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Preparation and properties of glass-ceramics from kaolin clay refining waste (Kira) and paper sludge ash

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Abstract

Glass-ceramics were prepared from mixtures of wastes generated from refining of silica sand and kaolin clay (Kira) and paper sludge ash. Kira and paper sludge ash were mixed in mass ratios of 55/45. The mixtures were melted at 1400 °C and quenched in water to obtain glasses. The quenched glasses were ground to <48 mesh and used to prepare glass-ceramics. Crystallization of the parent glass occurred above 950 °C, producing quartz solid solution at 1000 °C and cristobalite at 1100 °C as the major crystalline phases. The color of the glass-ceramics is white or slightly pale yellow. The four-point bending strengths of the as-fired glass-ceramics range from 63 to 66 MPa and the Vickers microhardness values from 6.0 to 6.4 GPa. The average linear thermal expansion coefficients of the glass-ceramics range from 6.3×10^{-6} /°C to 8.1×10^{-6} /°C (30–380 °C) and show non-linearity around the phase transition temperatures of quartz and cristobalite. The chemical durability of the resulting glass-ceramics is excellent in alkali but poor in acid solution. The glass-ceramics show rather better performance than commercial glass-ceramics even when prepared solely from wastes starting materials.

Keywords: C. Mechanical properties; D. Glass-ceramics; Kaolin clay waste; Paper sludge ash; Chemical durability

1. Introduction

As reported elsewhere [1,2], we have succeeded in preparing glass-ceramics using waste generated from refining kaolin clay and silica sand (called Kira) mixed with $CaCO_3$ [1] and dolomite ($CaMg(CO_3)_2$) [2]. The resulting glass-ceramics were shiny white with smooth surfaces. The major crystalline phases were wollastonite ($CaSiO_3$) in the Kira–$CaCO_3$ system, diopside ($CaMgSi_2O_6$) in the dolomite rich-sample and anorthite ($CaAl_2Si_2O_8$) in the dolomite-poor compositions within the Kira–dolomite system. The four-point bending strengths ranged from 73 to 130 MPa, being highest in the dolomite-rich sample. The Vickers microhardness values ranged from 6.6 to 7.6 GPa and were highest in the dolomite-poor sample.

The glass-ceramics prepared from Kira were found to show excellent mechanical and chemical durability properties with shiny white appearance and smooth surfaces. Thus, Kira is a suitable starting material for glass-ceramics. However, since the chemical constituents of Kira consist of SiO_2 and Al_2O_3, it is necessary to add components with glass modifier functions (limestone, dolomite, etc.) to obtain glass cullet. In order to develop glass-ceramics using various wastes as starting materials, it is preferable to prepare them using only wastes without the need to use virgin starting materials. We therefore have addressed the possibility of preparing glass-ceramics solely from waste materials. The additives to be mixed with Kira must contain alkali and/or alkaline earth elements; the candidate wastes are therefore steel making slag [3], incinerator ash [4], shell [5], paper sludge ash [6], etc. Some of these have been reported as forming glass-ceramics without further additives. One of the advantages of Kira glass-ceramics is their shiny white appearance due to the relatively low content of coloring components such as Fe_2O_3 and TiO_2. It is therefore preferable to select additives which themselves

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contain low contents of coloring components. On this basis, paper sludge ash was selected as the additive, since it consists of mainly SiO_2, Al_2O_3 and CaO, with only small amounts of Fe_2O_3 and TiO_2.

In this work, glass-ceramics were prepared using Kira and paper sludge ash as the starting materials and their mechanical properties, thermal behavior, chemical durability, etc. were determined and compared with materials prepared from Kira–$CaCO_3$ [1] and Kira–dolomite [2] systems.

2. Experimental

2.1. Preparation of glass-ceramics

The starting materials were Kira, which is generated as a coarse-grained residue of kaolin clay (refining corresponding to sample no. 1 in ref. [1]) and paper sludge (PS) ash, which is generated as incinerator ash by the Fuji Paper Making Union, Fuji, Shizuoka, Japan.

The batch composition was prepared by mixing 55 mass% of Kira with 45 mass% of PS ash, and was based on the eutectic composition in the $CaO–Al_2O_3–SiO_2$ system [7]. The components were mixed by wet ball milling for 24 h and dried at 110 °C overnight. The dried powder mixtures were melted at 1400 °C for 2 h in a Pt crucible and water-quenched to obtain granular glass. Glass powder samples were ground in an alumina ball mill and sieved to <48 mesh (310 μm). Pellets (10 mm in diameter) used in the crystallization experiments and testpieces (5 mm × 4 mm × 40 mm) used for property measurements were formed by uniaxial pressing at 98 MPa. The pellet samples were fired at 900–1250 °C for 10–480 min by inserting in a pre-heated furnace whereas the testpiece samples were fired at 1000, 1050 and 1100 °C for 4 h at heating and cooling rates of 5 °C/min.

2.2. Characterization

The chemical compositions of the samples were determined by X-ray fluorescence (RIX2000, Rigaku). X-ray measurements were performed using monochromated Cu Kα radiation (LaX XRD-6100, Shimadzu) to identify the crystalline phases. The glass transition and crystallization temperatures were determined from DTA analysis (Thermoplus, Rigaku) at a heating rate of 10 °C/min. The linear thermal expansion coefficients of the glass-ceramics were measured using a dilatometer (TMA8310, Rigaku). The sample sizes were 5 mm × 4 mm × 12 mm and the measurements were performed at 25–600 °C. The bulk densities of the glass-ceramics were measured by the Archimedes method using water.

The four-point bending strengths of the as-prepared glass-ceramics were measured on unpolished testpieces using a universal testing machine (AUTOGRAPH DCS-R-10TS, Shimadzu) at a crosshead speed of 0.5 mm/min. The reasons for using unpolished testpieces was to avoid chipping during polishing because of high content of glassy phase and also to obtain mechanical data for as-produced samples which are appropriate for their application as building materials. The average bending strength was obtained from measurements of 10 samples. The microhardness of the glass-ceramics was measured using a Vickers tester (MHT2, Matsuzawa Precision Machine) on samples polished using SiC powder (8000 mesh) with an indentation of 9.8 N for 15 s. The average value was obtained from 14 indentations.

The chemical resistance of the glass-ceramics was examined in acid and alkali solutions. The size of the samples was about 4.5 mm × 3.5 mm × 14 mm and the surfaces were polished using SiC powder (8000 mesh). Five pieces of sample were immersed in 100 ml of 1 mass% H_2SO_4 (about 0.1 mol/l) or 1 mass% NaOH (0.25 mol/l) at 90 °C for 24 h [8]. The samples were washed with deionized water, dried at 110 °C overnight and weighed. The chemical durability of the glass-ceramics was determined as the weight difference before and after the chemical leaching.

The microstructures of the glass-ceramics were observed using a SEM (JSM-5310, JEOL) at an accelerating voltage of 15 kV. The samples were polished using SiC powder (8000 mesh) and chemically etched for 1 min in 1 mass% HF (0.5 mol/l). The microstructures of the glass-ceramics after the chemical tests were also observed by SEM.

3. Results and discussion

3.1. Glass-ceramics

The chemical compositions of the Kira and PS ash samples are listed in Table 1. The major chemical component of the Kira is SiO_2 and the remaining components are Al_2O_3 (7.4 mass%), K_2O (3.2 mass%) and <1 mass% Fe_2O_3, TiO_2, MgO and Na_2O. Since the Kira is the coarse-grained residue of kaolin clay refining, it is higher in SiO_2 than other Kira wastes [1] and does not melt even at 1550 °C when mixed with $CaCO_3$. The major mineralogical constituents of the Kira are quartz (SiO_2) and microcline ($KAlSi_3O_8$) with a minor amount of kaolinite

Table 1
Chemical compositions of the starting materials

	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	TiO_2	P_2O_5	Others	Ig. loss
Kira	88.2	7.4	tr	0.1	3.2	0.1	0.2	0.1	tr	0.1	0.6
PS ash	32.6	27.3	27.1	7.1	0.2	0.1	0.7	1.4	0.9	0.8	1.8

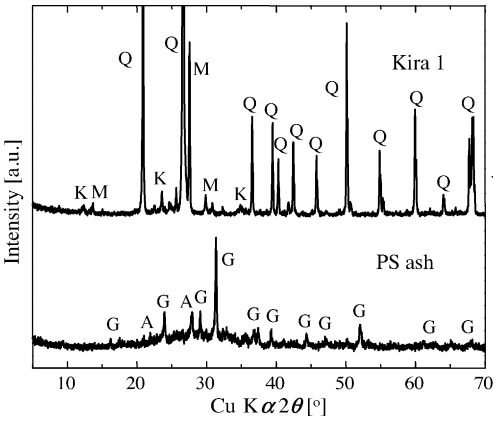

Fig. 1. XRD patterns of the starting materials, Kira and PS ash.

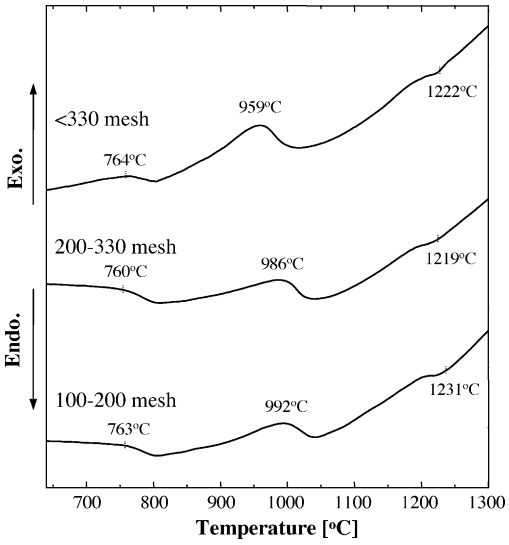

Fig. 2. DTA curves of PS glass samples with different particle size.

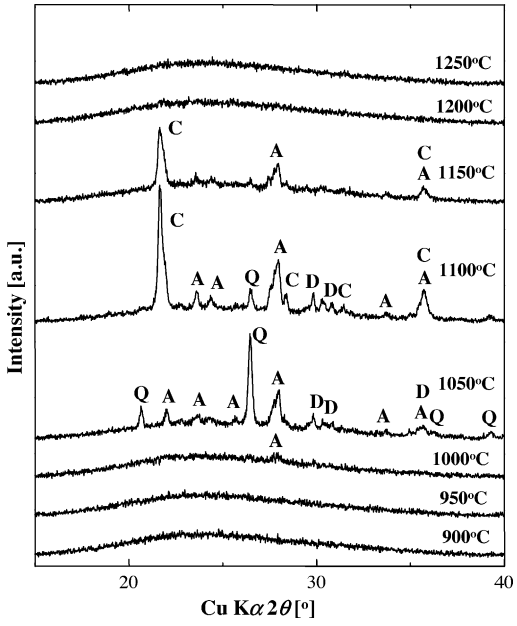

Fig. 3. XRD patterns of PS glass samples fired at various temperatures for 1 h.

$(Al_2Si_2O_5(OH)_4)$ as shown in Fig. 1. The major components of the PS ash are SiO_2 (32.6 mass%), Al_2O_3 (27.3 mass%) and CaO (27.1 mass%), totaling ≈90 mass%. The remaining components are MgO (7.1 mass%), TiO_2 (1.4 mass%), and <1 mass% P_2O_5, Fe_2O_3, K_2O and Na_2O. Since PS ash has been heated at about 900 °C, it contains the crystalline phases gehlenite ($Ca_2Al_2SiO_7$) and anorthite ($CaAl_2Si_2O_8$) as well as a considerable amount of amorphous material.

The granular glasses (PS glass) were transparent and pale yellow-green due to the small amount of Fe_2O_3 present in the sample. The chemical composition of glass sample is listed in Table 2 together with the data for CaO–Al_2O_3–SiO_2 glass (CC glass) produced from mixtures of Kira and $CaCO_3$ [1] and CaO–MgO–Al_2O_3–SiO_2 glass (CM glass) prepared from mixtures of Kira and dolomite [2]. Compared with the CC and CM glasses, the total of glass modifier components (CaO, MgO, Na_2O and K_2O) of the PS glass is lower.

The DTA curves of the PS glass powder samples of different grain sizes are shown in Fig. 2. The glass transition temperature (T_g) of the sample was observed at about 760 °C and was slightly higher than the CC glass sample (739 °C) and the CM glass sample (693 and 720 °C). This may be related to the higher SiO_2 content compared with the other glasses. Broad exothermic peaks due to crystallization are observed in the DTA curves at about 960–1000 °C. Weak endothermic peaks observed at about 1220–1230 °C are thought to correspond to the partial formation of a liquid phase.

The XRD patterns of the samples fired at various temperatures are shown in Fig. 3. Crystallization is observed in samples fired at ≥1000 °C. The major crystalline phases are quartz (SiO_2) and/or cristobalite (SiO_2) with smaller amounts of anorthite ($CaAl_2Si_2O_8$) and diopside ($CaMgSi_2O_6$). The quartz is observed below 1050 °C and the cristobalite above 1050 °C. Formation of quartz by firing at high temperatures (∼1000 °C) under an ambient atmosphere is rather unusual. Judging from the XRD peak positions of the quartz ($2\theta = 26.40$–$26.46°$), this is thought to be not pure SiO_2 ($2\theta = 26.67°$) but a quartz solid solution (quartz (SS))

Table 2
Chemical compositions of the present glass and comparison with ref. [2]

Glass	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	TiO_2	P_2O_5	Others	Ig. loss
PS	64.3	16.2	12.8	3.3	1.6	0.1	0.4	0.8	0.4	0.1	0.6
CC	57.9	12.3	26.8	0.1	2.4	tr	0.4	tr	tr	tr	tr
CM1	52.9	16.2	17.7	9.5	3.1	0.2	0.4	tr	tr	tr	tr
CM2	60.4	17.9	11.6	5.3	4.1	0.2	0.5	tr	tr	tr	tr

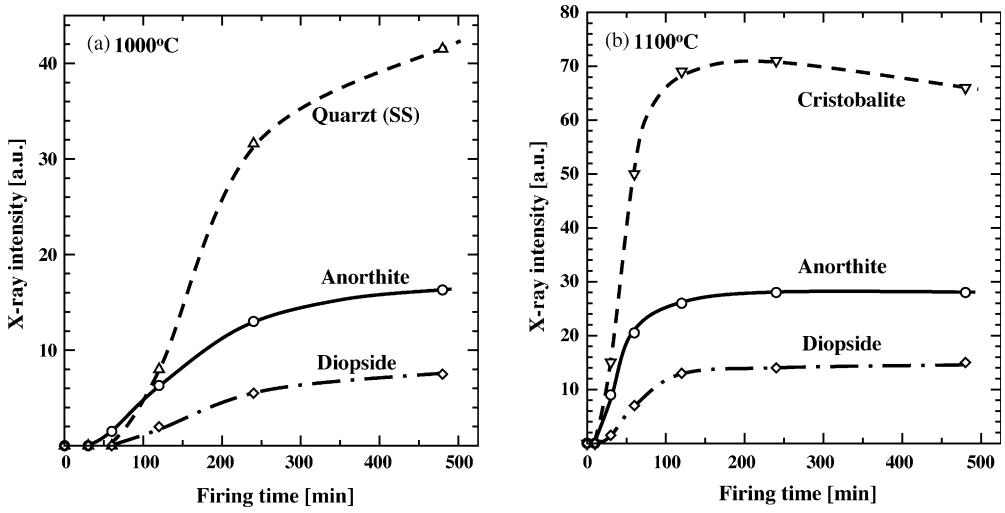

Fig. 4. Changes of the XRD peak intensities of crystalline phases in the samples fired at 1000 °C (a) and 1100 °C (b) as a function of firing time. The peaks used for the calculations are $2\theta = 21.7$, 26.5, 27.9 and 29.8° for cristobalite, quartz (SS), anorthite and diopside, respectively.

phase incorporating Mg and Al which can be represented by the chemical formula $Mg_{x/2}Al_xSi_{1-x}O_2$ [9]. At higher firing temperatures, it transforms about 1100 °C to cristobalite, a high-temperature phase of SiO_2 commonly formed by firing various silicas at high temperatures. The crystalline phases disappear on firing at 1200 °C, being re-converted to glassy phase. Fig. 4 shows the changes in the crystalline phase contents in samples fired at 1000 and 1100 °C as a function of firing time. Firing at 1000 °C causes the XRD peak intensities of quartz (SS), anorthite and diopside to increase gradually with longer firing times. By contrast, the XRD peak intensities increase steeply within 1–2 h and become almost constant after 2 h upon firing at 1100 °C. Thus, the firing temperature exerts a significant influence on the crystallization rates and amounts of the crystalline phases. These results are considerably different from those of the CC and CM glass-ceramics [1,2], which show a very steep increase in the XRD peak intensities within short times, i.e. 10 min in the CC and CM1 samples and 60 min in the CM2 sample. The time–temperature–transformation (*T*–*T*–*T*) curve of the PS glass sample is shown in Fig. 5, together with that of the CC glass sample. The crystallizing region of PS glass appears to be narrower than that of CC glass [1]. These differences are thought to be related to the SiO_2 content of the glass samples, suggesting a more stable glassy state results from a higher SiO_2 content.

The photographs of as-pressed samples and these fired at various temperatures are shown in Fig. 6. The sample fired at 950 °C shows sintering due to viscous flow of the compacted glass powder, giving it a glassy appearance with a pale yellow-green color. As is evident from Fig. 3, no crystalline phases are observed by XRD in this sample. Upon firing at

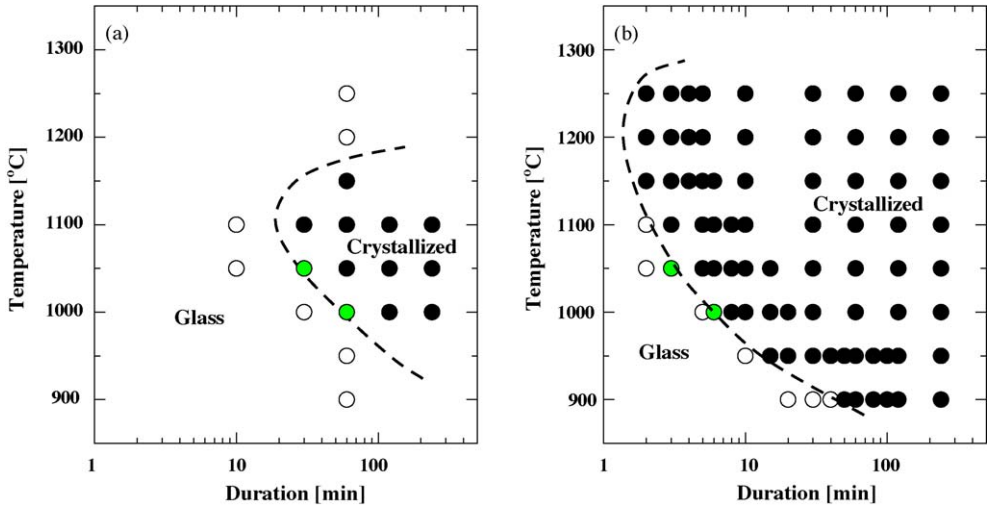

Fig. 5. Temperature–time–transformation (*T*–*T*–*T*) curves of the present PS glass (a) and CC glass (b) [1]. Open, hatched and solid circles represent glassy state, very small amount of crystallization and crystallized samples, respectively.

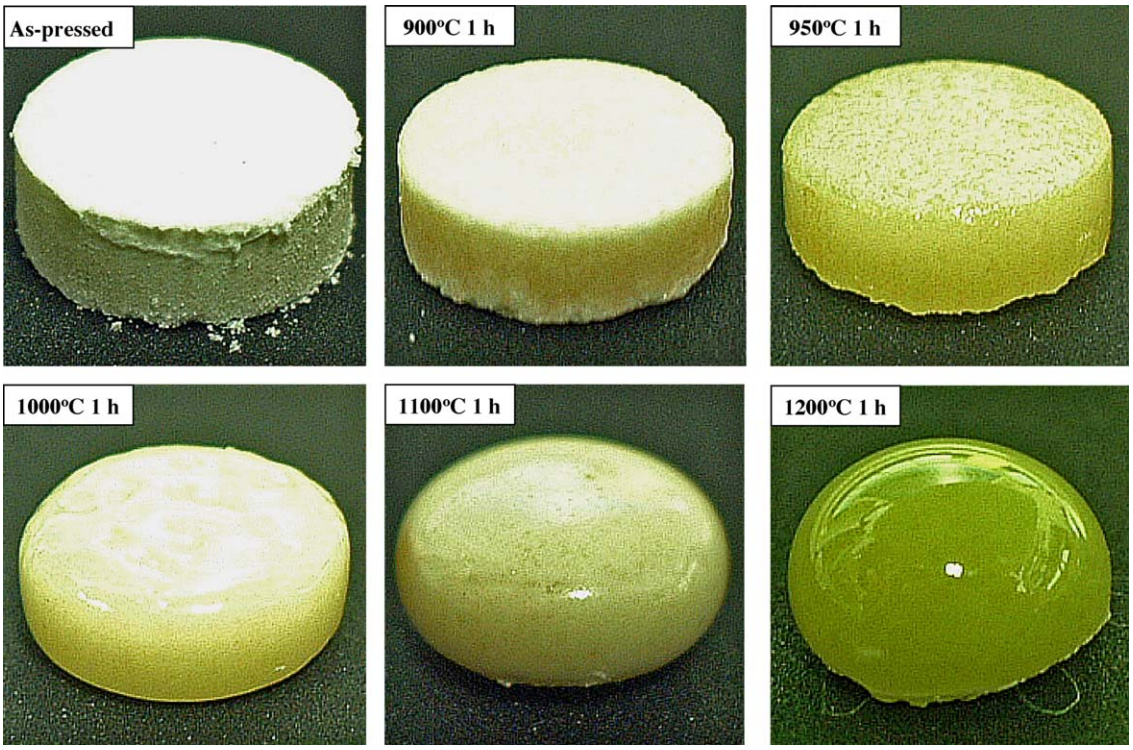

Fig. 6. Appearance of samples as-pressed and fired at various temperatures for 1 h.

1000 °C, the appearance of the sample becomes white due to crystallization. The present PS samples are seen to have rather rough surfaces at this temperature, but the surfaces become smooth upon firing at 1100 °C, thought to be due to the higher viscosity of the glassy phase in the matrix with a higher SiO_2 content. The shape of these glass-ceramic samples becomes rounded at higher firing temperatures due to the lowering of the viscosity of the glassy matrix phases. The deformation is similarly large in CC glass-ceramics [1] and CM glass-ceramics [2] although the higher viscosity at $\leq$1100 °C and large deformation at higher temperature is attributed to the lower melting point of the present glassy matrix compared with the CC and the CM glass-ceramics. On firing at 1200 °C, the sample become shiny and smooth with a yellow-green color and hemispherical shape, indicating a glassy state (Fig. 3).

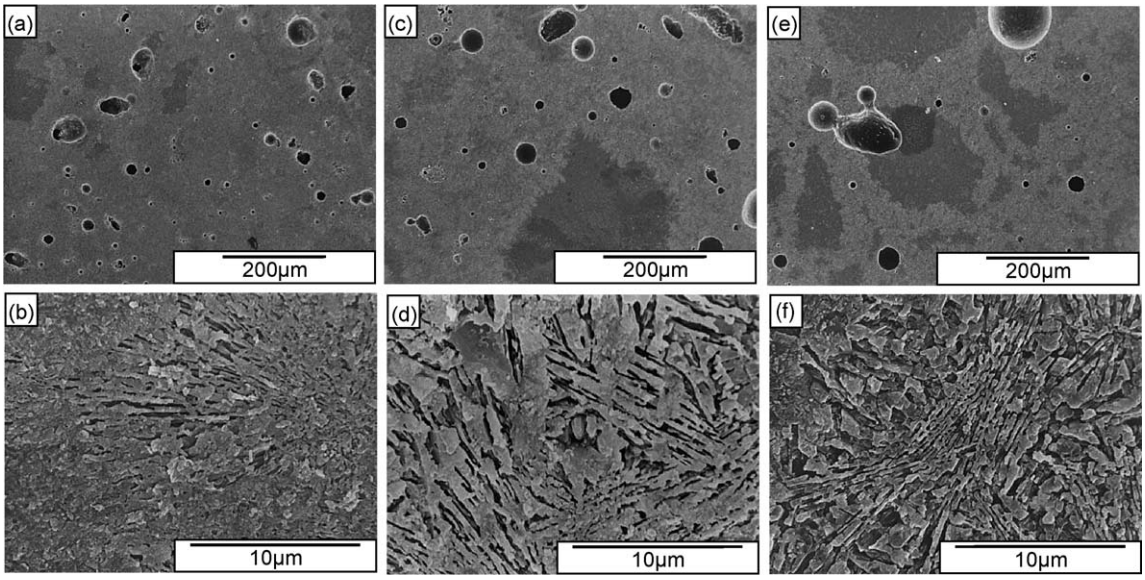

Fig. 7. Microstructures of polished and HF-etched samples observed at low and high magnifications fired at 1000 °C for 1 h (a and b), 1050 °C for 1 h (c and d) and 11000 °C for 1 h (e and f).

Table 3
Various properties of the present glass-ceramics compared with refs. [1,2]

Properties	Present glass-ceramics			Ref. [1]	Ref. [2]	
	PS1000	PS1050	PS1100	CC	CM1	CM2
Bulk density (g/cm^3)	2.50	2.47	2.46	2.56	–	–
Bending strength (MPa)	65 (4)[a]	63 (5)	66 (3)	81 (8)	130 (14)	73 (14)
Vickers hardness (GPa)	6.4 (3)	6.1 (3)	6.0 (1)	6.6 (3)	7.4 (8)	7.6 (5)
Linear thermal expansion ($\times 10^{-6}$/°C)	6.3	7.2	8.1	5.2	6.7	4.7
Weight loss in acid (mg/cm^2)	4.7 (4)	7.7 (2)	8.4 (2)	0.31 (2)	0.4	1.3
Weight loss in alkali (mg/cm^2)	0.71 (9)	0.80 (4)	0.85 (4)	1.60 (3)	2.3	1.4
Crystalline phase	Q > A, D[b]	Q > C, A, D	C > A, D	W	D > A	A > D

[a] The numbers in parentheses represent the standard deviation in the last decimal place.
[b] Q: quartz (SS); A: anorthite; D: diopside; C: cristobalite; W: wollastonite.

The microstructures of the samples fired at 1000, 1050 and 1100 °C determined on the polished and HF-etched surfaces are shown in Fig. 7. Large pores (~100 μm) are seen in the microstructures of the three samples. In the high-magnification photographs, slit shaped etching patterns observed in the surfaces are thought to correspond to a selectively leached glassy phase. The slit shaped patterns are aligned radially and thought to result from crystal growth from the surface to the center of the glass particles.

3.2. Properties of the glass-ceramics

The various properties of the present glass-ceramics are listed in Table 3 together with the corresponding data for the CC and CM glass-ceramics [1,2]. The bulk densities of the present glass-ceramics decrease from 2.50 to 2.46 g/cm^3 with higher firing temperature. This is attributed to the change of the major crystalline phases from quartz solid solution (2.60 g/cm^3) to cristobalite (2.33 g/cm^3). The bulk densities of the present PS glass-ceramics are lower than those of the CC glass-ceramics (2.56 g/cm^3), reflecting the lower densities of the major crystalline phases (quartz (SS) and cristobalite) than that of $CaSiO_3$ (2.90 g/cm^3), the main crystalline phase of the CC glass-ceramics. The higher porosity of the present glass may be a factor in this result.

The four-point bending strengths of the present PS glass-ceramics are 63–66 MPa and are lower than those of the CC and CM glass-ceramics. The low-bending strengths are attributed to the difference in the major crystalline phases and also to the presence of large closed pores (~100 μm) in the microstructure (Fig. 7). The presence of these pores is due to the higher viscosity of the glassy phase in the PS glass-ceramics. Although the resulting bending strengths of the present PS glass-ceramics are lower than in the CC and CM glass-ceramics, the strength is still slightly higher than that of commercial glass-ceramics (50 MPa). The Vickers micro-hardness values of the PS glass-ceramics range from 6.0 to 6.4 GPa. These values are lower than those reported for the CC and CM glass-ceramics [1,2] for similar reasons to those discussed in connection with the bending strength data.

The thermal expansion curves of the PS glass-ceramics are shown in Fig. 8. All the curves show non-linearity, and this anomalous behavior is related to the phase transitions of the major crystalline phases in the samples. In the sample fired at 1000 °C (PS1000), the major crystalline phase is quartz (SS) which shows anomalous expansion in the vicinity of 500 °C, as for quartz [10]. By contrast, the thermal expansion of the sample fired at 1100 °C (PS1100) shows anomaly at ~200 °C similar to that seen in cristobalite [10]. The thermal expansion coefficients calculated by averaging these curves between 30 and 380 °C are 6.3×10^{-6}/°C in the sample PS1000 and 8.1×10^{-6}/°C in the PS1100 sample. These values are higher than for the CC glass-ceramics because of the influence of these anomalies. However, since the thermal expansion of PS1000 in the low-temperature range is not large, this would not be a disadvantage in building material applications which only involve repeated temperature variations in the vicinity of room temperature.

The weight loss values of the PS glass-ceramics after leaching in acid and alkali solutions are 4.7–8.4 and 0.7–0.9 mg/cm^2, respectively. The leaching rates calculated from these data are 5.4–9.8 $\times 10^{-8}$ and 0.8–1.0 $\times 10^{-8}$ g/cm^2 s, representing thicknesses of 0.2–0.4 and 0.03–0.04 nm/s, respectively. The weight loss values in acid are apparently higher than those in alkali. The values in acid are higher than in CC and CM glass-ceramics while those in alkali are lower

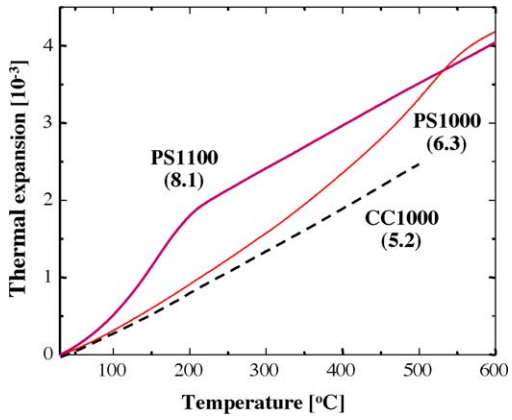

Fig. 8. Thermal expansion curves of PS glass-ceramics fired at 1000 (PS1000) and 1100 °C (PS1100), and that of CC glass-ceramics (CC1000) [1]. The numbers (*a*) in parentheses represent thermal expansion coefficients of $a \times 10^{-6}$/°C.

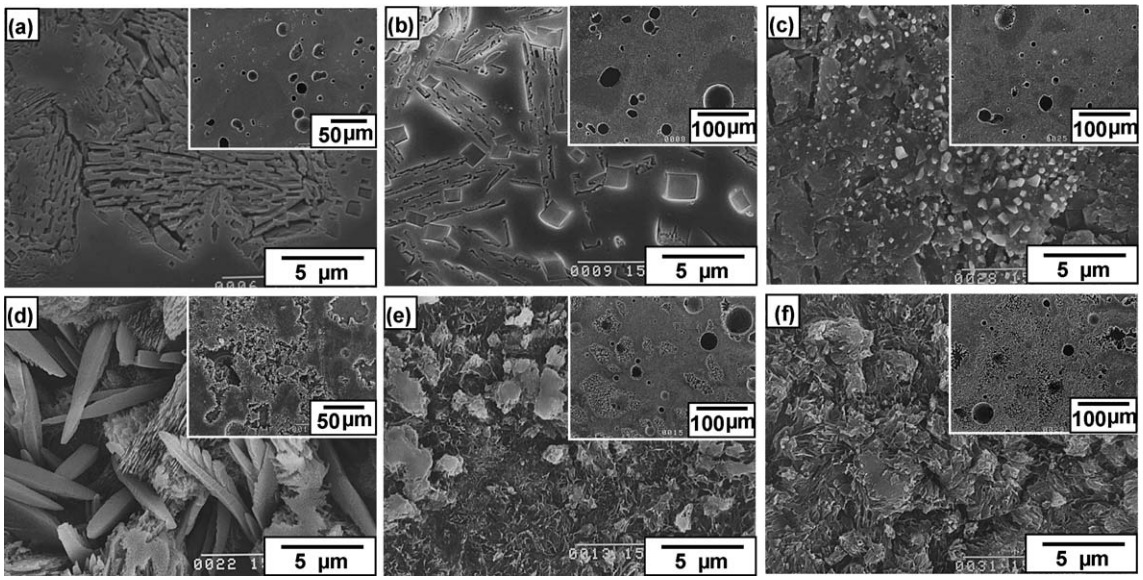

Fig. 9. SEM micrographs of surfaces of the glass-ceramics (PS1000) after chemical treatment in H_2SO_4 ((a) PS1000; (b) PS1050; and (c) PS1100) and NaOH ((d) PS1000; (e) PS1050; and (f) PS1100).

[1,2]. Since the weight loss values of the PS glass-ceramics are higher than for commercial glass-ceramics (3.4 mg/cm^2), this is a disadvantage from the points of view of the importance of acid rain. The microstructures of the PS glass-ceramics after leaching in acid and alkali solutions are shown in Fig. 9. In the acid-leached samples, the surfaces appear to be flat at low magnification, but high magnification, many etched regions are seen with many crystalline grains exposed by the surface leaching. The prismatic pores are thought to be generated by selective leaching of crystalline diopside which is more soluble in acid than the other crystalline phases and the glassy matrix. The shapes of the crystalline grains are found to be similar in PS1000 and PS1050 (relatively large acicular grains) but different in PS1100 (small equiaxed grains). By contrast, the leached texture is clearly observed even at low magnification in the alkali-leached samples. At high magnification, a heavily corroded texture is observed in PS1000. The needle and platy crystals take on the appearance of sharpened pencils and chapped-like surfaces, respectively. The microstructures of PS1050 and PS1100 become similarly rough with surfaces consisting of tangled terrace structures. Although the weight loss values are much higher in acid than in alkali solution for the three samples, the microstructures observed by SEM appear to be more leached in alkali than in acid solution.

Comparing the various properties of the present PS glass-ceramics with the two other glass-ceramics containing Kira (made from $CaCO_3$ [1] and dolomite [2]), most of the data for the PS glass-ceramics are slightly inferior to the other glass-ceramics but similar to those of commercial glass-ceramics. Taking into account the advantage of starting materials which are solely wastes, the present glass-ceramics have the advantage of being a more environmental-friendly material.

4. Conclusion

Glass-ceramics were prepared from mixtures of wastes generated from kaolin clay refining (Kira) and paper sludge (PS) ash. The following results were obtained:

(1) Mixtures of Kira and PS ash in the mass ratio of 55/45 can be melted at 1400 °C, from which glass powder can be prepared by quenching the melt in water.
(2) The glass transition temperature of 760 °C is a little higher than those previously reported for CC and CM glass-ceramics [1,2].
(3) Crystallization occurs at 1000 °C and the crystallized region obtained from the *T–T–T* curve is apparently narrower than for CC glass. The major crystalline phase is quartz solid solution at 1000 °C, transforming to cristobalite at 1100 °C.
(4) The present glass-ceramics were white in color, with surfaces and shapes which changed from rough to smooth and more rounded with higher firing temperatures.
(5) The four-point bending strengths and Vickers microhardness values are 63–66 MPa and 6.0–6.4 GPa, respectively. These mechanical properties are slightly inferior to those reported for CC and CM glass-ceramics [1,2].
(6) The thermal expansion coefficients of the PS glass-ceramics fired at 1000, 1050 and 1100 °C determined between 30 and 380 °C were 6.3×10^{-6}, 7.2×10^{-6} and 8.1×10^{-6} /°C, respectively. These values are higher than those reported for CC and CM glass-ceramics [1,2] due to anomalous expansion accompanying the phase transitions of quartz solid solution and cristobalite.

(7) The chemical durability of the PS glass-ceramics is excellent in alkali but relatively poor in acid.

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