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Waste fluorescent glass and shell derived glass-ceramics

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We prepared glass-ceramics by using fluorescent glass and waste shell as starting materials to recycle waste fluorescent glass containing harmful Hg to human body and waste shell, and to resolve environmental problems. Pressed specimens after quenching and grinding were heat treated at 800°C, 900°C and 1000°C for 1 h, respectively. β-wollastonite, gehlenite and sodium calcium silicate were observed by X-ray diffraction studies. Surface morphology and chemical composition were evaluated by field emission-scanning electron microscopy and energy dispersive X-ray spectrometer.

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1. Introduction

Wollastonite ($CaSiO_3$) is an important substance in ceramic and cement industries. A host of favorable properties such as low shrinkage, good strength, lack of volatile constituents, body permeability, fluxing characteristics, whiteness, and acicular shape renders wollastonite useful in several ceramic and other applications.

Recycling more recently has been extended to other types of byproducts, such as fly ash generated from coal- and oil-fired electric power stations, and fly ash from power plant urban solid waste incinerators [1]. Some of these glass-ceramic materials became commercial products [2] or were developed up to the preindustrial stage [3]. Their main applications are in field of abrasion-resistant materials, i.e., industrial floor coverings, wall facings, abrasion-resistant linings, and high-temperature insulators. Moreover, the low cost and availability of the raw materials make them very attractive from an economical point of view. Specially, as known in the art shaped products composed of wallostonite crystals have excellent properties exhibiting no deterioration at high temperatures of above 1000°C. Therefore, the products are expected to be useful as thermal insulating materials and refractories, and in road construction compositions, but there have been proposed no useful and economical method of preparation, as far as we knew [4].

Recently, the industrial and domestic wastes and their potential impacts on humans and the environment during management and disposal continue to pose one of the most challenging problems facing society. Approximately, above 0.6 million ton of glass waste are generated in South Korea on an annual basis including glass containers, light bulb, plate glass and automobile glass [5]. Thus, huge opportunity exists to convert this generating glass waste from an environmental and economic burden to a profitable, value-added resource. Specially, many unsalable and unuseful waste fluorescent glasses containing harmful Hg to human body is currently wasted without any recycling process.

In our study, to recycle waste fluorescent glass and resolve environmental problems, we prepared glass-ceramics reinforced by wallastonite. Further, as a calcium source to obtain glass-ceramics, we used waste shell. Throughout our work, crystallinity and morphological properties were analyzed with variation of the heat-treatment temperatures.

2. Experimental procedure

Fluorescent glass and waste shell (Mokpo, Chonnam, South Korea) were used as starting material. Waste fluorescent glass cullet and shell were carefully washed to remove Hg attached on glass cullet and to remove contaminant in shell, and dried at 110°C for 24 h in

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air. Glass composition used in our work is shown in Table I. The composition of the mother glasses used in this study were fixed at glass cullet : shell = 4 : 1 in weight ratio. About 30 g powder mixture of these composition was put in a alumina crucible and melted in a box-type SiC electric furnace at 1300°C for 1 h in air. To quench, the melts were rapidly poured into a water bath at room temperature and dried at 110°C for 24 h in air. Composition of the quenched glass is shown in Table II. The quenched glass was ground in an agate mill and pressed into a disk 0.5 cm thick.

The formed glass disks were heated up to 800°C, 900°C and 1000°C at a rate of 5°C/min for 1 h, respectively, in a tube-type electric furnace and allowed to cool inside of the furnace. The heat-treated specimens were cleaned with ethyl alcohol in an ultrasonic cleaner and dried at 110°C for 24 h in air. Fig. 1 shows the experimental procedure in this study.

Crystallinity was analyzed by X-ray diffraction (XRD, Rigaku Co., D-Max-1200, Jpn.) with Cu K_α radiation ($\lambda = 1.54056$ Å) generated at 40 kV and 30 mA, in the $10° < 2\theta < 50°$ range at a scan speed of 2° 2θ/min. Morphology and composition of the specimens were evaluated by using a field emission-scanning electron microscopy (FE-SEM, S-4700, Hitachi Co., Jpn.) equipped with an energy dispersive X-ray spectrometer (EDX) that has a robinson type backscattered electron detector. To analyze chemical durability, the specimens were immersed in 20 mL acidic solution (1 N H_2SO_4) at 80°C for 48 h. Durability was analyzed by the measurement of weight change.

TABLE I Composition of the waste glass used in this work

Element	Line	% (wt)
O	K_α	29.55
Na	K_α	11.01
Mg	K_α	1.79
Al	K_α	2.02
Si	K_α	47.04
K	K_α	2.02
Ca	K_α	6.57
Total		100.00

TABLE II Composition of the quenched glass

Element	Line	% (wt)
C	K_α	12.55
O	K_α	20.66
Na	K_α	7.55
Mg	K_α	0.60
Al	K_α	0.95
Si	K_α	33.40
K	K_α	2.07
Ca	K_α	22.23
Total		100.01

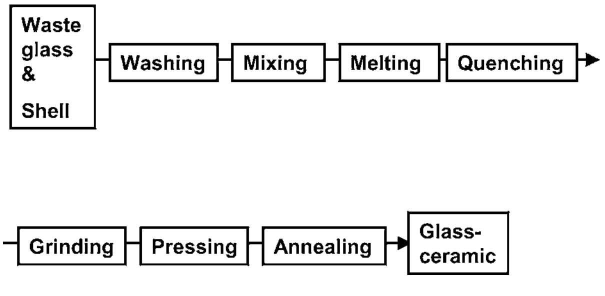


Figure 1 Process of glass-ceramic preparation.

3. Results and discussion

Fig. 2 shows the XRD results and chemical composition of shell used in our work. As clearly seen in Fig. 2, only $CaCO_3$ peaks such as (111), (021), (121), (012), (200), (031), (112), (112) + (130), (211), (122) + (220), (221), and (041) + (202) of the shell can be recognized. Composition of the shell was also investigated by EDX. It is apparent that shell used in this work was identified as calcium carbonate, containing mainly calcium and others such as oxygen and carbon, with orthorhombic structure (JCPDS File 41-1475).

The XRD results on the glass ceramics heat-treated at various temperatures showed that a mixture of phases, such as β-wollastonite ($CaSiO_3$, JCPDS File 27-0088), gehlenite ($Ca_2Al_2SiO_7$, JCPDS File 20-0199) and sodium calcium silicate ($Na_2Ca_3Si_6O_{16}$, JCPDS File 16-0690) at low temperature, i.e., 800°C and 900°C, were present. Peak intensities corresponding to the sodium calcium silicate and the gehlenite phases gradually decreased and disappeared with increase of the heat-treatment temperature from 800°C and 900°C to 1000°C. As shown in Fig. 3, the peak

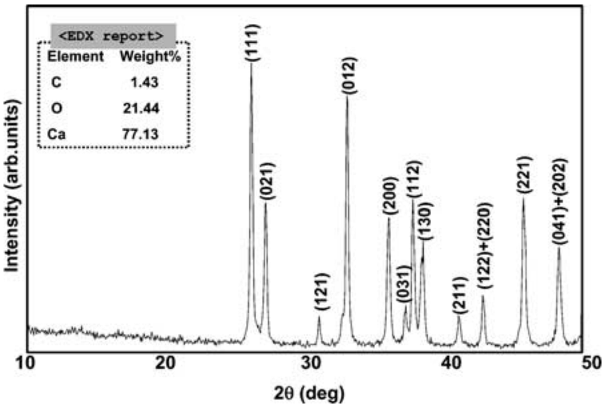


Figure 2 XRD pattern and composition for the shell used in this work.

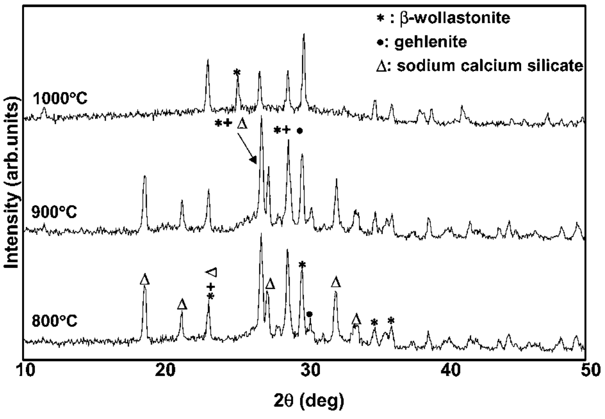


Figure 3 XRD patterns for the glass-ceramics heat treated at 800°C, 900°C and 1000°C.

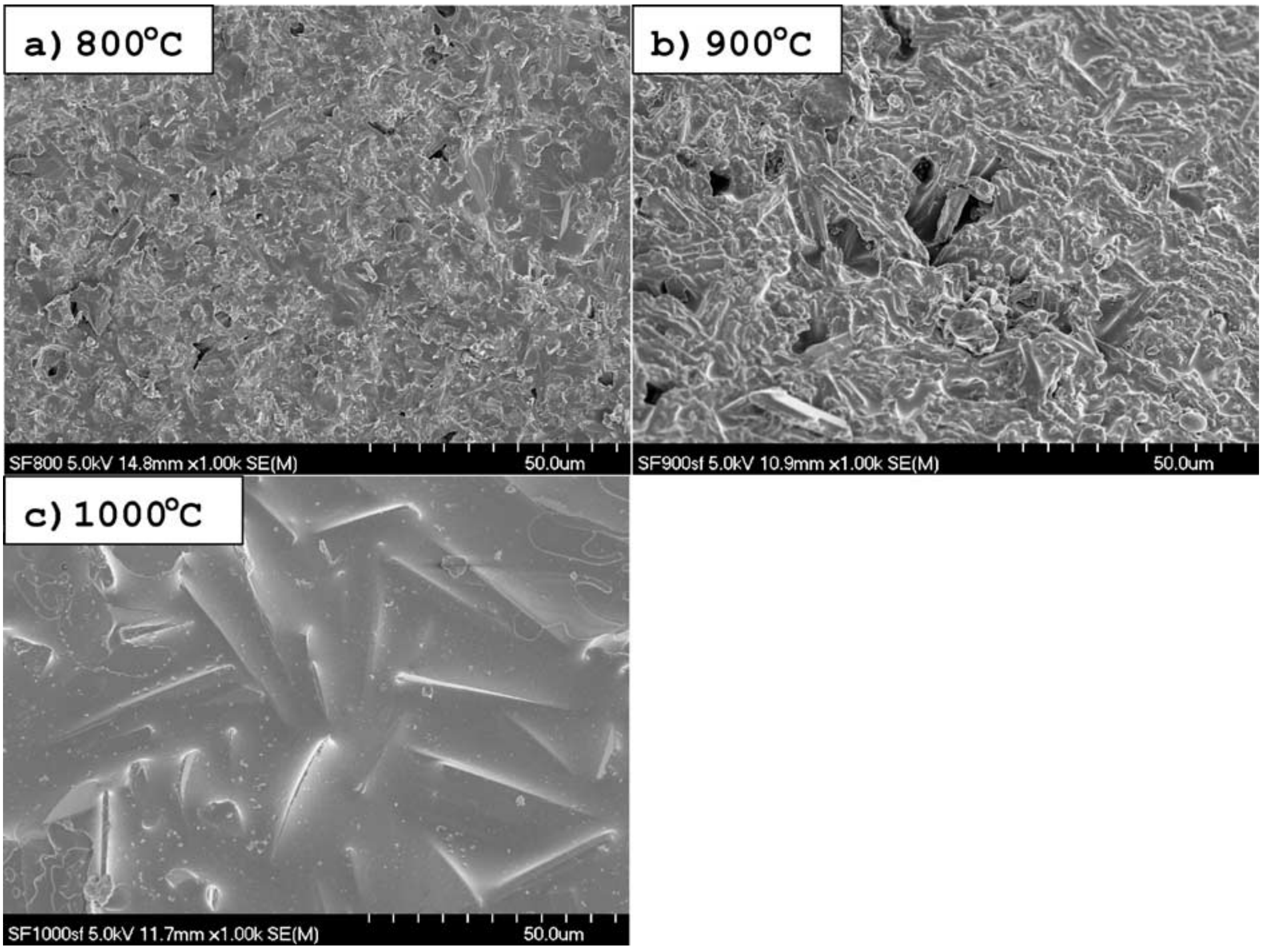


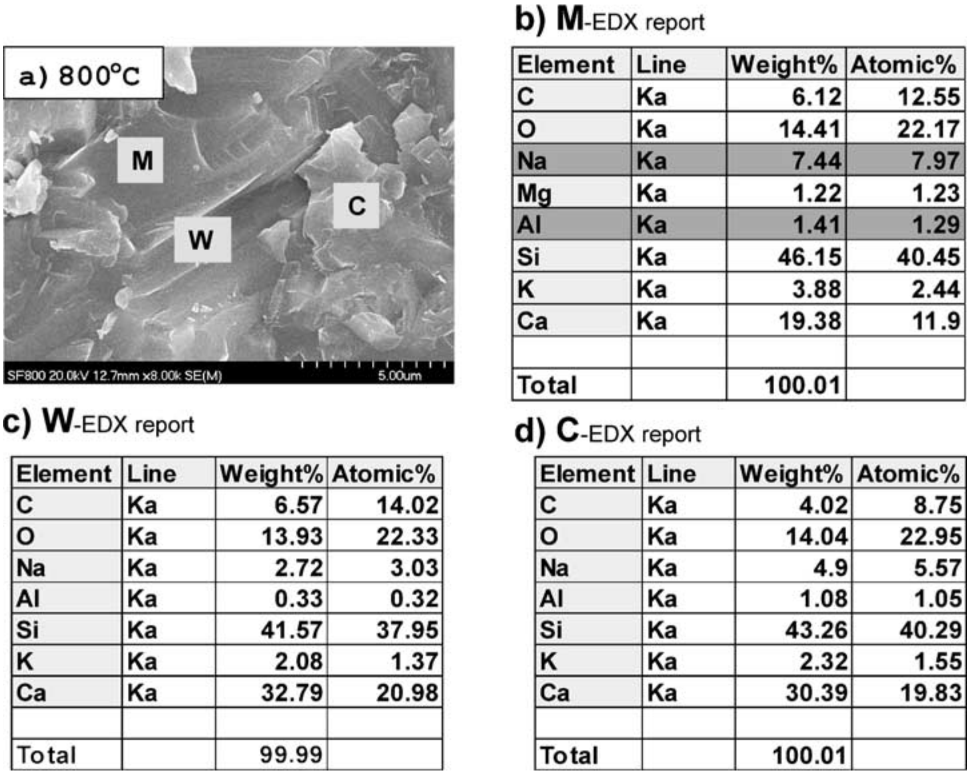
Figure 4 Surface morphology of the glass-ceramics heat treated at 800°C (a), 900°C (b) and 1000°C (c).

at around $2\theta = 30^\circ$ corresponding to gehlenite and the peaks at around $2\theta = 19$, 21, 32.6 and 34° corresponding to sodium calcium silicate dramatically decreased with increase of the heat-treatment temperature. On the contrary, as shown in Fig. 3, with increase of the heat-treatment temperature, small increase of the intensities for the peaks at around $2\theta = 23^\circ$ and 30° corresponding to mixture of sodium calcium silicate and β-wollastonite, and β-wollastonite, respectively, was visible. Newly formed peak at around $2\theta = 25^\circ$ corresponding to β-wollastonite, were identified. However, peaks at around 27° and 29°, which correspond to sodium calcium silicate + β-wollastonite and gehlenite + β-wollastonite decreased with increase of the heat-treatment temperature at 1000°C. We assume that this appearance might be due to decrease of the gehlenite and the sodium calcium silicate owing to formation of the β-wollastonite. At 1000°C, we confirmed highly crystallized glass-ceramic by β-wollastonite.

Fig. 4 shows surface morphology of the glass-ceramics at various heat-treatment temperatures. Morphological analysis of the specimen heat treated at 800°C and 900°C shows that well-crystallized whisker-type crystals were densely aggregated in matrix. However, with increase of the heat-treatment temperature at 1000°C, partially distributed whisker-type phase was increased to about 20–30 μm in length.

In order to more clearly investigate crystal composition, we performed EDX analysis for the same area used in morphological analyses. At 800°C, EDX analysis of the conglomerate-like crystals (denoted C in Fig. 5a) indicated the presence of 2 or 3 phases such as β-wollastonite, gehlenite and sodium calcium silicate (see Fig. 5d), whereas the whisker-type crystal (denoted W in Fig. 5a) in the matrix was mainly composed with β-wollastonite (see Fig. 5c). However, as heat-treatment temperature increase to 1000°C, the conglomerate-like crystals composed by various phases were disappeared, while, from the whisker-type crystal, the crystal growth was identified, as shown in Fig. 6. From above FE-SEM and EDX results, we concluded that, as heat-treatment temperature increase, the conglomerate-like crystals probably composed by β-wollastonite, gehlenite and sodium calcium silicate were converted to β-wollastonite phases.

On the previous XRD result, with increase of the heat-treatment temperature, decrease of the peak intensities corresponding to the gehlenite and the sodium calcium silicate was reasonable, since composition of the conglomerate-like crystals was exactly evaluated by EDX. However, at 1000°C, there is no compositional data for the aluminum and sodium, which mainly existed in gehlenite and sodium calcium silicate phases, although our specimen heat-treated at 1000°C mainly composed by the β-wollastonite phases. Thus, we suspect diffusion of the sodium and aluminum from crystal to glass matrix, since, in the preparation of glass-ceramics, there is no report on the volatilization of



b) **M**-EDX report

Element	Line	Weight%	Atomic%
C	Ka	6.12	12.55
O	Ka	14.41	22.17
Na	Ka	7.44	7.97
Mg	Ka	1.22	1.23
Al	Ka	1.41	1.29
Si	Ka	46.15	40.45
K	Ka	3.88	2.44
Ca	Ka	19.38	11.9
Total		100.01	

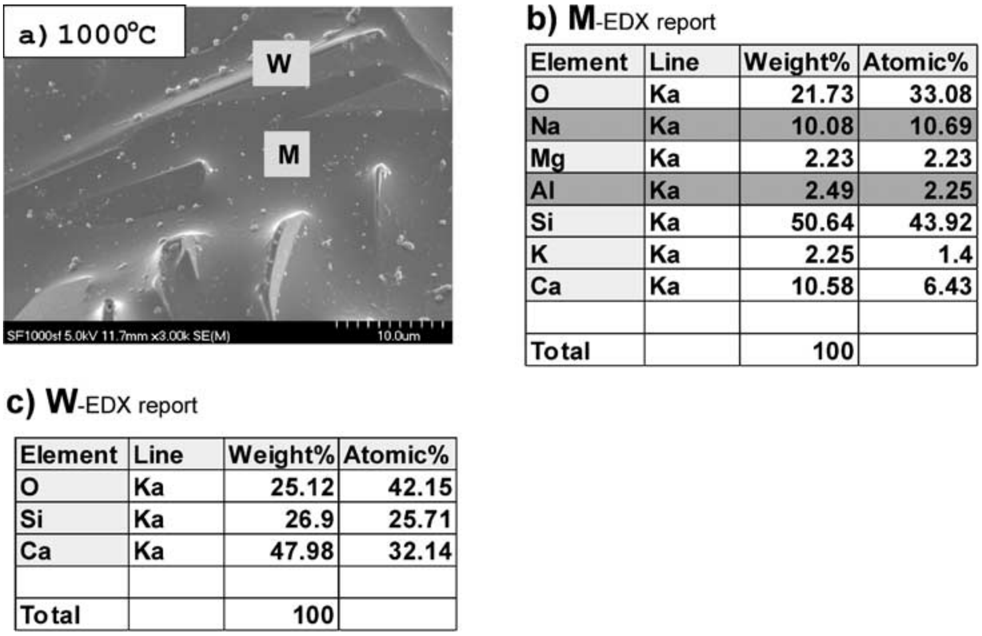
c) **W**-EDX report

Element	Line	Weight%	Atomic%
C	Ka	6.57	14.02
O	Ka	13.93	22.33
Na	Ka	2.72	3.03
Al	Ka	0.33	0.32
Si	Ka	41.57	37.95
K	Ka	2.08	1.37
Ca	Ka	32.79	20.98
Total		99.99	

d) **C**-EDX report

Element	Line	Weight%	Atomic%
C	Ka	4.02	8.75
O	Ka	14.04	22.95
Na	Ka	4.9	5.57
Al	Ka	1.08	1.05
Si	Ka	43.26	40.29
K	Ka	2.32	1.55
Ca	Ka	30.39	19.83
Total		100.01	

Figure 5 Surface morphology and chemical composition at higher magnification of the glass-ceramics heated at 800°C.



b) **M**-EDX report

Element	Line	Weight%	Atomic%
O	Ka	21.73	33.08
Na	Ka	10.08	10.69
Mg	Ka	2.23	2.23
Al	Ka	2.49	2.25
Si	Ka	50.64	43.92
K	Ka	2.25	1.4
Ca	Ka	10.58	6.43
Total		100	

c) **W**-EDX report

Element	Line	Weight%	Atomic%
O	Ka	25.12	42.15
Si	Ka	26.9	25.71
Ca	Ka	47.98	32.14
Total		100	

Figure 6 Surface morphology and chemical composition at higher magnification of the glass-ceramics heated at 1000°C.

sodium and aluminum during heat-treatment at 1000°C, as far as we knew. In order to detect diffusion of the sodium and aluminum, we performed EDX analysis for the glass matrix (denoted M in Figs 5 and 6). As shown in Figs 5 and 6, amount of the sodium and aluminum in the glass matrix significantly increased with increase of the heat-treatment temperature (compare Fig. 5b with Fig. 6b). This is the strong evidence that conversion of the phases from the gehlenite and the sodium calcium silicate to the β-wollastonite was promoted by the high temperature heating. Moreover, calcium content in matrix at 800°C decreased with increase of the heat-treatment temperature at 1000°C. This is another evidence of the growth of the β-wollastonite phases, since formation of the β-wollastonite needed more calcium ions.

Fig. 7 shows chemical durability of the specimens. To calculate the weight change, we define the degree of the chemical durability as follows,

$$\text{Weight change (\%)} = [(W_1 - W_2)/W_1] \times 100$$

where W_1 and W_2 are the weights of the specimen before and after immersion. In Fig. 7, weight loss of the

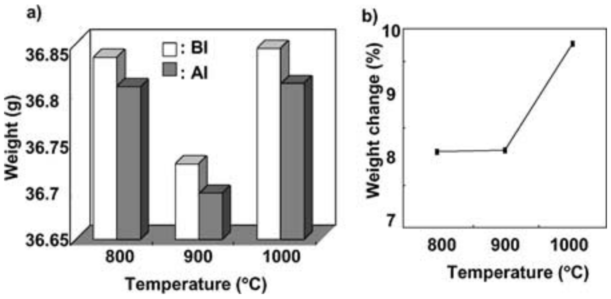


Figure 7 Weight (a) and weight change (b) of the specimen before (BI) and after (AI) immersion.

specimen heat treated at 1000°C exhibited small increase. However, since it is difficult to analyze exact durability because of small weight change, we could not clearly explain variation of the durability by weight gaining only.

Further study is still needed to investigate the relationship between heat-treatment temperature and durability as well as mechanical strength in order to apply for practical usage.

4. Conclusion

To recycle waste fluorescent glass and shell, we prepared glass-ceramics reinforced by β-wollastonite, gehlenite and sodium calcium silicate. With increase of the heat-treatment temperature, the conglomerate-like crystals composed by mixture of the β-wollastonite, gehlenite and sodium calcium silicate in matrix decreased. Whisker-type β-wollastonite crystals in glass matrix significantly increased in length with increase of the heat-treatment temperature from 800°C to 1000°C.

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