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Characterization of Sodium Borosilicate Glasses Containing Fluorides and Properties of Sintered Composites with Alumina

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Recently, alumina/glass composites have been applied as a substrate material for hybrid IC and LSI multi-chip packaging. In this study, the characterization of sodium borosilicate glasses containing NaF and AlF_3 and the preparation of the resulted glass/alumina composites have been examined and the effects of the addition of fluorides on the thermal and dielectric properties of the sintered composites have been studied. The sintering temperature of specimens was lowered by about 100-150°C by the addition of fluorine compared with the specimens without fluorine. The specimens containing fluorine showed slightly lower dielectric constants than those of the specimens without fluorine.

Key words : Fluorides, Sodium borosilicate glass, Alumina, Sintering temperature, Dielectric constant.

I. Introduction

Substrate material using glass/ceramic composites[1-5] has been studied because it can be sintered at low temperature and its properties can be modified to suit the operating device environment.[6-10] However, few systematic researches for improving its properties by changing the base glass composition have been studied. This study was based on the theory[11-15] that "fluoride addition is effective in lowering the dielectric constant".

In this study, the possibility of using glasses containing NaF and AlF_3 as the starting material for low-sintering-temperature substrates is examined from the viewpoints of the loss characeristics of each fluoride for heat-treatment, the effects of the addition of fluorides on the structural characteristics of the glasses, and the thermal and dielectric properties of the sintered composites.

The glass/alumina sintered composite was prepared from sodium borosilicate glass powder containing fluorides such as AlF_3 and NaF and Al_2O_3 powder. The effects of additives on the properties have been mainly examined in the later part of this paper.

II. Experimental Procedure

1. Preparation of glass and glass/alumina sintered composites

α-alumina powder (particle size ; below 5 mm) with purity of over 99.7% and sodium borosilicate glass powder containing fluoride (NaF, AlF_3) were used as starting materials. The compositions of base glass used in this study, and F/Si and Na/Si for each glass composition are also listed in Table. 1.

NaF was added by substituting the equal molar amount of Na_2O in a glass while an extra amount of AlF_3 was added 5-10% to a base glass with a prescribed composition. Each glass batch was melted by heating in a upright type electric furnace at 1200°C for 1hr under nitrogen gas flow (200 cc/min). Thin flakes were obtained by quenching the melt with a twin roller, and they were crushed into fine powder under 10 μm. A sintered specimen without fluoride was prepared, and its properties such, as dielectric constant and sintering temperature were compared to those for fluoride-added specimens. Both powders were mixed at a weight ratio of 1:1, pressed into the shape of pellets of 20 mm in diameter and approximately 1.5 mm thick with a pressure of 450 $Kgcm^{-2}$. In order to obtain the glass/alumina sintered composities, the specimens were heat treated at 5°C/min for 1hr at temperatures ranging from 600°C to 900°C in air or nitrogen atmosphere.

2. Measurements

In order to measure the sintering temperature of sintered bodies, apparent and bulk density of the sintered bodies[16,17] were examined. In this study, we defined sintering temperature as the temperature that the apparent density agrees with the bulk density, that is to say, open pores become extinct. Crystalline phases were identified by X-ray diffractometry using Ni filtered Cu Kα radiation. Thermal expansion rate and dielectric constant were investigated as typical properties. Rectangular bars (5×10~15×1.5 mm) cut from disk-like sintered bodies were subject to thermal expansion measurement. Au electrodes (10 mm in diameter) were attached to each face of pellets, and C was measured at 1 MHz by an LF impedance analyzer (4129 A, Hewlett-parkard Ltd), and the dielectric constants were calculated from C using ε=

$(C \times d)/(\varepsilon_0 \times S)$ equation.[15]

Residual fluorine was analyzed for the glasses and the glass/alumina sintered bodies in which four kinds of glass compositions (Sample No.1,2,3,7) were selected from those showed in Table 1. Quantitative analysis was conducted by EPMA (Shimadzu Co. EPMA-870 Q). The acceleration voltage was 20 kV, and the holding time for each spot was 5 min. The X-ray intensity was corrected by the ZAF1 method.[19,20] BaF_2 was used as a standard material in this measurement.

III. Results

1. *Composition of glass and properties of glass/alumina sintered composites*

Eleven types of glass compositions were used in the present study. Seven were added with NaF by substituting the Na_2O. The other four were added with an extra amount of AlF_3, up to 5 or 10 wt%. The resultant glass /alumina sintered bodies could be classified as to whether or not they precipitated nepheline (Na_2O-Al_2O_3-$2SiO_2$), which can be ascribed to the composition of the raw material (Fig. 1). The properties of glass and glass/alumina sintered bodies were listed in Table 2 and 3. With respect to dielectric constant and thermal expansion coefficient, relative values are normalized by the alumina values. In accordance with this result, the change of glass composition is one of the effective factor on the crystalline phase formation during heat-treatment and the change in dielectric and thermal properties of the composites.

Table 1. Classification of Sodium Borosilicate Glasses Containing Fluorides

	Sample No.	Glass Composition SiO_2:	B_2O_3:	Na_2O:	Na_2F_2	AlF_3	F/Si(Na/Si)	
*1	No.1	60	30	5	5	-	0.17(0.33)	*3
	No.2	70	15	7.5	7.5	-	0.21(0.43)	*4
	No.3	60	20	10	10	-	0.33(0.67)	*4
	No.4	50	30	10	10	-	0.40(0.80)	*4
	No.5	60	15	12.5	12.5	-	0.42(0.83)	*5
	No.6	60	10	15	15	-	0.50(1.00)	*5
	No.7	40	40	10	10	-	0.50(1.00)	*4
*2	No.8	60	30	10	-	5	0.25(0.33)	
	No.9	60	30	10	-	10	0.50(0.33)	
	No.10	40	40	20	-	5	0.38(1.00)	
	No.11	40	40	20	-	10	0.75(1.00)	

*1 : NaF added compositions
*2 : AIF3 added compositions
*3 : The compositions on the minimum curver of thermal expansion coefficient
*4 : The compositions on the minimum curver of chemical duability and Tf
*5 : The compsitions are unrelated *3 and *4

2. *Quantitative analysis of fluorine*

It is expected that the fluorine was evaporated during glass melting and sintering process. The amount of fluorine in the glass and glass/alumina sintered body was analyzed by EPMA measurement. In order to control the evaporation loss of fluorine, all the glass containing fluoride were prepared in nitrogen atmosphere.

On the other hand, the effect of preparation of atmosphere on the residual fluorine was investigated using sintered composites prepared in both air and nitrogen gas. The specific value (the ratio of F to Si in mole%), the amount of residual fluorine which obtained by EPMA measurement, is shown in Figs. 2 and 3. According to this result, the loss in fluorine could be controlled to a certain extent by the sintering atmosphere.

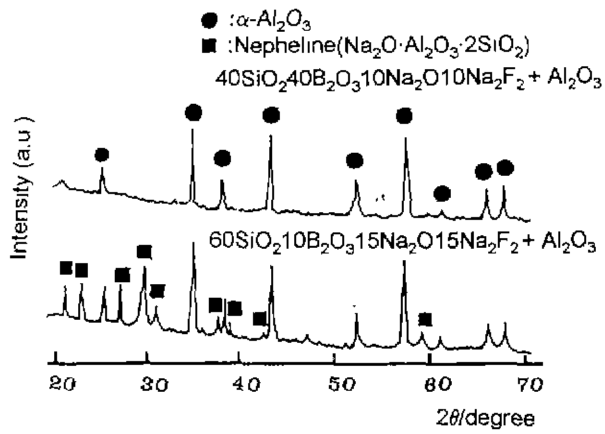

Fig. 1. XRD patterns of the sodium borosilicate glasses/Alumina sintered composites containing NaF.

Table 2. Properties of Sodium Borosilicate Glasses/Al_2O_3(1:1) Sintered Composites Containing NaF

Glass Compositions SiO_2	B_2O_3	Na_2O	Na_2F_2	Crystallines	Sintering temp. (°C)*1	Relative Density(%)	V/V_0 *2	ε *3	α *4
60	30	5	5	None	750	82.0	11.2	0.54	0.83
40	40	10	10	None	600	88.6	14.6	0.41	1.13
60	10	15	15	Nepheline	700	83 2	7.3	0.62	0.91
60	15	12.5	12.5	Nepheline	700	81 7	9.3	0.84	0.84

*1 · The temperature when apparent density and bulk density are equalized
*2 · Shrinkage
*3, *4 · Calculated from Al_2O_3=1

Table 3. Properties of Sodium Borosilicate Glasses/Al_2O_3(1:1) Sintered Composites Containing NaF_3

Glass Compositions				Crystallines	Sintering temp. (°C)*1	Relative Density(%)	V/V_0*2	ε*3	α*4
SiO_2	B_2O_3	Na_2O	Na_2F_2						
60	30	10	5	None	750	87.6	25.5	0.75	1.02
60	30	10	10	None	650	87.4	31.1	0.74	1.02
40	40	20	5	None	600	89.7	29.4	0.94	1.28
40	40	20	10	None	600	84.5	40.6	0.69	1.21

*1 : The temperature when apparent density and bulk density are equalized
*2 : Shrinkage
*3, *4 : Calculated from Al_2O_3=1

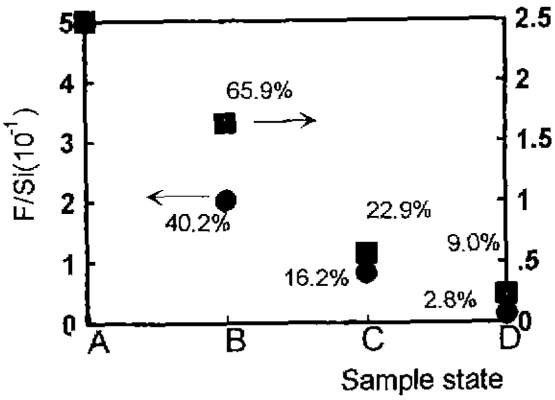

Fig. 2. The quantitative analysis of the residual fluorine after heat-treatment for sintered composites containing NaF.
□ : $40SiO_240B_2O_310Na_2O10Na_2F_2$
○ : $70SiO_215B_2O_37.5na_2O7.5Na_2F_2$
A : Raw materials, B : Glass
C : Glass/Al_2O_3(in N_2), D : Glass/Al_2O_3 (in Air)

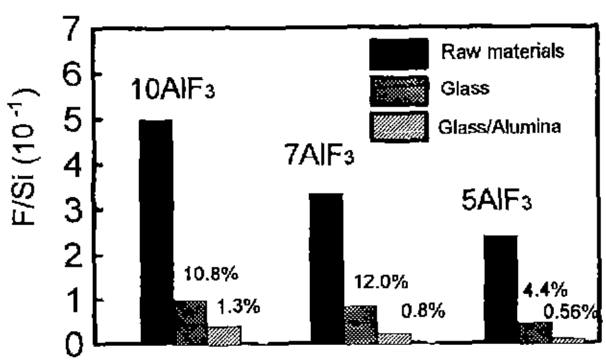

Fig. 3. The quantitative analysis of the residual fluorine after the heat-treatment for glasses and glass ($60SiO_230B_2O_310Na_2O$)/Alumina sintered composites containing AlF_3.

IV. Discussion

1. Change in crystal phase and thermal expansion rate depending on the glass composition (B/Na and Na/Si ratio)

(1) Segregation of crystalline phase depending on the glass composition

From the results of XRD analysis, glass composition is divided into two types, with and without nepheline segregation depending on the B/Na ratio.

1) Glass composition without nepheline crystal

Only α-Al_2O_3 was seen in XRD profile when the amount of B_2O_3 was larger than Na_2O at glass composition (B/Na ≥ 1). This can be ascribed to the softening (Softening point ; approximately 520-600°C) of glass instead of crystallization.

2) Glass composition with nepheline crystal

Nepheline phase was formed in composite when the amount of B_2O_3 was less than that of Na_2O (B/Na < 1). The reaction between glass component (SiO_2, Na_2O) and Al_2O_3 particle was thought to bring about nepheline crystal.

(2) Change in thermal expansion rate depending on the glass composition

In B/Na ≥ 1 composition range, the thermal expansion rate substantially changes according to Na/Si ratio or the amount of alkaline. For example, the thermal expansion rate (1.13) of the composite using No.7 glass (Na/Si=1.0) is larger than that (0.83) of the composite using No.1 glass. This can be ascribed to the increase in ionic bond rather than covalent bond in the glass according to the addition of alkaline modifier.

In B/Na < 1 composition range, nepheline phase increased with a increase in Na_2O amount in the glass phase. Similar to the composition range in which no nepheline phase appears, as described before, the thermal expansion rate was dependent on glass composition (Na/Si). In other words, the thermal expansion rate (0.91) of the composite using No.6 glass (Na/Si=1.0) was larger than that (0.84) using No.5 glass.

2. Change in properties depending on F/Si in glass

(1) The evaporation of fluorine

Quantitative analysis on the glass/alumina sintered bodies was conducted by EPMA. The results were as follows. The residual fluorine in the sintered body treated in nitrogen atmosphere was 3 or 5 times as large as that treated in air. The residual amount of fluorine also depended on the types of additive fluorine (NaF, AlF_3). The fluorine loss of AlF_3-added samples was expected to be lowered than that of samples with NaF, because the vapor pressure of the latter is higher than that of the former (the later 1 mmHg at 1177°C, the former 1 mmHg at 1238°C). The residual rate of fluorine in NaF-added composite sintered body was approximately 10 times larger than that added with AlF_3 (before sintering the former was over 4 times larger than the latter). These results can not be explained by the difference in vapor pressure between AlF_3 and NaF.

Another explanation on these results can be made as follows. A glass component ion (Al^{3+}) increases when added AlF_3, while a glass modifier ion (Na^+) increases when doped with NaF. This is the most substantial difference between AlF_3-added glass and NaF-added glass. In NaF-added glass, the cation (Na^+) introduced by NaF would promote the formation of terminal oxygen as well as ionic bond. The anion (F^-) apart from the cation (Na^+) would connect with Si forming the glass network, which would result in a more stable glass network. In AlF_3-added sample, the doped cation (Al^{3+}) substitute the network Si^{4+}. The resultant Si^{4+} connected with the anion ($3F^-$) derived from AlF_3, forming SiF_4 with high vapor pressure (-144.0°C). This result can be explained by the evaporation of SiF_4. This explanation on the loss mechanism of fluorine from glass structure is summarized in Fig. 4 and this is also thought to interpret the anomalous residual fluorine by EPMA to some extent.

(2) Properties of samples with different types of fluorine

Based on the quantitative analysis of fluorine, the effect of fluoride addition on the properties of sintered composite was examined. The sintering temperature can be lowered by 100-150°C with NaF addition. Fig. 5 shows the comparison in sintering temperature of composites with or without NaF. Fig. 6 illustrates the difference in dielectric constant between samples with or without NaF. On the whole, the dielectric constant of fluorine containing samples was lower than that of non-added samples. This can be ascribed to residual fluorine or an increase in porosity due to the evaporation of predicts reacted with the glass component such as SiF_4. The results are shown in Fig. 7. Fig. 7 illustrates the changes in dielectric constant and density of No.1 glass/alumina sintered composites with sintering temperature. Sintered body became dense when heated at around 700°C at which the dielectric constant also exhibited a high value. A further increase in heating temperature

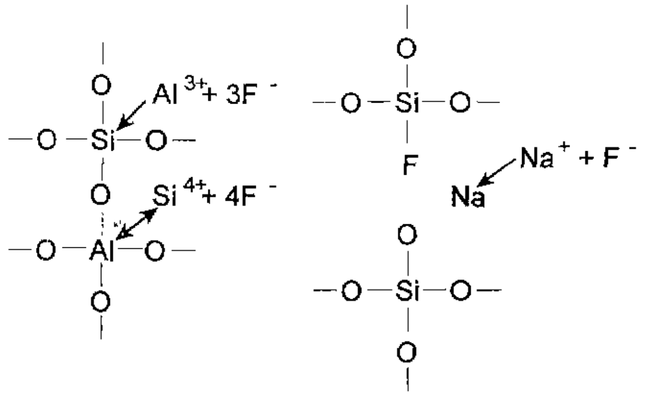

Fig. 4. Assumptive explanation on the loss mechanism of each fluorine from glass inter structure.

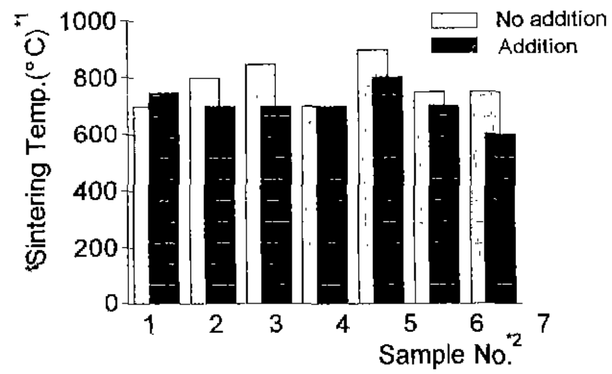

Fig. 5. Comparison in sintering temperature of sodium borosilicate glasses/alumina composites with or without NaF.
*1 : The temp. when apparent density and bulk density are equalized
*2 : See Fig. 1

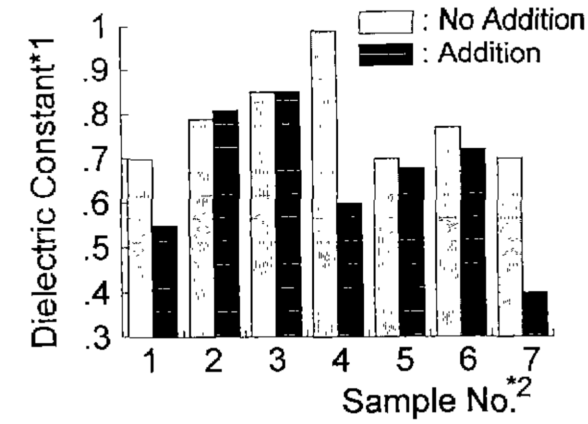

Fig. 6. Comparison in dielectric constant of sodium borosilicate glasses/Al_2O_3 composites with or without NaF.
*1 : Normalized to Al_2O_3(=1)
*2 : See Fig. 1

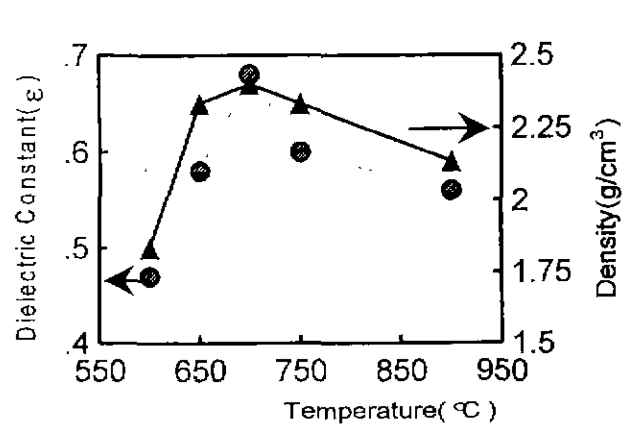

Fig. 7. The changes of dielectric constant and density of NaF containing No 1 containing No. 1 glass/alumina sintered composites with heat treatment temperature.

lead to a decrease in dielectric constant. This trend almost corresponded to the change in density. Accordingly, the dielectric constant is thought to be dependent on the pores existing in the sintered body.

The difference in dielectric constant depending on dopants NaF or AlF_3 will be discussed. For example, the dielectric constants obtained for composite sintered bodies using No.6 glass (F/Si=0.50) and No.9 glass (F/Si=0.50) were 0.62 and 0.74, respectively. Accordingly, this discrepancy in dielectric constant in spite of the same F/Si ratio in glass can be ascribed to the difference in residual fluorine (approximately 20% in the former, 1% in the latter). As described in section 4-2, the amount of residual fluorine is different between NaF added system and AlF_3 added system. That is, the NaF added system containing considerable amount of fluorine exhibited lower dielectric constant. In other words, the dielectric constant in the present system can be controlled by changing the fluorine amount in sintered bodies.

V. Summary

Glass/ceramics sintered composites were fabricated using alumina and sodium borosilicate glass containing fluoride. The results are as follows.

1) Glass composition such as B_2O_3 or Na_2O substantially affect the nepheline segregation and properties. When the amount of Na_2O was larger than that of B_2O_3 (B/Na) in glass, nepheline was formed from the glass composite (Na_2O, NaF or SiO_2) and Al_2O_3. The thermal expansion rate increased with Na/Si ratio.

2) The amount of residual fluorine was larger in the sample prepared in a nitrogen atmosphere than that in air. The types of fluoride in the starting material also affected the residual amount. Although the F- from NaF connected to the Si in the glass network, resulting in a stable glass structure, the F- from AlF_3 reacted with Si^{4+} substituted by Al^{3+}. The resultant SiF_4 was lost by evaporation.

3) The sintering temperature of specimens was lowered by about 100-150°C by the addition of fluorine compared with the specimens without fluorine. The specimens containing fluorine showed slightly lower dielectric constants than those of the specimens without fluorine. This can be ascribed to the increase in porosity due to the evaporation of SiF_4 formed between fluorine and glass component.

References

1. Rao R. Tummala "Ceramics and glass-ceramic packging in the 1990s,' *J. Am. Ceram. Soc.*, **74**, 895-908 (1991).
2. Y. Shimada, K. Utsumi and M. Suzuki, IEEE Transactions on Components, Hybrids and manufacturing technology, CHMT-6, [4], 382-88 (1986).
3. B. Ryu and I. Yasui, "Thermal and dielectrical properties of silica/glass composites with the controlled amount of tridymite," *J. Ceramic Soc. Jpn.*, **101**, 579-582 (1993).
4. David G. Wirth "Ceramic Substrates," Engineered materials handbook - Ceramics and glasses, The materials information society.
5. B. Kim and K. Lee, "Synthesis and characterization of cordierite glass-ceramics for low firing temperature substrate," Proc. 9th Korea-Japan Seminar on New Ceramics, 183-187 (1992).
6. B. Ryu and I. Yasui, "The crystallization behaviour of two types of glasses based on anorthiew composition $CaO-Al_2O_3-2SiO_2$," Proc. 4th Int. Sympo. on the Nucleation and Crystallization in Liquids and Glasses, Am. Cerm. Soc. (1992).
7. B. Ryu. and I. Yasui, Proc. 9th Korea-Japan Seminar on New Ceramics "Investigation of $CaO-Al_2O_3-2SiO_2$ glass as substrate materials," 155-159 (1992).
8. Y. Shimada, Y. Yamashita et al, "Low dielectric constant multilayer glass-ceramic substrate with Ag-Pd wiring for VLSI package," 37th ECC, May (1987).
9. L. M. Sheppard, Aluminium Nitride; "A versatile but challenging material," *Cerm. Bull.*, **69**[11], 1801 (1990).
10. R, R, Tummala, Microelectronics Packaging Handbook, Van Norstrand Reinhold, (1989).
11. I. Yasui, "Optical materials-amorphous and single crystal," Dai Nippon Tosho, 113-117 (1991).
12. A. G. Clare and J. M. Parker, "The effect of refractive index modifies on the thermal expansion coefficient of fluoride glasses," *Physics and Chemistry of Glasses*, **30**[6], 205-210 (1989).
13. G. M. Singer and M. Tomozawa, "Cordierite-based oxyfluoride glasses and glass ceramics, Part 1 Glasses," *Physics and Chemistry of Glasses*, **30**[3], June 86-95 (1989).
14. G. M. Singer and M. Tomozawa, "Cordierite-based oxyfluoride glasses and glass ceramics, Part 2 Glass ceramics," *Physics and Chemistry of Glasses*, **30**[3], June 95-102 (1989).
15. G. M. Singer and M. Tomozawa, "Cordierite-based oxyfluoride glasses and glass ceramics, Part 3 crystallization of the glasses," *Physics and Chemistry of Glasses*, **30**[3], June 102-109 (1989).
16. Y. Muzutani, et al, "Experiment of materials science," U-CHIDA ROGAKUHO 137-139 (1987).
17. I. Yasui, et al, "Characterization technics of ceramics," Japan Ceramics Society, 2-5 (1986).
18. D. G. Holloway "The phycal properties of glass," Wykeham Publication Ltd, 66-68 (1976).
19. Y. Gouji and K. Sato, "Enerry dispersion type X-ray analysis," Gakkai Shuppan Ctr., 110-114 (1989).
20. I. Uchiyama, T. Watanabe and S. Kimoto, "X-ray micro analyzer" Nikkan Kougyou, 110-172 (1977).