O U R N A L O F

Ceramic Processing Research

# Recycling of glass waste and shells by the fabrication of glass-ceramics reinforced by a whisker-type wollastonite phase

Byung-Hoon Kim, Jun-Hyung An, Yeon-Hum Yun<sup>a</sup>, Bo-An Kang<sup>a</sup>, Young-Sun Jeon<sup>a</sup> and Kyu-Seog Hwang<sup>a,\*</sup>

Department of Materials Science & Engineering, Chonnam National University, 300 Yongbong-dong, Buk-gu, Gwangju 500-757, Korea

<sup>a</sup>Department of Photonics Engineering and Institute of Photolectronic Technology, Nambu University, 864-1 Wolgye-dong, Gwangsan-gu, Gwangju 506-824, Korea

Glass-ceramics showing a high mechanical strength reinforced by whisker-type wollastonite crystals were prepared by a milling and heat-treatment process using various glass waste and shells as starting materials. In order to blend the starting materials and to accelerate the interaction between the glass and shell during annealing, mechanical milling using a disk-type mill was employed. Formation of whisker-type  $\beta$ -wollastonite crystals was observed in the glass matrix using a X-ray diffraction analysis and a field emission-scanning electron microscope. On increasing the annealing temperature from 800°C and 900°C to 1000°C, the compressive strength of the specimens increased.

Key words: glass-ceramic, wollastonite, waste glass, shell.

### Introduction

Glass-ceramics are of particular interest because of their high melting temperature, low thermal expansion, good oxidation resistance and low dielectric constant [1]. Up to now, a number of reports have been published on glass-ceramics using waste materials such as coal ash, iron and steel slag [2-6].

Some of these glass-ceramics have become commercial products [7], or have been developed up to a preindustrial stage [8]. Their main applications are in the field of abrasion-resistant materials, i.e., as 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.

Calcium silicate (wollastonite,  $CaSiO_3$ ) is an important substance in the ceramic and cement industries. It has a host of favorable properties such as low shrinkage, good strength, lack of volatile constituents, and whiteness. The growing demand for wollastonite in recent years is attested by the steady increase in production [9].

In this work, to resolve environmental problems from waste and to prepare high-mechanical strength materials, we fabricated wollastonite-reinforced glass-ceramics using glass waste and shells. Various waste glasses such as from light bulbs, plate glass and bottles, and shells were used as  $SiO_2$  and CaO sources, respectively. The

crystallinity, surface morphology and compressive strength of the specimens as a function of the heat-treatment temperature were analyzed.

## **Experimental Procedure**

Wollastonite-reinforced glass-ceramics with high mechanical strength were prepared from various waste glass and shells. The chemical composition of the glass mixture used in this work is given in Table 1. The composition of the mother mixtures were fixed at glass waste:shell=4:1 in weight ratio. In order to obtain a fine powder, the mixture was ground by disk-type mill (Retsch GmbH & Co. KG., D-42781 HAAN, TYPE:RS1, Germany) for 3 h. The ground mixture was pressed into disks 10 mm thick by hand pressure.

The formed specimens were annealed up to  $800^{\circ}$ C,  $900^{\circ}$ C and  $1000^{\circ}$ C at a rate of  $5^{\circ}$ C/min for 1 h, in a furnace and allowed to cool inside the furnace.

The crystallinity was analyzed by X-Ray diffraction (XRD, Rigaku Co., D-Max-1200, Jpn.) with CuK $\alpha$ 

 Table 1. The chemical composition of the glass waste used in this work

Composition	% (wt)
SiO <sub>2</sub>	75.91
Na <sub>2</sub> O	14.15
CaO	4.91
MgO	1.62
$Al_2O_3$	1.58
K <sub>2</sub> O	1.83

<sup>\*</sup>Corresponding author: Tel : +82-62-970-0110

Fax: +82-62-972-6200

E-mail: khwang@mail.nambu.ac.kr

radiation. The fracture-surface morphology of the specimens was evaluated using a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Jpn.). The chemical composition of the specimens was analyzed using an energy dispersive X-ray spectrometer (EDS). The compressive strength of the specimen was examined by universal tester (Instron 4302, Instron Co., England).

# **Results and Discussion**

Figure 1 shows the XRD patterns of specimens after heating at 800°C (a), 900°C (b) and 1000°C (c). The results showed that a mixture of phases, such as  $\beta$ wollastonite (CaSiO<sub>3</sub>, JCPDS File 27-0088) and sodium calcium silicate (SCS) (Na<sub>2</sub>Ca<sub>3</sub>Si<sub>6</sub>O<sub>16</sub>, JCPDS File 16-0690) were present. At 800°C, it is difficult to identify XRD peaks corresponding to  $\beta$ -wollastonite. On increasing the annealing temperature to 1000°C, the peak intensity corresponding to  $\beta$ -wollastonite (2 $\theta$ =29-30°) was greatly increased. However, some peaks from the SCS phase were still identified in the specimen after annealing at 1000°C.

Figure 2 shows FE-SEM images of the glass-ceramics heat-treated at 800°C (a), 900°C (b) and 1000°C (c). At 800°C, much unreacted powders can be seen probably due to the low annealing temperature. It was difficult to obtain whisker-type wollastonite crystals in the specimen annealed at 800°C. Surface morphological analysis of the specimen annealed at 900°C exhibited that pores in the matrix were partially distributed. On increasing the annealing temperature to 1000°C, whisker-type phases were grown in matrix. At the same time, the unreacted particles and partially distributed pores seen in the matrix at 800°C and 900°C disappeared. We can conclude that low-temperature annealing at 800°C and 900°C is inefficient for improving interaction between the glass and shell, resulting in the existence of unreacted powders and observable pores in glass matrix.

To investigate the crystal composition of the whisker-



**Fig. 1.** XRD patterns of the specimens heat-treated at  $800^{\circ}$ C (a),  $900^{\circ}$ C (b) and  $1000^{\circ}$ C (c).

type wollastonite-reinforced specimen annealed at 1000 °C, we performed EDS analysis on the fracture-cross section. Strong peaks corresponding to silicon and calcium were detected for the whisker-type phase. However, as in clearly shown in Fig. 3(c), the sodium ion content in the glass matrix had increased, while a relatively weak peak intensity corresponding to calcium ions was identified. From this result, we can confirm the formation of the wollastonite phase in the glass matrix for the specimen annealed at 1000°C.

Figure 4 shows the compressive strength of the specimens heat-treated at 800°C, 900°C and 1000°C. On increasing the annealing temperature from 800°C and 900°C to 1000°C, the compressive strength increased from ~195 MPa to ~351 MPa. Generally, glass-ceramics reinforced by whisker-type  $\beta$ -wollastonite show high mechanical strength. As previously shown in Fig. 2, the lower mechanical strength for the specimens containing



Fig. 2. FE-SEM images of the specimens heat-treated at  $800^{\circ}C$  (a),  $900^{\circ}C$  (b) and  $1000^{\circ}C$  (c).



Fig. 3. EDS analysis of crystal (b) and matrix (c) for the specimen heat-treated at 1000°C.



**Fig. 4.** Compressive strength of the present specimen heat-treated at 800°C, 900°C and 1000°C.

pores and unreacted powders in the glass matrix after annealing at 800°C and 900°C than that of the specimen annealed at 1000°C was expected.

# Conclusions

Using a mechanical milling and annealing procedure with glass waste and shells as starting materials, we can obtain a  $\beta$ -wollastonite-reinforced glass-ceramic at 1000°C having a high mechanical strength for practical

usage. On increasing the annealing temperature from 800°C and 900°C to 1000°C, specimens containing unreacted powders and pores in the glass matrix were converted to highly-crystallized glass-ceramcis with whisker-type wollastonite.

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#### References

- L. Barbieri, A.M. Ferrari, I. Lancellotti, C. Leonelli, J.M. Rincòn, and M. Romero, J. Am. Ceram. Soc. 83[10] (2000) 2515-2520.
- M. Tanaka and S. Suzuki, J. Ceram. Soc. Jpn. 107[7] (1999) 621-632.
- E. Mazzucato and A.F. Gualtieri, Phys. Chem. Minerals 27 (2000) 565-574.
- 4. A.R. Boccaccini, M. Petitmermet, and E. Wintermantel, Am. Ceram. Soc. Bull. 76[11] (1997) 75-78.
- E.D. Zanotto and E. Müller, J. Non-Cryst. Solids 130 (1991) 220-221.
- P. Alizadeh and V.K. Marghussian, J. Eur. Ceram. Soc. 20 (2000) 775-782.
- M.W. Davies, B. Kerrison, W.E. Gross, M.J. Robson, and D.W. Wichall, J. Iron. Steel Inst. 208 (1970) 348.
- 8. P. Rogers and J. Robertson, Interceram. 38 (1989) 37.
- 9. K.C. Rieger, Amer. Ceram. Soc. Bull. 74[6] (1995) 160-161.