Crystallization evolution, microstructure and properties of sewage sludge-based glass–ceramics prepared by microwave heating

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ABSTRACT

A Microwave Melting Reactor (MMR) was designed in this study which improved the microwave adsorption of sewage sludge to prepare glass–ceramics. Differential scanning calorimetry (DSC), X-ray diffraction (XRD), and scanning electron microscopy (SEM) were used for the study of crystallization behavior and microstructure of the developed glass–ceramics. DSC and XRD analysis revealed that crystallization of the nucleated specimen in the region of 900–1000 °C resulted in the formation of two crystalline phases: anorthite and wollastonite. When the crystallization temperature increased from 900 to 1000 °C, the tetragonal wollastonite grains were subjected to tensile microstresses, causing the cracking of crystal. Al ions substituted partially Si ions and occupied tetrahedral sites, giving rise to the formation of anorthite. The relationship between microwave irradiation and crystal growth was studied and the result indicated that the microwave selective heating suppressed the crystal growth, giving apparent improvements in the properties of the glass–ceramics. The glass–ceramics products exhibited bending strength of 86.5–93.4 MPa, Vickers microhardness of 6.12–6.54 GPa and thermal expansion coefficient of 5.29–5.75×10^{-6}/°C. The best chemical durability in acid and alkali solutions was 1.32–1.61 and 0.41–0.58 mg/cm^2, respectively, showing excellent durability in alkali solution.

1. Introduction

One of the main environmental problems is the safe disposal of the huge amount of sewage sludge that is produced every day in wastewater treatment plants [1]. Among the methods of the treatment of sewage sludge, glass–ceramics preparation seems to be a promising one for converting sewage sludge into novel materials that possess attractive mechanical and chemical properties [2]. Sewage sludge containing large amounts of CaO, SiO$_2$, and Al$_2$O$_3$ can be a good raw material for glass–ceramics production. By controlling the initial composition and by suitable heat treatment, a variety of crystalline phases will be obtained [3]. They exhibit bending strength, Vickers microhardness, fracture toughness, chemical durability and thermal shock resistance superior to those of glass, and in some cases traditional ceramics [4,5]. It should be noted that the chemical energy of the organic components in sewage sludge could be recovered during the prepared procedure of glass–ceramics as an auxiliary energy source. The

chemical energy in sewage sludge can be recovered during the prepared procedure of glass–ceramics as an auxiliary energy source, reducing the emission of CO$_2$ which is favorable to Kyoto Protocol [6]. Other advantages of this technology are the possibility of immobilizing heavy metal ions (held in the framework of glass or encapsulated into the crystallization phase) [7], the large reduction of volume (vary between 40 and 90%), and the flexibility of treatment procedure (which may accept different types of sewage sludge, either municipal or industrial) [8]. Preparing glass–ceramics by the conventional technology is an energy-intensive process, with the process temperature as high as about 1300 °C and the process time required as several hours [9]. Economic analysis of a glass–ceramics preparation system which can process 0.5–1.0 ton of sewage sludge per hour showed that the operating costs of this unit ranged from US$100–420 per ton, including labor, fuel and maintenance [10]. Another critical point in glass–ceramics preparation is the difficulty in controlling the size and the type distributions of the crystals due to the thermal inertia of the conventional heating [11].

To overcome these drawbacks, microwave heating has been developed as an alternative technology for the preparation of dense structural glass–ceramics, which is characterized by shorter reaction time, reduced energy consumption, and suppressed crystal size. It was found that the treatment temperature was decreased

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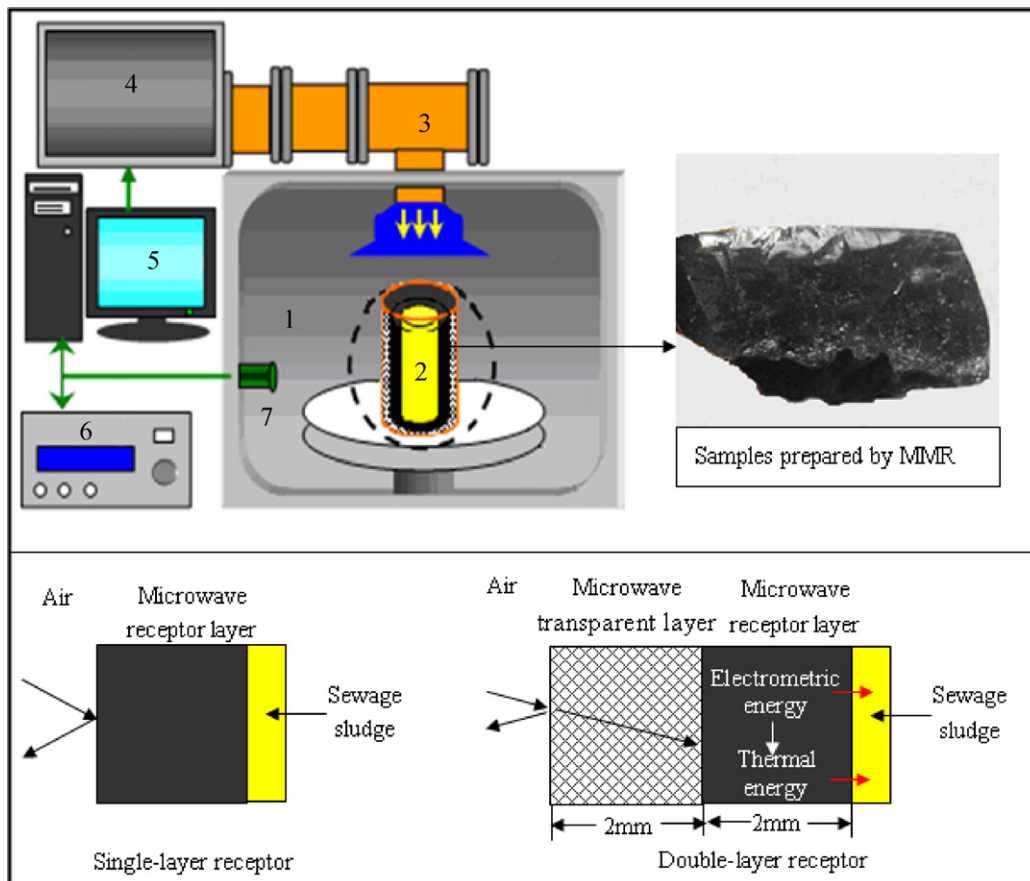
Fig. 1. A schematic of the microwave preparation reactor assembly: (1) microwave cavity; (2) Microwave Melting Reactor (MMR); (3) waveguide; (4) magnetron; (5) PC with fuzzy logic algorithm; (6) power governor; (7) infrared radiation thermometer.

from 1300 °C to 1000 °C when a glass–ceramics was sintered from barium aluminosilicate glass in microwave field [12]. It was also reported that an abrasion resistant glass–ceramics was developed from the MgO–Al$_2$O$_3$–TiO$_2$ system in 20 min by microwave heating [13]. Moreover, more uniform and strong bonding was observed in the glass–ceramics prepared by microwave, indicating that microwave energy suppressed the grain growth in crystal phase due to a fast heating rate and apparent low-temperature crystallization [8].

Sewage sludge is a poor receptor of microwave energy to achieve the temperature necessary for preparing glass–ceramics. It has been proved that microwave-induced preparation is possible, if an effective receptor is added into the raw sludge. The temperature of sewage sludge can achieve 1200 °C in microwave field when it was homogeneously blended with microwave receptor, such as graphite and char [9]. However, there are fundamental disadvantages of this method when it is applied in glass–ceramics preparation. The chemical composition of the samples shows uncontrollable changes in virtue of adding microwave receptor, leading to the poor properties of the products. In addition, the microwave receptor could not be recovered due to the encapsulation of silicate matrix in the glass–ceramics, increasing the operating cost of the procedure. Attempts termed as "hybrid microwave sintering" were also made to set around the sample directly to initially heat the material at room temperature [14]. However, the temperature of sewage sludge could not reach high enough owing to the significant reflection loss on the interface between microwave receptor layer and the air surrounding it.

To solve these problems, a new Microwave Melting Reactor (MMR) was designed in this study for preparing glass–ceramics

from sewage sludge. In MMR, microwave absorption of sewage sludge can be improved by the double-layer structure and the required temperature can be achieved in a very short of time, usually in a few minutes. A wave-transparent layer was introduced into the MMR system to decrease the reflection coefficient of the interface between the air and the MMR. Another important property of the powder was the low thermal conductivity which could give the sample a good heat insulation quality. The double-layer structure in MMR provides the even distribution of temperature and electromagnetic field in the samples, favoring the production of glass–ceramics with desired qualities. Further researches presented in this paper were focused on: (1) investigating the influence of heat-treatment schedule on the crystallization behavior and microstructure of the microwave-prepared glass–ceramics, (2) defining the evolution of crystallization in microwave field which were hardly found by applying the conventional procedures, and (3) gaining an insight into the chemical and physical properties of the glass–ceramics prepared by microwave in comparison to that obtained from conventional process.

2. Experimental

2.1. The design of MMR

The 2.45 GHz microwave furnace, which consisted of a rectangular multimode cavity, a continually adjustable power supply (0.50–2.7 kW), a temperature controlling system, and a Microwave Melting Reactor, was used for microwave heating experiment. As shown in Fig. 1, the Microwave Melting Reactor (MMR) consisted of a wave-absorbing layer and a wave-transparent layer. The

wave-transparent layer is the surface layer which plays an important role in avoiding the reflection loss of the incident wave on the front surface between the reactor and air. The wave-absorbing layer beneath it absorbed the incident wave transmitted through the wave-transparent layer and transformed the electromagnetic energy to thermal energy. In terms of optimizing the MMR performance, the material properties and the thickness of each layer are most important parameters to design the reactor structure.

Active carbon, a well known microwave receptor, was filled in the microwave-absorption layer. The material filled in microwave-transparent layer was selected according to the expression for reflection coefficient as given in Eq. (1) [15]:

$$R = \left| \frac{\eta_2 - \eta_1}{\eta_2 + \eta_1} \right| \tag{1}$$

where R is the reflection coefficient, η_1 and η_2 are the characteristic impedances of the air and the material filled in microwave-transparent layer, respectively. It is clear that the value of η_2 should be close to the value of η_1 for decreasing the reflection coefficient of the incident wave. Based on the results of our preliminary experiments, ferric oxides mixed with aluminum oxides ($Fe_2O_3/Al_2O_3 = 1:1$) were adopted as the materials filled in the microwave-transparent layer. Before filled into the microwave-transparent layer, the Fe_2O_3 and Al_2O_3 grains were ground using a mill to obtain a mixed powder with particle size $\leq 75.0\,\mu m$. The mixture powder had the properties of both lower characteristic impedance and higher microwave transmission rate, decreasing the reflection coefficient of the interface between the air and the MMR. Another important property of the powder is the low thermal conductivity which gives the sample a good heat insulation quality.

The thicknesses of microwave-transmission layer and microwave-absorption layer were determined according to the penetration depth (D_E, depth of the microwave energy penetrates into a material). D_E can be calculated by the Fresnel formula [8]:

$$D_E = \frac{\lambda_0}{\pi \sqrt{\varepsilon_r} tg\delta} \tag{2}$$

where λ_0 is the length of electromagnetic wave in vacuum, ε_r is the material dielectric constant, and $tg\delta$ is the dielectric loss tangent. According to the calculation of Eq. (2), both the optimal thicknesses of microwave-transmission layer and microwave-absorption layer were determined as 2 mm. The glass preparation from sewage sludge has been carried out to test the behavior of MMR in microwave heating. It was observed that the temperature of the specimen required for preparing glass was reached (1300 °C) and parent glass was prepared successfully in this reactor.

2.2. Parent glass production

Sewage sludge used in experiments was collected from urban wastewater treatment plants in Harbin, China. Selected chemical characteristics and the heavy metal contents of this sludge are given in Table 1. The dehydrated sewage sludge (moisture content was 79.8%) which contained small hard particles were crushed in a mortar and then heated at 1000 °C until the sludge samples reached constant weight to remove the volatile components. Sewage sludge must be mixed with additives to lower the melting temperature from its melting around 1500 °C. In our experiments, CaO and waste glass were used as effective additives. The chemical compositions of the sewage sludge, waste glass and raw materials were examined by X-ray fluorescence spectroscopy (XRF) and the results are shown in Table 2, indicating that the formed glass should be in the SiO_2–CaO–Al_2O_3 ternary phase system. Fig. 2 shows the phase diagram of the CaO–Al_2O_3–SiO_2 system. The chemical compositions of raw materials for preparing glass–ceramics could be located in the

Table 1
Chemical characteristics of sewage sludge.

Proximate analysis (wt.%)						
A[a]	V[a]	Ca[a,b]	O[c]	H[a,b]	N[a,b]	S[a,b]
24.50	75.50	39.40	24.43	5.71	4.75	1.18

Heavy metal content in dry sewage sludge (ppm)						
Cr	Cd	Cu	Pb	Zn	Fe	Ni
143	4.75	138	59.9	700	10,200	38.7

A: ash content; V: volatile matter content.
[a] Dry base.
[b] Ash free basis.
[c] Calculated by difference.

wollastonite–anorthite subsystem (the region marked by hatching in Fig. 2). The batch composition, prepared by mixing 52.0 wt.% of the raw sludge with 21.0 wt.% of CaO and 21.0 wt.% of waste glass, was chosen on the basis of the eutectic composition (CaO 38.0, Al_2O_3 20.0 and SiO_2 42.0 mass%) [16].

Additionally, 6.0 wt.% TiO_2 were added to the base glass composition as nucleating agents. Mixtures obtained above were melted by microwave processing and conventional processing respectively. In the microwave process, glasses were prepared by melting sewage sludge in a corundum crucible at 2000 W microwave power for 10 min and then cooled naturally to room temperature. In the conventional process, glasses were prepared by melting the mixture in an alumina crucible at 1450 °C for 2 h after which melts were preheated at 600 °C to reduce thermal shock. The results of XRD analysis for sewage sludge, parent glasses obtained from these two different heating processes are shown in Fig. 3.

2.3. Glass–ceramics production

It is important to determine nucleation and crystal growth temperatures precisely for effective conversion of glasses to glass–ceramics. Differential scanning calorimetry analysis (DSC) is performed using a calorimeter (STA449C, NETZSCH) with α-Al_2O_3 as standard sample. The glass powders are heated from room temperature to 1100 °C with the rate of 10 °C/min in order to detect the nucleation and crystallization temperatures. According to the results of DSC, heat-treatment schedule for the microwave-produced parent glass should include a nucleation stage at 760 °C for 30 min followed by a crystal growth stage at different temperatures (900 °C, 950 °C and 1000 °C) for 60 min in microwave irradiation. For conventional glass, sample should be held at nucleation temperature (820 °C) for 90 min and then heated to crystallization temperature (1000 °C) for 120 min in electric furnace. Fig. 4 shows the processes of glass–ceramics preparation by microwave and conventional methods. The types of the crystalline phases were characterized by X-ray with Cu Kα radiation (XRD: P|max-γβ, Rigaku, Japan). The step length was 0.02° with scanning speed of 5°/min in the range of 10–90° (Cu Ka = 1.5418 A). The schemes of glass–ceramics preparation by microwave and conventional heating are shown in Fig. 4.

2.4. Methods to evaluate glass–ceramics properties

Several techniques were used to evaluate the properties of glasses and glass–ceramics. The morphology of the crystalline phases made in thermal glass treated was investigated using a scanning electron microscope (SEM, S-4700, HITACHI). Archimedes' method was employed to measure the apparent density of the glass–ceramics. Hardness and fracture toughness were measured by an indentation method using the Vickers indenter. Vickers hardness was measured with loads of 100–1000 g with loading
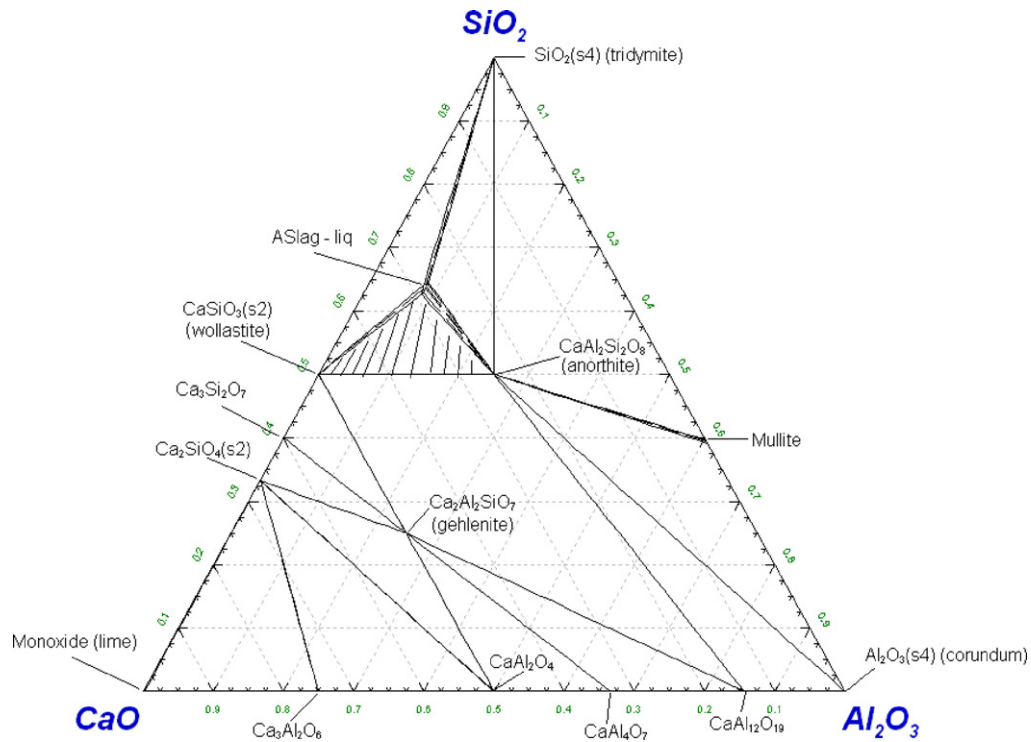
Fig. 2. Phase diagram of the CaO–Al$_2$O$_3$–SiO$_2$ system. The chemical compositions of sewage sludge correspond to the eutectic point marked by hatching (CS, wollastonite; CAS$_2$ anorthite).

times of 10 s. Bending strength was obtained from a four-point method with spans of 20 and 40 mm at a cross-head speed of 100 mm/min, as designated by American Society of Testing Materials (ASTM) E855-90 [17]. The thermal expansion coefficient (20–400 °C) was measured by TMA with a heating rate of 10 °C/mm in atmosphere. Chemical durability was measured following the designation of American Society of Testing Materials (ASTM) C279-88 [18]. First, powdered specimens were prepared in particle sizes of 4.75–6.75 mm. 20.0 g specimen powder was then immersed into 100 ml of 1 mass% H$_2$SO$_4$ (about 0.10 mol/l) or 1 mass% NaOH (0.25 mol/l) and boiled on a hot plate for 48 h. The specimens were dehydrated and acid/alkali durability was estimated by measuring the weight loss of powders.

2.5. Methods of heavy metal leaching tests

Leaching tests of sewage sludge and glass–ceramics were subjected to the toxicity characteristic leaching procedure (TCLP) method according to the US Environmental Protection Agency [19]. The sludge and glass–ceramics samples were manually crushed (<9.00 mm) and placed in a flask. The extraction solution consisted of acetic acid diluted in distilled water with a pH value of 4.93. Extraction fluid was added into the flask to keep a liquid-to-solid ratio of 20. The flask is tightly closed and stored at 25 °C for 18 h. The resultant solutions were filtered through 0.6 μm filters and the concentration of heavy metals in the solution was determined by ICP. A Perkin Elmer A Analyst 200 ICP operated at 13.56 MHz (using Ar and N$_2$ gases) was used for the measurements.

3. Results and discussion

3.1. Thermal analysis of the parent glass

The glass transition temperature (Tg) and crystallization temperature (Tc) of the parent glasses prepared by microwave process

and conventional process were determined from the DSC traces as shown in Fig. 5. The DSC profiles from the different processes showed different individual properties with regard to peak position and intensity. For the glass prepared by microwave process, an intense exothermic peak (Tc) was observed at 969.5 °C which was attributed to crystallization from the parent glass. In the case of conventional heating, Tc peak was clearly evident at about 985.1 °C. Apparently, microwave irradiation gave rise to the lower temperature of Tc. It was also noted that the exothermic peak of microwave prepared glass had higher intensity than that of conventionally prepared glass, demonstrating that microwave irradiation played an important role in enhancing bulk heterogeneous crystallization. The important differences between the DSC curves of the two glass samples may be attributed to the less required energy for crystallizing when microwave was used in the preparation of the glass–ceramics. Crystallization was a process to consolidate partial glass into strong crystal phases by supplying sufficient thermal energy to overcome the energy barrier between the glass and the crystal. The principle of microwave heating was to apply an electromagnetic field to the sludge samples, causing violent agitation in atoms thus raising the product's temperature. The atoms with continual rapid motion decreased strength of the bonds within the glass network or directly precipitated from glass as nuclei, resulting in the reduction of energy barrier for crystallization.

It must be noted that the glass transition temperatures Tg were difficult to determined due to their weak peaks in the DSC curves of both microwave and conventional prepared samples. Weaker intensity of Tg peak for microwave-prepared glass probably associated with its higher crystallization capability. When glassy phases transformed to crystalline phase(s), the molecular rearrangement phenomenon occurred preceding glass crystallization i.e. precrystallization stage [20]. Regarding the kinetics, heating absorption was necessary in this stage, which was called the activation energy of crystallization (E). The heating absorption was recorded in the DSC curve as endothermic peak and the corresponding temperature
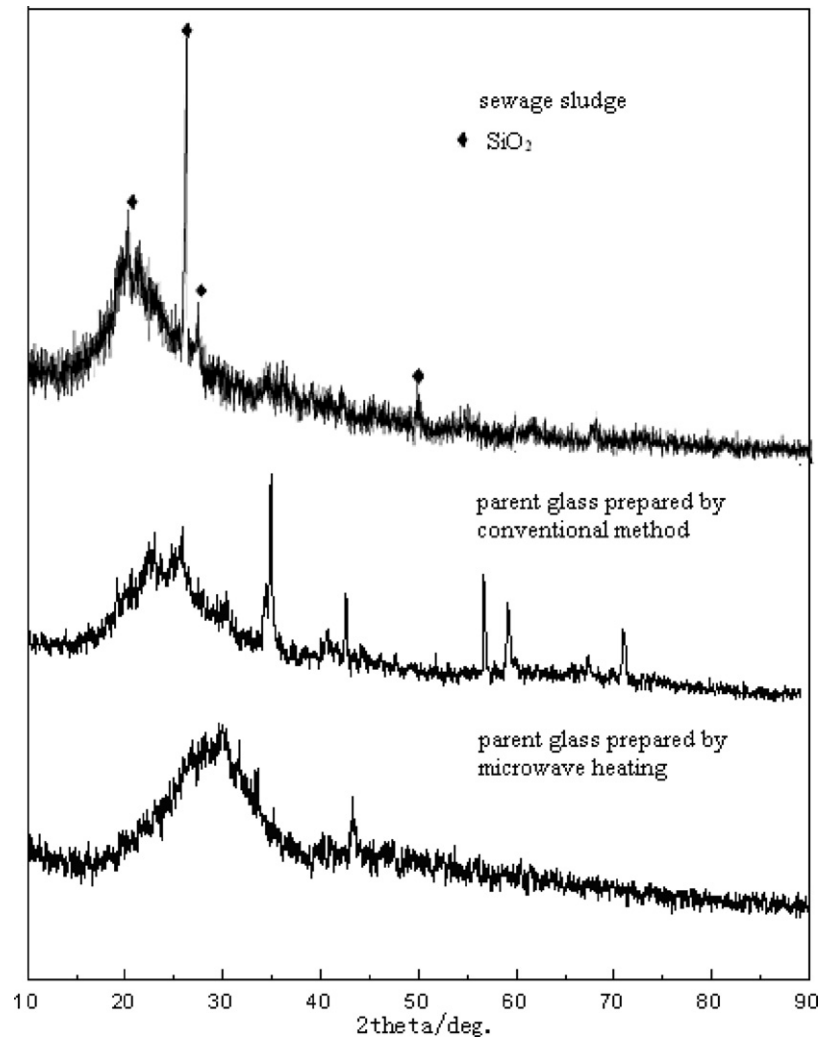
Fig. 3. XRD patterns for sewage sludge, parent glass obtained from conventional and microwave heating.

was Tg [21]. The increased heat absorption during precrystallization stage resulted in the higher intensity of the Tg peak, indicating the lower crystallization capability of the parent glass. On the contrary, decreased heat absorption caused insignificant Tg

Fig. 4. The scheme of glass–ceramics preparation by microwave and conventional heating in the present study.

peak, suggesting the higher crystallization capability of the parent glass.

3.2. XRD analysis of the glass–ceramics

X-ray diffraction analysis (XRD) was carried out to identify the crystalline phases in both the conventional and microwave-processed samples crystallized at 1000 °C. For the conventional samples, there was only one major crystalline phase, anorthite, which had intensive XRD lines at 23.4, 24.3 and 28.6 Å (Fig. 6(a)). For the microwave samples, XRD measurement showed the precipitation of anorthite as a major crystalline phase and the precipitation of a small amount of β-spodumene solid solution in all the glass–ceramics after the heat treatment (Fig. 6(b)–(d)). The disappearance of wollastonite phase in conventional sample might be explained by thermal inertia of the conventional process which prolonged the duration at high temperature for molten glass, leading to early phase separation and crystallization in glass phase. Furthermore, the X-ray diffraction lines for microwave sample were progressively sharper and more distinct. This behavior might be related to the microwave irradiation, which was believed to decrease the viscosity of the glassy matrix phase and enhance crystallization as discussed above.

To design the optimized heat-treatment schedule of microwave process, XRD patterns of microwave glass–ceramics obtained at
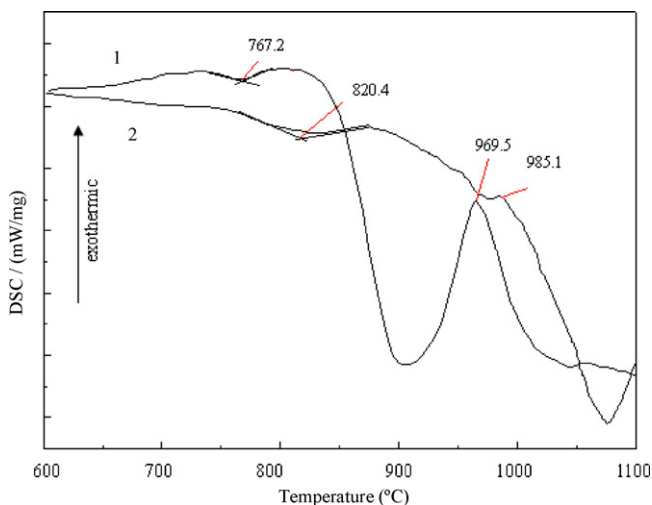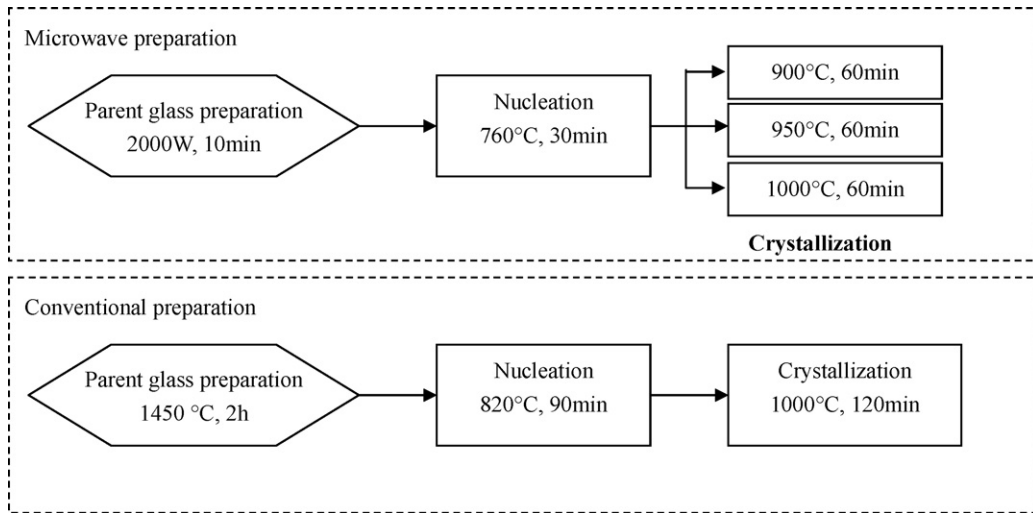
Fig. 5. DSC curves (heating rate 10 °C/min) corresponding: (1) parent glass prepared by microwave heating; (2) parent glass prepared by conventional heating, respectively.
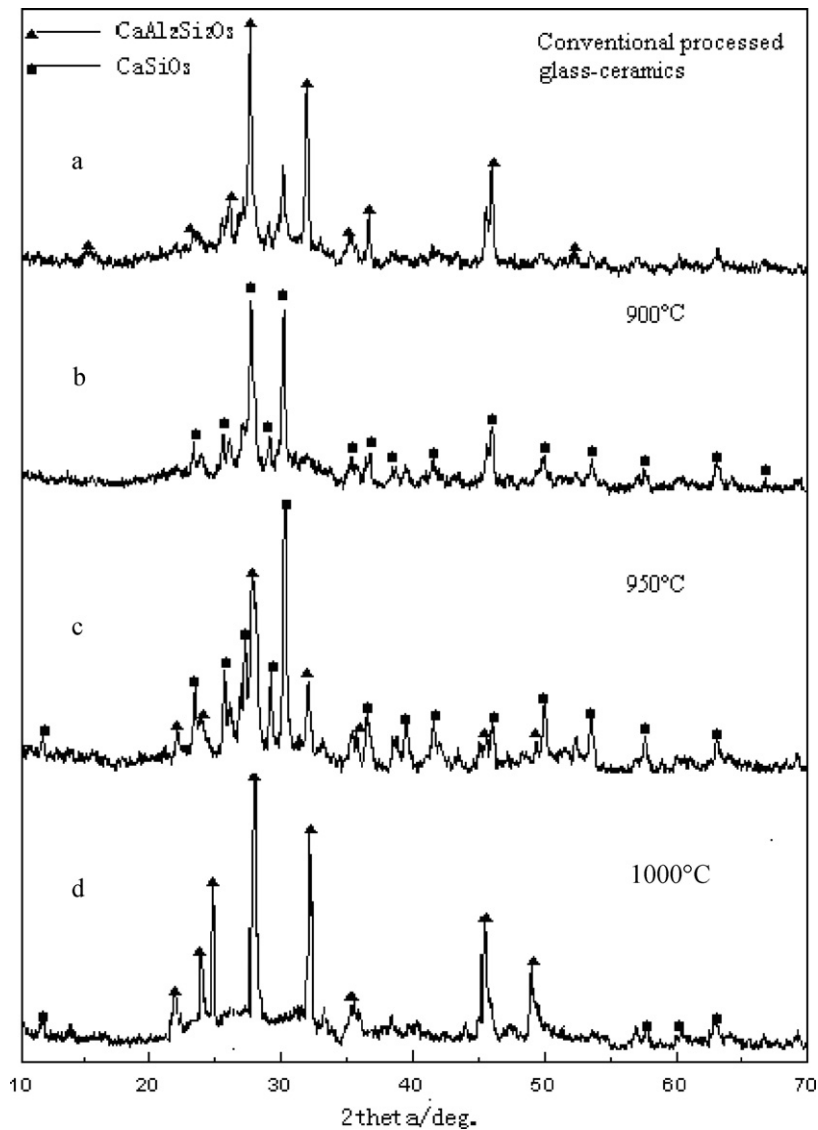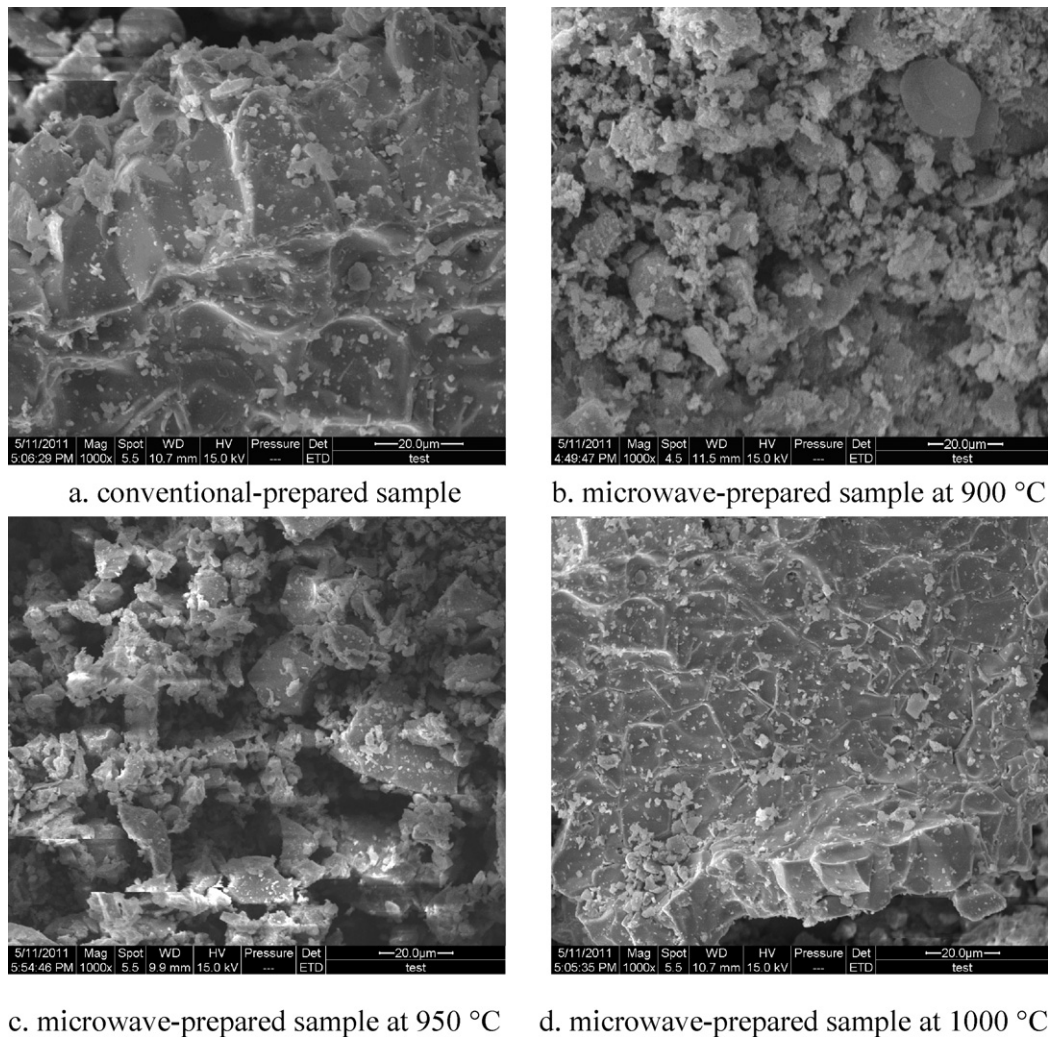

Fig. 6. XRD patterns of the glass–ceramics obtained from (a) conventional process and microwave process at (b) 900 °C, (c) 950 °C and (d) 1000 °C.

a. conventional-prepared sample

b. microwave-prepared sample at 900 °C

c. microwave-prepared sample at 950 °C

d. microwave-prepared sample at 1000 °C

Fig. 7. SEM micrographs of the glass–ceramics obtained from conventional process and microwave process (a: conventional-prepared sample; b: microwave-prepared sample at 900 °C; c: microwave-prepared sample at 950 °C; microwave-prepared sample at 1000 °C).

different crystallization temperature were also studied. The XRD results of microwave-prepared samples at 900, 950 and 1000 °C suggested a consecutive transformation of the parent glass into crystalline phases. The X-ray pattern of the sample obtained at 900 °C is basically composed of low intensity peaks of wollastonite ($CaSiO_3$). A further temperature increase to 950 °C enhanced the intensity of the wollastonite peaks and weakly new phase of anorthite ($CaAl_2Si_2O_8$) was observed. When the glasses were crystallized at 1000 °C, the prepared sample was predominantly composed of anorthite with residual glassy phase, implying that the main crystalline phase had changed from wollastonite to anorthite. From the figure, it was obvious that the anorthite peak intensity was a function of crystallization temperature. The peak intensity increased while crystallization temperature increased, indicating a temperature dependence of anorthite crystallization. According to the theory of stable energy of glass structure unit [22], the crystallization process of CaO–Al_2O_3–SiO_2 system was assumed in this paper. At 900 °C, the free Ca^{2+} was prone to unite [SiO_4] in order that wollastonite was first formed in glass–ceramics [23]. When the temperature reached 1000 °C, the structure unit Ca[SiO_4] was forced to rearrange and unite [AlO_4] to form anorthite as the main crystalline phase in glass–ceramics.

3.3. SEM analysis of the glass–ceramics

The microstructural features of both conventionally and microwave processed glass–ceramics crystallized at 1000 °C were analyzed by SEM as shown in Fig. 7. To determine the influence of crystallization temperature on microwave-processed glass–ceramics, the SEM micrographs of microwave processed samples crystallized at 900 °C and 950 °C are also exhibited in Fig. 7. It appeared that microwave process produced finer sized crystallites in the glass–ceramics than that evolved by the conventional heat treatment process. The results revealed that rapidity of microwave method avoided undesirable grain growth and provided a finer and uniform microstructure, which was an attractive feature for the processing of glass–ceramics. The similar results might be found in other literatures [12,14]. Mahajan et al. [24] reported that high-density ceramic materials were obtained in 4 h of cycle time for microwave sintered sample whereas it took 22 h for conventional method.

It should also be noticed that the heat-treatment schedules had significant effect on the microstructure of glass–ceramics obtained from microwave process. For sample crystallized at 900 °C, needle-like wollastonite-2 M crystal grains were observed. When the crystallization temperature increased to 950 °C, not only

Table 2
Mineral chemical composition of sewage sludge, waste glass and resulting glass–ceramics (wt.%).

Sample	SiO_2	Al_2O_3	MgO	CaO	K_2O	Na_2O	TiO_2	Fe_2O_3	P_2O_5	Others
Sewage sludge	47.62	18.34	2.50	7.91	2.74	1.33	0.81	8.29	7.16	3.29
Waste glass	70.63	3.25	–	10.66	–	15.44	–	0.02	–	–
Glass–ceramics	39.62	10.21	1.30	27.34	1.42	3.92	6.42	4.31	3.72	1.74

the amount of crystal grains increased but also the length of the grain became short, suggesting that wollastonite-TC appeared. The conversion process of the wollastonite phase was also described by Toya et al. [25]. They considered that the crystalline phase formed at 900 °C was wollastonite-2 M (the low temperature phase of $CaSiO_3$), gradually transforming to wollastonite-TC (the high temperature phase of $CaSiO_3$) at $\geq$950 °C, the vicinity of the phase transition temperature. When the crystallization temperature increased to 1000 °C, the glass–ceramics reached an almost stationary microstructure consisting of flake-like crystals. According to the results of XRD, these crystals should attribute to anorthite.

Based on the SEM results, a particular process model of glass–ceramics preparation from sewage sludge by microwave heating was developed. During the fabrication of parent glass, the interaction between air and hot glass might induce the occurrence of active radicals (for example Si–OH) and hetero-matters (for example silica gels) on the surface of glass [12]. It has been reported that the active radicals and hetero-matters could act as the nuclei and bring the nucleation energy lower [26–28]. Accordingly, under the synergetic actions of the above factors, the surface of glass would be homogeneously nucleated and then preferentially deposited wollastonite-2 M as initial crystals. During microwave process, the microwave power was absorbed by parent glass itself and hence, the rise of heat content in the bulk of glass took place at a faster rate compared to that of the near surface region. Thus, the temperature of the bulk was much higher than that of the surface, leading to a latent heat release from bulk to the surface. Under the effect of latent heat release during crystal growth, the initial crystals did not grow evenly in all directions. Instead, the growth would be orientated along directions with lower latent heat release impact. When primary dendrite crystals grew along the surface orientation, the impact of latent heat release was so weak that crystallization grew faster and the crystallite size became larger. Larger crystallite size led to decrease in their bonding area and thereby, the extent of reinforcement to the glass matrix decreased, causing the decrease of the measured hardness. Therefore, the glass–ceramics obtained at 900 °C had slight poor mechanical property.

In fact, the wollastonite-2 M phase was thermodynamically unstable but kinetically favorable and as a result, this phase appeared first. When the crystallization temperature reached 950 °C, wollastonite-2 M was replaced by the slower growing, but thermodynamically favored wollastonite-TC phase. Since the wollastonite-TC crystals grew perpendicularly to interface between the surface and bulk, the effect of latent heat release became stronger, and then, the crystallization proceeded slower and the crystalline size became finer. The area fraction enhancement of fine crystallites provided more rigidity and localized strong bonding which could cause an apparent increase in the hardness value of the glass–ceramics. When the crystallization temperature increased to 1000 °C, hydrostatic compressive microstresses developed in crystal phase owing to the much higher latent heat release from the bulk to the surface. The tetragonal wollastonite grains were subjected to tensile microstresses, causing the cracking of the Si–O bond. Al ions substituted partially Si ions in the structure of wollastonite and occupied sites, giving rise to the formation of tetrahedral anorthite.

3.4. Physical and chemical properties

The various properties of the resultant glass–ceramics obtained from conventional process and microwave process with different crystallization temperatures are listed in Table 3. The bending strengths of the microwave processed glass–ceramics ranged from 86.5 to 93.3 MPa, showing no apparent relationship with the crystallization temperature. These bending strengths were relatively higher compared with those prepared using conventional method (70.2 MPa), which might be attribute to the differences in the microstructures among the specimens. Undesirable grain growth was avoided in microwave process for its high heating rate and negligible thermal inertia which provided a finer and uniform microstructure [29]. Therefore, crystalline distribution in a microwave-processed sample was roughly uniform, and the impressed pressure value on every microscopic part was almost the same.

In addition, the fine, compact and homogeneous distribution of crystals in microwave samples also led to remarkably higher values of Vickers' microhardness than that of conventional ones. The highest one, which was generated at 950 °C and did not increase in number at higher temperature, was close to 6.54 GPa, thus being comparable to that of commercial glass–ceramics for applications in the building industry [30].

The chemical durability of glass–ceramics was important if the materials were to be considered as a potential building material. The weight losses of the microwave processed glass–ceramics after leaching in acid and alkali solutions were in the range of 1.32–1.61 and 0.41–0.58 mg/cm^2, respectively. The weight losses in acid were higher than those in alkali, indicating higher chemical durability of the microwave processed glass–ceramics to alkali than to acid. The weight losses of the conventionally processed glass–ceramics after leaching in acid and alkali solutions were 1.20 and 0.91 mg/cm^2 for acid and alkali, respectively. The glass–ceramics obtained from microwave process thus had slightly lower chemical durability to acid but significantly higher durability to alkali than the conventional ones. This difference might be due to the differences in crystalline amount of the glass–ceramics samples from different processes. The weight loss in acid solution was well known to be generated by selective leaching of the crystalline $CaSiO_3$ phases which were more soluble in acid than the glassy matrix [22]. Since the crystalline phase in microwave samples consisted of wollastonite (α-$CaSiO_3$ and β-$CaSiO_3$) with lower durability in acid, the degree of leaching increased and resulted in a slight lower chemical durability to acid [25]. By contrast to the slightly lower chemical durability to acid, microwave processed glass–ceramics exhibited excellent durability to alkali leaching. This might be due to the low glass content in the microwave sample, which was more soluble in alkali than in acid.

The thermal expansion coefficients of the microwave glass–ceramics ranged from 5.29×10^{-6}/°C to 5.75×10^{-6}/°C, a little lower than that of the sample obtained from conventional process (6.21×10^{-6}/°C). The present thermal expansion was also lower compared to the values reported for various glass–ceramics, giving the present materials an enhanced ability to suppress thermal stress in applications involving building materials.

Table 3
Physical and chemical properties of the glass–ceramics obtained from conventional process and microwave process at different crystallization temperatures.

Property	Microwave-prepared glass–ceramics[a]			Conventional glass–ceramics[a]	Commercial glass–ceramics[b]
	900 °C	950 °C	1000 °C		
Bending strengths (MPa)	86.5 ± 0.2	93.4 ± 0.2	91.6 ± 0.4	70.2 ± 0.2	82.0
Vickers' hardness (GPa)	6.12 ± 0.05	6.54 ± 0.03	6.41 ± 0.02	6.28 ± 0.03	5.80
Acid weight loss (mg/cm^2)	1.61 ± 0.02	1.53 ± 0.03	1.32 ± 0.02	1.20 ± 0.01	1.32
Alkali weight loss (mg/cm^2)	0.41 ± 0.01	0.53 ± 0.01	0.58 ± 0.01	0.91 ± 0.02	1.00
Thermal coefficient ($\times 10^{-6}$/°C)	5.75 ± 0.03	5.31 ± 0.01	5.29 ± 0.04	6.21 ± 0.03	6.70

[a] The presented value (mean value ± standard deviation) is average of five results.
[b] Data from Ref. [30].

Table 4
TCLP results of the glass–ceramics samples.

TCLP results (mg/l)	Cu	Pb	Zn	Cd	Cr	As
Sewage sludge	8.21	2.11	22.21	0.451	1.54	–
Glass–ceramics (900 °C)	–	0.00537	1.21	0.00213	–	–
Glass–ceramics (950 °C)	–	–	–	–	–	–
Glass–ceramics (1000 °C)	–	–	–	–	–	–
Regulatory standard of EPA	50.0	3.00	50.0	0.300	1.50	1.50

3.5. Leaching characteristics of heavy metals

TCLP results of the developed glass–ceramics are given in Table 4. Any heavy metal concentration could not be detected in the extraction solutions of the samples prepared at 950 and 1000 °C, while small concentrations of Pb, Zn and Cd ions which were lower than the limits suggested by EPA [19] were detected in the extraction solutions of samples prepared at 900 °C. Consequently, heavy metals were sufficiently stabilized by preparing glass–ceramics, according to the US EPA standards. It seemed that high bonding strength of anorthite was responsible for this behavior. During the crystallizing process, the nuclei formed at the preferred sites and absorbed ions from the silicate matrix. Heavy metal ions, such as Zn^{2+} and Pb^{4+}, replaced Si^{4+} or Al^{3+} ions and held in the crystalline phase through the bonding strength of crystal systems. Correspondingly, the stabilities of heavy metals strongly depended on the type of the crystal which had different bonding strength. The bonding strength of anorthite systems could reach $189.45–208.62 \times 10^4$ kJ/mol [31], while the value of wollastonite was only $2.75–5.75 \times 10^4$ kJ/mol [32]. Anorthite which consisted in the 950 and 1000 °C samples was an ideal crystalline matrix for the immobilization of heavy metals in the production of glass–ceramics materials.

4. Conclusion

The presented MMR with double-layer structure was used for preparing glass–ceramics from sewage sludge. Glass–ceramics based on $CaO–Al_2O_3–SiO_2$ system was developed successfully. Attractive physical and chemical properties of the microwave-processed glass–ceramics were observed, such as higher bending strengths (86.5–93.4 MPa) and lower thermal expansion coefficient (5.29×10^{-6}/°C). The leaching tests of heavy metals in the glass–ceramics showed that 950 and 1000 °C samples which contained anorthite as main crystal immobilized the heavy metal ions effectively. A model of crystal growth in the microwave field was developed in this study and the results indicated that microwave heating generated a latent heat release, which suppressed the crystals growth, causing an improvement in the glass–ceramics properties.

References

[1] H.C. Xu, P.j. He, G.Z. Wang, L.M. Shao, D.j. Lee, Anaerobic storage as a pretreatment for enhanced biodegradability of dewatered sewage sludge, Bioresour. Technol. 102 (2011) 667–671.
[2] J.A. Roethera, D.J. Daniela, D.R. Amutha, D.E. Deeganc, C.R. Cheesemanb, A.R. Boccaccinia, Properties of sintered glass–ceramics prepared from plasma vitrified air pollution control residues, J. Hazard. Mater. 173 (2010) 563–569.
[3] J.A. Perez, R. Terradas, M.M. Seijas, R. Martinez, Inertization of industrial wastes in ceramics materials, Ind. Ceram. 16 (1996) 17–21.
[4] P.A. Bingham, R.J. Hand, G. Forder, Vitrified metals finishing wastes. I. Composition, density and chemical durability, J. Hazard. Mater. 119 (2005) 125–133.
[5] P.A. Bingham, R.J. Hand, Vitrification of toxic wastes: a brief review, Adv. Appl. Ceram. 105 (2006) 21–31.
[6] P.A. Bingham, R.J. Hand, S.D. Forder, A. Lavaysierre, Vitrified metal finishing wastes. II. Thermal and structural characterization, J. Hazard. Mater. 122 (2005) 129–138.
[7] T.W. Cheng, Effect of additional materials on the properties of glass–ceramics produced from incinerator fly ashes, Chemosphere 56 (2004) 127–131.
[8] E.G. Pan, A.A. Ravaev, Microwave synthesis of advanced dental ceramic–alloy materials, Mater. Lett. 58 (2004) 2679–2683.
[9] A. Domínguez, J.A. Menéndez, M. Inguanzo, J.J. Pís, Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating, Bioresour. Technol. 97 (2006) 1185–1193.
[10] T. Garcia, J. Valles, Heavy metal-rich wastes sequester in mineral phases through a glass–ceramic process, Chemosphere 68 (2007) 1946–1953.
[11] A. Karamanov, M. Pelino, Induced crystallization porosity and properties of sintereds diopside and wollastonite glass–ceramics, J. Eur. Ceram. Soc. 28 (2008) 555–562.
[12] S. Das, A.K. Mukhopadhyay, S. Datta, G.C. Das, D. Basu, Hard glass–ceramic coating by microwave processing, J. Eur. Ceram. Soc. 28 (2008) 729–738.
[13] S. Das, A.K. Mukhopadhyay, S. Datta, D. Basu, Evaluation of microwave processed glass–ceramic coating on nimonic superalloy substrate, Ceram. Int. 36 (2010) 1125–1130.
[14] Z.J. Huang, M. Gotoh, Y. Hirose, Improving sinterability of ceramics using hybrid microwave heating, J. Mater. Process. Technol. 209 (2010) 2446–2452.
[15] Z. Zhang, Z. Wang, L. Wang, Design principle of single- or double-layer wave-absorbers containing left-handed materials, Mater. Des. 30 (2009) 3908–3912.
[16] T. Toya, A. Nakamura, Y. Kameshima, A. Nakajima, K. Okada, Glass–ceramics prepared from sludge generated by a water purification plant, Ceram. Int. 33 (2007) 573–577.

[17] ASTM Designation, Standard test methods for bend testing of metallic flat materials for spring applications involving static loading, E 855-90, 1979, pp. 734–741.

[18] ASTM Designation, Standard specification for chemical-resistant masonry units, C279-88, 1979, pp. 137–138.

[19] USEPA, Method 1311: Toxicity Characteristic Leaching Procedure. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, third ed., US Environmental Rotection Agency, Office of Solid Waste, US Government Printing Office, Washington, DC, 1992.

[20] G.A. Khater, The use of Saudi slag for the production of glassceramic materials, Ceram. Int. 28 (1) (2002) 59–67.

[21] P. Goharian, A. Nemati, M. Shabanian, A. Afshar, Properties, crystallization mechanism and microstructure of lithium disilicate glass–ceramic, J. Non-Cryst. Solids 356 (2010) 208–214.

[22] J.D. Luan, A.M. Li, T. Su, X.B. Cui, Synthesis of nucleated glass–ceramics using oil shale fly ash, J. Hazard. Mater. 173 (2010) 427–432.

[23] F. Peng, K. Liang, A. Hu, Nano-crystal glass–ceramics obtained from high alumina coal fly ash, Fuel 84 (2005) 341–346.

[24] S. Mahajana, O.P. Thakura, D.K. Bhattacharyaa, K. Sreenivas, A comparative study of $Ba_{0.95}Ca_{0.05}Zr_{0.25}Ti_{0.75}O_3$ relaxor ceramics prepared by conventional and microwave sintering techniques, Mater. Chem. Phys. 112 (2008) 858–862.

[25] T. Toya, Y. Kameshima, A. Yasumori, K. Okada, Preparation and properties of glass–ceramics from wastes (Kira) of silica sand and kaolin clay refining, J. Eur. Ceram. Soc. 24 (2004) 2367–2372.

[26] J. Zhou, Y. Wang, A novel process of preparing glass–ceramics with pseudo-bioclastic texture, Ceram. Int. 34 (2008) 113–118.

[27] I. Gutzow, R. Pascova, A. Karamanov, J. Schmelzer, The kinetics of surface induced sinter crystallization and the formation of glass–ceramics materials, J. Mater. Sci. 33 (1998) 5265–5273.

[28] P.W. McMillan, Glass–Ceramics, second ed., Academic Press, London, UK, 1979.

[29] L. Barbieri, A. Karamanov, A. Corradi, I. Lancellotti, M. Pelino, J. Ma Rincon, Structure, chemical durability and crystallization behavior of incinerator-based glassy systems, J. Non-Cryst. Solids 354 (2–9) (2008) 521–528.

[30] W. Holand, G. Beall, Glass–Ceramic Technology, The American Ceramic Society, Westerville, OH, 2002.

[31] F.H. ElBatal, M.A. Azooz, Y.M. Hamdy, Preparation and characterization of some multicomponent silicate glasses and their glass–ceramics derivatives for dental applications, Ceram. Int. 35 (2009) 1211–1218.

[32] M. Montazerian, P. Alizadeh, B.E. Yekta, Processing and properties of a mica–apatite glass–ceramic reinforced with Y-PSZ particles, J. Eur. Ceram. Soc. 28 (2008) 2693–2699.