

## Effect of Al<sub>2</sub>O<sub>3</sub> filler addition on sintering behavior of low-firing BaO-B<sub>2</sub>O<sub>3</sub>-ZnO glass ceramic system

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### Abstract

The sintering behavior of BaO-B<sub>2</sub>O<sub>3</sub>-ZnO, which is Pb-free glass-ceramic system, was examined as functions of the composition and the amount and particle size of Al<sub>2</sub>O<sub>3</sub> filler. Different kinds of modifiers were added and Al<sub>2</sub>O<sub>3</sub> fillers with different particle sizes (1.5 μm and 4.5 μm) were added. The glass frit-filler composites were sintered in the temperature range 520~580 °C. X-ray diffraction results revealed that some of the composites crystallized during sintering. Dielectric constant and thermal expansion coefficient the glass-ceramics were analyzed.

### 1. Introduction

As the society enters rapidly to the information-oriented society, the need of various display devices increases for an effective information distribution. The expectation of plasma display panel (PDP) as the proper display device for the need has been increased. Barrier rib material in PDP device is made up of glass frit-ceramic composites, and PbO glass system has been popular which is sinterable at low temperature. However, recent nature protection issues restrict the wide use of PbO system, so the development of materials, which can replace the PbO system, is urgent. BaO-B<sub>2</sub>O<sub>3</sub>-ZnO system which is Pb-free was reported as the appropriate material of low temperature sintering.[1]

Required characteristics for barrier rib material are low sintering temperature below 600 °C, dielectric constant below 15 and its thermal expansion coefficient is 7~9×10<sup>-6</sup>/°C which is

almost the same with that of the glass substrate.[2-3] The PDP barrier rib is a composite of glass frit and filler, and Al<sub>2</sub>O<sub>3</sub> is mainly used as its filler. Barrier rib materials have different characteristics according to the kinds of fillers added. Densification of this composite occurs by viscous sintering mechanism.[4] The densification rate depends on the viscosity of glass, and the viscosity depends on the composition of glass and kinds of fillers added in the glass.[5] Particularly this relative viscosity depends on the amount and particle size of fillers.[6-9]

In this study, BaO-B<sub>2</sub>O<sub>3</sub>-ZnO glass-ceramic system is investigated for the application to PDP barrier rib. This system is a glass-ceramic that crystallizes during sintering. Generally glass-ceramic has high mechanical strength and low thermal expansion coefficient. Crystallization during sintering results in the softening temperature of glass frit high, which prevents deformation of barrier rib during re-heating.[10] The object of this study was to determine the effect of glass frit composition and particle size of Al<sub>2</sub>O<sub>3</sub> filler on densification behavior of the glass-ceramic.

### 2. Experimental procedure

High purity raw materials of BaCO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub> and ZnO were melted for 1 h at 1200 °C after mixing. The molten glass was quenched on a steel plate. The glass frit was ball-milled with zirconia ball. The mean particle size of the glass frit was 1.4 μm. The softening and crystallization temperatures of the frit were measured by using

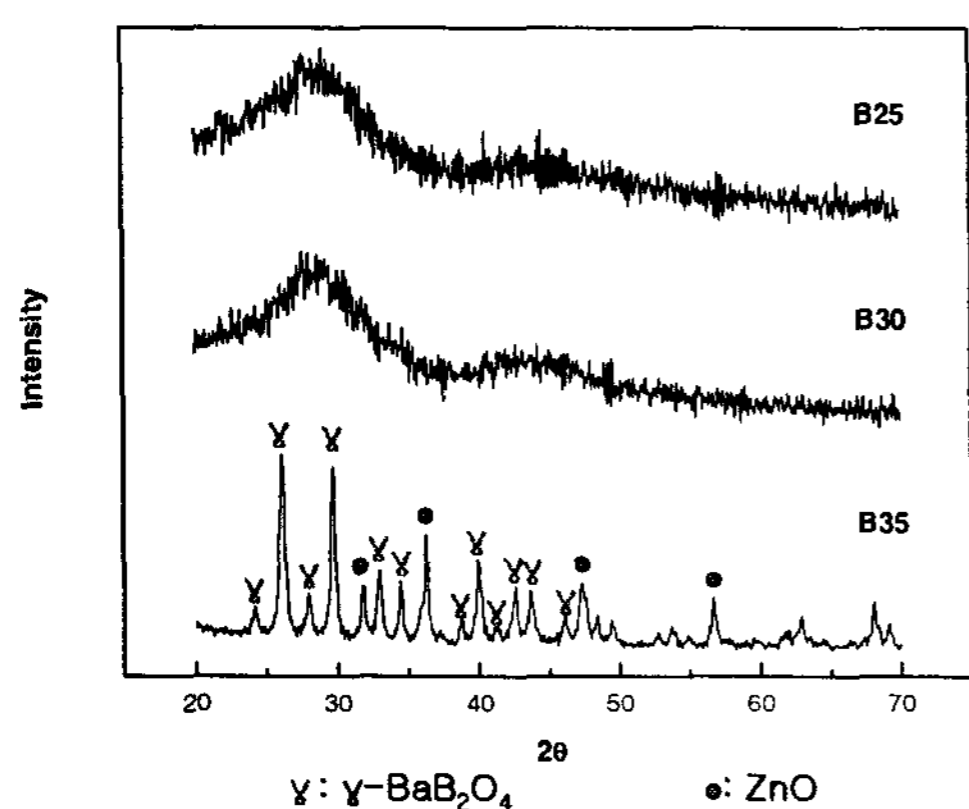
Differential Scanning Calorimetry. Composites of the glass frit and  $\text{Al}_2\text{O}_3$  with different particle sizes of  $4.5\mu\text{m}$  and  $1.5\mu\text{m}$  were prepared, then pressed under the pressure of 100MPa in order to form pellets. The pellets were sintered at 520-580°C for 1 h. The density of pellet was measured by the Archimedes method. Microstructure, phase development and thermal expansion coefficient of pellets were examined.

### 3. Result and discussion

Table 1 shows the compositions of glass frit by changing the amounts of BaO and ZnO with the fixed amount of 40mol%  $\text{B}_2\text{O}_3$ .

**Table 1 Compositions of BaO- $\text{B}_2\text{O}_3$ -ZnO glass ceramic and state of those after quenching (mol%)**

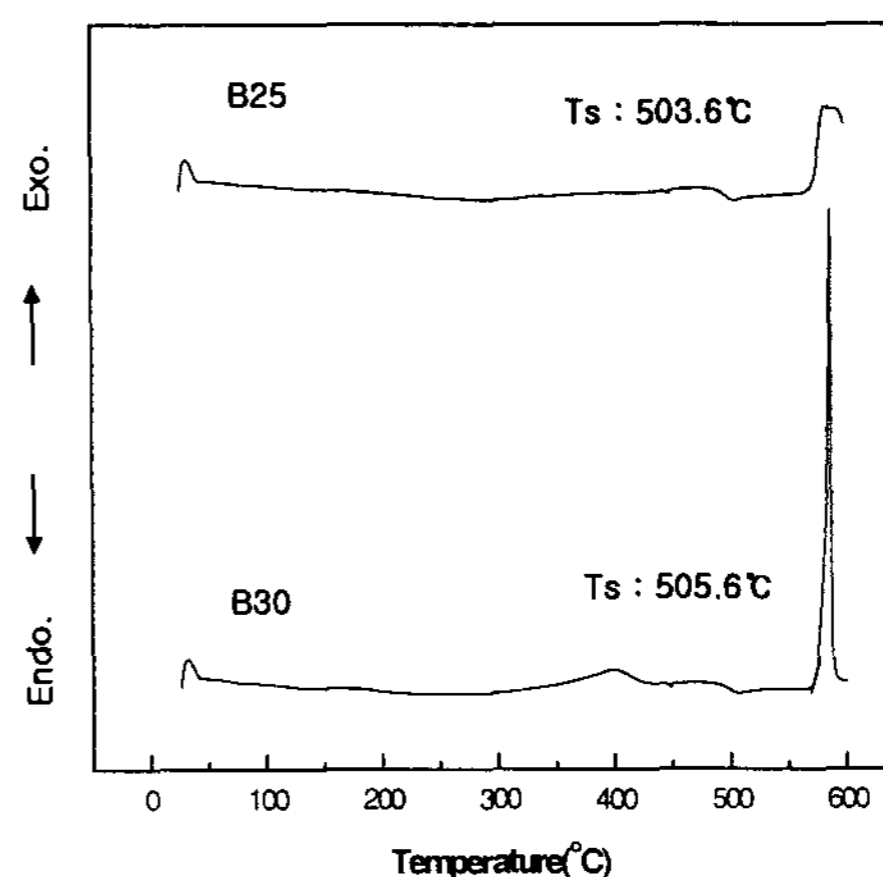
	BaO	$\text{B}_2\text{O}_3$	ZnO	State
<b>B25</b>	25	40	35	Glassy
<b>B30</b>	30	40	30	Glassy
<b>B35</b>	35	40	25	Crystallized



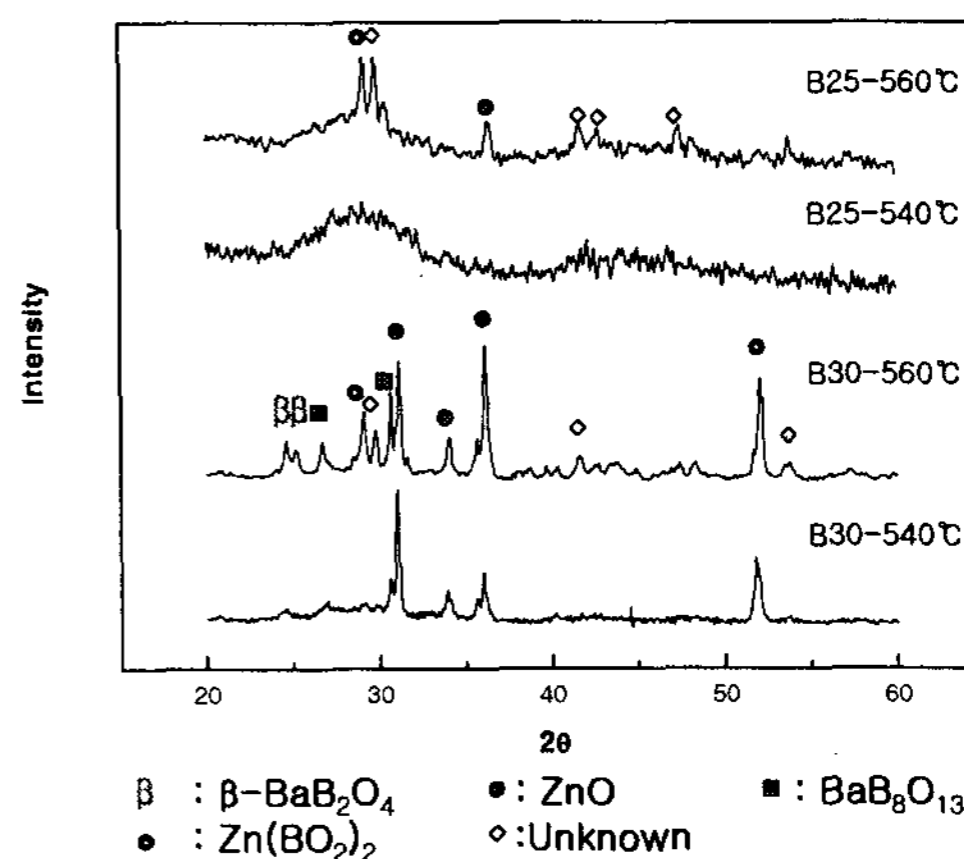
**Fig. 1 XRD result of B25, B30 and B35 powder after quenching**

Fig. 1 shows the X-ray diffraction results of the compositions in Table 1 after melting and quenching. B25 and B30 were in glass state after quenching. However, in case of B35, diffraction peaks were shown which implies that B35 has crystallized after quenching. The phases, which were produced after quenching of B35, are  $\gamma$ - $\text{BaB}_2\text{O}_4$  and ZnO. Fig. 2 is DSC analysis results of B25 and B30 which are in glass state. DSC of B25

shows one exothermic peak at 560°C that explains the crystallization phenomena at that temperature. In case of B30, two exothermic peaks at 400°C and 560°C were observed. The softening temperature ( $T_s$ ) of B25 and B30 is 504°C and 506°C, respectively. The  $T_s$  of B25 is lower than that of B30.



**Fig. 2 TG-DTA result of B25 and B30**

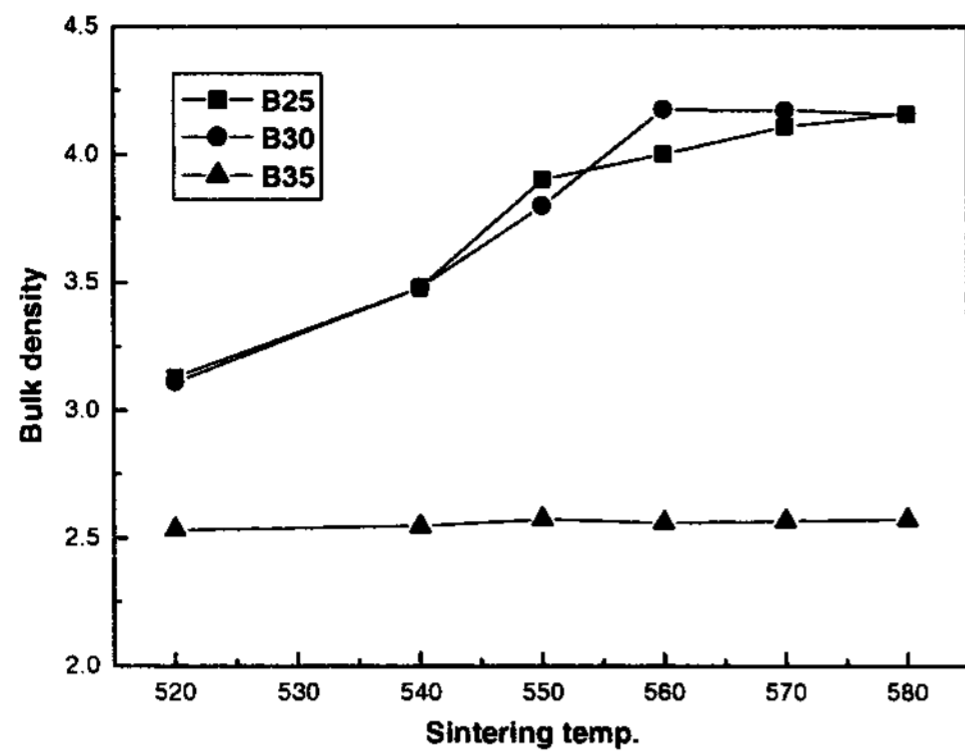


**Fig. 3 XRD result of B25 and B30 after sintering**

Fig. 3 shows the XRD result of B25 and B30 after sintering. In case of B25, it was in the amorphous state when it was sintered at 540°C and crystallized to  $\text{Zn}(\text{BO}_2)_2$ , ZnO and unknown phases at 560°C. In case of B30 crystallization already initiated when sintered at 540°C. The crystallized phases were ZnO and  $\text{Zn}(\text{BO}_2)_2$  and those phases seem to crystallized from 400°C since the DSC result revealed an exothermic reaction peak at 400°C which corresponds to the

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crystallization of the phases. Another exothermic peak was shown near 560 °C, which corresponds to the crystallization of  $\beta$ -BaB<sub>2</sub>O<sub>4</sub> and BaB<sub>3</sub>O<sub>18</sub> phases as observed in XRD result in Fig. 3.

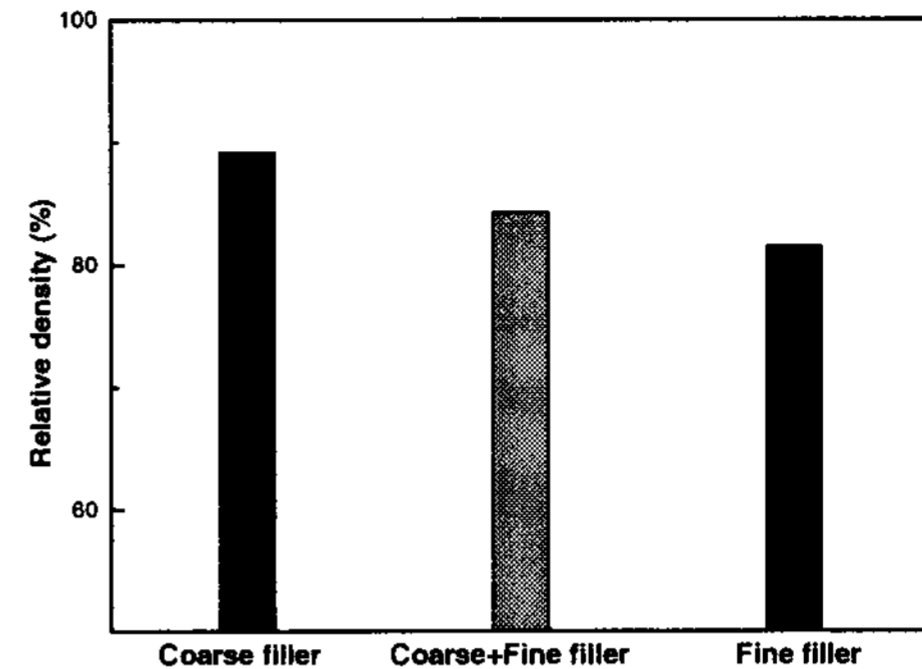


**Fig. 4 Bulk densities of B25, B30 and B35 after sintering at various temperatures**

Fig. 4 shows the bulk density of B25, B30 and B35 after sintering. We can see the softening temperature of B30 is higher than that of B25. But the densification of B30 proceeded at lower temperature than B25. The density of B25 continuously increased up to 580 °C and seemed still did not reach to the maximum density. It is because the crystallization retarded densification. While in case of B30, even though the crystallization has also proceeded at 560 °C, the maximum density was achieved at 560 °C then the density decreased slowly at higher temperatures. It is thought due to the composition change of glass frit as the crystallization proceeds. Density decreasing above 560 °C is thought to be the expansion of closed pores. In case of B35, no densification was proceeded in the temperature range sintered.

B30 composition was selected as the glass frit because B30 revealed low sintering temperature. Fig. 5 shows the relative density of B30 glass frit-Al<sub>2</sub>O<sub>3</sub> filler composite sintered at 560 °C. Coarse and fine fillers with particle sizes of 4.5 μm and 1.5 μm were used and the amount of the filler was fixed to 20 vol%. When the filler is mixed with the glass frit, three different mixtures are prepared, that is, coarse filler only, fine filler only, and

coarse plus fine filler with a ratio of 1:1 were added to the glass frit. According to Eiler's relative viscosity model [11] for concentrated suspensions, the relative viscosity is higher as the amount of filler in composite is increased, and the relative viscosity depends on the physical properties of the filler.



**Fig. 5 Relative density of B30 with 20 vol.% of Al<sub>2</sub>O<sub>3</sub> filler after sintering at 560 °C**

It is known that the densification is faster when the viscosity is low.[12] The relative density of B30 without filler was 94.8% after sintering at 560 °C. When 20 vol% of filler was added the relative densities of the composites with coarse, fine and coarse plus fine filler were 89.2%, 81.5%, and 84.3%, respectively. This relative density represents the smaller particle size of filler results in lower relative density.

**Table 2 Dielectric constant and thermal expansion coefficient of B30 added Al<sub>2</sub>O<sub>3</sub> 20vol% after sintering at 560 °C**

Vol.% / Filler	Filler		
	Coarse	Coarse + Fine	Fine
Dielectric constant	10	9	9
Thermal expansion coeff. (×10 <sup>-6</sup> /°C)	7.2	7.5	8.0

Table 2 shows the dielectric constant and thermal expansion coefficient of the sintered composites. The dielectric constant of Al<sub>2</sub>O<sub>3</sub> is

11~12, and that of B30 after sintering at 560°C is 10. The dielectric constant of the composites was thought to be in between the dielectric constants of Al<sub>2</sub>O<sub>3</sub> and B30. However, the dielectric constant of the composites containing fine fillers revealed low dielectric constant of 9. It is believed due to pores in the sintered body of which the relative density was low.

The thermal expansion coefficient of Al<sub>2</sub>O<sub>3</sub> is 6.5×10/°C and that of B30 is 9.4×10/°C. The composite that has higher density showed lower thermal expansion coefficient. Generally, pores in the sample leads to low thermal expansion coefficient. But our results were not agreed with the general trend. It is believed to be cause by the densification during thermal expansion coefficient measurement process. When the measurement is proceeded, the sintered sample experiences heat treatment which provides driving force of the densification.

#### 4. Conclusion

1) Although the amount of modifier was the same, crystallization of the glass frit was easier when the amount of BaO increased.

2) The crystallized glass frit after quenching was hardly densified, and the densification of the frit in glass state proceeded slowly as the sintering temperature increased.

3) The composite with coarse filler showed higher relative density due to the lower relative viscosity.

4) The composite with higher relative density showed higher dielectric constant but lower thermal expansion coefficient.

#### 5. Acknowledgement

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