norcross, GA), operating on bulk or finely crushed samples, respectively. Three density values were used to calculate the amount of open and closed porosity.

The compressive strength (σ_c) of the sintered ceramics was measured at room temperature on an Instron (1121 UTM, Instron Danvers, MA) with a crosshead speed of 1 mm/min. The reported data are the average and standard deviation after testing 6 specimens.

The leachability of heavy metals from the VBA-based glass-ceramics was assessed according to EN 12457-4 [19]. The leached heavy metal content was measured by inductively coupled plasma mass spectroscopy (ICP-MS, Agilent 7500 cx) and ion chromatography (IC, Dionex ICS 2000).

Optical stereomicroscopy (AxioCam ERc 5 s Microscope Camera, Carl Zeiss Microscopy, Thornwood, New York, USA) was used for morphological characterization of the sintered glass-ceramics. Microstructural characterization of green and selected sintered glass-ceramics was performed by Secondary Electron (SE) imaging using Scanning Electron Microscopy (SEM, XL30-FEG (Philips), with 15 kV acceleration voltage.

The pore volume and pore size distribution of selected green and sintered samples were measured based on the Barrett-Joyner-Halenda (BJH) N₂ adsorption method, using the Tristar 3000 micrometric instrument and the V6.08 software.

Selected sintered samples (cylindrical discs with diameter of 30 mm and thickness of 5 mm) were coated with conductive silver paste and connected to metal wires, in turn attached to a GW INSTEK LCR-819 precision LCR meter (frequency range: 12 Hz – 100 kHz) and an Agilent 4285 precision LCR meter (frequency range: 75 kHz – 30 MHz), for AC measurements. The measured resistance R, given by the geometry of the samples and according to Ohm's law, yielded an estimation of the electrical conductivity. The measured capacitance C, given by the geometry and the parallel plate capacitor configuration, yielded an estimation of the relative permittivity.

3. Results and Discussion

3.1 Characterization of raw materials

The chemical composition of VBA and SLG is summarised in Table 2 and is expressed by oxides. VBA is mainly composed of Si, Ca, Al, Fe elements and minor quantities of Na, Mg and Ti not exceeding 10 wt%. Microwave vitrification of BA followed by air quenching yielded a high amount of amorphous phase content (94 wt%) with minor amounts of crystalline phases, such as anorthite, corundum, pyroxene, wollastonite, quartz and metallic iron. The particle size distribution of VBA-as received and SLG as well as their specific surface are reported on Table 3.

Table 2: Normalized chemical composition (wt%) of VBA and SLG based on XRF data

Compound	VBA	SLG
SiO ₂	50.4	71.9
CaO	19.9	7.5
Al ₂ O ₃	10.8	1.2
Fe ₂ O ₃	10.2	0.3
Na ₂ O	0.7	14.3
MgO	2.4	4.0
SO ₃	11.2	/
TiO ₂	1.3	0.1

Table 3: Particle size distribution and Blaine surface of VBA and SLG.

	D ₁₀ (μm)	D ₅₀ (μm)	D ₉₀ (μm)	Specific surface area (cm ² /g)
VBA	1.4	13.6	73.7	4000 ± 200
SLG	1.4	15.1	41.1	3831 ± 93

3.2 Characterization of VBA-based porous materials

3.2.1 Characterization of green samples

DSC-TGA was performed to assess the crystallization temperature of the VBA-based green samples. Figure 1 presents the thermal analysis and weight loss of the 1M/green porous material, which was used as a reference material, since the thermal analysis of the two other VBA-based formulations (2.5M/green and 1M/SLG/green) was comparable. The endothermal peak at around 150 °C corresponds to the release of physically bound water and the exothermal peak at around 250 °C to the surfactant burnout, that both are in accordance with the respective weight losses [14][20]. The following weight gain could be attributed to the oxidation reactions, i.e. changes in the oxidation state of iron. The glass transition temperature (T_g), reported to be around 660 °C for a similar VBA composition [20] was not clearly observed from the DSC curve. A small exothermal crystallization peak around the crystallization temperature (T_c) was observed for all porous samples approximately at 880 °C. The crystallization temperature was considered as a reference to define the aimed temperature for the sintering experiments, which were performed around the T_c (equal to 900 °C) and T_c minus 100°C (equal to 800 °C).

Figure 1: Weight loss by thermogravimetric thermal analysis and heat flow by differential scanning calorimetry of the 1M/green porous material.

The dilatometry curve of the 1M/green porous material upon heating revealed a clear T_g (embodied figure) around 600 °C, as shown in Figure 2, which also marks the onset of densification. At 800 °C, densification stops after an overall linear shrinkage of 14.54%, triggering crystallization which continues up to the melting point of the crystalline phase (at approximately 1000 °C).

Figure 2: Dilatometry curve of the 1M/green porous material upon heating.

The XRD spectra of the as received VBA and the green porous materials are presented in Figure 3. The low crystallinity of VBA is confirmed by the broad ‘amorphous halo’ centered around 2θ . Decomposition of the calcium-bearing phases combined with CO_2 from air exposure led to the formation of calcite (CaCO_3 , PDF#05-0586) and the excess of Na^+ ions from the activating solution resulted in sodium carbonate hydrate formation (thermonatrite, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, PDF#76-0910). The XRD patterns of the porous green materials revealed newly formed phases (e.g. thermonatrite, calcite), the appearance of which increases with increasing activating solution concentration from 1M to 2.5M. Sodium carbonate detection was limited in the green material produced from VBA mixed with SLG compared to the other green materials. This is potentially an effect of the absence of excess Na^+ ions in the activating solution.

The as received VBA, green and sintered porous glass-ceramics were investigated by FTIR, as presented in Figure 4. Sintered 1M/SLG/900 was selected for the measurement as a compromise of activation with low molarity solution and good mechanical and physical properties, as presented in section 3.2.2.

VBA has two broad absorption bands, centered at 699 cm^{-1} and 929 cm^{-1} , associated with the silicate network, as reported for aluminosilicates [21]. The absorption band at 699 cm^{-1} can be correlated to the symmetric Si-O-T (T=Al, Si) stretching vibration between 560 cm^{-1} and 800 cm^{-1} [22,23], whereas the absorption band at 929 cm^{-1} is associated with the Si-O-T (T=Al, Si) asymmetric vibration occurring at $1200\text{-}950 \text{ cm}^{-1}$ [19-21].

Comparing the recorded spectra in the $825\text{-}1167 \text{ cm}^{-1}$ region, a slight shift could be observed towards lower wavenumbers of the VBA absorption band at 929 cm^{-1} and an increased intensity of the absorption peak at 944 cm^{-1} , after alkali activation and pre-curing step. According to Peys et al. [26], the dissolution of a synthetic ternary slag ($\text{CaO-FeO}_x\text{-SiO}_2$) entails a decrease in intensity of the Si-O-T band, which is associated with the starting material, and the emergence of a new band linked to the formation of an inorganic polymer network. Alkali-activation and pre-curing of VBA resulted in the formation of new bands in the $1200\text{-}1458 \text{ cm}^{-1}$ region and at 1650 cm^{-1} , 2872 cm^{-1} , 2954 cm^{-1} and 3400 cm^{-1} , as indicated by the square frames. The atmospheric carbonation of the material generated asymmetric C-O stretching bands of the carbonate ion (CO_3^{2-}) polymorphs on the shoulder of the Si-O-T absorption band (around 1457 cm^{-1}) and in the $1200\text{-}1458 \text{ cm}^{-1}$ region. The stretching and bending bands around 1650 cm^{-1} and 3400 cm^{-1} correspond to the O-H groups, indicating the presence of H_2O or surface O-H groups. In addition, the band divided in two main peaks at 2872 cm^{-1} and 2954 cm^{-1} can be assigned to the C-H₂ stretching vibration of the organic surfactant. Triton X-100 is composed of a polar alcohol group, which is linked to an aliphatic group and an aromatic ring. As such, the peak at 1510 cm^{-1} can be associated with the stretching modes of the aromatic ring of the surfactant [27].

Figure 3: X-ray diffraction patterns of the as-received and activated VBA.

The IR spectrum of the sintered porous material bears some differences compared to that of VBA. The Si-O-T stretching peak does not present a hump anymore, but on the contrary several consecutive sharper peaks appear. As reported in literature [28], the incorporation of iron causes a distortion of the Si-network. Along with the incorporation of other network modifying elements (e.g. Ca, Fe, Na and Mg), in view of the formation of new crystalline phases (Fig.3), it is possible that these factors account for the appearance of several distinguishable peaks [29]. The absence of the C-O, O-H groups and C-H₂ bands is due to their decomposition during sintering [30].

Figure 4: FTIR spectra of as-received (black), 2.5M/green (red), 1M/green (green), 1M/SLG/green (blue), and sintered 1M/SLG/900 (cyan) VBA.

Figure 5: Secondary electron micrographs of a) 2.5M/green, b) 1M/green and c) 1M/SLG/green materials.

Figure 6: EDS elemental mapping of the 1M/green material (scale bar length is 10 μm).

The formation of an inorganic polymer structure is confirmed by the scanning electron micrographs of the green materials presented in Figure 5. EDS mapping of the 1M/green porous material (Figure 6) was used as a reference to evidence the development of a (C,N)-A-S-H type of binder phase (indicated by 1 on the BSE image) and low or unreacted phases (e.g. quartz, indicated by 2 on the BSE image), that can be confirmed by the concentrated regions of silicon. The grey (cracked) phase between the particles is the polymer mounting resin that filled the pores of the material. The particles indicate both the binder phase and the unreacted particles. EDS mapping corroborates the XRD identified phases for the green samples in Figure 3.

3.2.2. Characterization of sintered porous VBA-based glass-ceramics

Sintering of green VBA-based materials promoted a substantial crystallization, evident from the reduction of the amorphous halo and the emergence of a multitude of diffraction peaks, especially when increasing the temperature from 800 °C to 900 °C, as shown in Figure 7.

The peaks are consistent with the phases already found in trace amount in VBA, as well as the newly formed phases. More precisely, wollastonite (CaSiO_3 , PDF#76-0925), clinopyroxene ($\text{Ca}(\text{Mg}_{0.6}\text{Fe}_{0.2}\text{Al}_{0.2})(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_6$, PDF#72-1379), albite-anorthite solid solution ($\text{Ca}_2\text{Na}(\text{Al},\text{Si})_2\text{Si}_2\text{O}_8$, PDF#20-0528) and a melilite solid solution ($\text{Ca}_{1.96}\text{Na}_{0.05}(\text{Mg}_{0.24}\text{Al}_{0.64}\text{Fe}_{0.12})(\text{Si}_{1.39}\text{Al}_{0.61}\text{O}_7)$, PDF#72-2128) could be detected after sintering at 800 °C and 900 °C. Quartz, already present in VBA, was detected in the porous material sintered at 800°C but not at 900 °C. The formation of iron oxides (hematite, Fe_2O_3 , PDF#33-0664) and magnetite (Fe_3O_4 , PDF#75-1610) can be attributed to the oxidation of the pre-existing metallic iron. The formation of hematite and magnetite was favored for the porous materials produced from pure VBA (Figure 7a and Figure 7b), potentially because of the

tendency of TiO_2 and MgO elements to form spinels. Melilite solid solution was favored at low temperature, in the presence of stronger activation (2.5M NaOH); the intensity of pyroxene and wollastonite peaks increased upon sintering at 900 °C. The addition of SLG, although possessing a lower CaO content than VBA, seems to have enhanced the formation of wollastonite (Figure 7c). This can be potentially justified by the exchange of Ca^{2+} ions from the albite-anorthite solid solution with the extra Na^+ ions from SLG.

Figure 7: Crystalline phase evolution in the sintered porous glass-ceramic: a) 2.5M; b) 1M and c) 1M/SLG.

Optical micrographs of the porous glass-ceramics sintered at 800 °C and 900 °C are presented in Figure 8. All materials exhibited an almost completely open porosity, quite homogeneously distributed and confirmed by the porosity data in Table 4. This effect can be attributed to the sintering, which is more evident in Figure 9, comparing the particle structure of 1M/green with the sintered microstructure of 1M/900. For the same material the pore size distribution in the strut network was measured by the BJH method (Figure 10), in order to better reveal the impact of sintering on the strut porosity. Decrease in strut pore volume is noticed for the sintered 1M/900 in the mesopore region. In addition, the average pore diameter in the strut structure increases from 11.08 ± 0.08 nm for the 1M/green to 12.49 ± 0.04 nm, although the difference is not substantial, for the 1M/900, potentially because of the agglomeration of small pores (in the mesoporosity region) into larger pores [31].

The total porosity of the material approached 70 vol%, except for the porous samples produced from VBA and activated with a 1M solution, which were visibly less porous in the green state (see Figure 5b). The strength of the green porous material could not be measured because of the fragility of the material, whereas the compressive strength of the sintered equivalents could be measured (Table 4).

Figure 8: Optical micrographs of sintered porous VBA-based materials; a) 2.5M/800, b) 2.5M/900, c) 1M/800, d) 1M/900, e) 1M/SLG/800 and f) 1M/SLG/900.

Figure 9: SE-SEM images of a) 1M/green and b) 1M/900 porous material.

Figure 10: Pore size distribution in the strut network of the 1M/green and 1M/900 porous material.

Table 4: Physical and mechanical properties of porous sintered VBA-based materials

Material	ρ_{geom} (g/cm ³)	ρ_{apparent} (g/cm ³)	Total porosity (%)	Open porosity (%)	σ_c (MPa)
2.5M/800	0.83 ± 0.03	2.77 ± 0.01	70 ± 0.03	70	1.3 ± 0.2
2.5M/900	0.84 ± 0.08	2.78 ± 0.08	69.8 ± 0.01	69.8	1.9 ± 0.2
1M/800	0.97 ± 0.03	2.78 ± 0.01	65.3 ± 0.01	65.2	2.3 ± 0.8
1M/900	0.99 ± 0.03	2.75 ± 0.00	63.9 ± 0.06	63.9	3.0 ± 0.7
1M/SLG/800	0.89 ± 0.01	2.74 ± 0.01	67.5 ± 0.05	67.5	2.1 ± 0.6
1M/SLG/900	0.76 ± 0.26	2.74 ± 0.02	67.5 ± 0.01	67.4	2.7 ± 0.7

Figure 11: Specific compressive strength (open symbols), total porosity (filled symbols) and compressive strength (half-open symbols) of the porous glass-ceramics fired at different temperatures.

According to Table 4, both 1M/900 and 1M/SLG/900 exhibited the highest strength, equivalent to 3.0 MPa and 2.7 MPa, respectively. However, Figure 11 shows that this is due to the reduced or similar porosity (in the case of 1M/SLG/900) and the resulting stronger network, of the abovementioned samples, sintered at 900 °C. When referring to the strength-to-density ratio (specific strength), general trends are found for both sintering and activation conditions. The specific strength increased when increasing the sintering temperature from 800 °C to 900 °C, which agrees with the previously discussed enhanced vitrification and crystallization. As already reported, SLG addition could improve the compressive strength of waste-derived porous glass-ceramics [15], because of the additional silicates forming a more stable and compact network. Both compressive strength and specific compressive strength data are comparable to those reported for other waste-derived porous glass-ceramics [15] and lightweight construction materials, such as aerated concrete [32]. It should be mentioned that the processing route presented herein includes more steps than the production of aerated concrete or expanded clay aggregates. Every process though, is associated with advantages and disadvantages and thus optimization is imperative before upscaling, so that the process becomes more sustainable in an industrial environment. The main advantage of the specific process is the use of a low molarity activating solution, comparing to other alkali activated materials as for instance inorganic polymers, which is related to a significant decrease in cost and environmental impact.

The most promising porous glass-ceramics (1M/900 and 1M/SLG/900) were compared with the as received VBA, in terms of their leaching behavior. The leaching data, obtained according to the EN 12457-2 procedure, are reported in Table 5.

The measured leaching values of As, Ba, Mo and Cr are higher in the porous glass-ceramics compared to the as-received VBA. This can be assigned to a number of factors, including the formation of new crystalline phases during sintering or the weak immobilization of As and Mo in the porous glass-ceramic structure, as has been reported for Fe-rich based inorganic polymer [33]. Notwithstanding, all release values remained well below the threshold allowed for waste acceptable at landfills for inert waste, according to the European Norm 2003/33/EC, 2003 [19].

Considering the presence of magnetite and hematite, known as semiconductors, 1M/SLG/800 was characterized in terms of electrical conductivity and relative permittivity. The electrical conductivity was constant in the whole frequency range (75 kHz-30 MHz) at 0.9 ± 0.1 S/m, a value of the order of that of Si and Ge semiconductors [32]. The relative permittivity evidenced particularly high levels (exceeding 50000), with a marked increase with decreasing frequency, as shown in Figure 12 (a relative permittivity exceeding 200000 is noted at 50 Hz). This behavior could be raised by the coexistence of electronic and ionic conductivity. In the produced porous materials, the presence of an electron flow could be attributed to electron exchanges ('electron hopping') between iron sites possessing a different valence (Fe^{2+} and Fe^{3+}), feasible in magnetite [34] as well as in hematite [35]. In addition to that, the ionic contribution could arise from the hopping of modifier cations (e.g. Na^+ , Mg^{2+}) present in the glass network [36].

Table 5: Leaching test results on selected porous VBA-based glass-ceramics (mg/kg).

Element	Limit values for inert waste[19]	VBA	1M/900	1M/SLG/900
Arsenic	0.5	0.0049	0.0062	0.0202
Barium	20	0.0173	0.2786	0.1061
Cadmium	0.04	0.0006	<0.0002	<0.0002
Chromium	0.5	0.0053	0.1711	0.1637
Copper	2	0.0383	0.0160	0.0097
Lead	0.2	0.0159	<0.0047	<0.0047
Mercury	0.01	<0.0004	<0.0004	<0.0004
Molybdenum	0.5	<0.0033	0.3383	0.4379
Nickel	0.4	0.0014	<0.0014	<0.0014
Selenium	0.1	<0.0122	<0.0122	<0.0122
Zinc	4	0.0203	<0.0203	<0.0203

High relative permittivity values are typical for percolative ceramic/metal dielectric composites (Ceramic matrix composites, i.e. composites featuring conductive metal particles in a ceramic matrix), which are also difficult to control because of their high dielectric loss values, being highly conductive (owing to electrical leakage by conductive carriers) [37]. Simultaneous occurrence of electrical conductivity, open porosity and iron oxide dispersed phases in the aforementioned porous materials appears appealing for possible applications in electro-catalytic reactions, such as water splitting for hydrogen and oxygen evolution [38], integrating also a pre-processing step to assure a high-purity product.

Figure 12: Relative permittivity of porous 1M/SLG/800 as a function of frequency.

4. Conclusions

Porous glass-ceramics with up to 70 vol% porosity and 3 MPa compressive strength were synthesized, using a microwave process as a purification step to produce a vitrified BA (VBA) precursor. The formation of highly porous bodies relied on intensive mechanical stirring of VBA powder in a weak alkaline medium, with the addition of a surfactant, followed by sinter-crystallization at moderate temperatures (800 °C or 900 °C). Besides silicates, the developed porous glass-ceramics featured the formation of hematite and magnetite, formed by the oxidation of metal particles presented in the VBA. Although sinter-crystallization did not lead to the stabilization of all heavy metals in the nearly completely amorphous VBA, the leaching values for all porous materials were below the EU thresholds specifications. The highest strength-to-density ratio was found for the porous 1M/SLG/900, in which the valorization of VBA was coupled with the reuse of 10 wt% SLG waste, in a 1M NaOH alkalinity medium. Based on the high open porosity (up to 70%), as well as the acceptable compressive strength (above 1 MPa), the VBA-based porous glass ceramics could be potentially used for thermal or acoustic insulators. The presence of hematite and magnetite in the porous 1M/SLG/800 glass-ceramic yielded a moderate electrical conductivity of 0.9 ± 0.1 S/m and high relative permittivity exceeding 50000 (in the 20-200 Hz frequency range), can set the baseline for novel applications of porous VBA/SLG-based glass-ceramics beyond building materials, such as electro-catalytic reactions.

351

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