Low Temperature Sintering and Dielectric Properties of $BiNbO_4$ and $ZnNb_2O_6$ Ceramics with Zinc Borosilicate Glass

Kwan-Soo Kim, Shin Kim, and Sang-Ok Yoon[a]
Department of Ceramics Engineering, Kangnung National University, Jibyeon-dong, Kangnung-si, Kangwon 210-702, Korea

Jong Guk Park
Department of Electrical Engineering, Kangwon National University, Gyo-dong, Samcheok-si, Kangwon 245-711, Korea

[a]E-mail : soyoon@kangnung.ac.kr

(Received January 31 2007, Accepted October 9 2007)

Low temperature sintering behavior and microwave dielectric properties of the $BiNbO_4$- and the $ZnNb_2O_6$-zinc borosilicate glass (ZBS) systems were investigated with a view to applying the composition to LTCC technology. The addition of 10~30 wt% ZBS in both systems ensured successful sintering below 900 ℃. For the $BiNbO_4$-ZBS system, the sintering was completed when 15 wt% ZBS was added whereas 25 wt% ZBS was necessary for the $ZnNb_2O_6$-ZBS system. Secondary phase was not observed in the $BiNbO_4$-ZBS system but a small amount of Zn_2SiO_4 with the willemite structure as the secondary phase was observed in the $ZnNb_2O_6$-ZBS system. In terms of dielectric properties, the application of the $BiNbO_4$- and the $ZnNb_2O_6$-ZBS systems sintered at 900 ℃ to LTCC were shown to be appropriate; $BiNbO_4$-15 wt% ZBS (ε_r = 25, $Q\times f$ value = 3,700 GHz, τ_f = -32 ppm/℃) and $ZnNb_2O_6$-25 wt% ZBS (ε_r = 15.8, $Q\times f$ value = 5,400 GHz, τ_f = -98 ppm/℃).

Keywords : $BiNbO_4$, $ZnNb_2O_6$, LTCC, Zinc-borosilicate, Dielectrics

1. INTRODUCTION

Due to a rapid growth in the mobile telecommunication industry, microwave devices have been required to have a small volume and to be used at higher frequency. To meet these requirements, miniaturized devices such as multi chip modules (MCM) and surface mounting device (SMD) are intensively developed using the multi layer process (MLP) and the co-firing technique. Silver with low electrical resistance is applied as electrodes of low temperature co-fired ceramics (LTCC) because it can be heat-treated in ambient atmosphere. Due to the low meting point of silver (about 960 ℃), the sintering of LTCC have to be conducted about 900 ℃. To reduce the sintering temperature of dielectric materials, there are lots of studies to use mixture of low melting temperature glasses as a flux agent and ceramics as filler[1,2].

Bismuth-based dielectric ceramics are well known as low-firing materials and have been studied for multilayer capacitors. Since Kagata et al.[3] reported the microwave dielectric properties of $BiNbO_4$, one of the compounds in the Bi_2O_3-Nb_2O_5 system, (ε_r= 43, $Q\times f$ values= 10,000~17,000 GHz) with sintering aids, various attempts have been undertaken to improve the microwave dielectric properties of $BiNbO_4$, such as the substitution of lanthanide for Bi, the solid solutions of $Bi(Nb_{1-x}Ta_x)O_4$, $Bi(Nb_{1-x}Sb_x)O_4$ and the addition of various sintering aids[4-7]. Furthermore, $BiNbO_4$ has a merit of relatively low sintering temperature about 1000℃.

On the other hand, niobium based, columbite-type compounds such as MNb_2O_6 (M = Zn, Mg, Ca, Mn, Cu and Co) with an orthorhombic structure have been investigated for application in microwave devices. These compounds have very low loss and middle dielectric constant. Among them, $ZnNb_2O_6$ exhibits superior dielectric properties: ε_r= 25, $Q\times f$ value= 83,700 GHz and τ_f= -56 ppm/℃ [8-10]. Moreover, because sintering temperature is very low as 1150 ℃, it is expected that the sintering temperature can be easily reduced to below 1000 ℃. $ZnNb_2O_6$ ceramic with sintering aids are, therefore, promising candidates for low-temperature sintering dielectrics applied in multilayer microwave devices. However, a few studies on solid solution between $BiNbO_4$-$ZnNb_2O_6$ or sintering aids added $BiNbO_4$ and $ZnNb_2O_6$ systems were reported.

In this study, low temperature sintering behavior and microwave dielectric properties of zinc-borosilicate glass (ZBS) added $BiNbO_4$ and $ZnNb_2O_6$ ceramics were investigated in the view point of the application to LTCC materials.

2. EXPERIMENTAL MODUS OPERANDI

To prepare $BiNbO_4$ and $ZnNb_2O_6$ ceramics power, the proper ratio of Bi_2O_3, ZnO and Nb_2O_5 powders (High Purity Chemical Laboratory, Japan, Purity 99.9 %) were ball-milled for 24 hr and then calcined at 800 ℃ for 2 hr. Zinc-borosilicate glass (ZBS) was prepared by a quenching method after a melting process of powder mixtures of ZnO, B_2O_3, and SiO_2 (High Purity Chemical Laboratory, Japan, purity 99.9 %) at 1300 ℃ for 30 min. $BiNbO_4$ and $ZnNb_2O_6$ ceramics composed of 10~20 and 15~30 wt% ZBS were ball-milled for 24 hr and then dried. The disk type specimens with a 15 mm in diameter were prepared by a pressing of powder mixtures under 1,500 kg/cm^2 and sintering processes at between 800~925 ℃ with an interval of 25 ℃ for 2 hr. The phase analysis was carried out by an X-ray diffractometer (MO3XHF, Mac science) using a Cu target and within 2 theta range of 10~80 °. The microstructures were observed by a FE-SEM (S-4200, Hitachi). The dielectric constant (ε_r) and the quality factor ($Q\times f$ value) were measured by Hakki-Coleman method using a network analyzer (HP8720ES) and specimens which were placed between two parallel metal plates; the resonant frequency, the half power bandwidth which was recorded at 3 dB level of the resonant peak, and the insertion loss were measured. The temperature coefficient of resonant frequency (τ_f) was measured using an invar cavity in the temperature range of between 25 and 85 ℃[11].

3. RESULTS AND DISCUSSION

The deformation temperature of the zinc borosilicate glass (ZBS, $65ZnO\text{-}25B_2O_3\text{-}10SiO_2$ in wt% and 60.3-27.1-12.6 in mol%, respectively), i.e., the temperature at the maximum value of thermal expansion curve, was determined as 588 ℃, which was similar with the value in the literature; $60ZnO\text{-}30B_2O_3\text{-}10SiO_2$ (in mol%)[12]. Density, deformation point and dielectric properties of zinc borosilicate glasses were summarized in Table 1 and these glasses showed similar properties except $Q\times f$ value and τ_f.

Table 1. Density, defoemation point and dielectric properties of zinc borosilicate glasses.

	65Z25B10S	60Z30B10S
Density (g/cm^3)	3.57	3.60[a]
Deformation point (℃)	588	582
Dielectric constant, (ε_r)	6.53	7.56
Resonant frequency (GHz)	17.1	15.5
Q	261	93
Q×f *value* (GHz)	4 465	1 439
τ_f (ppm/℃)	-10	-21
Remarks	this work	ref. 12

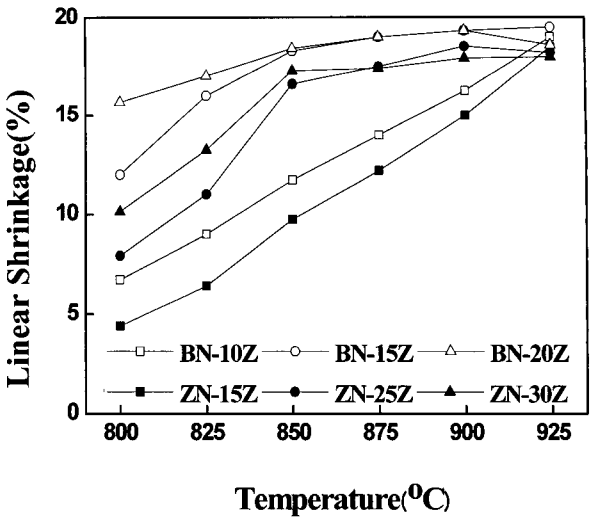

Fig. 1. Linear shrinkage of the $BiNbO_4$- and the $ZnNb_2O_6$-ZBS systems as a function the sintering temperature.

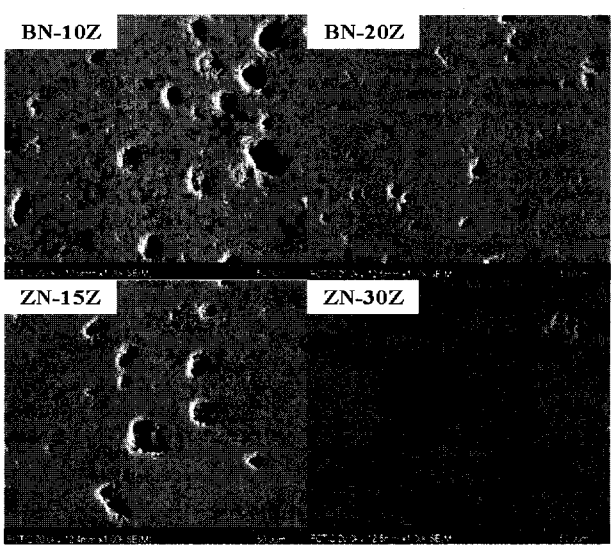

Fig. 2. Microstructures of some specimens for the $BiNbO_4$- and the $ZnNb_2O_6$-ZBS systems sintered at 900 ℃.

The linear shrinkage behavior of the $BiNbO_4$ (denotes as BN)- and the $ZnNb_2O_6$ (ZN)-xZ systems was shown in Fig. 1 as a function of the sintering temperature; x in -

xZ indicates the amount ZBS in wt%. The linear shrinkage of both systems increased with the increase of ZBS content and the sintering temperature. The shrinkage was completed below 900 ℃ for the specimens of BN-15Z and ZN-25Z (in ZBS vol%; 8 and 18, respectively) but the relative density was about 90 % of theoretical density both systems. As shown in Fig. 1, the ZN-xZ system exhibited lower shrinkage than the BN-xZ system having the relatively low sintered temperature at 1000 ℃. The low shrinkage of the ZN system might be related to the presence of secondary phases as well as the relatively low sinterability. The sintering behavior could be interpreted as the one-stage sintering. It is, moreover, considered that the non-reactive liquid phase sintering (NPLS) occurred in these ceramic-glass systems[13,14] although there was a small amount of secondary phase was observed in the ZN-xZ system as shown in Fig. 3. The NLPS is one of the liquid-assisted sintering (LAS) [15]; LAS distinguishes between the NLPS, where a glass phase content of at least 20-40 vol% is necessary for the densification and a reactive liquid phase sintering, where a glass content <20 vol% is sufficient. In this study, it is considered that small amount of glass was sufficient for the densification due to the relatively high sinterability in both systems although the NLPS occurred. The densification in the NLPS was proposed 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 the 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.

Figure 2 shows the microstructures of some specimens in both systems which were sintered at 900 °C. It is understandable that the amount of the closed pore decreased as the increase of the ZBS content, indicating that the liquid phase promoted the densification and then the pore filling resulted in. Generally, for the glass-ceramic sintering process, the densification is due to the viscous flow, which instigates the coalescence of powders and removes the pores in bodies. Accordingly, the viscosity of glass has an influence on the densification behavior. B_2O_3 is recognized as a typical glass network former that has a lower glass transition temperature[16].

The powder X-ray diffraction patterns of both systems sintered at 900 ℃ are shown in Fig. 3. A single phase of $BiNbO_4$ was observed in the BN-xZ system, indicating that there were no reactions between $BiNbO_4$ and ZBS. For the ZN-xZ system, $ZnNb_2O_6$ ceramics was formed as the main phase and a small amount of Zn_2SiO_4 with the willemite structure was observed as the secondary phase.

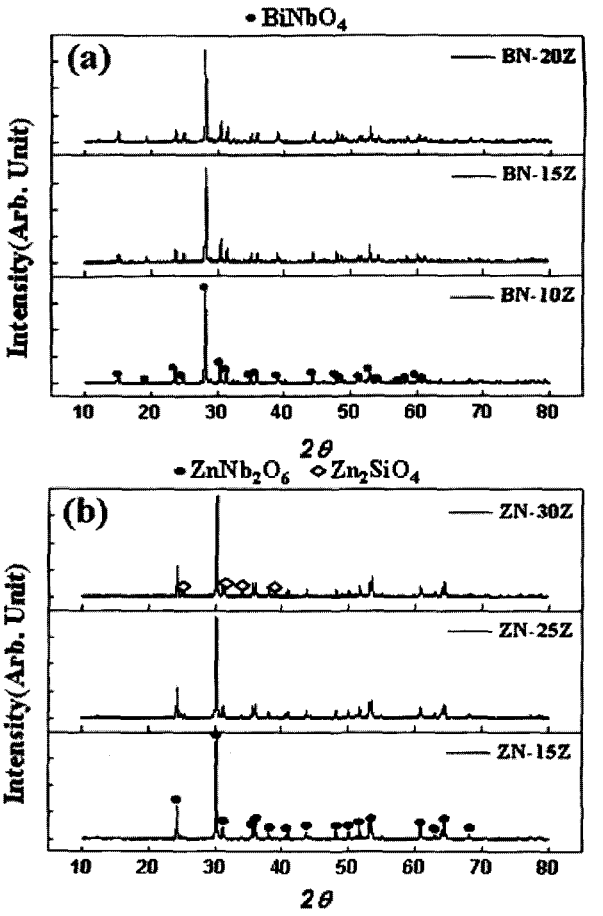

Fig. 3. The Powder XRD patterns of (a) the $BiNbO_4$- and (b) the $ZnNb_2O_6$-ZBS systems sintered at 900 ℃.

The dielectric constant (ε_r) of the BN- and the ZN-xZ systems as a function of the sintering temperature is shown in Fig. 4. As the sintering temperature increased, the increase of the dielectric constant increased; the increase might be caused by the densification because the similar behavior was observed in the plot of the linear shrinkage against the sintering temperature as shown in Fig. 1. In this study, the dielectric constant of BN-15Z and ZN-25Z (in ZBS vol%; 8 and 18, respectively) was measured as 24.6 and 15.8, respectively when the sintering was conducted at 900℃ which were lower than the calculated value of about 40.1 and 21.7 using the logarithmic mixing rule [17] of Eq. (1) with the data of the ZBS (6.53), $BiNbO_4$ (43), and $ZnNb_2O_6$ (25),

$$\log K = V_i * \log K_i \quad (1)$$

where, V_i and K_i are the volume fraction and the dielectric constant of phase i, respectively. The difference between the measured and calculated values might be caused by the presence of pores. Generally, the

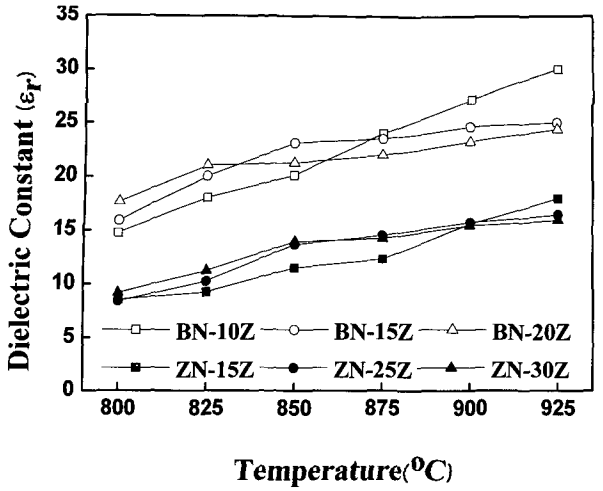

Fig. 4. Dielectric constant of the $BiNbO_4$- and the $ZnNb_2O_6$-ZBS systems as a function of the sintering temperature.

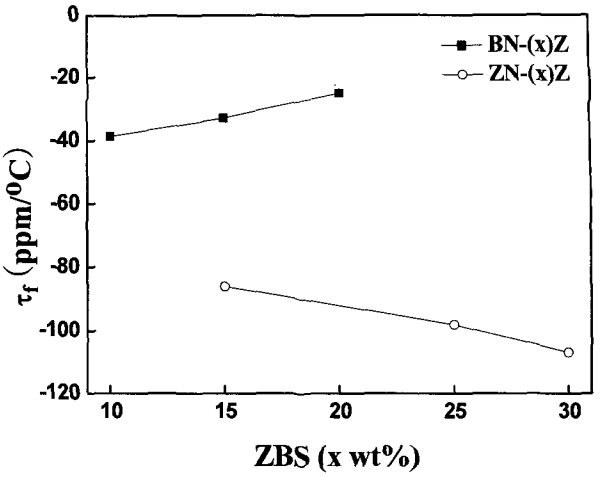

Fig. 6. Temperature coefficient of resonant frequency of the $BiNbO_4$- and the $ZnNb_2O_6$-ZBS systems as a function of ZBS contents sintered at 900℃.

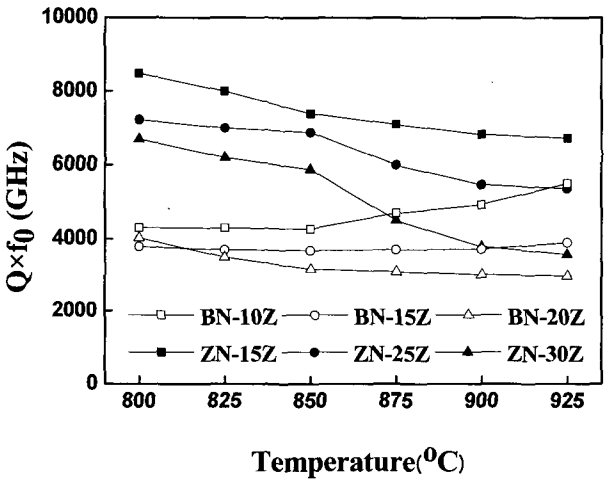

Fig. 5. $Q\times f$ value of the $BiNbO_4$- and the $ZnNb_2O_6$-ZBS systems as a function of the sintering temperature.

dielectric constant is affected by the density; the ε_r value of porous ceramics showed low values since it of pores was a unit (ε_r=1).

The $Q\times f$ value of both systems as a function of the sintering temperature is shown in Fig. 5. The $Q\times f$ value in both systems decreased as the increase of the amount of ZBS content, indicating that the $Q\times f$ value might be affected by the presence of the glassy phase having high loss, i.e. low quality factor. For a material having high quality factor and low dielectric loss, it is necessary to reduce the attenuation constant; it is known that the anharmonicity in the lattice vibration affects the attenuation constant for perfect crystals (i.e., intrinsic loss) whereas dislocations, pores, defects, grain boundaries, and secondary phases have an influence on the attenuation constant for poly-crystals (i.e., extrinsic loss)[13]. In general, the amounts of pores and grain boundaries decrease with increasing of the density and then dielectric losses are reduced.

Figure 6 shows the temperature coefficient of resonant frequency (TCF, τ_f) of both systems sintered at 900 ℃ as a function of ZBS content. The TCF of BN-xZ went toward the positive side as the increase of the ZBS content. This result was that the sinterability increased with the increase of ZBS content as shown Fig. 1., in addition, $BiNbO_4$ specimens were transformed from the orthorhombic to triclinic phase at 1040 ℃. E. S. Kim et al.[18] was reported that $BiNbO_4$ with with 0.03 wt.% CuV_2O_6 of the temperature coefficient of resonant frequency (TCF) was changed from −35.7 ppm/℃ for triclinic phase to −3.4 ppm/℃ for orthorhombic phase; the increase of TCF with phase transition of $BiNbO_4$ was due to the increase of bond strain resulting from the [Nb-O] octahedral distortion of $BiNbO_4$. The TCF of $ZnNb_2O_6$ ceramic decreased as the increase of the ZBS glass content. In addition, the TCF of Zn-xZ was shown than ZBS (-10 ppm/℃) and $ZnNb_2O_6$ (-56 ppm/℃). It is considered that the change of the glass composition by dissolution of Nb^{+5} might cause the further decrease of TCF. A detailed study is necessary to confirm this suggestion.

Consequently, for the $BiNbO_4$- and the $ZnNb_2O_6$-ZBS systems the application as materials for microwave dielectrics of LTCC could be possible because the below 900 ℃ sintering was conducted in both systems. The improvement of TCF is, however, necessary for the application. Therefore, the addition of materials having positive TCF, such as TiO_2, might be an effective method for the improvement.

4. SUMMARY

In this study, sinterability and microwave dielectric properties of the $BiNbO_4$- and the $ZnNb_2O_6$-ZBS systems were investigated as a function of zinc-borosilicate glass content. In terms of dielectric properties, the application of both systems sintered at 900 ℃ to LTCC were shown to be appropriate; $BiNbO_4$-15 wt% ZBS (ε_r= 25, $Q\times f$ value = 3,700 GHz, τ_f= -32 ppm/℃) and $ZnNb_2O_6$-25 wt% ZBS (ε_r = 15.8, $Q\times f$ value = 5,400 GHz, τ_f= -98 ppm/℃).

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 funded by the Ministry of Education & Human Resources Development, Republic of Korea.

REFERENCES

[1] T. Takada, S. F. Wang, S Yoshikawa, S. T. Tang, and R. E. Newnham, "Effect of glass addition on BaO-TiO_2-WO_3 microwave ceramics", J. Am. Ceram. Soc., Vol. 77, No. 7, p. 1909, 1994.

[2] V. Tolmer and G. Desgardin, "Low-temperature sintering and influence of the processing on the dielectric properties of $Ba(Zn_{1/3}Ta_{2/3})O_3$", J. Am. Ceram. Soc., Vol. 80, No. 8, p. 1981, 1997.

[3] Kagata, H., Inoue, T., Kato, J., and Kameyama, I., "Low-fire bismuth-based dielectric ceramics for microwave use", Jpn. J. Appl. Phy., Vol. 31, p. 3152, 1992.

[4] S. K. Ko, K. Y. Kim, B. H. Kim, and W. Choi, "Experimental fabrication of low pass filter of $BiNbO_4$ ceramics", J. of KIEEME(in Korean), Vol. 11, No. 4, p. 281, 1998.

[5] O. A. Shlyakhtin, A. V. Orlov, and Y. J. Oh, "Liquid phase low temperature sintering of niobate and cerate fine powders", J. Electroceram., Vol. 17, No. 2-4, p. 405, 2006.

[6] C. L. Huang and M. H. Weng, "Low-fire $BiTaO_4$ dielectric ceramics for microwave applications", Mater. Lett., Vol. 43, p. 32, 2000.

[7] N. Wang, M. Y. Zhao, and Z. W. Yin, "Effects of Ta_2O_5 on microwave dielectric properties of $BiNbO_4$ ceramics", Mater. Sci & Eng. B, Vol. 99, p. 238, 2003.

[8] M. Maeda, T. Yamamura, and T. Ikeda, "Dielectric characteristics of several complex oxide ceramics at microwave frequencies", Jpn. J. Appl. Phys., Vol. 26, p. 76, 1987.

[9] H. J. Lee, K. S. Hong, and S. J. Kim, "Dielectric properties of MNb_2O_6 compounds (Where M = Ca, Mn, Co, Ni, OR Zn)", Mater. Res. Bull., Vol. 32, No. 7, p. 847, 1997.

[10] Y. Zhang, J. Wang, Z. Yue, Z. Gui, and L. L, "Effect of Mg^{2+} substitution on microstructure and microwave dielectric properties of $(Zn_{1-x}Mg_x)$-Nb_2O_6 ceramics", Ceram. Int., Vol. 30, p. 87, 2004.

[11] B. W. Hakki and P. D. Coleman, "A Dielectric Resonator Method of Measuring Inductive Capacities in the Millimeter Ranger", IRE. Trans. on Microwave Theory Tech., MTT-8, p. 402, 1960.

[12] J.-M. Wu and H.-L. Huang, "Microwave properties of Zinc, Barium and Lead borosilicate glasses", J. Non-Cryst. Solids, Vol. 260, p. 116, 1999.

[13] K. G. Ewsuk, L. W. Harrison, and F. J. Walczak, "Sintering glass-filled ceramic composites : Effet of glass properties", p. 969 in Ceramic Transaction, Vol. 1(B), edited by G. L. Messing, E. R. Fuller, Jr., and H. Hausner, Am. Ceram. Soc. Westerville, OH, Vol. 1(B), p. 969, 1988.

[14] K. G. Ewsuk, "Sintering maps for ceramic-filled glass composites", edited by K. M. Nair, R. Pohanka, and R. C. Buchaman, Am. Ceram. Soc. Westerville, OH, Vol. 19, p. 123, 1990.

[15] S. Kemethmuller, M. Hagymasi, A. Stiegelschmitt, and A. Roosen, "Viscous flow as the driving force for the densification of low-temperature co-fired ceramics", J. Am. Ceram. Soc., Vol. 90, p. 64, 2007.

[16] J. H. Jean and T. K. Gupta, "Devitrification inhibitors in borosilicate glass and binary borosilicate glass composition", J. Mater. Res., Vol. 10, No. 5, p. 1312, 1995.

[17] W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, "Introduction to ceramics 2nd edition", John Wiley and Sons, New York, p. 947, 1976.

[18] E. S. Kim and W. Choi, "Effect of phase transition on the microwave dielectric properties of $BiNbO_4$", J. Eur. Ceram. Soc., Vol. 26, p. 1761, 2006.