

Properties of $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass-ceramic system prepared by spray pyrolysis

Jin Man HAN, Dae Soo JUNG, Jang HEUI and Yun Chan KANG[†]

Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Korea

$\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LZAS) glass-ceramic system was studied in the high temperature spray pyrolysis. Small amount of P_2O_5 was used as nucleation agent. Fine-sized $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glass powders with amorphous phase and spherical shape were formed by spray pyrolysis at temperatures between 1300 and 1500°C. The mean size of the glass powders prepared at a temperature of 1500°C was 0.7 μm . The glass transition temperature (T_g) of the glass powders was 551.2°C. The two crystallization exothermic peaks were observed at 703.8 and 923.8°C. Densifications of specimens occurred at sintering temperatures of 800 and 900°C, in which interconnected network microstructure was formed by tiny dendritic crystals. The specimens sintered at temperatures of 600 and 700°C had $\text{LiAl}(\text{SiO}_3)_2$ crystal structure. On the other hand, the specimens sintered at temperatures between 800 and 1000°C had $\text{LiAlSi}_2\text{O}_6$ (β -spodumene) crystal structure.

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1. Introduction

Glass-ceramics are used in various fields including electronics, biomedical, optical, etc.¹⁾⁻⁵⁾ Glass-ceramics are polyphase materials consisting of at least one crystalline phase and a glass phase. Glass-ceramics are produced by partial crystallization of the glass systems. Nucleation and growth of crystals in the glass matrix produce the glass-ceramics. The various oxides such as TiO_2 , ZrO_2 , and P_2O_5 are generally used as nucleation agents.^{1),2)}

$\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LZAS) glass-ceramics are widely studied because of their adjustable thermal expansion coefficients (TECs). Therefore, LZAS glass-ceramics with various compositions were studied as sealant materials of metals in various application fields. Lu et al. studied the effect of heat treatment condition on crystallization behavior and thermal expansion coefficient of $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5$ glass-ceramics, in which P_2O_5 was used as nucleation agent.¹⁾ Demirkesen et al. studied the effect of Al_2O_3 additions on the thermal expansion and crystallization behaviors of $\text{Li}_2\text{O}-\text{ZnO}-\text{SiO}_2$ glass-ceramic.^{3),4)}

In previous studies, LZAS glasses with various compositions were prepared by conventional melting and quenching method and subsequently converted to glass-ceramics by nucleation and crystallization processes in the condition of controlled heating process. Reagent-grade materials of Li, Zn, Al, and Si components were mixed uniformly by mixing apparatus. After mixing, the powders were put into Pt or Pt/Rh crucible and molten in the temperature range of 1400–1500°C for several hours, and then the molten glass was quenched into distilled water to form cullet. The cullet was dried and milled to the glass powders. The LZAS glasses prepared by conventional melting and quenching method had large size and irregular morphology.

Spray pyrolysis is one of the more promising processes for the preparation of improved ceramic and metal powders.⁶⁾⁻¹⁰⁾ Spray pyrolysis was also applied to the preparation of glass powders.¹¹⁾⁻¹⁴⁾

The glass powders with amorphous phases were directly prepared by high temperature spray pyrolysis even at short residence time of glass powders inside the hot wall reactor as several seconds. The glass powders prepared by spray powders had sub-micron size, spherical shape and non-aggregation characteristics. The prepared glass powders had also narrow size distribution even without sieving process. However, glass-ceramic systems were not well studied in the spray pyrolysis.

In this study, $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LZAS) glass powders were directly prepared by high temperature spray pyrolysis. Small amount of P_2O_5 was used as nucleation agent. The effect of preparation temperature on the morphologies, crystal structures, and thermal properties of the powders were investigated. The crystallization behavior of the prepared glass powders under controlled heating process was investigated.

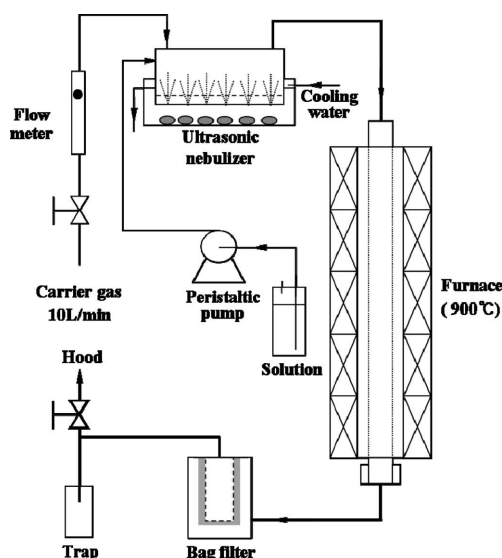


Fig. 1. Schematic diagram of the ultrasonic spray pyrolysis process.

[†] Corresponding author: Y. C. Kang; E-mail: yckang@konkuk.ac.kr

2. Experimental procedure

Glass powders with a 12 mass% Li_2O –20 mass% ZnO –15 mass% Al_2O_3 –51 mass% SiO_2 –2.0 mass% P_2O_5 composition were directly prepared by high-temperature spray pyrolysis. **Figure 1** shows the schematic diagram of the spray pyrolysis process. The spray pyrolysis equipment used consisted of six ultrasonic spray generators that operated at 1.7 MHz, a 1,000-mm-long tubular alumina reactor of 50-mm ID, and a bag filter. The glass powders were prepared by spray pyrolysis at temperatures between 1000°C and 1500°C. The spray solutions were obtained by adding lithium nitrate, zinc nitrate, aluminum nitrate, TEOS (tetraethyl orthosilicate), and nitric acid to distilled water. The overall solution concentration was 0.5 M. The spray solution was atomized with ultrasonic spray generators and intro-

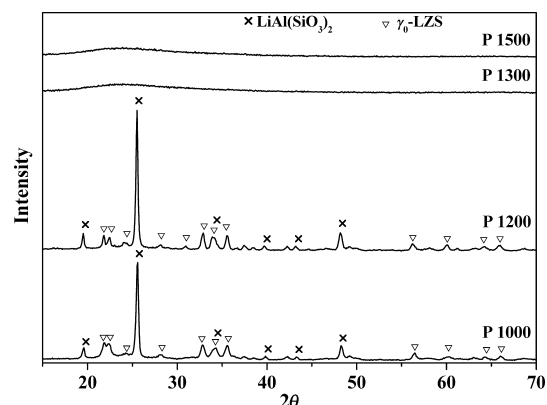


Fig. 2. XRD patterns of the powders prepared by spray pyrolysis.

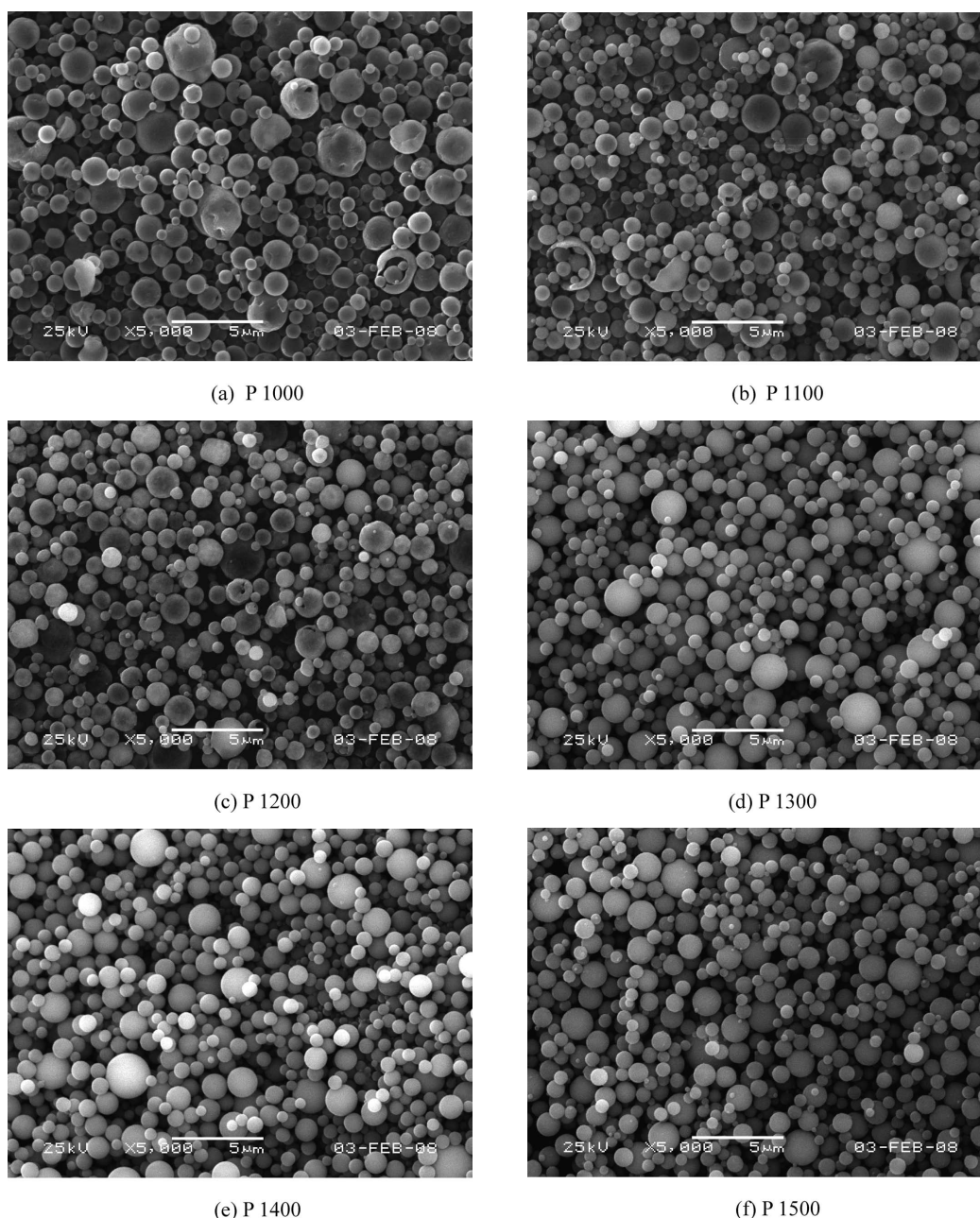


Fig. 3. SEM photographs of the powders prepared by spray pyrolysis at different temperatures.

duced into a hot reaction column, where the droplets were dried, decomposed, and melted. Rapid quenching of the melted glass outside of the reactor formed the glass powder. The flow rate of air used as a carrier gas was 10 L/min. The glass powders were added with a 5% polyvinyl alcohol (PVA) solution and pressed into disc-shaped compact with a 15 mm diameter using uniaxial press of 1000 kg force. The samples were then heat treated at 400°C for 2 h to eliminate the PVA, followed by sintering at temperatures between 700 and 1000°C for 2 h and cooled naturally to room temperature while furnace power was off.

The thermal properties of the prepared glass powders were studied using differential scanning calorimeter (DSC, Netzsch, STA409C, Germany). The morphologies of the glass powders and sintered pellets were investigated using scanning electron microscopy (SEM, JEOL, JSM-6060, Japan). The crystal structures of the powders were studied using X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu K α radiation ($\lambda = 1.5418 \times 10^{-10}$ m). The compositions of the glass powders were analyzed by using energy dispersive X-ray (EDX). Surface areas of the powders were measured by Brunauer–Emmett–Teller (BET) method using N₂ as adsorbate gas.

3. Results and discussion

The crystal structures of the powders prepared by spray pyrolysis at various temperatures were shown in Fig. 2. The powders prepared at temperatures of 1000 and 1200°C had XRD peaks of LiAl(SiO₃)₂ (JCPDS # 31-0706) as main crystal structure. However, the powders prepared at temperatures of 1300 and 1500°C had broad peaks between 20 and 30° in the XRD patterns. Therefore, glass material without crystal structure was formed at a preparation temperature of 1300°C by melting and quenching process.

Figure 3 shows the SEM photographs of the powders prepared at various temperatures. The residence time of the powders inside the hot wall reactor was changed from 0.46 to 0.33 s when the temperature of the reactor was changed from 1000 to 1500°C. The powders had spherical shapes and micron sizes irrespective of the preparation temperatures. Evaporation of powders did not occur even at a high temperature of 1500°C. Nano-sized glass powders were formed by chemical vapor deposition process if evaporation of some components of powders occurred.^{12,13} One powder was formed from one droplet. However, the mean sizes and inner structures of the powders were

affected by the preparation temperature. The mean sizes of the powders prepared at temperatures of 1000 and 1500°C were 0.95 and 0.72 μ m. The powders prepared at low temperatures below 1200°C had hollow morphologies. On the other hand, the powders prepared at temperatures above 1300°C had dense structures and fine sizes. In the XRD patterns as shown in Fig. 2, the glass materials were prepared at temperatures above 1300°C. Glass materials with amorphous phase were formed by melting and quenching process. Therefore, melting of the powders inside the hot wall reactor occurred at temperatures above 1300°C. Melting of the powders produced the glass powders with dense structures and fine sizes. Figure 4 shows the BET surface areas of the powders prepared at various temperatures. The BET surface areas of the powders decreased from 4.89 to 2.23 m²/g when the reactor temperature was changed from 1000 to 1300°C. Formation of glass phase by melting of the powders decreased the BET surface areas of the powders.

Figure 5 shows TG and DSC curves of LZAS glass powders prepared by spray pyrolysis at a preparation temperature of 1500°C. The glass transition temperature (T_g) of the glass powders was 551.2°C. The two crystallization exothermic peaks were observed at 703.8 and 923.8°C. The thermal properties of the glass powders prepared by spray pyrolysis were different with those of the powders prepared by conventional melting and quenching process.⁵ The total weight loss of the powders in the temperature range of 40–1000°C was 0.67%.

Figure 6 shows the SEM photographs of surfaces of the specimens sintered at various temperatures. The specimens were prepared from the glass powders obtained by spray pyrolysis at a temperature of 1500°C. Sintering between the powders started at a temperature of 700°C. On the other hand, the spherical morphology of the glass powders maintained at a sintering temperature of 700°C. Densifications of specimens occurred at sintering temperatures of 800 and 900°C, in which interconnected network microstructure were formed by tiny dendritic crystals. The shapes of crystals formed at sintering temperatures of 900 and 1000°C were different. Figure 7 shows the XRD patterns of the specimens sintered at various temperatures. The specimens sintered at temperatures of 600 and 700°C had XRD peaks of LiAl(SiO₃)₂ (JCPDS # 31-0706) as main crystal structure. On the other hand, the specimens sintered at temperatures between 800 and 1000°C had XRD peaks of LiAlSi₂O₆ (β -spodumene, JCPDS # 130251) as main crystal structure.

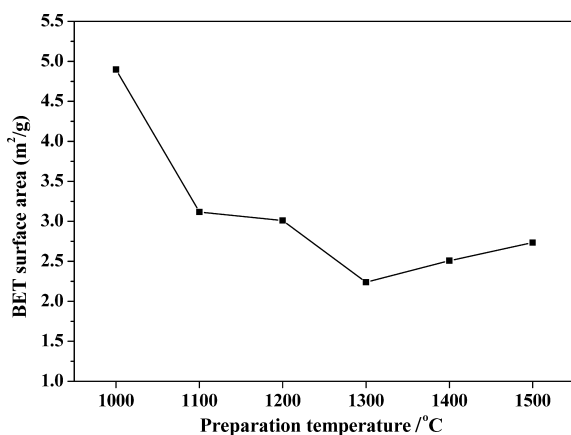


Fig. 4. BET surface areas of the powders prepared by spray pyrolysis at different temperatures.

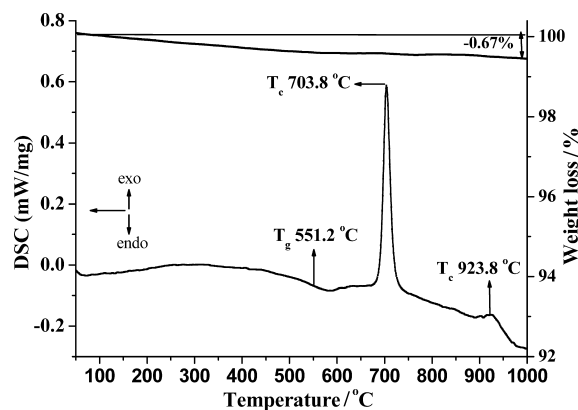


Fig. 5. TG/DSC curves of the glass powders prepared by spray pyrolysis.

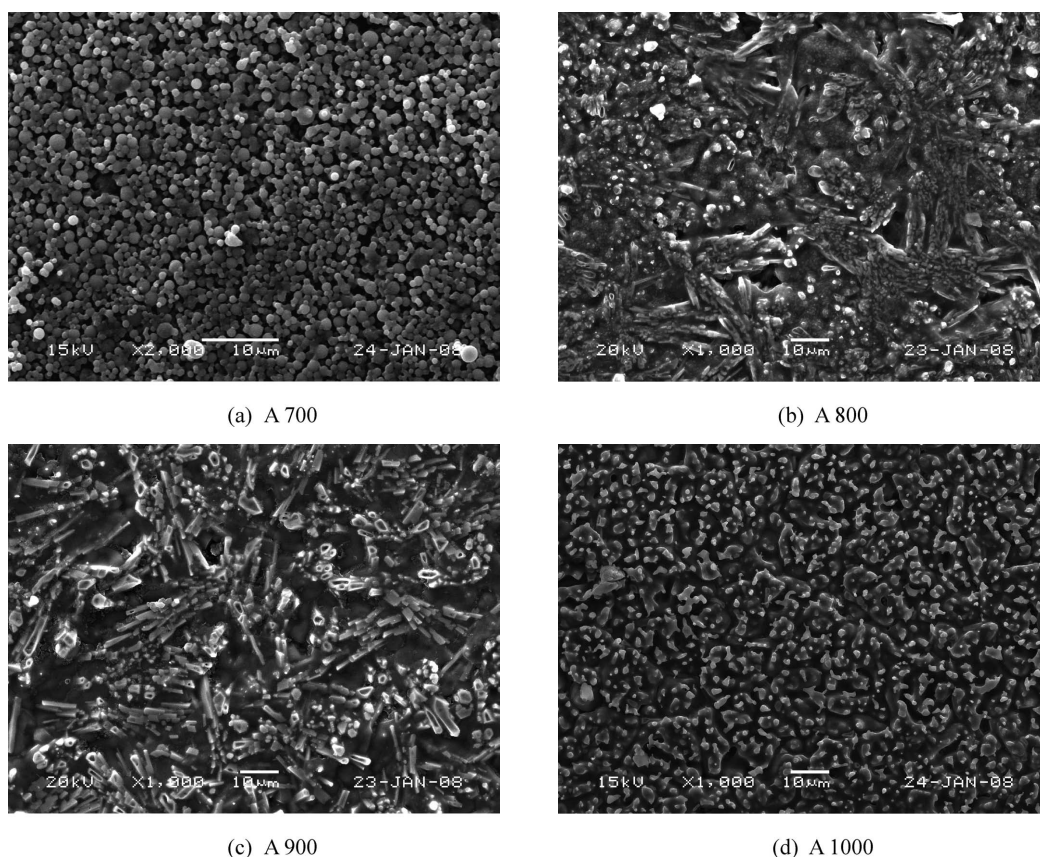


Fig. 6. SEM photographs of the specimens sintered at different temperatures.

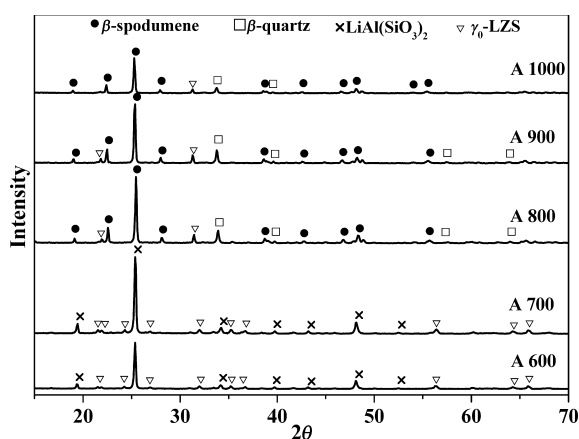


Fig. 7. XRD patterns of the specimens sintered at different temperatures.

4. Conclusion

Sintering characteristics of $\text{Li}_2\text{O}-\text{ZnO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (LZAS) glass powders prepared by high temperature spray pyrolysis were investigated. In the spray pyrolysis, the LZAS glass powders were directly prepared by melting and quenching process at preparation temperatures above 1300°C . One glass powder was formed from one droplet. Therefore, the mean size of LZAS glass powders could be controlled by changing the concentration of the spray solution. The crystallization behaviors of the prepared glass powders under controlled heating process were investigated from the microstructures and crystal structures of

the sintered specimens.

References

- 1) A. X. Lu, Z. B. Ke, Z. H. Xiao, X. F. Zhang and X. Y. Li, *J. Non-Cryst. Solids*, **353**, 2692–2697 (2007).
- 2) B. I. Sharma, M. Goswami, P. Sengupta, V. K. Shirkhande, G. B. Kale and G. P. Kothiyal, *Mater. Lett.*, **58**, 2423–2428 (2004).
- 3) E. Demirkesen, Z. E. Erkmen and N. Yildiz, *J. Am. Ceram. Soc.*, **82**[12], 3619–3621 (1999).
- 4) E. Demirkesen and E. Maytalan, *Ceram. Int.*, **27**, 99–104 (2001).
- 5) M. Goswami, P. Sengupta, K. Sharma, R. Kumar, V. K. Shirkhande, J. M. F. Ferreira and G. P. Kothiyal, *Ceram. Int.*, **33**, 863–867 (2007).
- 6) T. C. Pluym, T. T. Kodas, L. M. Wang and H. D. Glicksman, *J. Mater. Res.*, **10**, 1661–1673 (1995).
- 7) Y. C. Kang, I. W. Lenggoro, K. Okuyama and S. B. Park, *J. Electrochem. Soc.*, **146**, 1227–1230 (1999).
- 8) Y. C. Kang, H. S. Roh and S. B. Park, *Adv. Mater.*, **12**, 451–453 (2000).
- 9) G. L. Messing, S. C. Zhang and G. V. Jayanthi, *J. Am. Ceram. Soc.*, **76**, 2707–2726 (1993).
- 10) A. Gurav, T. Kodas, T. Pluym and Y. Xiong, *Aerosol Sci. & Tech.*, **19**, 411–452 (1993).
- 11) J. S. Cho, D. S. Jung, S. K. Hong and Y. C. Kang, *J. Ceram. Soc. Japan*, **116**[5], 600–604 (2008).
- 12) S. K. Hong, H. Y. Koo, D. S. Jung, I. S. Suh and Y. C. Kang, *J. Alloy. Compd.*, **437**, 215–219 (2007).
- 13) H. Y. Koo, S. K. Hong, I. S. Suh and Y. C. Kang, *Mater. Lett.*, **61**, 3669–3672 (2007).
- 14) J. S. Cho, S. K. Hong, D. S. Jung and Y. C. Kang, *J. Ceram. Soc. Japan*, **116**[2], 334–340 (2008).