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# Properties of Wollastonite-Reinforced Glass-Ceramics Made from Waste Automobile Glass and Waste Shell

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**Abstract**

Wollastonite-type glass ceramics were prepared by milling and firing at various temperatures using an automobile waste glass and waste shell as starting materials. Powder mixture ground by disk-type ball mill for 3 hours was pressed into a disk. The pressed specimen was fired at 850°C, 950°C and 1050°C for 1 hour in air. From FE-SEM observation, with an increase of the firing temperature from 850°C to 1050°C, whisker-type phase was grown to about 10 μm in length. Specimen fired at 1050°C showed the formation of well-crystallized whisker-type wollastonite grains and the highest compressive strength.

**Key words**: glass-ceramics, automobile waste glass, shell, wollastonite

## 1. Introduction

Wollastonite 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 ceramics and other application. The growing demand for wollastonite in recent years is attested by the steady increase in production worldwide.[1-4)]

Natural wollastonite particles are limited by the condition of the deposits, so the material can be synthesized artificially.[1)] Synthesized wollastonite reinforced glass-ceramics[5)] is used for various purposes and is needed to study the appropriate way.

To solve environmental problems from waste materials, in this work, we prepared wollastonite reinforced glass-ceramics using waste materials, such as automobile waste glass and shell. The starting material was thoroughly ground to increase the interaction between the powders. Automobile glass and shell were used as sources of Si and Ca, respectively. Crystallinity and morphological properties of the specimens with variation of the firing temperature were analyzed. Mechanical strengths and densities of the specimens were also measured.

## 2. Experimental Procedure

Wollastonite reinforced glass-ceramic was prepared from automobile waste glass and shell. Chemical composition evaluated by an energy dispersive X-ray spectrometer (EDS) of the automobile waste glass used in this work was given in Table 1. Automobile glass and shell (Mokpo, Chonnam, South Korea) were carefully washed in water bath to remove contaminant, and dried in dry oven at 100°C for 24 hours. The weight ratio of automobile waste glass with respect to shell was 4. To obtain a fine powder, the mixture was ground in disk-type ball mill (Retsch GmbH & Co. KG., D-42781 HAAN, TYPE : RS1, Germany) for 3

**Table 1.** Chemical composition of automobile waste glass used in this work.

| Composition | $SiO_2$ | $Na_2O$ | CaO | MgO | $Al_2O_3$ | $K_2O$ |
|---|---|---|---|---|---|---|
| wt% | 77.51 | 13.09 | 4.83 | 1.59 | 1.66 | 1.32 |

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hours. The particle size distribution was derived from the particle size analyzer (PSA, Malvern Ins. Lab., MS 1002). Most of the particles fell into in the size 0.1-1 μm range. The ground mixture was pressed into a disk with 10 mm thickness and 5 mm diameter.

The formed specimen was fired at up to 850°C, 950°C and 1050°C with heating rate 5°C/min for 1 hour in air (flow rate: 150~200 mL/min), respectively, in a box-type furnace and allowed to cool inside of the furnace. After firing, the specimen was cleaned with ethyl alcohol in an ultrasonic bath and dried at 100°C for 12 hours in air.

Crystallinity was analyzed by X-ray diffraction (XRD, Rigaku Co., D-Max-1200, Japan) with CuKα radiation (λ=1.54056 Å) generated at 40 kV and 30 mA. Morphology and composition of the specimens were evaluated by using a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan) equipped with an EDS. Compressive strength and density were examined by universal tester (Instron 4302, Instron Co., England) and electronic densimeter (ED-120T, MFD BY A&D Co. Ltd., Japan).

## 3. Results and Discussion

Fig. 1 shows the XRD result of the shell used in this work. As clearly shown in Fig. 1, $CaCO_3$ peaks of the shell can be recognized. It seemed that the major compound of the waste shell was $CaCO_3$.

Fig. 2 shows the XRD patterns of specimens fired at various temperatures. The XRD revealed β-wollastonite ($CaSiO_3$), gehlenite ($Ca_2Al_2SiO_7$) and sodium calcium

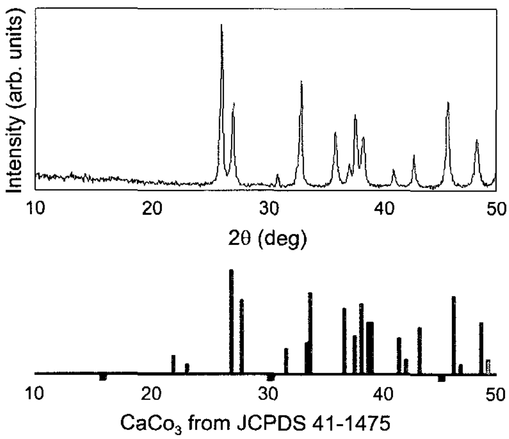


**Fig. 1.** XRD patterns of waste shell and $CaCO_3$.

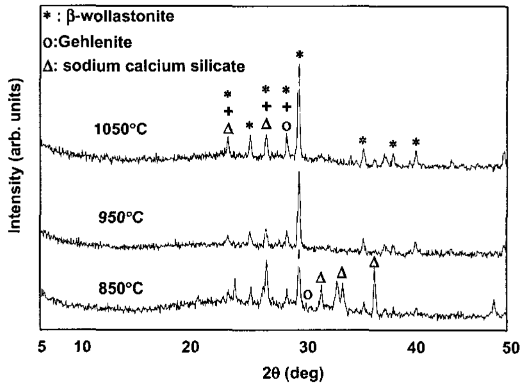


**Fig. 2.** XRD patterns of glass-ceramics fired at 850°C, 950°C and 1050°C for 1 h in air.

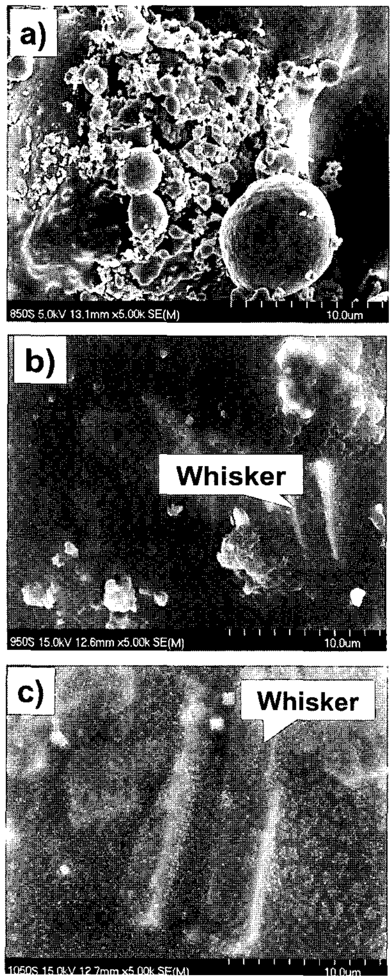


**Fig. 3.** FE-SEM images (× 5,000) of the specimens fired at 850°C (a), 950°C (b) and 1050°C (c).

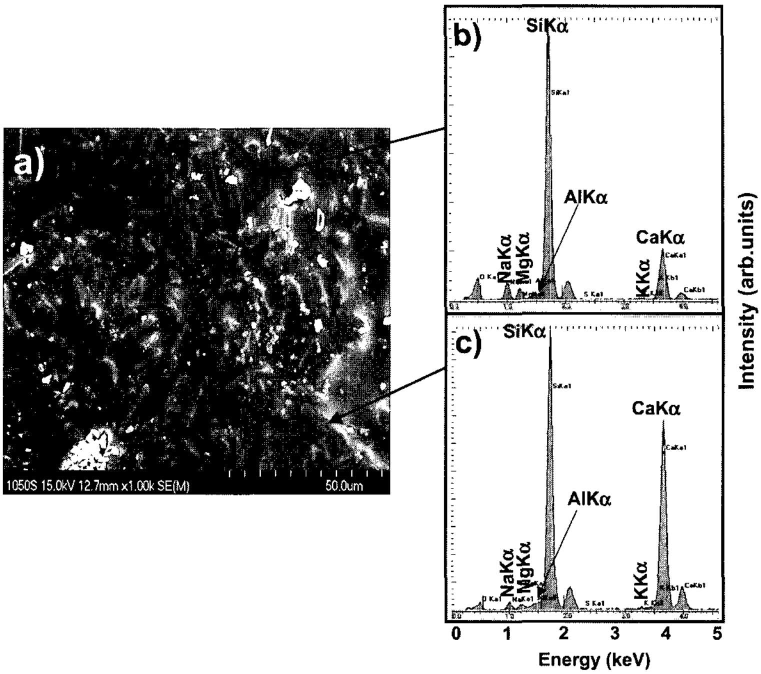


**Fig. 4.** FE-SEM image (a) and EDS analysis (b) and (c) of the specimen after firing at 1050°C.

silicate (SCS) ($Na_2Ca_3Si_6O_{16}$) phases. Peak intensity corresponding to SCS (2θ=30~40°) decreased with increasing the firing temperature from 850°C to 1050°C. With increase in firing temperature, peak intensity at 2θ=29~30°, corresponding to β-wollastonite, slightly increased. The highest peak intensity of β-wollastonite was obtained by firing at 1050°C.

Fig. 3 shows FE-SEM images of the glass-ceramics fired at various temperatures. Morphological analysis of the specimen fired at 850°C shows that round-shape grains were partially distributed in matrix. At 950°C, whisker-type crystals were identified. With increase of the firing temperature to 1050°C, whisker-type phase was grown to about 10 μm in length.

To investigate crystal composition of well-grown whisker-type crystal in matrix, EDS analysis for the specimen fired at 1050°C was carried out. As shown in Fig. 4, the whisker-type crystal in the matrix was mainly composed with β-wollastonite [see Fig. 4 (c)], while, as shown in Fig. 4 (b), EDS analysis of the matrix indicated the presence of silicate glass containing Ca, Al, Na and Mg as an additive. It seems that formation of the whisker-type β-wollastonite was promoted by addition of shell as a Ca source and high-temperature heat-treatment. From

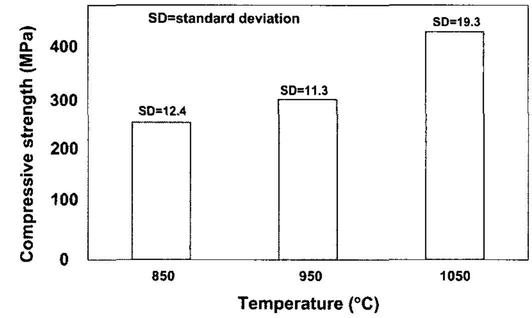


**Fig. 5.** Compressive strength of the specimens fired at 850°C, 950°C and 1050°C.

our previous report,[6] as annealing temperature increased, the round-shape grains composed by β-wollastonite, gehlenite, and SCS were converted to whisker-type β-wollastonite. At 1000°C, therefore, we confirmed highly crystallized glass-ceramics by β-wollastonite with a waste fluorescent glass and shell by XRD, FE-SEM and EDS. Furthermore, as an increase of annealing temperature from 800°C to 1000°C, calcium content in matrix at 800°C decreased. This is an evidence of the growth of the β-wollastonite phases, since formation of the β-wollastonite needed more calcium ions.[6]

Fig. 5 shows the compressive strength of the specimens

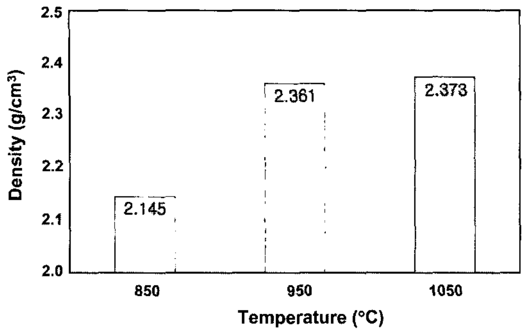


**Fig. 6.** Density of the specimens fired at 850°C, 950°C and 1050°C.

fired at 850°C, 950°C and 1050°C, respectively. The compressive strength increased with firing temperature from 850°C to 1050°C. Generally, the glass-ceramics reinforced with whisker-type wollastonite showed a high mechanical strength.

Fig. 6 shows the densities of the samples fired at 850°C, 950°C and 1050°C. As shown in Fig. 6, it is difficult to obtain high-density compact by firing at 850°C. With increase in firing temperature to 950°C and 1050°C, the density of the specimens increased from 2.145 to 2.361 and 2.373 g/cm$^3$, respectively. Since, with increase of the heat-treatment temperature, small increase of peak intensity corresponding to β-wollastonite could be related to high compressive strength. We assume the existence of another effect on the compressive strength of our specimens because the density and compressive strength of the sample fired at 850°C were lower than those of specimens fired at 950°C and 1050°C. From above results of the density and compressive strength, it was believed that as firing temperature increases, pores between the starting materials probably remaining in matrix at low-temperature gradually disappeared at 950°C and 1050°C, resulting in high density and high compressive strength. Moreover, we could obtain the relationship between the pore in matrix and the firing temperature by using a FE-SEM observation.[6]

In this work, we obtained whisker-type wollastonite reinforced glass-ceramic with high compressive strength for the practical use compared with that of gray cast iron bars (572 Mpa, ASTM Class 20).[7]

## 4. Conclusion

Whisker-type β-wollastonite reinforced glass ceramics showing a high compressive strength were prepared using milling and firing with an automobile waste glass and waste shell as starting materials. The highest XRD peak intensity of the wollastonite was obtained by heating at 1050°C. Formation of the whisker-type wollastonite was promoted by addition of shell as a CaO source and firing at high temperature. We obtained high strength glass-ceramic to apply for practical usage, such as building materials.

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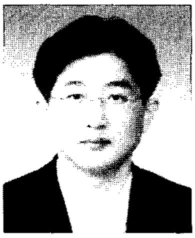

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