Valorization of industrial wastes for the production of glass ceramics

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Abstract

In the present experimental study, CaO-Al_2O_3-SiO_2glass ceramics were produced by mixing four different binary compositions ofindustrial wastes, namely fly ash, red mud andmetallurgical slag.Molten glasswas first producedin alumina crucibles at 1300and 1500^oC and then cast in stainless steel moulds. After cooling, glass was pulverized and used for the production of glass ceramics which wereprepared in disks anduniaxially pressed at 60 MPa. The chemical composition of the raw materials as well as the sintering temperature affected microstructure, porosity, compressive strength, Vickers hardness and linear thermal expansion coefficient of the produced glass ceramics. The potential leaching of hazardous elements from glass ceramics was investigated by Toxicity Characteristics Leaching Procedure (TCLP) test, their chemical stability was studied by immersion in distilled water, simulated acid rain solution and seawater for a period up to one month, while their structural integrity was assessed according to ASTM standard C1262-10. The use of analytical techniques, namely X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Differential Thermal Analysis (DTA) and Fourier Transform Infrared Spectroscopy (FTIR) provided significant insights on the microstructure of glass ceramics.

Keywords

Glass Ceramics, industrial waste, compressive strength, porosity, microhardness

Introduction

Valorization of industrial wastes and by-products has emerged as an important environmental issue since industrial development generatestonnes of hazardous wastes which have high content of toxic elements, including heavy metals and metalloids. Today, the need for the development of efficient management approachesfocusing on reduction of the volume of wastes, immobilizationofhazardous elements andenergy savings is of high priority.Vitrification, which aims at the conversion of wastes into a stable glassy matrixthrough thermal treatment, has so far attracted significant attention due toits successful applicationin a variety of wastes including fly ashes, metallurgical, municipaland even radioactive wastes(Aloisi et al. 2006,Erol et al. 2009).Most of the derived glassesexhibit high chemical inertness(Binhussain et al. 2014) andnoticeable potential for immobilization ofhazardous elements(Leroy et al.2001).

Another advantage of wastevitrification is the production of glass ceramics from the vitrified materials.Glass ceramics are polycrystalline materials produced by controlled crystallization of a glass matrix and typically consist of a crystalline phase (30-95% w/w) and a residual glassy phase. When adjusting different process parameters such as chemical composition, particle size distribution, treatment time and temperature, tailor made glass ceramics for specific applications can be produced. Based on their favourable properties such as high mechanical strength in elevated temperature, high microhardness, high chemical inertness and low thermal expansion coefficient, glass ceramics can become suitable for a variety of applications including, but not limited to, construction materials, ceramic tiles, catalytic supports, lightweightaggregatesand sensors(Zhang et al. 2007,Dong et al. 2009, Tang et al. 2014).

Several studies are available in literature investigatingvitrificationof different wastes. Blast furnace slag was the first silicate waste used as potential raw material for the synthesis ofglass ceramics. The end product, called slag sital, was produced from the vitrification of slag via two-stage heat treatment. The use

of fly ash for the production of ceramics with improved mechanical, chemical and physical properties has been also studied (Rincón et al. 1999, Erol et al.2008,Wang et al. 2014).The microstructure and properties of glass ceramics were studiedby Differential Thermal Analysis (DTA) based on the crystallization behaviour of fly ash (Leroy et al. 2001).CaO-Al_2O_3-SiO_2(CAS) glass ceramics have been producedfrom incinerator fly ash throughcombustion and powder sintering(Cheng & Chen 2003). Both processes resulted in the production of ceramics at 900-950$^oC$with good mechanical and physical properties.

In other studies, different wastes have been investigatedin orderto produce glass ceramics. The effect of the presence of glass cullet and float dolomite in fly ash powder mixtures was studied by Barbieri et al.(1999) and the presence of alkaline-earth elements was found to improve their mechanical properties. The effect of various additives on the properties of glass ceramics made from several silicate wastes has been also studied (Rozenstaucha et al.2006). Glass ceramics developed using mixtures of fly ash, peat, clay and waste glass exhibitedhigh relative density (2.4 g/cm^3) and mechanical strength (72MPa).

However, the main drawback of the production of glass ceramics using wastes as raw materials is the high temperature required for glass melting. In order to substantially reduce melting temperature and the associated production cost, several approaches were considered bymixing materials of different compositions. Thus, industrial wastes including slags, red mud, galvanic glass microspheres, acid neutralizationsaltsand medical wastes can be mixed with or without the addition of natural raw materials, e.g. clay, alumina – silicon carbideand silica sandto produce glass ceramics with lower production costs, sufficient physical and mechanicalproperties(eg. compressive strength as high as 80 MPa) andlowcontent of hazardous elements(Francis et al. 2013,Mymrin et al. 2014).

In the present study, CaO-Al_2O_3-SiO_2 glass ceramics were producedby mixing high calcium fly ash, red mud andlow calcium ferronickel slag.Fourdifferent binary compositions were tested and the

effect of mineralogyand temperature on microstructure, porosity and mechanical and physical properties wasinvestigated.

Experimental design

Materials

The raw materials used for the production of glass ceramics were: i)fly ash form thethermal power plant of Ptolemais, NWGreece, ii) red mud from “Aluminum of Greece”, Agios Nikolaos, prefecture of Veotia, Greeceand iii) electric arc furnace slag from the “LARCO S.A” ferronickel plant, Larymna, prefecture of Lokris, Greece.Table 1 shows the chemical analysis of the raw materials used in the form of oxides and trace elements, as derived from anX-Ray fluorescence energy dispersive spectrometer (XRF-EDS) Bruker-AXS S2 Range Type.Loss on ignition (LOI) was determined by heating raw materials at 1050 ^{o}C for 4h.

X-Ray Diffraction (XRD)analysis of raw materials, as well as of glasses and glass ceramics,was carried out using a Bruker D8 Advance diffractometer with a Cu-Kα radiation and a scanning range from 3^{o} to 70^{o} 2θ,with step 0.03^{o} and 4s/step measuring type. Qualitative analysis was performed using the DIFFRACplus Software (Bruker AXS) and the PDF database.

Fly ash used in the present studyis classified as class C (SiO_2+Al_2O_3+Fe_2O_3>50%), while the main crystalline phases detected by XRDareportlandite, anorthite, calcite and quartz. Red mud is a by-product of alumina production by the Bayer process, while its volume and composition may vary widely and depend on the type of bauxite treated. Red mud used consists mainly of iron and aluminum oxides. Ferronickel slag consists of forsterite and fayalite (olivines),quartz, anorthite and cristobalitewhileitsamorphous content exceeds 50%.Commercial silica sand, of 98% purity, obtained from Athens, Greece, was also used in some tests.

Table1. Chemical analysis (% w/w) of raw materials

Component	Fly ash	Red mud	Slag
$Fe_2O_{3(tot)}$	5.6	41.65	43.83
SiO_2	33.4	9.28	32.74
Al_2O_3	13.1	15.83	8.32
CaO	31.85	10.53	3.73
MgO	3.67	1.13	2.76
MnO	0.18	-	0.41
Na_2O	0.46	2.26	-
K_2O	0.76	0.21	-
P_2O_5	-	0.12	-
TiO_2	0.71	4.73	-
SO_3	6.58	0.3	0.45
Cr_2O_3	0.06	0.09	3.07
C	-	-	0.11
Ni (mg/kg)	460	1055	1000
Co (mg/kg)	68	-	200
LOI	2.7	12.77	-
Total	99.13	99	95.54

All materials weregroundprior to use in a FRITSCHpulverizer(Germany)and the average particle size was determined by laser particle analysis using a MASTERSIZER S, Malvern Instrument.The mean particle size of the raw materials used for the production of glasses varied from 30 to45 μm, while for the production of glass ceramics the mean particle size of glasses varied between 30 and 80μm.

Glass Synthesis

The binary compositions and the experimental conditions used for the synthesis of glassesare shown in Table 2. The presence of fly ash and silica sand enhancesthe glass forming ability of the mixture,while the

presence of red mud and slag provide Fe which actsas network modifier for the crystalline structure and facilitates the formation of crystalline phases such as diopside, wollastonite and enstatite (Erol et al. 2009). In order to decrease both the melting temperature of the mixture and the viscosity of molten glass, 10% w/w of borax (Sigma Aldrich, Germany) and 10% w/w of sodium carbonate (Fluka, Germany) werealso added in two cases.Glass synthesis was carried out in alumina cruciblesafter heating the mixture for 2hat 1300or 1500^{o}C. Molten glass was cast in stainless steel moulds.

Table 2. Binary compositions and experimental conditions used for glass synthesis

Composition	PFA(%)	RM (%)	SK (%)	SS (%)	Borax/Sodium Carbonate(%)	Temperature (^{o}C)
50P50RM	50	50	-	-	-	1500
90P10RM	90	10	-	-	-	1500
90P10SS	90	-	-	10	10/10	1500
90P10SK	90	-	10	-	10/10	1300

PFA: Ptolemais fly ash, RM: red mud, SS: silica sand, SK:slag

Glasses were analysed by Differential Thermal Analysis (DTA) to investigate the crystallization process and determine both glass transition (T_g) and crystallization peak temperature (T_c). DTA analysis was performed using a Perkin Elmer Pyris DTA/TG analyser, while samples were heated from 40 to 1200^{o}C with a constant rate of 10 ^{o}C/min.

Glass ceramics production

The pulverized glasses were used as raw materials for the production of glass ceramics. Four different glass ceramics were prepared in disks and uniaxially pressed at 60 MPa (sample dimensions ⌀30 mm

diameter, h ~15-25 mm). The use of pulverized materialsimproves processing and the functional characteristics of the final products.

The green samples were dried at 110^{o}C and then sintered for 2h at temperatures varying between800 and 1000^{o}C, with a heating rate of 3^{o}C/min. Open porosity and bulk density of the sintered glass ceramics were measured by mercury porosimetry (MicromeriticsAutopore IV 9500); measurements were done in triplicate. The standard deviation in all cases was less than 5%. The compressive strength was determined using an MTS 800 load frameas the average of three measurements. Vickers microhardness measurements were performed by FM-800 Future-Tech microhardness tester.Samples were polished using diamond paste and a load of 500 g was selected. To obtain reproducible results 10 indentations were made on each sample. Dilatometric studies of glass ceramics produced after sintering at 900^{o}C were also performed to determine the coefficient of thermal expansion (CTE) between 40 and 600^{o}C on a Netzsch DIL 402C dilatometer.

The functional groups present inglass ceramics were identified using FTIR analysis on KBr pellets (each sample was mixed with KBr at a ratio 1:100 w/w and pressed to obtain a disc) with a Perkin Elmer Spectrum 1000 spectrometer. The microstructure of the samples was determined by Scanning Electron Microscopy (SEM) using a JEOL 6380LV scanning electron microscope equipped with an EDS INCA microanalysis system.

The toxicity of glass ceramics was investigated by subjecting samples to TCLP (Toxicity Characteristics Leaching Procedure) test (US EPA, 1990). The concentration of Cr,Ni,Zn,Cd,Pb andCuin the extract was determined using an Agilent Technologies 7500c x inductively coupled plasmamass spectrometry (ICP-MS) analyser (Agilent Technologies,Santa Clara, CA, USA).

The chemical stabilityof glass ceramics was investigated by immersion of samples in distilled water, simulated acid rain (H_2SO_4:HNO_3 60:40 % w/w, pH 3) and seawater for 1day,7days and 1 month. After immersion for the predetermined period the samples were weighted and the weight loss was calculated.

The structural integrity of the specimens was assessed by employingtwo 48 h freeze-thaw cycles, with -10^{o}Cand 80^{o}C as temperature extremes, according to ASTM standard C1262-10.Weight loss and compressive strength have been also determined after the end of the tests.

Results and Discussion

Mineralogy of glass ceramics

Glasses were initially prepared and chemically characterized as shown in Table 3, in order to optimize the process of glass ceramics production.The XRD patterns of glass and glass ceramics produced after sintering of glass powder at different temperatures are presented in Figures 1-4. The patterns indicate that by increasing sintering temperature from 800 to 1000 ^{o}Ccrystalline phases are developed and the relative intensity of the peaks is also increased, whilethe amorphous content, indicated by the wide shoulder shown between 17-38^{o}, is reduced in accordance with the chemical composition of the raw materials. Addition of 10% w/w silica sand to fly ash for the synthesis of glass (G-90P10SS) causes the formation of diopside, feldspars, brownmillerite and chromitein the respective glass ceramic (GC-90P10SS). The formation of new phases depends on the sintering temperature. It is shown in Figure 1 that at higher sintering temperature (1000^{o}C) diopside and feldspar peaks become more intense while chromite and brownmilleriteare also detected in glass ceramics.

When fly ash and slag (90 and 10% w/w, respectively) are used for the synthesis of glass(G-90P10SK) nepheline, brownmillerite and gehleniteare identified at temperature higher than 900 ^{o}Cin the respective glass ceramic (GC-90P10SK), due to the presence of Si, Ca and Fe in the raw material(Figure 2).Glasses and the respective glass ceramicsproduced aftersintering at 800 ^{o}C show higher amorphicity as indicated by the shoulder shown between 17^{o} and 38^{o} 2θ. As temperature increases the intensity of peaks of enstatite and nepheline also increases.

Table 3. Chemical analysis (%) of glasses

	G-50P50RM	G-90P10RM	G-90P10SS	G-90P10SK
Na_2O	0.13	0.52	9.22	6.32
MgO	1.74	2.14	1.96	3.70
Al_2O_3	22.81	18.93	6.16	8.27
SiO_2	15.94	35.91	46.96	26.53
P_2O_5	0.15	0.14	0.10	0.07
SO_3	0.00	0.15	0.85	0.33
K_2O	0.61	1.24	0.96	0.73
CaO	22.31	19.03	15.90	15.14
TiO_2	3.16	1.53	0.42	0.71
MnO	0.05	0.03	0.01	0.15
Fe_2O_3	24.18	6.81	4.13	16.15
NiO	0.05	0.02	0.01	0.04
CuO	-	0.01	-	-
ZnO	0.01	-	-	0.01

According to the XRD patterns of G-50P50RM and G-90P10RM glasses and the respective glass ceramics (GC-50P50RM,GC-90P10RM) (Figures 3 and 4, respectively), similar crystalline phases i.e. gehlenite, enstatite and wollastonite are identified. The phases remained after sintering are gehlenite and hematite. Noother crystalline phases (quartz, anhydrite, gibbsite and lime) were detected due to precipitation and dissolution reactions that tookplace during sintering. The amount of glassy phase was decreased in glass ceramics produced after sinteringat 1000 ^oC, while the intensity of wollastonite and enstatitepeaks has increased. The presence of Na-Fe crystalline phases in glass ceramics is due to the high Fe content in the starting raw materials and is typical ofglass ceramics derived from $CaO\text{-}Al_2O_3\text{-}SiO_2$ (CAS) wastes (Ilic et al. 2003, Xu et al. 2010, He et al. 2013).

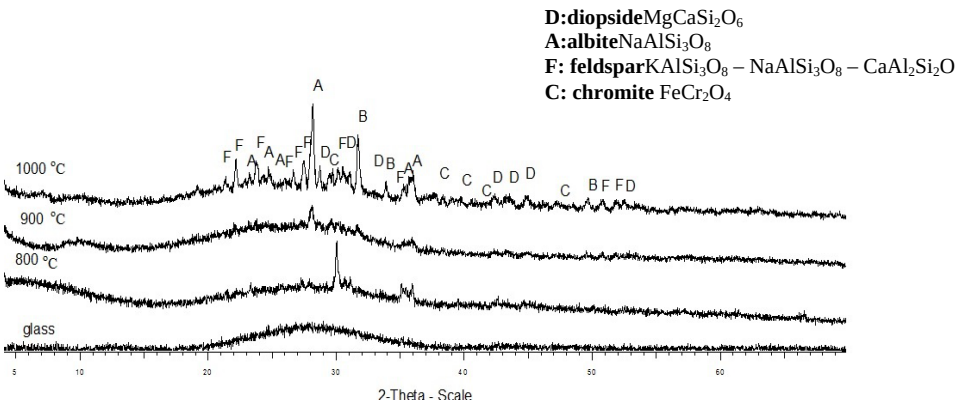

Figure 1. XRD patterns of G-90P10SS glass and the produced glass ceramics (GC-90P10SS) at 800, 900 and 1000^{o}C

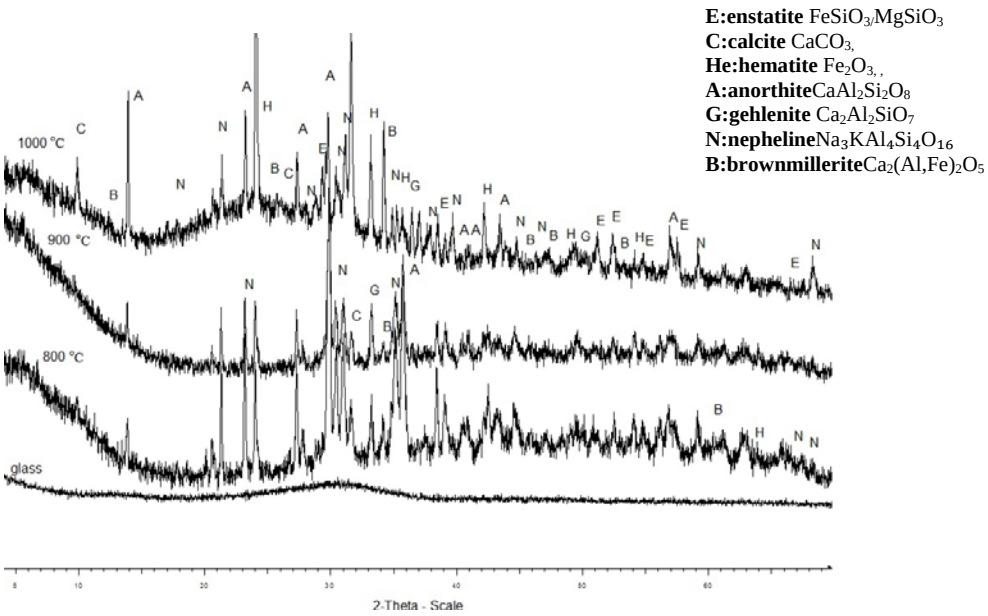

Figure 2.XRD patterns of G-90P10SK glass and the produced glass ceramics(GC-90P10SK) at 800, 900 and 1000^{o}C

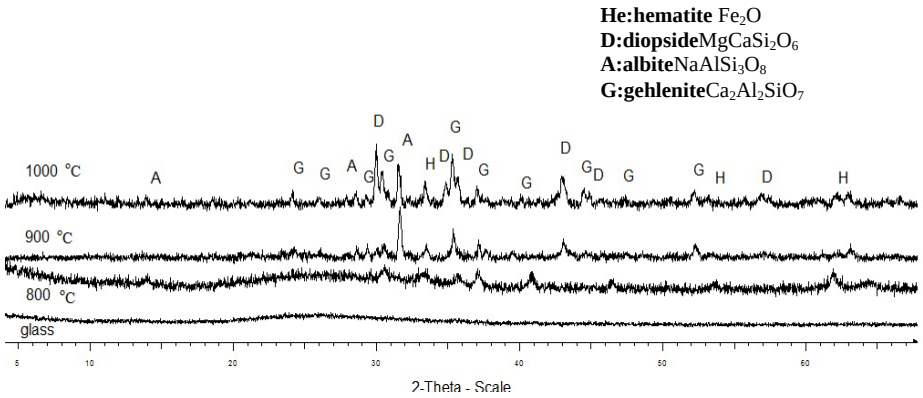

Figure 3. XRD patterns of G-50P50RM glass and the produced glass ceramics (GC-50P50RM)at 800, 900 and 1000^{o}C

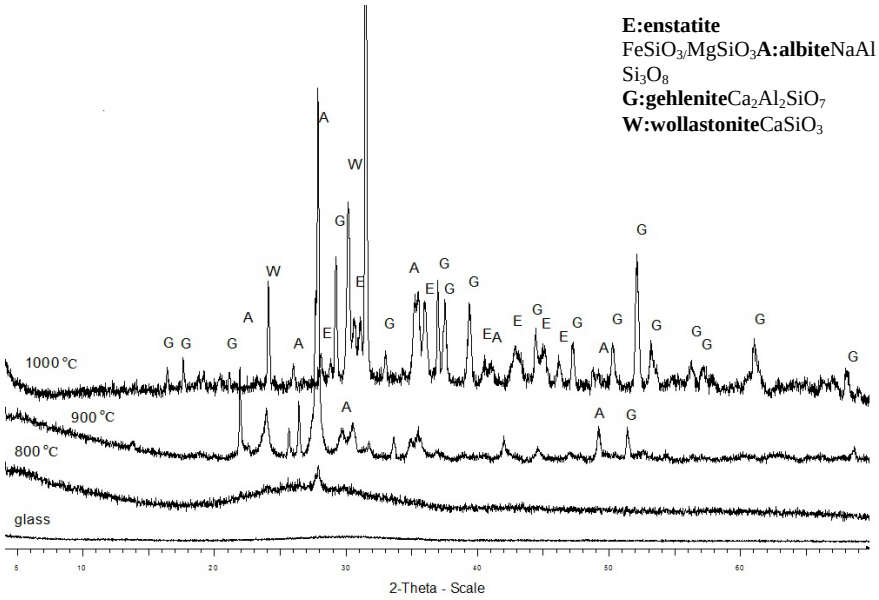

Figure 4. XRD patterns of (G-90P10RM) glass and the produced glass ceramics (GC-90P10RM)at 800, 900 and 1000^{o}C

Microstructure of glass ceramics

Figure 5presentsSEM images and element spectrums (EDS analysis) of glass ceramics produced after sintering at 900 ^{o}C of glasses producedfrom fly ash, red mud and slag. It is shown that in all specimenscrystal particles of different size and shape are distributed in a glassy phase. In glass ceramics(GC-90P10SS)produced after sintering of glass produced from fly ash and silica sand, a homogeneous microstructure and a very uniform dispersion of grains into the main glass matrix areshown (Figure 5a). A rigid network of well-connected grains has been developed indicating that this glass exhibitsgoodsinterability. Based on the EDS analysis,shown in Figure 5b, it is deduced thatthe elongated dark crystals correspondto diopside (D)and the small white grains correspond to chromite(Cr). Figure 5c shows themicrostructure of glass ceramicsproduced after sintering of glass produced from red mud and fly ash(GC-90P10RM), where the amount of glassy phase is uniformly distributedand fills the interparticle voids. Mostgrains are elongated and the intrergraincontact isclearlyvisible. The needle shapedcrystals correspond to wollastonite(W), as also confirmed in Figure 5d. In glass ceramics (GC-90P10SK) produced after sintering of glass produced from fly ash and slag, Figure 5e,it is shown that spherical and laminar shaped grains are uniformly distributed into the glassy phase. Spherical particles varying in size from 2.5 to5.5 μm correspond to enstatite(E) and laminar particles with a mean particle size of 5μm to brownmillerite(B), as also deduced from Figure 5f which is similar to Figures 5b and 5d.

The study of the microstructure of glass ceramics produced after sinteringof glass at 1000 ^{o}C(data not shown) reveals a denser structure where larger particles are embedded intothe crystalline matrix. The amount of glassy phase was decreased as sintering temperature increased. In all cases the results are consistent with XRD patterns.

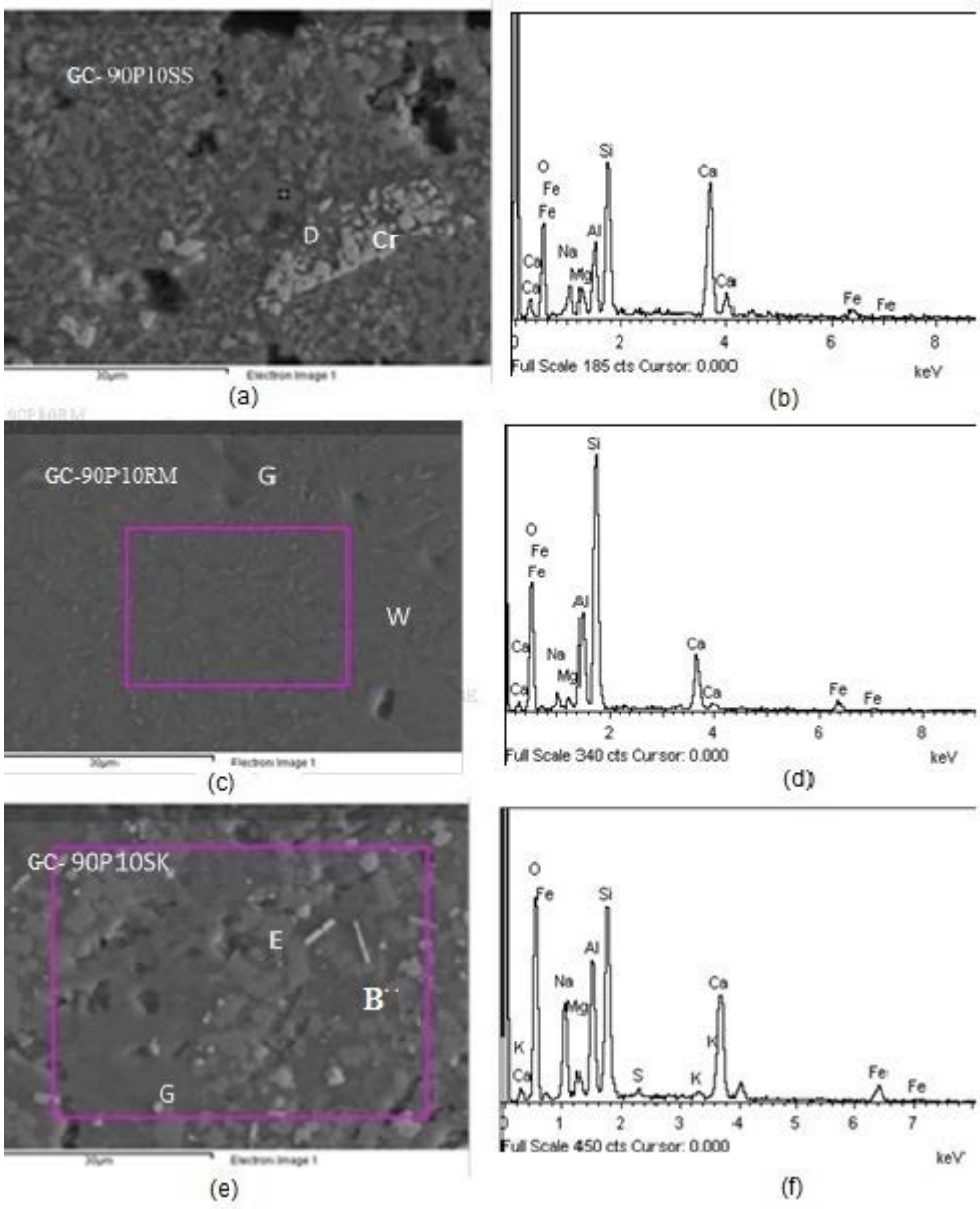

Figure 5. SEM imagesand elemental spectrums (EDS analysis) of GC-90P10SS (a,b), GC-90P10RM (c,d) and GC-90P10SK (e,f) glass ceramics produced after sintering glass powderat 900 ^{o}C

Effect of thermal treatmentof glasses

The behaviour of the glass powder during heating was investigated through DTA, where glass transition (T_g) and crystallisation temperatures (T_c)were determined (Figure 6). It is shown that in all samples T_g and $T_c$stronglydepend on compositionof raw materials. In glasses withhigh Fe content (G-50P50RM andG-90P10SK), namely 25% and 15%respectively, the endothermic peaks at 600 and 700^{o}Cindicate the glass transition temperature, while the exothermic peaks at 716^{o}C for the glassproduced fromslag and fly ash (G-90P10SK) are probably related to decomposition of calcite.The exothermic peaks around 850^{o}C, shown in both specimens, are also related to iron content.For the G-90P10RMglass produced from raw materials containing very little red mud a shift of T_c and T_g temperatures to higher values (910 and820 ^{o}C, respectively) is observed.

For the glasses produced from raw materials with higher SiO_2 content (G-90P10SS), T_g is below 600 ^{o}C and T_c is at 700 ^{o}C. Both temperatures were shifted to lowest values while peaks become more intense when compared to the respective glasses produced from raw materials with high Fe content (G-50P50RM, G-90P10SK). In the latter case T_g is around 700 ^{o}C and T_c at 900 ^{o}C for G-50P50RM while for the glass G-90P10SK T_g is 630 ^{o}C andT_c at 720 ^{o}C respectively. The higher temperatures of crystallization and glass transition are evident in G-90P10RM glass where T_g is 850 ^{o}C, and crystallization temperature is around 910 ^{o}C. This decreasing trend in temperature is also related to the initial particle size of the powderedglass which is around 30 μm for G- 90P10SS sample, while for the coarser G-90P10RM sample with a mean particle size of 80μm, crystallization peak temperature is almost 150 ^{o}C higherand reaches 910 ^{o}C. Based on the DTA results the selected sintering temperature for all glasses was decided to be 100 ^{o}C higher than glass transition temperature to ensure that sinter-crystallization process is completed.

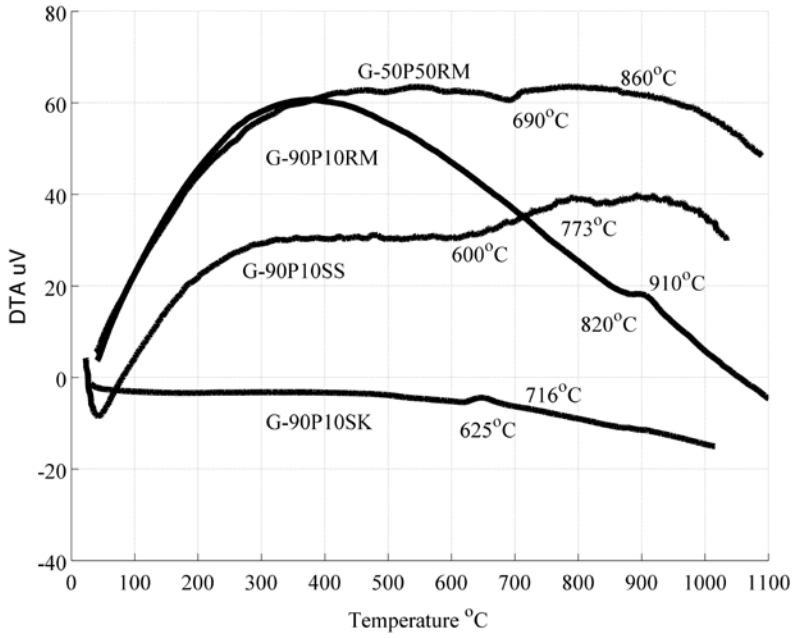

Figure 6.DTA of glasses

FTIR analysis

Figures7-10present the FTIR spectra of raw materials, the produced glasses as well as the respective glass ceramicsproduced at 900°C.The identified FTIR bands are consistent with infrared data of commercial silicate glasses and glass ceramics (Elbatal et al. 2009).The spectracan be divided in three main regions, includinghigh frequency bands between 1000-1100cm^{-1}, many mid frequency bands between 480and 700 cm^{-1}, and lower frequency and weaker bands up to 2000cm^{-1}.The intensity of the peaks of the produced glass ceramics varies depending on the glass composition.

Peaks inglassescontaining low $SiO_2$and high $Al_2O_3$and CaOcontent as well as in the respective glass ceramics become weaker in high and mid frequency bands, while atlow frequency bands show higher intensity(Atalay et al.2001).The band seen at 480^{-1} cm in all glassescan be attributed to the bending motions of the aluminosilicates and the formation of Fe phases. Peak intensity is stronger for glasses with

high Si/Al ratio such as the G-90P10SS.A doublet of peaks between 600and800 cm^{-1} is mainly due to Si–O–Si symmetric stretching of bridging oxygen between SiO_4tetrahedra. The band at around1000 cm^{-1}isattributed to asymmetric stretching vibrations of the silicate tetrahedral network.The strong band seen at around 1400$cm^{-1}$is more dominant for glass ceramics with high Ca content like GC-50P50RMand is due to atmospheric carbonation, asymmetric stretching and out of plane bending modes of CO_3 contained in $CaCO_3$(Zaharaki et al. 2010).

Weaker bands shown mostly for glass ceramicsat 2400cm^{-1} are probablydue to the presence of Fe phases. Peak intensity gets stronger as Fe content increases, as it is evidentfor glass ceramics produced aftersintering of glasses containing fly ash, red mud and slag (GC-50P50RM, GC-90P10SK).Finally, small bands seen at 3600 cm^{-1}, are associated to stretching vibrations of the –OH bond or to the presence of silalon (SiOH) (Komnitsas et al. 2009). FTIR results of the present studyconfirm the silicate glass ceramics structure (Liao etal. 2015).

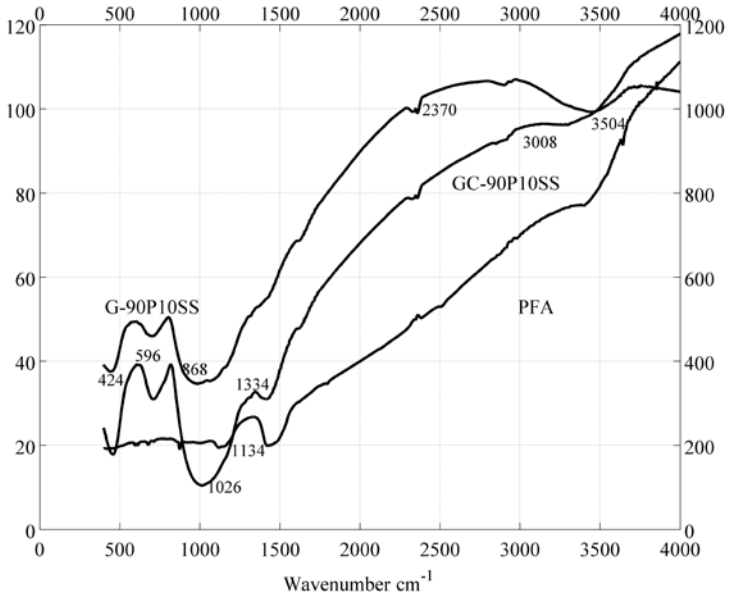

Figure 7.FTIR spectra of Ptolemais fly ash, G-90P10SSglass and GC-90P10SS glass ceramic

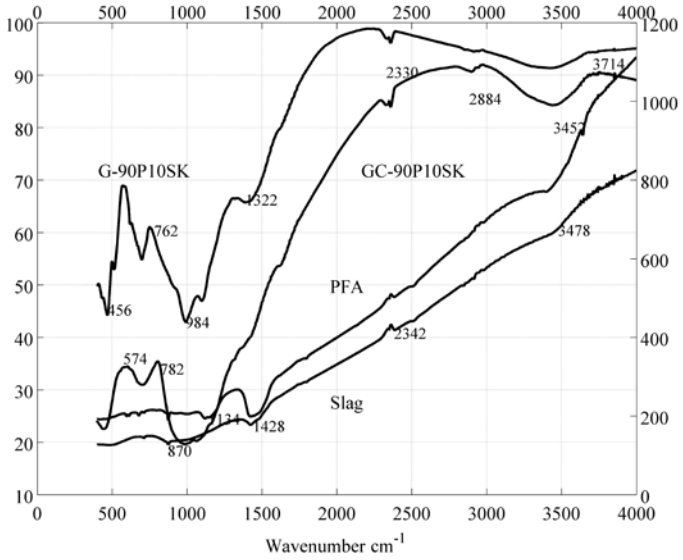

Figure 8. FTIR spectra of Ptolemais fly ash, slag, G-90P10SK glassandGC-90P10SKglass ceramic

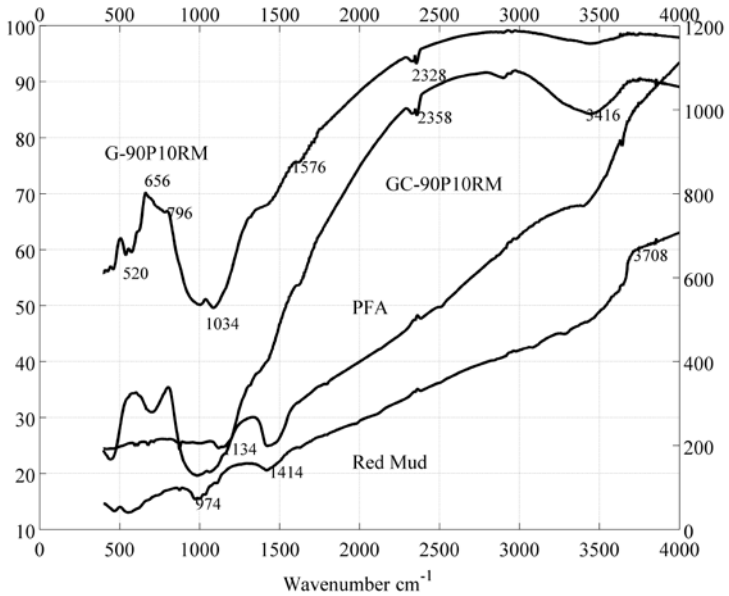

Figure 9. FTIR spectra of Ptolemais fly ash, red mud,G-90P10RMglass and GC-90P10RM glass ceramic

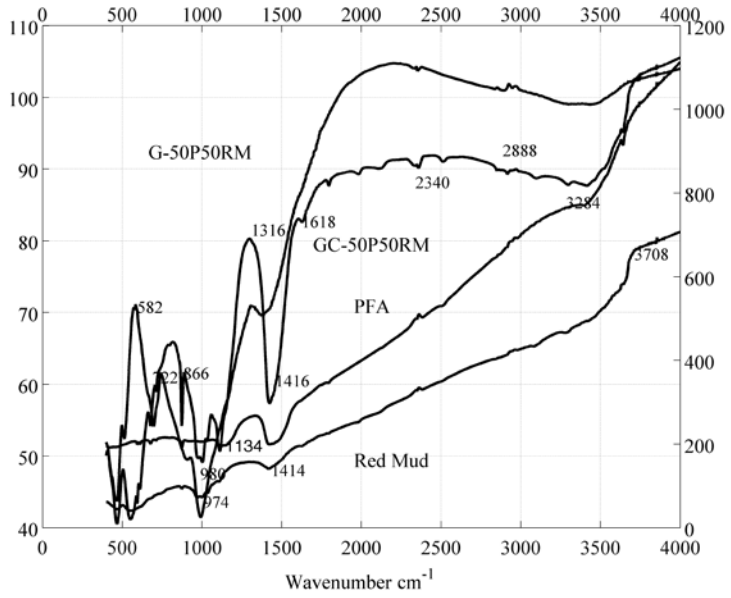

Figure 10. FTIR spectra Ptolemais fly ash, red mud,G-50P50RMglass, andGC-50P50RM glass ceramic

Physical and mechanical properties

The open porosity and bulk density ofglass ceramics produced after sintering of glass powderat 800, 900 and1000 ^{o}C, are presented in Table 4. The results indicate that the increase of sintering temperature results in an increase of bulk densityand a respective noticeable decrease of porosityfor all glass ceramics.

Table 4. Open porosity and bulk density of glass ceramics

	Open porosity, %			Bulk density, g/cm^3		
Composition	800^{o}C	900^{o}C	1000^{o}C	800^{o}C	900^{o}C	1000^{o}C
GC-50P50RM	36.68	11.28	6.47	1.84	1.87	1.92
GC-90P10RM	32.29	23.03	15.66	1.84	2.02	2.13
GC-90P10SS	31.37	2.43	2.02	1.76	2.37	2.37
GC-90P10SK	22.68	4.11	2.62	2.18	2.33	2.35

During sinteringof the glass powder, the pores developintergrain contacts due to diffusion kinetics, thus resulting in densification of the final product and a further decrease of porosity. Thebetter packing of particles, as shown inSEM analysis, results in a more homogeneous structure and in gradual decrease of porosity intheproduced glass ceramics.Sintering of powdered glasses, with a meanparticle size of 20μm, also results inbetter rearrangement of grains, faster diffusion kinetics and early densification. The well-developed crystalline structure of glass ceramics was also observed in XRD patterns.However, glass ceramics produced after sintering of glasses produced from red mud and fly ash, such as GC-90P10RM and GC-50P50RM with high CaO content (> 20%), exhibited higher values of porosity, ranging between 6 and 36%, while the highest value was recorded at the lower sintering temperature. This trend in porosity was also observed in other studies where high residual porosity(30%) was reported in glass ceramicsproduced from fly ash, silica sand and metallurgical slag (Karamanova et al. 2011, Binhussain et al. 2014).

Bothopen porosity and bulk density of glass ceramics are strongly affected by the chemical composition of the raw materials, their particle size and the degree of crystallization. The lowervalues ofporosity, in the range of around 2-4.1 %,wereobtained forceramics,i.e. GC-90P10SS,produced from glasses with high Si/Al ratio(Si/Al:6.62).

Mechanical properties of glass ceramics, namely compressive strength and Vickers microhardness,were also determined.Compressive strength is affected by the sintering temperature and the particle size of the powdered glass, factors which affectthe final microstructure of glass ceramics. As the sintering temperature increases from 800 ^{0}C to 1000 ^{o}C porosity values decrease and the compressive strength shows a noticeable increase reaching the maximum value of 194MPa for the glass ceramic producedafter sintering of glass produced fromfly ash and 10% w/w silica sand (90P10SS) (Table 5).

Table 5. Mechanical properties of glass ceramics

	Compressive strength (MPa)			Vickers microhardness(HV)			CTE 20-600^{o}C (10^{-6}/K)
Composition	800^{o}C	900^{o}C	1000^{o}C	800^{o}C	900^{o}C	1000^{o}C	
GC-50P50RM	21	20	23	257	321	353	2.38
GC-90P10RM	16	49	72	380	447	524	2.78
GC-90P10SS	30	115	194	550	620	732	4.91
GC-90P10SK	10	30	58	584	614	704	1.82

Vickers microhardness values are also high for all glass ceramics produced after sintering at 1000 ^{o}C. The maximum value,exceeding730 HV, was obtained for glass ceramicGC-90P10SSindicating that the presenceof Siin the raw materials improves substantially both the mechanical and physical properties of the final products.According to He et al. (2013), the increase in theCaO content in glasses results in an increase of both hardness and compressive strength of the produced glass ceramics due to the crystallization of wollastonitewhichis beneficial for the development of a homogeneous microstructure. This observation is in agreement with the results of the present study where wollastonite is the dominant phase in glass ceramic GC-90P10RM which exhibitedhighhardness and compressive strength, 524 HV and 72MPa respectively.

Increase of sintering temperature also resulted in higher values of hardness varying from 257 to 524HV for specimensproduced from raw materials containing red mud(GC-50P50RM, GC-90P10RM), and from 550HV to 732HV for glass ceramics produced from raw materials containing slag and silica sand (GC-90P10SS, GC-90P10SK).

Based on the values of porosity (>23%), bulk density (1.84-2.13gr/cm^{3})and compressive strength (21-72MPa) glass ceramics produced from raw materials containing suitable amounts of red mud and fly ash (GC-50P50RM, GC-90P10RM) can be used as filters, catalytic materialsand lightweightceramics.(Shao et al. 2004, Ribeiro &Labrincha 2008, Cetin et al. 2015). According to a previous study (Nanko,1998) open porosity higher than 30%, high mechanical strength, narrow particle

size distribution and high chemical resistance are required in order to use porous materials as filters and catalysts. On the contrary, glass ceramics produced from silica sand (GC-90P10SS) and slag (GC-90P10SK) exhibiting higher density,lower porosity and high compressive strengthmay be used as construction materials. Leroy et al. 2001, mentioned that recommended values of density, compressive strength and CTE for commercial bricks are 1.65-2.08 g/cm^3, 4.8-27.6 MPa and 4.5-9 10^{-6}/K respectively, while for building tiles compressive strength should be in the range26-44MPa.

Dilatometric studies have been also performed and the coefficient of thermal expansion (CTE) has been determinedforthe temperature range of 20-600^{o}C. As it is shown in Table 5, CTE values are considered relatively low,while the highest value of 4.91*10^{-6}/Kis obtained for ceramics withthe highest alkali content, almost 12 %(GC-90P10SS). Thesevaluesareconsistent with the results obtained by Ribiero et al. (2008), who alsoobserved that the higher CTEare relatedtothe presence of alkalis in the glassy phase.

In Table 6 the main properties of the glass ceramics produced in the present study are compared with the results published in earlier studies indicating the high valorization potential of high calcium fly ash, low calcium ferronickel slag and red mud for the production of glass ceramics with properties suitable for a number of applications.

Potential toxicity of glass ceramics

The TCLP results of the raw materials and the producedglass ceramics, in terms of Cr and Ni which show noticeable leachability in the raw materials, namely fly ash and slag respectively,are presented in Table 7.

Table 6. Comparison of properties of various glass ceramics

Raw material	Crystallization	Compressive	Density	Porosity	Reference

	temperature ^{o}C	strength MPa	g/cm^3	%	
Fly ash	1150-1200		1.93-3.19	0.3-15	Erol et al. 2008
Fly ash, waste glass	950-1100	26-76	1.6-2.2		Lu et al. 2014
Fly ash, silica sand	750-950	65-70(bending strength)	2.9-3		Yang et al. 2009
Aluminum waste, waste glass, clay, peat ash	1080-1180	32-42	2.5-2.94		Lodins et al. 2011
Slag, kaolin, quartz	1200-1220	3-28	2.1-2.34	39-49	Karamanova et al. 2011
Fly ash, red mud, silica sand	910-950		2.8-2.9	6-10	Erol et al. 2000
Fly ash, slag, silica sand, clay	900-1200	20-73	1.8-2.68	5-35	Binhussainetal. 2014
Fly ash, red mud, slag, silica sand	*800-1100*	*10-115*	*1.8-2.35*	*2-36*	*Present study*

Table 7. Concentration of heavy metals (mg/L) in the TCLP extract of raw materials and glass ceramics produced after sintering at 900 ^{o}C

Element	GC-50P50RM	GC-90P10RM	GC-90P10SS	GC-90P10SK	Slag	Fly ash	Red mud	*US EPA limit*
Cr	0.25	<DL	0.77	2.81	<DL	678.9	<DL	5
Ni	0.09	0.21	0.18	<DL	429.5	<DL	<DL	-

DL: Detection Limit

It is shown that for both elements their leachability in the produced ceramics is either below detection limit or negligible. The highest concentration, in terms of Cr, is shown for the GC-90P10SK glass ceramic, 2.81 mg/L, which is well below the respective TCLP limit of 5 mg/L. No TCLP limit for Ni is available.

The substantial decrease of leachabilityof heavy metals inglass ceramics is mainly attributed to the increase in the degree of crystallinity and the entrapment of heavy metal ions ina well-developed crystalline structure (Yang et al. 2009; Vu et al. 2011; Rozenstrauha et al. 2013).The leachability of other

elements such as Cu, Zn, Cd and Pbwas not determined since it wasbelow detection limit in the raw materials used.

Structural integrity of glass ceramics

The % weight loss ofglass ceramicsproduced after sintering at 900^{o}C,after immersion in distilled water(pH 6.5), simulated acid rain(pH 3) and seawater (pH 8.2) for 1, 7 and 30 d is shown in Table8.The results indicate that longer than 7 days immersion period does not result in noticeable increase in weight loss for all specimens and solutions tested.The highest weight loss, as anticipated, was recorded for specimens immersed in simulated acid rain solution, which simulates a highly corrosive environment. The slightly higher weight loss of glass ceramics immersed in sea water, compared to distilled water, is attributed to the effect of chlorine ions present in seawater (Komnitsas et al. 2007).

Table 8. Weight loss (%) of glass ceramics produced after sintering at 900^{o}C

Specimen	Distilled water			Simulated acid rain			Seawater		
	1d	7d	30d	1d	7d	30d	1d	7d	30d
GC-50P50RM	1.70	1.77	2.84	4.78	5.27	6.06	3.02	4.33	5.94
GC-90P10RM	2.14	2.22	3.33	8.49	8.99	9.96	4.14	5.23	7.17
GC-90P10SS	0.88	0.92	0.98	2.78	3.39	4.16	1.27	1.44	1.56
GC-90P10SK	0.97	1.12	2.01	3.61	4.15	5.04	1.87	2.42	2.97

Glass ceramics produced from raw materials containing fly ash and red mud (GC-90P10RM, GC-50P50RMand GC-90P10SK), where gehleniteis present in lower or higher percentages, exhibited lowerchemical resistance and this is probably due to the gelatinization of gehlenite in acidic solutions (Cheng et al. 2002).The weight loss recorded is mainly attributed to the dissolution of the glassy phase.It

is thereforebelieved that the chemical stability of the produced glass ceramics depends on the degree of crystallinity and microstructure (Erol et al. 2008,Leroy et al. 2001, Cheng & Chen 2003).

Table 9shows the compressive strength and the weight loss of glass ceramics subjected totwo 48 hours freeze thaw cycles, using -10^{o}C and 80^{o}Cas temperature extremes, according to ASTM standard C1262-10.

Table 9. Weight loss and compressive strength of glass ceramics produced after sintering at 900 ^{o}C,according toASTM standard C1262-10

Specimen	Weight loss, %	Initial Compressive strength, MPa	Final Compressive strength, MPa	Compressive strength loss, %
GC-50P50RM	4.05	20	15	25
GC-90P10RM	3.11	49	38	22.4
GC-90P10SS	0.55	115	106	7.8
GC-90P10SK	2.04	30	26	13.3

Measurements show that weight loss is limited for all glass ceramicstested and varies between 0.55 and 4.05%.On the other hand, the loss of compressive strength is rather low for glass ceramics produced after sintering of glass produced from raw materials containing fly ash and either silica sand or slag (GC-90P10SS and GC-90P10SK). The first specimen maintained its compressive strength in remarkable levels (106 MPa). Finally, glass ceramics produced from raw materials containing red mud (GC-50P50RM, GC-90P10RM), although they exhibited low weight loss, exhibited higher loss of compressive strength which varied between 22 and 25%.

Conclusions

Glass ceramics with beneficial properties can be successfully produced through sintering of glasses derived from industrial wastes such ashigh calcium fly ash, low calcium ferronickel slag and red mud. In the present study, these three wastes were used for the production of glassesat 1300 and 1500 ^{o}C which were then pulverized and sintered between 800 and 1000 ^{o}Cfor the production of glass ceramics. The main crystalline phases detected in glass ceramicswerewollastonite,enstatite and diopside belonging to $CaO-Al_2O_3-SiO_2$ (CAS)system. A small amount of glassy phase remained in the matrix at 900 ^{o}C, while sintering at 1000 ^{o}C results in an increase ofcrystallinity and intensity of peaks associated mainly with Ca and Fe phases.Crystal particles of 2-5.5 μm were uniformly dispersed into the glassy matrixin all glass ceramics as indicated by the use of analytical techniques.

Sintering temperature affects porosity,microhardness, compressive strength andlinear thermal expansion coefficient of the produced ceramics.Also, the increase of sintering temperature results in increase of density, for which the maximum values(~2.35 g/cm^3) were acquired for glass ceramics produced from fly ash and silica sand or slag. Glass ceramics prepared from red mud and fly ash, with CaO content higher than 20%, show higher porositywhich reaches36.7%. Despite the increase of porosity, the compressive strength and the Vickers microhardnessof all glass ceramics are high reaching 194MPa and 732 HV respectively for specimen GC-90P10SS, which produced after sintering at 1000 ^{o}C. Low thermal expansion coefficient values, in the range of 1.8-4.9*10^{-6}/K, have been also measured. The concentration of heavy metals in the TCLP extracts of all glass ceramics is either negligible or well below the respective US EPA limits due to the increase of the degree of crystallinity in the final products and the entrapment of heavy metal ions in the crystalline structure. In addition, limited weight losswas recorded for glass ceramics immersed in distilled and seawater, which increased considerably but did not exceed 10% when specimens immersed in simulated acid rain solution. Finally, the loss of compressive strength of glass ceramics subjected to freeze-thaw cycles, according to ASTM standard C1262-10, varied

between 7.8 and 25%. It has to be underlined though that the lower value of compressive strength was 15 MPa (GC-50P50RM), while the higher,although reduced, reached 106 MPa (GC-90P10SS).

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