

Sintering behavior and microwave dielectric properties of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ system with zinc-borosilicate glass

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The sintering behavior and microwave dielectric properties of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ ($x = 0.4$ and 0.6)-ZBS glass system were investigated with a view to applying the composition to low temperature co-fired ceramic technology. The addition of 25wt% ZBS glass ensured successful sintering below 925°C. Except an α - PbO_2 type $ZrTiO_4$ solid solution, TiO_2 and monoclinic ZrO_2 were formed for the composition with $x = 0.4$ whereas $Zn_{1/3}Nb_{2/3}TiO_4$ was observed for $x = 0.6$. In addition, α - Zn_2SiO_4 and ZnB_2O_4 were crystallized from the zinc borosilicate glass. Non-reactive liquid phase sintering (NLPS) occurred and a one-stage sintering was conducted. The dielectric constant was affected by the densification, i.e., the porosity and it obeyed the logarithmic mixing rule. $Zr_{0.4}(Zn_{1/3}Nb_{2/3})_{0.6}TiO_4$ with 25wt% ZBS glass sintered at 925°C gave 27.7 as the dielectric constant (ϵ_r), 3,850 GHz in as the $Q \times f$ value, and +6.1 ppm/°C as the temperature coefficient of resonant frequency (τ_f).

Key words: $ZnNb_2O_6$, $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$, LTCC, Zinc-borosilicate, Dielectrics.

Introduction

Mobile and satellite communications have increasing demands on the development of microwave components. Dielectric resonators or duplexers are required with a size reduction, low insertion loss and temperature stability in the microwave frequencies. Therefore, dielectric materials for use in the microwave components are required to have a high dielectric constant (ϵ_r) and a high Q ($\approx 1/\tan\delta$) value [1, 2]. Moreover, in practical use, it is important to adjust the temperature coefficient of the resonant frequency (τ_f) of the dielectric resonator to 0 ppm/°C. In order to adjust τ_f to nearly zero, two or more compounds having positive and negative τ_f values are employed to form a solid solution or mixed phases [3, 4]. Recently, to meet requirements of miniaturization and multi-function, the development of microwave devices has been focused on multi chip modules (MCM). The multi-layered passive devices may be fabricated by green sheets sintered at low temperatures with conducting materials such as Ag and Cu with low melting temperatures of about <1000°C; these conducting materials could not be used with conventional dielectric materials having sintering temperatures of >1200°C. To reduce the sintering temperature of dielectric materials, there are many studies using mixtures of low melting temperature glasses as a fluxing agent and ceramics as filler [5, 6].

Niobium based, columbite-type compounds such as

MNb_2O_6 ($M = Zn, Mg, Ca, Mn, Cu$ and Co) have been investigated for application in microwave devices. These compounds with an orthorhombic structure have very low loss and middle dielectric constant. Among them, $ZnNb_2O_6$ exhibits superior dielectric properties: $\epsilon_r = 25$, $Q \times f$ value = 83,700 GHz and $\tau_f = -56$ ppm/°C [3, 7, 8]. Moreover, because the sintering temperature is as low as 1150°C, it is expected that the sintering temperature can be easily reduced to below 1000°C. $ZnNb_2O_6$ ceramic with sintering aids are, therefore, promising candidates for low-temperature sintering dielectrics applied in multilayer microwave devices [9, 10]. However, because the dielectric constant and the temperature coefficient of the resonant frequency of $ZnNb_2O_6$ ceramic is middle and a large negative value, respectively, it is necessary to improve the dielectric constant and to adjust to zero the temperature coefficient of the resonant frequency for practical applications [3, 11]. In contrast, $ZrTiO_4$ ceramics with an orthorhombic crystal structure were reported to have a high dielectric constant $\epsilon_r = 38\text{--}40$, $Q \times f$ value = 21,000~30,000 GHz and a positive τ_f value of +59 ppm/°C [1, 12]. Also, the ionic size of the Zn^{2+} ion (0.74 Å, CN = 6) and Nb^{5+} ion (0.64 Å, CN = 6) were similar to that of the Zr^{4+} ion (0.72 Å, CN = 6) [1, 13]. The tetravalent Zr^{4+} ion is, therefore, expected to be substituted by one-third of Zn^{2+} ions and two-thirds of Nb^{5+} ions in the $ZrTiO_4$ ceramics. In this study, the sintering and microwave dielectric properties of zinc-borosilicate glass (hereafter ZBS glass) added $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ ($x = 0.4$ and 0.6) systems with the substitution of ZrO_2 by $Zn_{1/3}Nb_{2/3}O_2$ systems were investigated in the view point of the application to LTCC materials.

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Experimental Procedure

To prepare $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ ($x = 0.4$ and 0.6) power (denotes as ZNx), the proper ratio of ZrO_2 , TiO_2 , ZnO , and Nb_2O_5 powders (purity 99.9%) were ball-milled for 24 hr and then calcined at $1000^\circ C$ for 2 hr. The powders of ZnO , B_2O_3 and SiO_2 of extra-pure reagent a grade were well mixed and the ZBS glass frit was obtained by a quenching method after a melting process at $1300^\circ C$. The deformation temperature of the ZBS glass was measured by a dilatometer (DIL 402, Netzsch). The ZNx-ZBS system composed of 25 and 30wt% glass (ZNx-25 and ZNx-30, respectively) was 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 $1,500\text{ kg/cm}^2$ and a sintering processes between $800\text{--}950^\circ C$ with an interval of $25^\circ C$ for 2 h. The phase analysis was carried out by an X-ray diffractometer (D/Max-2200, Rigaku, Japan) using a Cu-K with a 2theta range of $10\text{--}80^\circ$. The microstructures were observed by a FE-SEM (S-4200, Hitachi). The dielectric constant (ϵ_r) and the $Q \times f$ value were measured by the Hakki-Coleman method using a network analyzer (HP-8720ES) and specimens which were placed between two parallel metal plates; the resonant frequency, the half power bandwidth which was recorded at the 3dB level of the resonant peak, and the insertion loss were measured [14]. The temperature coefficient of the resonant frequency (τ_f) was measured using an invar cavity in the temperature range of between 25 and $85^\circ C$.

Results and Discussion

The deformation temperature of the ZBS glass, i.e., the temperature at the maximum value of the thermal expansion curve, was determined as $588^\circ C$, which was similar to the value in the literature; it of a zinc borosilicate glass with the composition of 60ZnO-30 B_2O_3 -10 SiO_2 (in mol%, Zn60B30Si10) was reported as $582^\circ C$ by Wu and Huang [15]. They also determined the dielectric constant (ϵ_r), the $Q \times f$ value, and the temperature coefficient of the resonant frequency (τ_f) of this glass as 7.56, 1,439 GHz (93 at 15.5Hz), and $-21\text{ ppm}/^\circ C$, respectively. Density,

Table 1. Density, deformation temperature and dielectric properties of ZBS glasses.

	ZBS glass	Zn60B30Si10
Density (g/cm^3)	3.57	3.60 ^a
Deformation point ($^\circ C$)	588	582
Dielectric constant, (ϵ_r)	6.53	7.56
Resonant frequency (GHz)	17.1	15.5
Q	261	93
$Q \times f$ value (GHz)	4 465	1 439
τ_f (ppm/)	-10	-21
Remarks	this study	ref. 15

^aref. 16

deformation point and dielectric properties of the ZBS glasses are summarized in Table 1 and these glasses showed similar properties except the $Q \times f$ value and τ_f .

The XRD patterns of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ -ZBS system containing 25 and 30wt% ZBS glass sintered at $925^\circ C$ are shown in Fig. 1; (a) $x = 0.4$; $Zr_{0.6}(Zn_{1/3}Nb_{2/3})_{0.4}TiO_4$ (denoted as ZN4) and (b) $x = 0.6$; $Zr_{0.4}(Zn_{1/3}Nb_{2/3})_{0.6}TiO_4$ (ZN6). In the compositions of ZN4-25 and -30 (25 and 30wt% ZBS glass, respectively), the crystalline phases of the α - PbO_2 type $ZrTiO_4$ solid solution, the rutile-type structure, and the monoclinic ZrO_2 were observed. Doped zinc and niobium might be substituted on Zr-sites in the $ZrTiO_4$ solid solution because related compounds were not detected. From the fact that the monoclinic ZrO_2 was formed as the secondary phase, the observed rutile-type structure may be TiO_2 in the basic of the stoichiometry of $ZrTiO_4$. And it is suggested that there were no reactions between the ZBS glass and TiO_2/ZrO_2 ; this suggestion is supported by the report that the ZBS glass acted as a non-reactive glass in the TiO_2 -ZBS system which was sintered at $900^\circ C$ [16]. On the other hand, the crystalline phases of the $ZrTiO_4$ solid solution and a rutile type $Zn_{1/3}Nb_{2/3}TiO_4$ were observed in the compositions of ZN6. These results indicated that the solubility limit for $Zn_{1/3}Nb_{2/3}$ on Zr-site might be less than 0.4 and the precipitated ZnO/Nb_2O_5 might form $Zn_{1/3}Nb_{2/3}TiO_4$ through the reaction with TiO_2 in the ZN6 compositions in which ZnO/Nb_2O_5 was heavily doped whereas TiO_2 and ZrO_2 were precipitated in the ZN4 compositions. In the study for the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ system ($0.2 \leq x \leq 1.0$) without additives which was sintered at 1250, Kim et al., stated that an α - PbO_2 type $ZrTiO_4$ solid solution was formed for the compositions up to $x = 0.35$ and a mixture of the α - PbO_2 type solid solution and the $Zn_{1/3}Nb_{2/3}TiO_4$ was formed for $x \geq 0.4$ [1]. The difference of the phases formed in the ZN4 might be

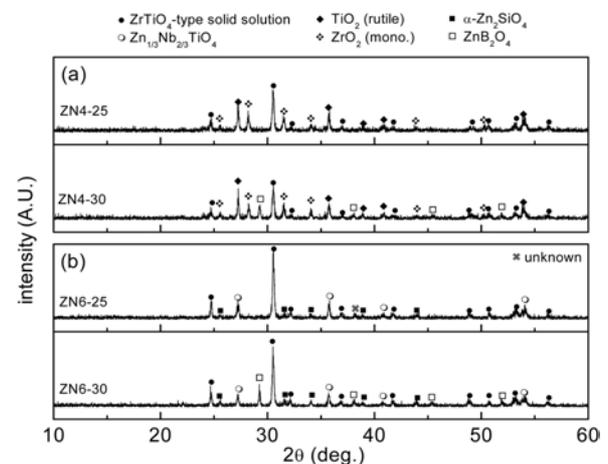


Fig. 1. Powder XRD patterns of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ -ZBS system sintered at $925^\circ C$; (a) with 25wt% (ZN4-25 and ZN6-25) and (b) with 30wt% ZBS glass (ZN4-30 and ZN6-30).

caused by the temperature of preparation. The crystalline phase of α - Zn_2SiO_4 with a hexagonal structure was observed in both systems. Among five polymorphisms, α - Zn_2SiO_4 was reported as the only stable phase at temperatures between 800°C and the liquidus in an atmospheric condition [17] and it might be crystallized the ZBS glass in this study. ZnB_2O_4 was also observed in the ZBS-rich compositions, i.e., ZN4-30 and ZN6-30.

The linear shrinkage behavior of the compositions for ZN4-25 and ZN6-25 as a function of the sintering temperature are shown in Fig. 2 along with the data of ZnNb_2O_6 -25wt% ZBS glass for comparison. From the facts that the deformation temperature of the ZBS glass was 588°C and the values of the linear shrinkage at 800°C were about 4% in both compositions, the sintering behavior could be interpreted as one-stage sintering. It is, moreover, considered that a non-reactive liquid phase sintering (NPLS) occurred in the ceramic-glass system where there were no reactions between glass and ceramic [18, 19]. The NLPS is one of the liquid-assisted sintering (LAS) schemes [20]; LAS is distinguished from NLPS, where a glass phase content of at least 20-40vol% is necessary for the densification and a reactive liquid phase sintering, where a glass content <20vol% is sufficient. The densification in the NLPS is 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 a density change 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. 2, on the other hand, ZN4 and ZN6 exhibited lower shrinkage than ZnNb_2O_6 which could be sintered at 1150°C. The low shrinkage might be related to the presence of secondary phases as well as the low sinterability of ZrTiO_4 . A similar behavior was obtained in the compositions for ZN4-30 and ZN6-30. Fig. 3 shows the microstructures of ZN4-25 and

ZN6-25 which were sintered at 800 and 925°C. It is understandable that the densification was promoted as the sintering temperature increased. A slight densification occurred partly at 800°C, which corresponded to the first stage of NPLS whereas a dense microstructure with a small amount of closed pores was obtained at 925°C.

The dielectric constant (ϵ_r) of ZN4-25 and ZN6-25 as a function of the sintering temperature is shown in Fig. 4 along with the data of ZnNb_2O_6 -25wt% ZBS glass. As the sintering temperature increased, the increase of the dielectric constant might be caused by the densification because the behavior of the dielectric constant against the temperature was similar with that of the shrinkage as shown in Fig. 2. The dielectric constants of ZN4-25 and ZN6-25 were measured as 24.8 and 27.7, respectively when the sintering was conducted at

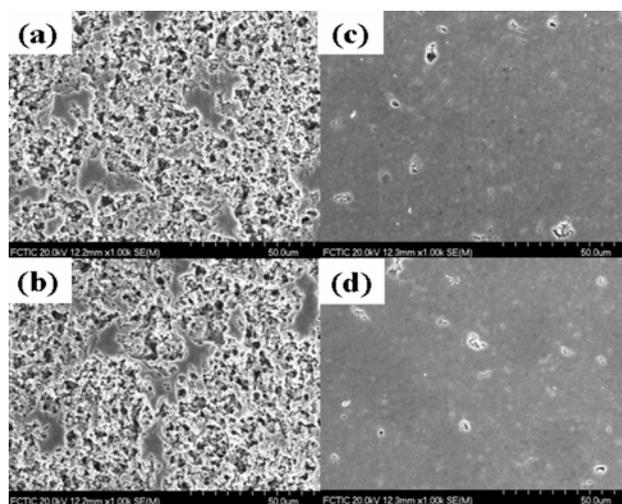


Fig. 3. Microstructures of the $\text{Zr}_{1-x}(\text{Zn}_{1/3}\text{Nb}_{2/3})_x\text{TiO}_4$ -25wt% ZBS glass system ($x = 0.4$ and 0.6) and 925°C; (a) $x = 0.4$ sintered at 800°C, (b) $x = 0.6$ at 800°C, (c) $x = 0.4$ at 925°C and (d) $x = 0.6$ at 925°C.

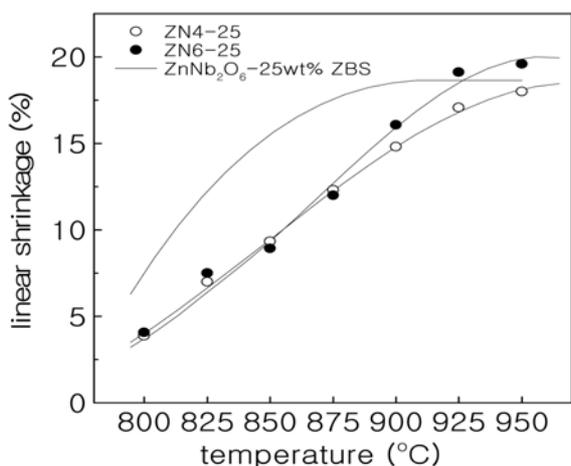


Fig. 2. Linear shrinkage of the $\text{Zr}_{1-x}(\text{Zn}_{1/3}\text{Nb}_{2/3})_x\text{TiO}_4$ -25wt% ZBS glass system ($x = 0.4$ and 0.6) as a function of the sintering temperature.

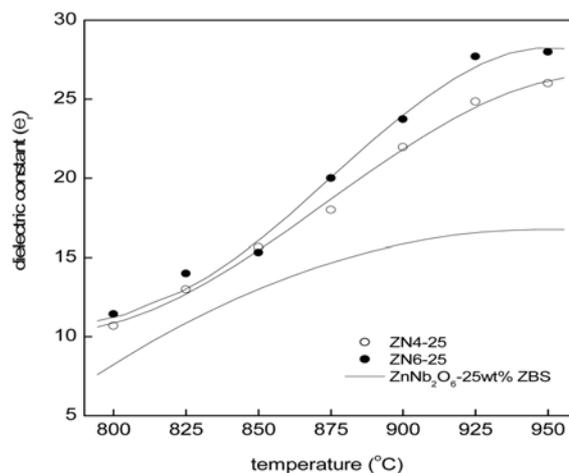


Fig. 4. Dielectric constant of the $\text{Zr}_{1-x}(\text{Zn}_{1/3}\text{Nb}_{2/3})_x\text{TiO}_4$ -25wt% ZBS glass system ($x = 0.4$ and 0.6) as a function of the sintering temperature.

925°C which were slightly higher than the calculated value of about 23.7 using the logarithmic mixing rule [21] of Eq. (1) with the data of the ZBS glass (6.53) and $Zr_{0.65}(Zn_{1/3}Nb_{2/3})_{0.35}TiO_4$ (44) [1],

$$\ln \varepsilon_{r,i} = \sum v_i \ln \varepsilon_{r,i} \quad (1),$$

where, $\varepsilon_{r,i}$ and v_i are the dielectric constant and the volume fraction of the i phase, respectively. It is considered that the reason for the high value for the measured specimens might be related with the formation of secondary phases having high dielectric constants such as TiO_2 (105) and $Zn_{1/3}Nb_{2/3}TiO_4$ (83). As expected, on the other hand, the dielectric constant of ZN4-25 and ZN6-25 were higher than that of $ZnNb_2O_6$ -25wt% ZBS glass. And the dielectric constant of $ZnNb_2O_6$ -25wt% ZBS glass also obeyed the logarithmic mixing rule; the dielectric constant was 16.50 when the sintering was conducted at 925°C which was similar with the calculated value of 15.75 using Eq. 1, indicating that the dependence of the dielectric constant on the relative amount of the phase present in the sintered specimens can be explained by the logarithmic mixing rule. The $Q \times f$ values of ZN4-25 and ZN6-25 along with $ZnNb_2O_6$ -25wt% ZBS glass as a function of the sintering temperature are shown in Fig. 5. For ZN4-25, the quality factor showed almost the same value of about 3,100 GHz although the density increased. It is considered that the dielectric loss of phase boundaries due to the formation of secondary phases might be one of the reasons for the low value. For a material having a 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 whereas dislocations, pores, defects, grain boundaries, and secondary phases have an influence on the attenuation constant for poly-crystals. ZN6-25 exhibited an increase up to a maximum point at 900°C and then a decrease with an increase of the sintering

temperature. The increase was correlated with the density whereas the decrease after the maximum was unclear. From the fact that the decrease of the quality factor was also observed in $ZnNb_2O_6$ -25wt% ZBS glass, it is considered that the large amount of the ZBS glass phase might also correspond to the inferiority of the quality factor. The temperature coefficient of the resonant frequency (τ_f) of ZN4-25 was +6.1 ppm/°C when the sintering was conducted at 925°C. This value is reasonable because τ_f of $Zr_{0.65}(Zn_{1/3}Nb_{2/3})_{0.35}TiO_4$, the ZBS glass, and TiO_2 was -3.0 [1], -10.0, and +465 ppm/°C, respectively. When ZN4-25, i.e., $Zr_{0.4}(Zn_{1/3}Nb_{2/3})_{0.6}TiO_4$ -25wt% ZBS glass, was sintered at 925°C, it showed good dielectric properties and the application of it to microwave devices may be shown to be appropriate; the dielectric constant (ε_r), the $Q \times f$ value, and the temperature coefficient of the resonant frequency (δ_f) was 27.7, 3,850 GHz, and +6.1 ppm/°C.

Conclusions

The sintering behavior and microwave dielectric properties of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ ($x = 0.4$ and 0.6)-ZBS glass system were investigated with a view to applying the composition to LTCC technology. The addition of 25wt% ZBS glass ensured successful sintering below 925°C. Except an α - PbO_2 type $ZrTiO_4$ solid solution, TiO_2 and monoclinic ZrO_2 were formed for the compositions with $x = 0.4$ whereas $Zn_{1/3}Nb_{2/3}TiO_4$ was observed for $x = 0.6$. In addition, α - Zn_2SiO_4 crystallized from the ZBS glass and ZnB_2O_4 was observed in the compositions with 30wt% ZBS glass. Non-reactive liquid phase sintering (NLPS) occurred and a one-stage sintering was conducted. The dielectric constant was affected by the densification, i.e., the porosity and it obeyed the logarithmic mixing rule. $Zr_{0.4}(Zn_{1/3}Nb_{2/3})_{0.6}TiO_4$ with 25wt% ZBS glass sintered at 925°C demonstrated 27.7 in the dielectric constant (ε_r), 3,850 GHz in the $Q \times f$ value, and +6.1 ppm/°C in the temperature coefficient of resonant frequency (τ_f).

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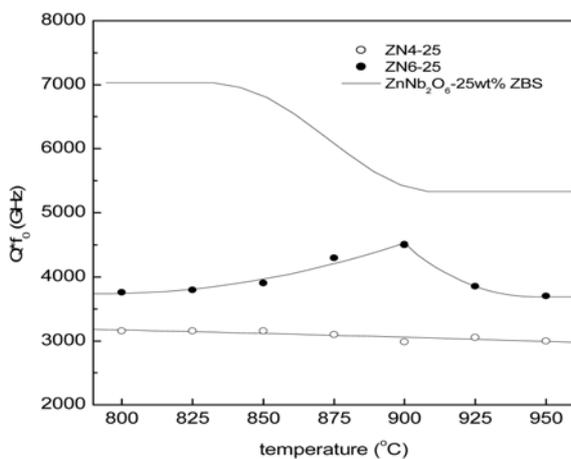


Fig. 5. $Q \times f$ value of the $Zr_{1-x}(Zn_{1/3}Nb_{2/3})_xTiO_4$ -25wt% ZBS glass system ($x = 0.4$ and 0.6) as a function of the sintering temperature.

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