

Chemical durability of β -wollastonite-reinforced glass-ceramics prepared from waste fluorescent glass and calcium carbonate

BYUNG-HOON KIM¹, BO-AN KANG², YEON-HUM YUN², KYU-SEOG HWANG^{2*}

¹Department of Materials Science and Engineering, Chonnam National University,
300 Yongbong-dong, Buk-gu, Gwangju 500-757, South Korea

²Department of Applied Optics and Institute of Photoelectronic Technology,
Nambu University, 864-1 Wolgye-dong, Gwangsan-gu, Gwangju 506-824, South Korea

We prepared glass-ceramics reinforced by β -wollastonite using waste fluorescent glass to resolve the environmental problem. Fluorescent glass and calcium carbonate were used as starting materials. The chemical durability of specimens heat-treated at 800 °C, 900 °C, and 1000 °C was analyzed by both measuring weight change and observing surface morphology. Specimen composition was determined with energy dispersive X-ray spectroscopy. As the heat treatment temperature was increased from 800 °C to 1000 °C, the chemical durability decreased, especially in the glass-matrix area. A compressive strength of about 250–350 MPa was sufficiently large for practical use.

Key words: *glass-ceramics; β -wollastonite; fluorescent glass*

1. Introduction

Wollastonite (CaSiO_3) is an important substance in the ceramic and cement industries. A host of favourable 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. The growing demand for wollastonite in recent years has been attested by a steady increase in production worldwide [1].

Conversion or inclusion in glass-ceramic systems has been used to extend recycling to several types of by-products, such as fly ash from coal- and oil-fired electric power stations and fly ash from urban solid waste incinerators [2]. Some of these

*Corresponding author, e-mail: khwang@mail.nambu.ac.kr.

glass-ceramic materials have become commercial products [3] or have been developed up to the pre-industrial stage [4]. Their main applications are in the field of abrasion-resistant materials, i.e., industrial floor coverings, wall facings, abrasion-resistant linings, and high-temperature insulators. Moreover, low cost and availability of the raw materials make them very attractive from the economic point of view. However, according to our knowledge no useful and economic method of their preparation has been devised as yet [5].

Recently, we have prepared glass-ceramics from waste fluorescent glass [6]. In this work, we investigate the chemical durability of glass-ceramics reinforced by β -wollastonite. The mechanical strength of these glass-ceramics has been determined.

2. Experimental procedure

Preparation of the specimens used in this study was similar to that described in our previous report [6]. Briefly, fluorescent glass and calcium carbonate (CaCO_3 , Duksan Co., Ltd., South Korea) were used to prepare β -wollastonite glass-ceramics. Table 1 shows the chemical composition of the fluorescent glass used. Waste fluorescent glass cullet was washed with water to remove attached Hg, and dried at 110 °C for 24 h in air. The compositions of the mother glasses of the glass-ceramics were fixed at glass cullet: $\text{CaCO}_3 = 4:1$ in weight ratio. About 30 g of powder mixture was put in an alumina crucible and melted in a box-type SiC electric furnace at 1300 °C for 1 h in air. In order to quench the glass, the melts were rapidly poured into a water bath at room temperature and dried at 110 °C for 24 h in air. The quenched glass was ground in an agate mill and pressed into a disk 0.5 cm thick and 3 cm in diameter. The green disks were heated in a tube-type furnace to 800 °C, 900 °C, and 1000 °C at a rate of 5 °C/min for 1 h, respectively, and then allowed to cool inside the furnace.

Table 1. The chemical composition of the fluorescent glass

Element	Content wt. %
O	29.55
Na	11.01
Mg	1.79
Al	2.02
Si	47.04
K	2.02
Ca	6.57
Total	100.00

To analyze their chemical durability, the specimens were immersed into 20 cm³ of acidic solution (0.5 M H_2SO_4) at 80 °C for 48 h. After this treatment, the specimens were successively washed with distilled water and dried at 80 °C for 24 h in air. The

chemical durability of the specimens was analyzed by both measuring weight change and observing surface morphology with field emission-scanning electron microscopy (FE-SEM, S-4700, Hitachi Co., Jpn.). Variations in chemical compositions at the surface of the specimens before and after immersing were evaluated by an energy dispersive X-ray spectrometer (EDX) equipped with a Robinson-type backscattered electron detector. Compressive strength was determined using a universal tester with a 0.5 mm/min crosshead speed (Instron 4302, Instron Co., England).

3. Results and discussion

Figure 1 shows the FE-SEM images of fractured cross sections of the sintered samples. Morphological analysis of the specimens at 900 °C and 1000 °C shows a dense structure. However, the structure of the sample sintered at 800 °C was porous with large particles throughout the sample. We assume that porous structure was caused by the vaporization of organics during heat treatment or by insufficient annealing.

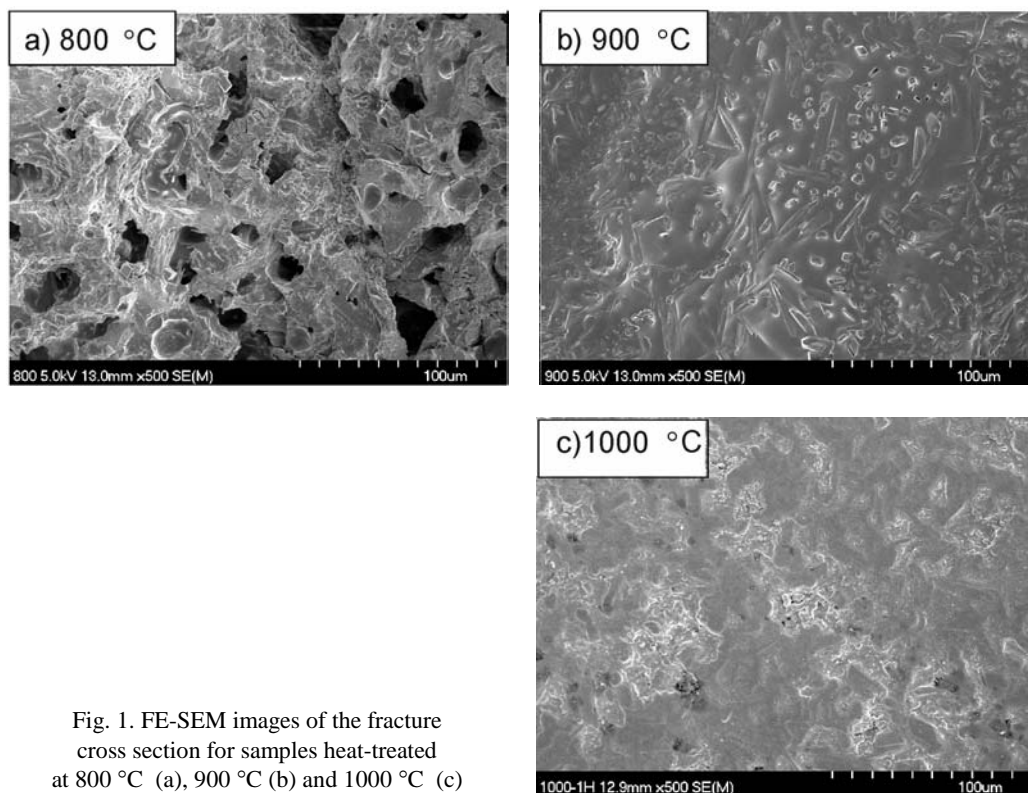


Fig. 1. FE-SEM images of the fracture cross section for samples heat-treated at 800 °C (a), 900 °C (b) and 1000 °C (c)

Table 2 shows the chemical durability of the specimens heat-treated at 800 °C, 900 °C, and 1000 °C. The chemical durability of these samples was not significantly affected by heat-treatment temperatures, although the weight loss of the sample heat-

treated at 1000 °C exhibited a small but significant increase. Since it is difficult to analyze the exact chemical durability of the samples due to their small weight changes before and after immersing, we were not able to explain the variations in the chemical durability by measuring weight gain alone.

Table 2. Weight changes of the glass-ceramics heat-treated at 800 °C (A), 900 °C (B) and 1000 °C (C) between before acid-immersion (BA) and after acid-immersion (AA)

Sample	BA (g)	AA (g)	Weight-loss (%)
A	36.985	36.947	0.1030
B	36.685	36.619	0.1060
C	36.376	36.335	0.1130

In order to obtain more insight into chemical durability, morphology and chemical composition at the surface of the samples were evaluated by FE-SEM and EDX before and after immersing the samples in acidic sol. Figures 2, 4, and 6 show the surface morphologies and chemical compositions of the glass-ceramics heat-treated at 800 °C, 900 °C and 1000 °C before acid-treatment. Si, Ca, Al, and alkali ions such as Na, Mg, and K were detected on the surfaces of all samples before acid-immersion. However, as is clearly seen in Fig. 6c, relatively small and strong peak intensities corresponding to Na and Ca, respectively, were identified on the surface grain for the sample heat-treated at 1000 °C. This is probably due to the formation of highly crystalline β -wollastonite. Simultaneously, as shown in Figs. 2 and 4, for samples heat-treated at 800 °C and 900 °C it is very difficult to detect variations in peak intensities between the glass-matrix (Figs. 2a and 4a) and grain-like area (Figs. 2b and 4b). It is clearly shown in Fig. 6 that as the heat-treatment temperature increased to 1000 °C, the amount of Na in the glass matrix confirmed by EDX was significantly larger than that in the whisker-type grains. Moreover, the calcium content of the glass-matrix at 800 °C and 900 °C significantly decreased with increasing heat treatment temperature. This is additional evidence of the growth of β -wollastonite crystals in the sample heated at 1000 °C, since the formation of β -wollastonite needs more calcium ions.

Figures 3, 5 and 7 show the surface morphologies and chemical compositions of glass-ceramics heat treated at 800 °C, 900 °C, and 1000 °C, respectively, after acid-immersion. Figs. 3 and 5 show that it is very difficult to identify variations in the amount of Na ions in the glass-matrix for samples heat-treated at 800 °C and 900 °C, whereas a significant decrease of Na ion concentration was detected in the grain-like area. On the contrary, at 1000 °C, as shown in Fig. 7, the amount of Na ions in the glass-matrix decreased after acid-immersion (compare Fig. 6b with Fig. 7b).

In order to compare ion contents more clearly, we determined the weight ratio (Na/Si) for different samples, as shown in Fig. 8. For the samples heat-treated at 800 °C and 900 °C, Na ion-diffusion was larger in the grain-like area than in the glass-matrix. The sample heat-treated at 1000 °C gave the opposite result, i.e., the glass-matrix exhibited larger Na-diffusion after acid-immersion.

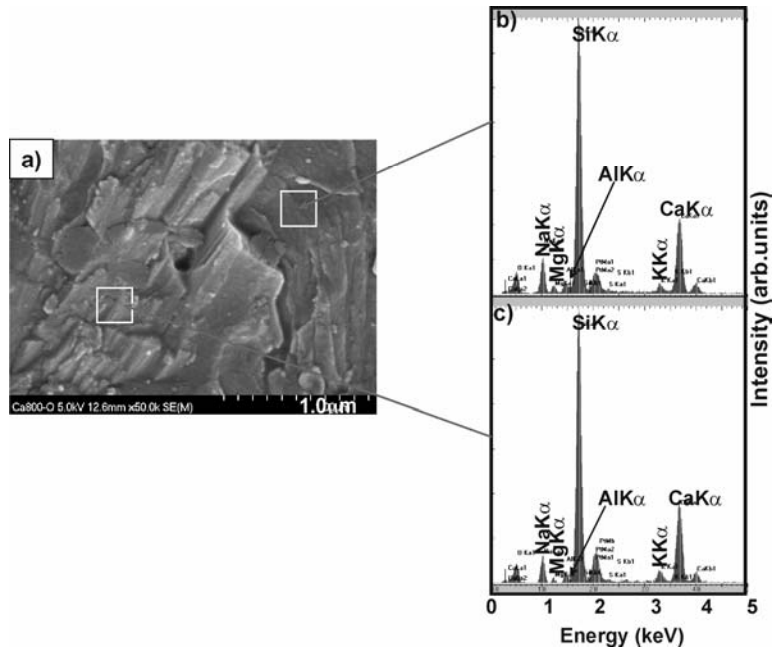


Fig. 2. FE-SEM image (a) and chemical composition of the surface (matrix (b) and grain (c)) of the glass-ceramic heat-treated at 800 °C, before acid-immersion

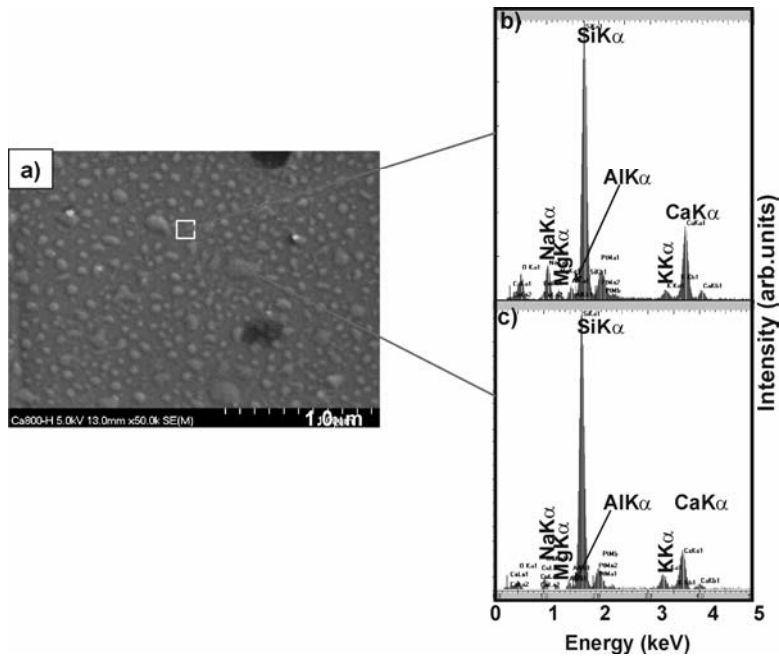


Fig. 3. FE-SEM image (a) and chemical composition of the surface (matrix (b) and grain (c)) of the glass-ceramic heat-treated at 800 °C, after acid-immersion

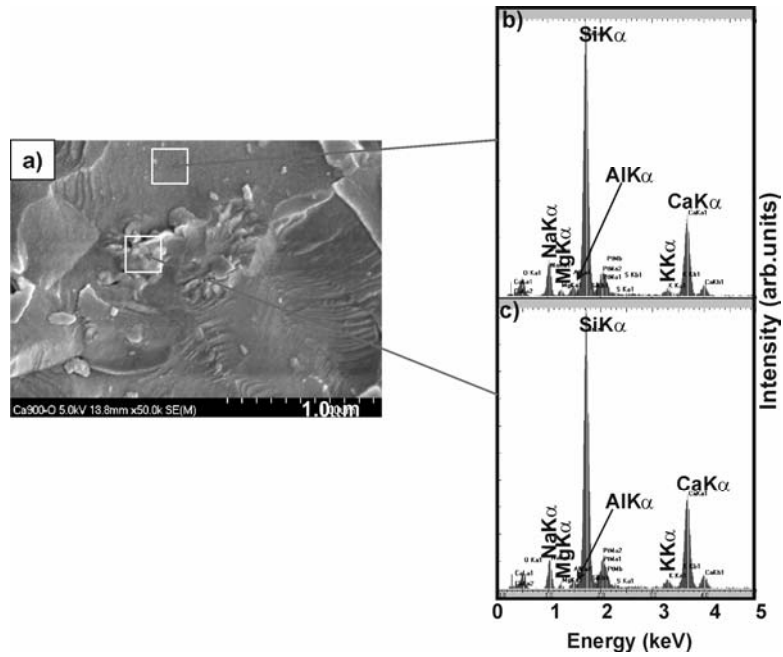


Fig. 4. FE-SEM image (a) and chemical composition of the surface (matrix (b) and grain (c)) of the glass-ceramic heat-treated at 900 °C, before acid-immersion

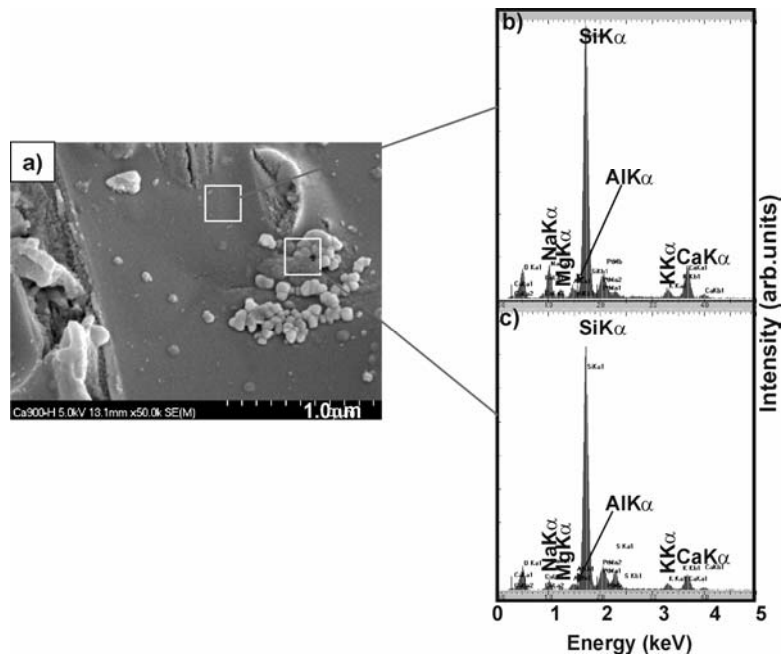


Fig. 5. FE-SEM image (a) and chemical composition of the surface (matrix (b) and grain (c)) of the glass-ceramic heat-treated at 900 °C, after acid-immersion

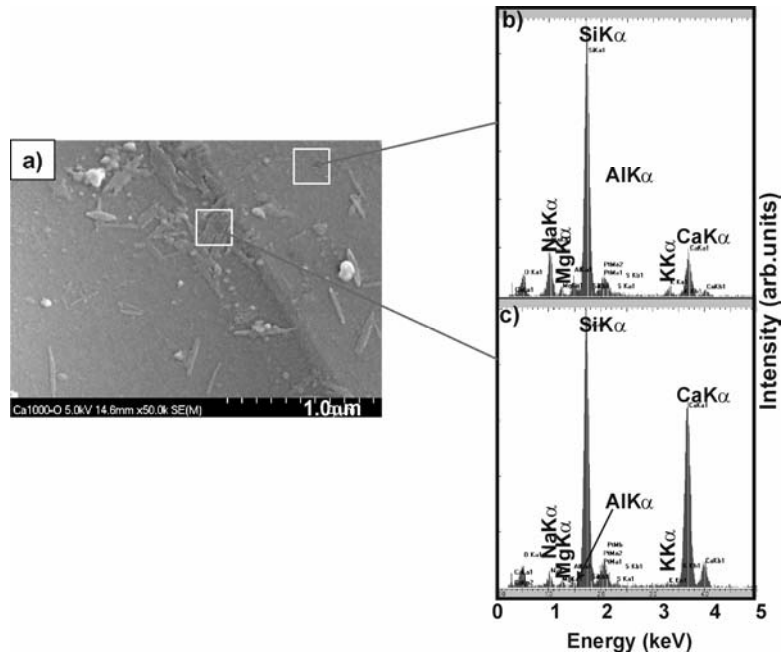


Fig. 6. FE-SEM image (a) and chemical composition of the surface (matrix (b) and grain (c)) of the glass-ceramic heat-treated at 1000 °C, before acid-immersion

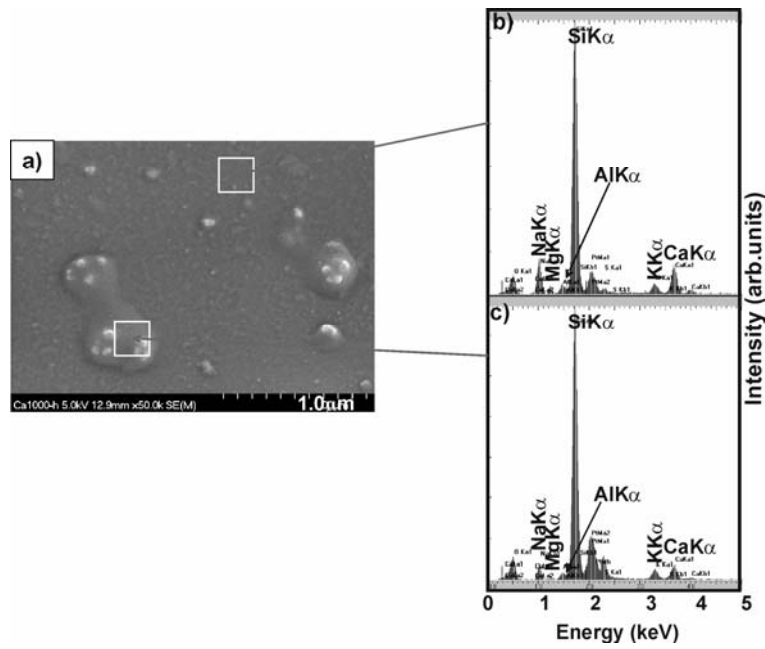


Fig. 7. FE-SEM image (a) and chemical composition of the surface (matrix (b) and grain (c)) of the glass-ceramic heat-treated at 1000 °C, after acid-immersion

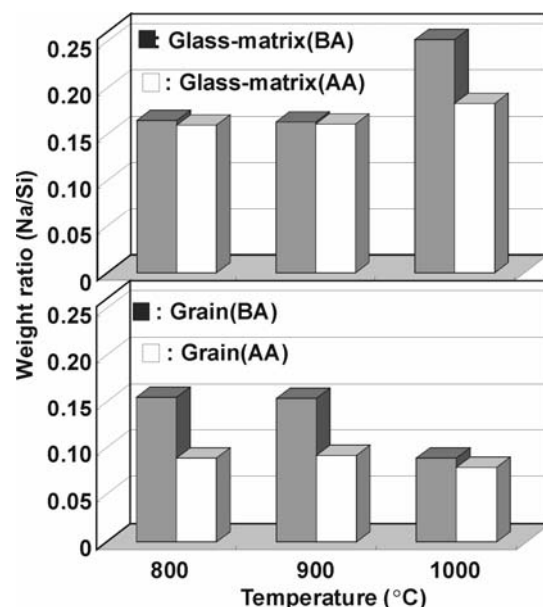


Fig. 8. Variation in the Na contents of the glass-ceramics surface at various temperatures between before (BA) and after acid-immersion(AA)

Generally, the chemical stability of glass-ceramic materials is affected by the composition of the crystalline phase and by the composition and amount of residual glass phase and its morphology. Alkali ions are much more stable in the crystalline phase than in the residual glass phase. Consequently, in order for glass-ceramic materials to have good chemical resistance, it is necessary that their residual glass phase contain low concentrations of alkali metal oxides in particular [7]. From our measurements of weight gain and EDX analysis, we conclude that the chemical durability of samples heat-treated at 800 °C and 900 °C was favourably improved, since their crystalline phase (grains) contained a larger amount of alkali ions (such as Na) as compared with the glass-matrix. On the other hand, it is assumed that chemical durability was decreased at 1000 °C, since the glass matrix contained relatively large amounts of alkali ions owing to diffusion during the high temperature heat treatment.

We also determined the compressive strength of samples heat-treated at 800 °C, 900 °C, and 1000 °C. The compressive strength of the samples decreased with increasing heat-treatment temperature, being 313.87, 230.33, and 226.6 MPa for the 800 °C-, 900 °C- and 1000 °C-heat-treated samples. Generally, glass-ceramics reinforced by whisker-type β -wollastonite crystals show high mechanical strength. However, in our work, the compressive strength was slightly decreased for samples heat-treated at 1000 °C, although well-crystallized β -wollastonite crystals were identified in the glass-matrix, as shown in our previous report [6]. Furthermore, samples treated at 800 °C, having a porous structure, showed a larger compressive strength. By com-

paring with the data for marble (110–170 MPa) [8], we conclude that our samples exhibit a compressive strength large enough for practical usage for all heat-treatment temperatures investigated. The samples treated at 800 °C are glass-ceramics with the potential to use light-weight resources having high strength.

Further experimental studies are needed to investigate chemical durability with other etching agents and in various conditions.

4. Conclusion

We prepared glass-ceramics reinforced with β -wollastonite from waste fluorescent glass and calcium carbonate. From FE-SEM and EDX analyses, we conclude that the glass-ceramics heat-treated at 800 °C and 900 °C showed favourable improvements in chemical durability, since their crystalline phase had a larger amount of alkali ions as compared with the glass-matrix. The compressive strength of the samples obtained at all investigated heat-treatment temperatures (800, 900 and 1000 °C) is large enough for practical usage. Samples treated at 800 °C are glass-ceramics with potentialities to use light-weight resources having high strength.

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