*Journal of Ceramic Processing Research. Vol. 9, No. 2, pp. 97~99 (2008)*

J O U R N A L O F
**Ceramic Processing Research**

# Microwave dielectric properties of lead borosilicate glass-$Al_2O_3$ composites

**Sang Ok Yoon[a], Kwan Soo Kim[a], Sang Heung Shim[b], Yun Han Kim[a] and Shin Kim[a,*]**
[a]*Department of Ceramic Engineering, Kangung National University, Kangnung 210-702, Korea*
[b]*Department of Electrical Engineering, Kangwon National University, Samcheok 245-711, Korea*

**A lead borosilicate (PBS) glass-$Al_2O_3$ composite was prepared and its microwave dielectric properties were investigated. Although the anorthite-type phase was observed above 800°C, this phase might have crystallized from the PBS glass because the PBS glass originally contained the constituents of the anorthite phase and a one-stage sintering behavior was conducted. The densification behavior was suggested to occur through a non-reactive liquid phase sintering. The dielectric constant ($\varepsilon_r$), the quality factor ($Q\times f_0$), and the temperature coefficient of the resonant frequency ($\tau_f$) of the 50 vol% PBS glass-$Al_2O_3$ composite sintered at 900°C were 9.26, 4 941 GHz, and −38 ppm/K, respectively.**

**Keywords: LTCC, Glass-Ceramic, $Al_2O_3$, Lead borosilicate, Composite.**

## Introduction

A number of studies of low temperature co-fired ceramics (LTCC) have been intensively investigated. There are two basic methods to prepare an LTCC [1, 2]. The first is to use crystallizable glasses as starting materials which undergo devitrification to crystalline phases during the firing process. Ideally no glass phases, hence, exist in the final microstructure. The properties of crystallizable glasses depend on the degree of crystallization, i.e., the thermal history. Cordierite-based glass, showing a low dielectric constant and good mechanical properties including strength and thermal expansion coefficient (TEC), is a material typical of crystallizable glasses [3]. The second method is to use a mixture of low melting temperature glasses working as a flux agent and ceramics as the filler. The final structure is composed of ceramic particles in a glass matrix, i.e. glass-ceramics. Generally, borosilicate glasses are used as flux materials due to their capability of glass formation at low temperature and good dielectric properties [4].

To diminish signal propagation delay, LTCC materials for the substrate are required to have a low dielectric constant [5]. Typical commercial LTCC materials have a low dielectric constant in a range of 4.7~9.7 which is similar to that of alumina (~9) [1]. The aim of this study is to prepare glass-$Al_2O_3$ ceramic composites with a low dielectric constant and a high quality factor using $Al_2O_3$ as filler and lead borosilicate glass as a flux agent and to investigate its microwave dielectric properties.

*Corresponding author:
Tel : +82-33-640-2900
Fax: +82-33-640-2244
E-mail: shinkim@kangnung.ac.kr

## Experimental Procedure

Powders of PbO, CaO, $SiO_2$, $B_2O_3$, and $Al_2O_3$ of extra-pure reagent grade were weighed in the weight percentage of 40, 5, 45, 5, and 5, respectively and well mixed in a dry condition. Lead borosilicate (PBS) glass was prepared by a quenching method after a melting process above 1400°C using an alumina crucible. The deformation temperature of the PBS glass was measured by a dilatometer (DIL 402, Netzsch). By disk milling and ball milling using zirconia balls in a wet condition, a glass frit was obtained. To prepare the glass-ceramic system, 10~50 vol% PBS glass frit and $Al_2O_3$ (purity 99.9% and average particle size 3 μm) were ball milled for 24 h and then dried. The disk type samples 15mm in diameter were prepared by pressing of powder mixtures under ca. 14 MPa and sintering at between 600 and 950°C for 2 h. The density based on Archimedes' method was measured. The phase analysis of the sintered glass-ceramics was carried out by an X-ray diffractometer (MO3XHF, Mac science) using a Cu-Kα target and a Ni filter within a 2θ range of between 10~80. The microstructures were observed by a FE-SEM (S-4200, Hitachi). Using a network analyzer (HP8720ES), the dielectric constant ($\varepsilon_r$) and the quality factor ($Q\times f_0$) were measured by the Hakki-Coleman method with disk-type samples which were placed between two parallel metal plates; the resonant frequency $f_0$, the half power bandwidth $\Delta f_{3dB}$, which was recorded at 3dB level of the resonant peak, and the insertion loss were measured [6]. The temperature coefficient of the resonant frequency ($\tau_f$) was measured using an Invar cavity in the temperature range of 25~85°C.

## Results and Discussion

The deformation temperature of PBS glass, i.e., the temperature at the maximum peak of the thermal expansion curve, was determined as 627°C. The dielectric constant ($\varepsilon_r$), the quality factor ($Q \times f_0$), and the temperature coefficient of the resonant frequency ($\tau_f$) of the PBS glass were 6.89, 1 123 GHz (90 at 12.490 GHz), and −23.9 ppm/K, respectively.

The linear shrinkage of the PBS glass-$Al_2O_3$ system containing 20~50 vol% glass as a function of sintering temperature is shown in Fig. 1. A large shrinkage above 15% was only observed in the composition of 50 vol% glass whereas the other compositions showed a relatively low shrinkage. When the sintering was conducted at 900°C, a porous microstructure was observed up to 40 vol% glass composition and a dense one was obtained in the composition of 50 vol% PBS glass as shown in Fig. 2. It is understandable that the necessary glass content in this system is at least 50 vol% for the densification. The glass content of nearly all commercial LTCC composites is, indeed, greater than 50 vol%, mostly between 63% and 85% [7]. Further investigation in this study was, hence, focused on this composition. The relative density of the 50 vol% PBS glass-$Al_2O_3$ composite showed an increase as the sintering temperature increased and then a plateau above 800°C as shown in Fig. 3; this behavior was in accord with the results of the linear shrinkage.

Figure 4 shows powder X-ray diffraction (XRD) patterns of the 50 vol% PBS glass-$Al_2O_3$ composite sintered between 700 and 900°C. $Al_2O_3$ was the only crystalline phase at 700°C and the anorthite-type phase was formed above 800°C. The formation temperature of the anorthite-type phase is in accord with the work of Lo et al. that it was detected at temperatures higher than 800°C [8]. The anorthite ($M^{2+}O \cdot Al_2O_3 \cdot 2SiO_2$) based glass-ceramic system has been intensively studied because it showed a relatively low dielectric constant

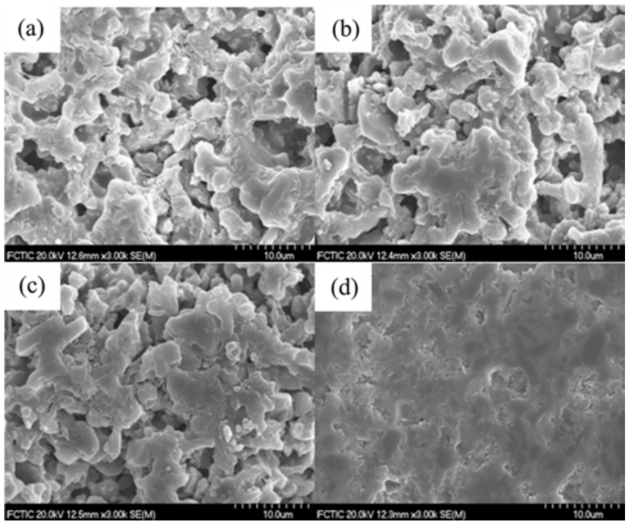


**Fig. 2.** Microstructures of the PBS glass-$Al_2O_3$ system sintered at (a) 700°C, (b) 800°C, and (c) 900°C.

(~9.1) and a high quality factor in a range of 1000~ 1200 at 0.5 GHz [9]. The T2000 tape dielectric of Motorola is well known as a specific commercial material for anorthite and it includes a specially-formulated $B_2O_3$-$K_2O$-$SiO_2$-CaO-SrO-BaO glass (TG glass), $Al_2O_3$ as a ceramic filler, and $TiO_2$ as a $\tau_f$ adjustment agent. On the other hand, it was suggested that anorthite crystallized from the PBS glass because the PBS glass originally contained the constituents of anorthite such as $Pb^{2+}$, $Ca^{2+}$, $Al^{3+}$, and $Si^{4+}$. This suggestion is supported by the one-stage sintering behavior for 50 vol% PBS glass-$Al_2O_3$ composite as shown in Fig. 2 as well as the low intensity of the diffraction peaks for the anorthite-phase as shown in Fig. 4. The densification, therefore, might occur through a non-reactive liquid phase sintering (NLPS) process which is a type of liquid-assisted sintering (LAS) [7]. LAS distinguishes between the NLPS, where a glass phase content of at least 20-40 vol% is necessary for the

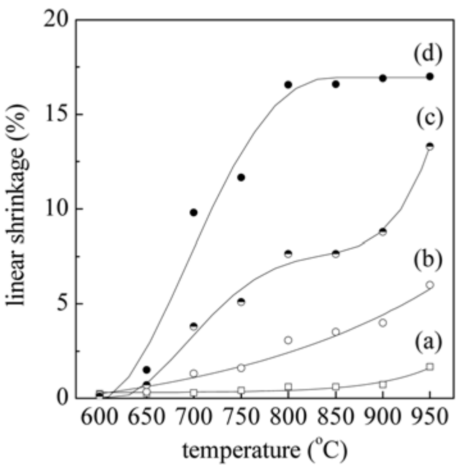


**Fig. 1.** Linear shrinkage of the PBS glass-$Al_2O_3$ system as a function of temperature.

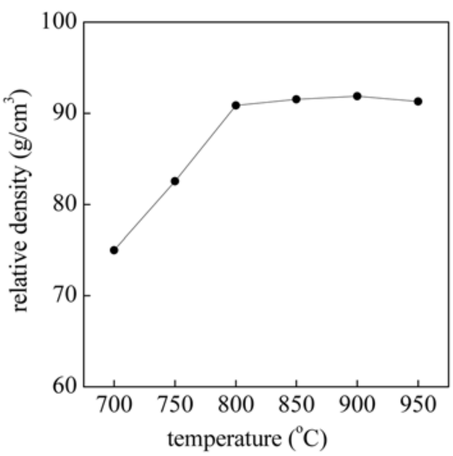


**Fig. 3.** Relative density of the 50 vol% PBS glass-$Al_2O_3$ composite as a function of sintering temperature.

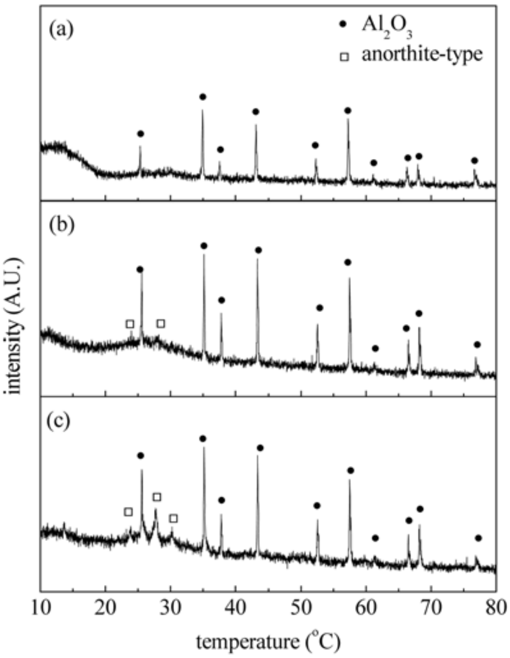


**Fig. 4.** Powder XRD patterns of the 50 vol% PBS glass-$Al_2O_3$ composite sintered at (a) 700°C, (b) 800°C, and (c) 900°C.

densification and a reactive liquid phase sintering, where a glass content <20 vol% is sufficient [7]. The densification in the NLPS was proposed to occur in three stages; the first stage is glass redistribution and local grain rearrangement where only slight densification occurs, the second is the main densification process including global rearrangement, glass redistribution, and closure of pores where a density from 65 to 90% of the theoretical density is accomplished, and the third is viscous flow where the residual porosity of about 10% is closed.

As shown in Fig. 5, the dielectric constant ($\varepsilon_r$) and the quality factor ($Q \times f_0$) of the 50 vol% PBS glass-$Al_2O_3$ composite gently increased as the sintering temperature increased from 3.89 to 9.26 and from 1460 to 4941 GHz, respectively, indicating that these were mainly affected by the porosity. The temperature coefficient of the resonant frequency ($\tau_f$) of the specimen sintered at 900°C was −38 ppm/K. It could be concluded that the application of the PBS glass-$Al_2O_3$ system to substrates may be shown to be appropriate after an improvement in $\tau_f$.

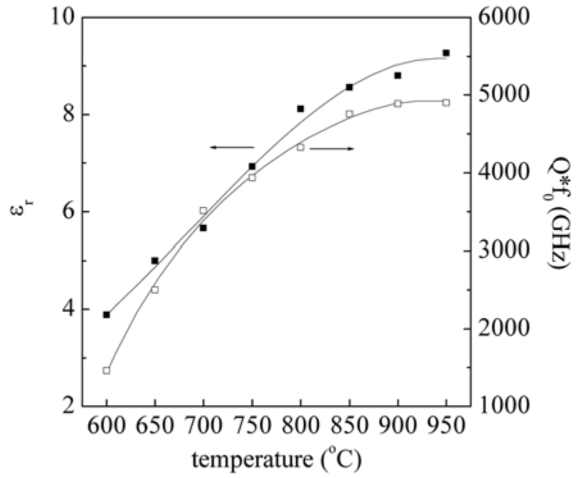


**Fig. 5.** Dielectric constant and quality factor of the 50 vol% PBS glass-$Al_2O_3$ composite as a function of sintering temperature.

## Summary

A lead borosilicate (PBS) glass-$Al_2O_3$ composite was prepared and its microwave dielectric properties were investigated. The deformation temperature of the PBS glass was 627 and the 50 vol% PBS glass-$Al_2O_3$ composite only showed a dense microstructure. Although the anorthite-type phase was observed above 800°C, it was suggested that this phase crystallized from the PBS glass because the PBS glass originally contained the constituents of the anorthite phase. This suggestion was supported by the one-stage sintering behavior as well as the low intensity of the diffracted peaks for anorthite. The densification behavior, therefore, could be suggested to occur through a non-reactive liquid phase sintering (NLPS) process The dielectric constant ($\varepsilon_r$), the quality factor ($Q \times f_0$), and the temperature coefficient of the resonant frequency ($\tau_f$) of the 50 vol% PBS glass-$Al_2O_3$ composite sintered at 900°C were 9.26, 4941 GHz, and −38 ppm/K, respectively.

## Acknowledgement

This research was supported in part by a grant from the Fine Ceramics Researcher Fosterage Program of the second stage of Brain Korea 21 Program and also partially supported by a grant from Gangwon Advanced Materials through a development project of industry necessity technology, Republic of Korea.

## References

1. Y. Imanaka, in “Multilayered Low Temperature Cofired Ceramics (LTCC) Technology” (Springer, 2005) p.21.
2. R.R. Tummala, J. Am. Ceram. Soc. 74[5] (1991) 895-908.
3. S.H. Knickerbocker, A.H. Kumar, and L.W. Herron, Am. Ceram. Soc. Bull. 72[1] (1993) 90-95.
4. J.-M. Wu and H.-L. Huang, J. of Non-Crystalline Solids 260 (1999) 116-124.
5. K. Fukuda, R. Kitoh, and I. Awai, Jpn. J. Appl. Phys. 32 (1993) 4584-4588.
6. B.W. Hakki and P.D. Coleman, IRE Trans. Microwave Theory Tech. MTT-8 (1960) 402-410.
7. S. Kemethmuller, M. Hagymasi, A. Stiegelschmitt, and A. Roosen, J. Am. Ceram. Soc. 90 (2007) 64-70.
8. C.-L. Lo, J.-G. Duh, B.-S. Chiou, and W.-H. Lee, J. Am. Ceram. Soc. 85 (2002) 2230-2235.
9. S.X. Dai, R.-F. Huang, and D.L. Wilcox Sr. J. Am. Ceram. Soc. 85 (2002) 828-832.