The Study of Low Temperature Firing Glass-Ceramics Substrate in Lithium Fluorhectorite

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Abstract

The Li_2O-MgO-MgF_2-SiO_2 glasses with addition of B_2O_3 were investigated in order to make glass-ceramics for low temperature firing substrate. Glasses were made by melting at 1450℃ in the electronic furnace and crystallized at 750℃. After the crystallization, crystal phases and microstructure were observed. The crystal phases were polycrystalline of lithium boron fluorphlogopite and lithium fluorhectorite. The crystal shape was changed to granule type from needle type with the increase in B_2O_3 contents. Average particle size of the glass-ceramics after water swelling was 3.77㎛. The optimum sintering temperature and sintering shrinkage of the substrate were 900℃ and 13.4vol%, respectively.

1. Introduction

Recently, the ceramics for the electronics has been rapidly grown due to its high reliability and ceramics has taken an important position in the materials industry.[1-2] Many researchers are interested in the developments of new materials or components with good mechanical, electrical and complex properties.[3-4]

In this study, the Li_2O-MgO-MgF_2-SiO_2 glasses as the substrate were studied for the effects of the B_2O_3 to the crystal phase, water swelling, sintering, and etc.

2. Experimental Procedures

The composition of base glass is Li_2O 6.0, MgO 10.8, MgF_2 16.7, SiO_2 66.5 by wt% and B_2O_3 was added to base glass 2.5 to 10wt%. Chemical composition of base glass is shown in Table 1. The raw materials were mixed in V-mixer for 30min. and melted in platinum crucible at 1450℃

for 1hour. Optimum nucleation and crystallization temperature were obtained by using differential thermal analyzer(DTA).

Nucleation temperature was obtained by Marrotta method. The heat treatment carried out at 490℃ for 2 hours with rate of 10℃ /min, subsequently crystallization was treated at 750℃ for 3 hours with rate of 5℃/min.

Table 1. Chemical composition of base glasses (wt%)

	Li_2O	MgO	MgF_2	SiO_2	B_2O_3
LB-1	6.00	10.80	16.70	66.50	0
LB-2					2.50
LB-3					5.00
LB-4					7.50
LB-5					10.00

Microstructure developed in the sample was investigated by SEM(JEOL, JSM-5200). Glass-ceramics powder was prepared by water swelling with magnetic stirrer. The average particle size of the glass-ceramics was analyzed by PSA(FRITSCH, analysette 22).

Composition of the glass-ceramics powder and organic additives to prepare slurry is shown in Table 2. Added polymers, were ethanol and toluene as a solvent and menhaden fish Oil[5] was used as a dispersion. Poly vinyl butyral and di-n-butyl phthalate were used as binder and plasticizer, respectively.[6-7]

The appropriate ratio of solvent : powder was 65 : 35 for the tape casting.

Table 2. Composition of casting slurry (wt%)

Powder	35
Ethanol / Toluene	25.5 / 25.5
Fish Oil (dispersant)	1.5
PVB (binder)	6
DBP (plasticizer)	6.5

Green sheet was prepared by doctor blade method. The blade height to process tapes was about 600㎛ with casting speed of 10cm/min. Green sheet was dried for 24, 48, 72 hours and their sizes were measured to study the shrinkage behavior.

To find out optimum sintering temperature of Glass-ceramics, substrate were sintered at 800, 900, and 1000℃. The microstructure in the sample were examined by SEM.

3. Results and Discussion

3.1 Thermal property of base glass

Transition temp.(T_g), softening temp. (M_g) and thermal expansion coefficient(α) of the glass samples are plotted as a function of the amount of added B_2O_3 in Fig. 1.

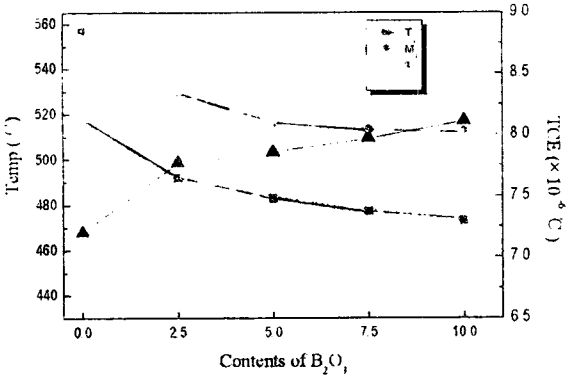


Fig. 1 The value of T_g, M_g and α in various composition

As B_2O_3 was added, transition temp. and softening temp. showed decreased gradually. On the contrary, thermal expansion coefficient was increased.

3.2 XRD patterns of glass-ceramics

Glass-ceramics was grinded to powder after heat treatment to investigate crystal phase. XRD patterns are shown in Fig. 2.

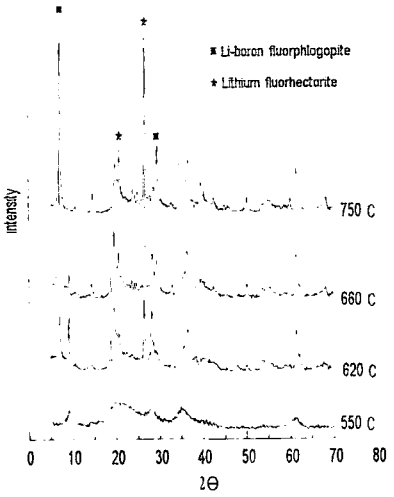
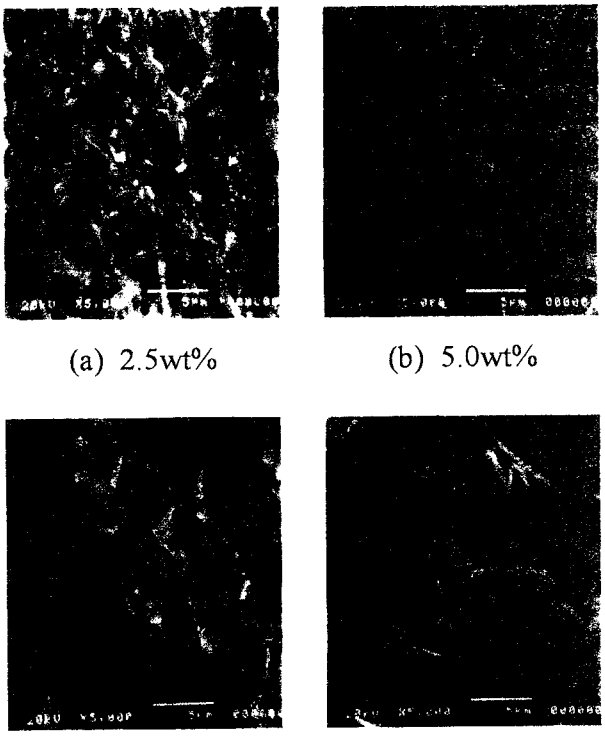


Fig. 2 XRD patterns of glass-ceramics crystallized at different temperatures

The crystal phases were polycrystalline of lithium boron fluorphlogopite and lithium fluorhectorite. The fraction of lithium fluorhectorite crystals increases as the heat-treatment temperature is elevated.

3.3 Microstructure of glass-ceramics

With the increase in the amount of B_2O_3 addition from 0 to 10.0wt%, surface crystal habit was changed needle type into granule type due to the increase of lithium boron fluorphlogopite crystal. The crystal shape surface is shown in Fig. 3.



(a) 2.5wt% (b) 5.0wt%

(c) 7.5wt% (d) 10.0wt%

Fig. 3. SEM photographs of glass-ceramics containing B_2O_3

3.4 Drying and sintering shrinkage of green sheet

Drying shrinkage rate is shown in Fig. 4. Linear shrinkage rate was increased with the increase in drying time. Sintering shrinkage rate is shown in Fig. 5.

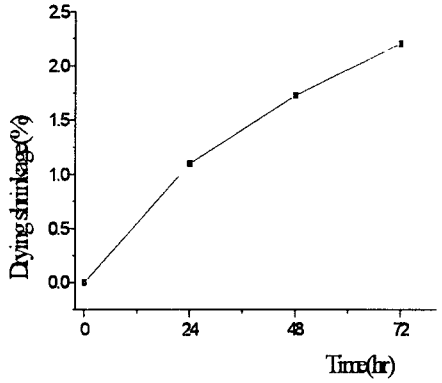


Fig.4. Drying shrinkage of green sheet at various time

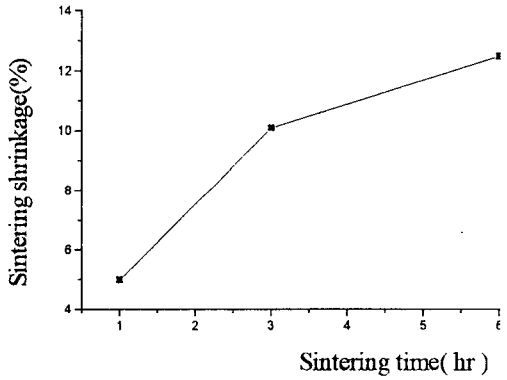
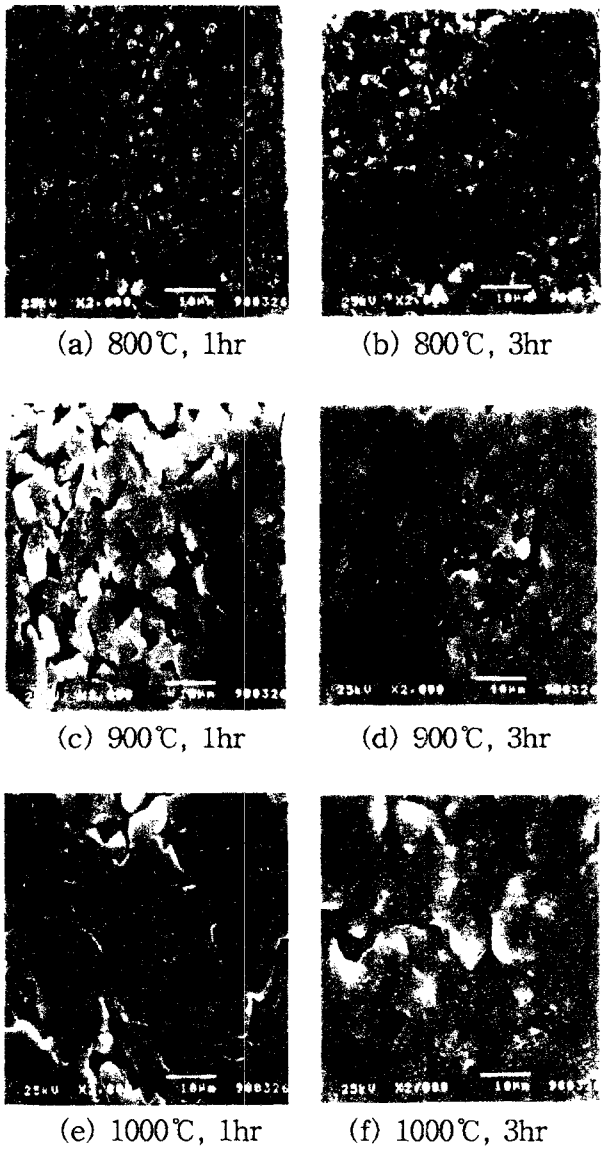


Fig. 5 Sintering shrinkage of green sheet followed by time

3.5 Microstructure of substrate

Green sheet was sintered at 800℃~1000℃ for 1hr~3hr to improve sintering properties. The microstructures in the heat-treated green sheet is shown in Fig.6.

The sintered face at 800℃ was shown and sintering at 900℃ was increased relatively. At 1000℃, the most of porosity disappeared, which means the sintering worked effectively.



(a) 800℃, 1hr (b) 800℃, 3hr

(c) 900℃, 1hr (d) 900℃, 3hr

(e) 1000℃, 1hr (f) 1000℃, 3hr

Fig.6. SEM photographs of glass ceramics

4. Conclusion

1. Main crystal phases in the glass-ceramics was lithium fluorhectorite and lithium boron fluorphlogopite phase.

2. With the increase of the amount of B_2O_3 addition from 0 to 10.0wt%, transition temp. decreased from 518℃ to 473℃ and softening temp. decreased from 557℃ to 512℃. Thermal expansion coefficient increased from 7.2×10^{-6}/℃ to 8.11×10^{-6}/℃.

3. The crystal shape was changed needle type into granule type with the addition of B_2O_3 and the property of water swelling was reduced. The average particle size of glass ceramics after water swelling was 3.77㎛.

4. Optimum sintering temperature and holding time were 900℃ and 3hours, respectively.

5. References

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