Journal of the Microelectronics & Packaging Society
Vol. 6, No. 3, p.35-39, 1999.

The Fabrication of Low Temperature Firing Substrate of Li_2O-MgO-MgF_2-SiO_2-B_2O_3 system

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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℃. The crystal phases were polycrystalline of lithium boron fluorphlogopite and lithium fluorhectorite. The crystal shape was changed to granule type from needle type with increasing B_2O_3 content. 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 13.4%, respectively.

1. Introduction

Recently, the ceramics for the electronics has been rapidly grown due to their high reliability and ceramics have 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, 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 weight% and B_2O_3 was added to base glass 2.5 to 10 weight%.(Table 1.) The raw materials were mixed in a V-mixer for 30min. and melted in a platinum crucible at 1450℃ for 1hour in an electronic furnace. Optimum nucleation temperature was obtained by Marrotta method[5]. The heat treatment carried out at 490℃ for 2 hours with rate of 1 0℃/min, subsequently crystallization was treated at 750℃ for 3 hours with rate of 5℃/min.

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

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

Composition of the slurry for tape casting is shown in Table 2. Added polymers, were ethanol and toluene as solvent and menhaden fish Oil[6] was used as a dispersion agent. Polyvinyl butyral and di-n-butyl phthalate were used as a binder and a plasticizer, respectively.[7-8] The appropriate ratio of solvent : powder was 65 : 35 for the tape casting.

Table 2. Composition of casting slurry (weight%)

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 for processing tapes was about 600㎛ with casting speed of 10cm/min. Green sheet was dried for 24, 48, 72 hours at 120℃ in dry oven and their drying shrinkages were measured. To find out optimum sintering temperature of glass-ceramics, the substrate were sintered at 800, 900, 1000℃ and then microstructure of the sample were examined by SEM.

3. Results and Discussion

Transition temperature(T_g), softening temperature (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.

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

Powder X-ray diffraction method was used after heat treatment to investigate crystal phase. XRD patterns are shown in Fig. 2. The crystal phases were polycrystalline of lithium boron fluorphlogopite and lithium fluorhectorite. The

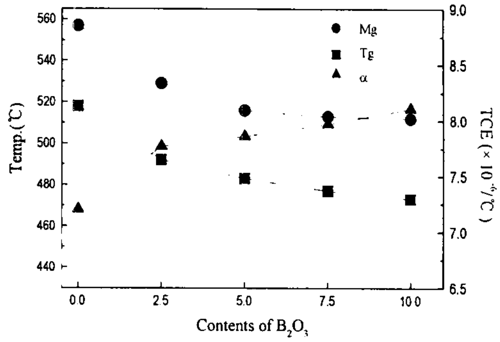


Fig. 1. The value of T_g, M_g and α in various composition

fraction of lithium fluorhectorite crystals increase as the heat-treatment temperature was elevated.

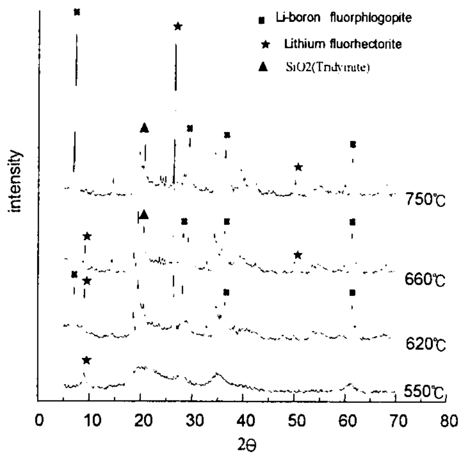
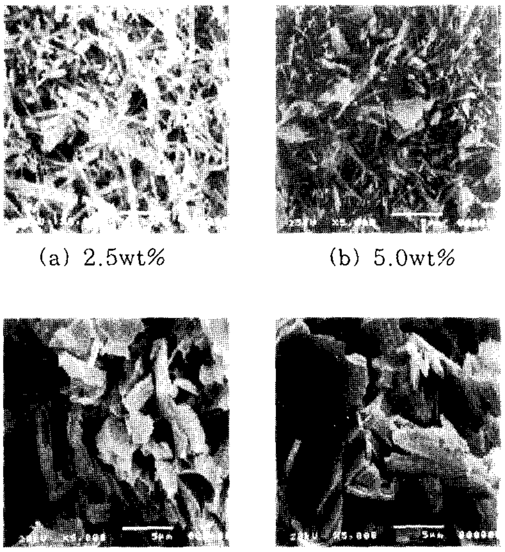


Fig. 2. XRD patterns of glass-ceramics crystallized at different temperatures

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

Powderization of the prepared glass-ceramics and necessary was conducted by water swelling. At this point of the procedure, the char-



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

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

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

acteristic of swelling was deteriorated as increasing of B_2O_3 added for decrease of firing temperature.[Fig. 4] The particle size of the glass-ceramics measured by PSA is shown in Fig. 5. The average particle size after water swelling was 3.77㎛.

Drying shrinkage rate is shown in Fig. 6. Linear shrinkage rate was increased

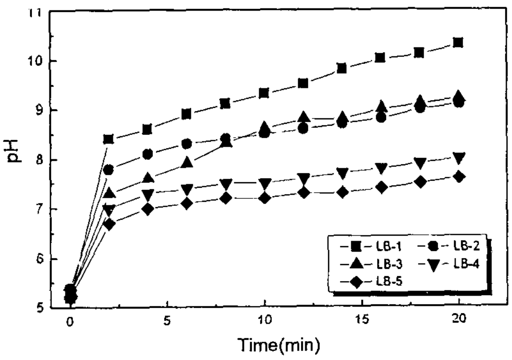


Fig. 4. Alkalinity of each glass-ceramics under magnetic stirrer condition

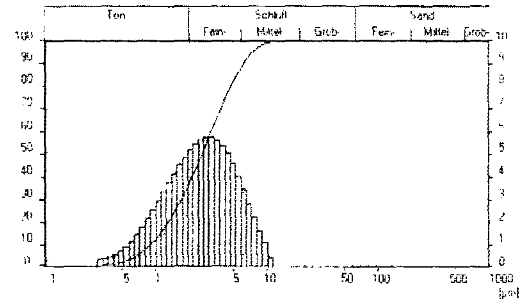


Fig. 5. Particle size distribution of glass-ceramic powder after water swelling (LB-2)

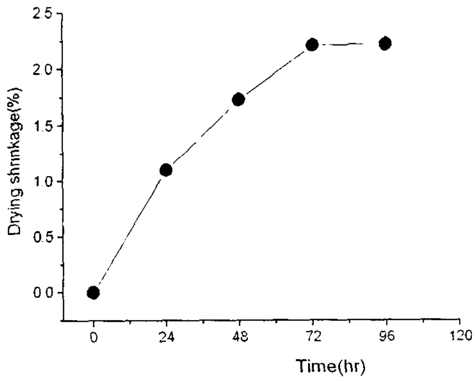


Fig. 6. Drying shrinkage of green sheet at various time

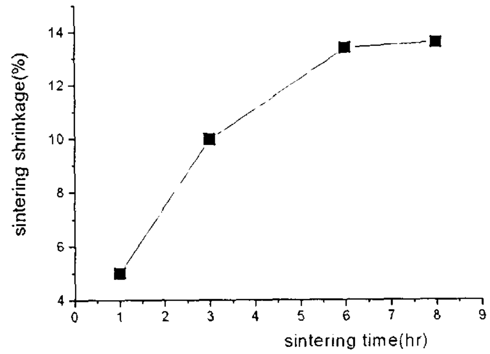
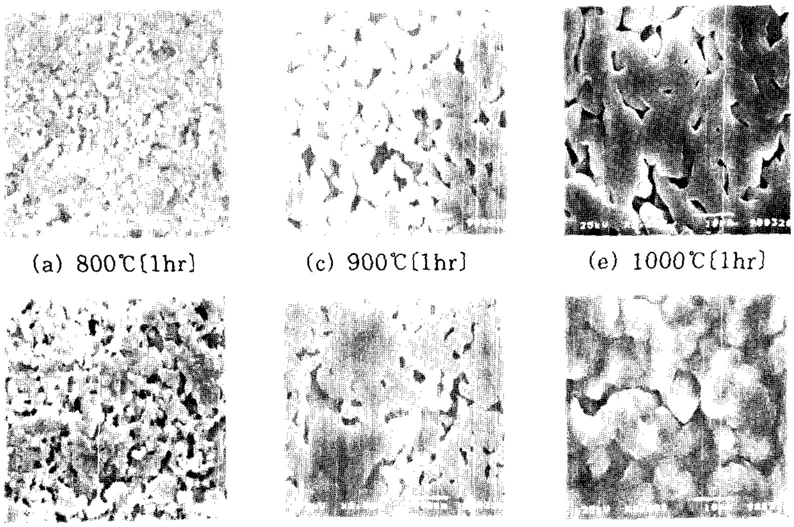


Fig. 7. Sintering shrinkage of green sheet followed by time(at 900℃)

with the increase in drying time. Sintering shrinkage rate is shown in



(a) 800℃(1hr) (c) 900℃(1hr) (e) 1000℃(1hr)

(b) 800℃(3hr) (d) 900℃(3hr) (f) 1000℃(3hr)

Fig. 8. SEM photographs of glass ceramics

Fig. 7. Linear shrinkage of sintering was 13.4% at 900℃ for 6hours.

Green sheet was sintered at 800℃~1000℃ for 1hr~3hr to find adequate sintering conditions. The microstructures of sintered sheet is shown in Fig. 8. The sample at 800℃ showed poor sinter with lots of pores. But sintered at 900℃ for 3hours and at 1000℃ for 1hour were shown well sintered surface in Fig. 8(c)(d)(e). At 1000℃ for 3hours, the sheet began to melt and demolished shape.

4. Conclusion

1. Main crystal phases in the glass-ceramics was lithium fluorhectorite and lithium boron fluorphlogopite phase and the crystal shape was changed needle type of lithium fluorhectorite into granule type of lithium boron fluorphlogopite with the addition of B_2O_3.

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

3. The rate of water swelling was reduced according to the B_2O_3 contents. 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.

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