

Effects of alkali-borosilicate glass additions on the microstructure and dielectric properties of $\text{Ba}_{0.88}(\text{Nd}_{1.40}\text{Bi}_{0.42}\text{La}_{0.30})\text{Ti}_4\text{O}_{12}$

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The microstructures and dielectric properties of $\text{Ba}_{0.88}(\text{Nd}_{1.40}\text{Bi}_{0.42}\text{La}_{0.30})\text{Ti}_4\text{O}_{12}$ / alkali-borosilicate glass composites were investigated in this study, with the volume percentage of the glass phase in the composite being either 50, 55, or 60 vol.%. Sintered density measurements indicated that the density increased with an increase in the sintering temperature for the composites with 50 and 55 vol.% glass additions, but, at a sintering temperature higher than 800 °C, the density decreased for the composite with a 60 vol.% glass addition. XRD patterns revealed that the peak of the highest intensity in the B(NBL)T crystal belongs to the (401) crystal plane, while that in the B(NBL)T/glass composites to the (320) crystal plane. Along with the change in crystalline preferred orientation, the lattice constants of the crystal also changed. SEM micrographs indicated that the B(NBL)T phase developed into columnar grains at sintering temperatures higher than 1260 °C. Moreover, when glass was added, the grain morphology changed, especially at sintering temperatures higher than 850 °C. When sintered at 950 °C for 2 hours, the composite with 55 vol.% glass yielded the highest dielectric constant ($\epsilon_r = 23.2$), the lowest dielectric loss ($\tan\delta = 4.1 \times 10^{-3}$), and a high $Q \times f$ value ($Q \times f = 1,620$ GHz, $Q = 1/\tan\delta$, $f = 6.67$ GHz).

Key words: Sintering; Microstructure-final, Dielectric properties, $\text{Ba}_{0.88}(\text{Nd}_{1.40}\text{Bi}_{0.42}\text{La}_{0.30})\text{Ti}_4\text{O}_{12}$, Structural applications.

Introduction

Electronic products have the trend toward miniaturization, lighter weight, and portability in order to fulfill the demand of personal communications [1, 2]. Considering the RF frequency range (1-30 GHz) which is used in current telecommunication and the suitable chip size in the current technologies (2-10 mm) [3], microwave components must be miniaturized in order to reduce the size of microwave devices. Among the microwave components, antennas are the ones whose sizes can be reduced substantially should the antenna circuitry be properly designed and the dielectric constant of the dielectric material surrounding the antenna circuitry be enhanced [4-5].

Most of well-known commercial microwave dielectric materials exhibit a high dielectric constant (ϵ_r), a high quality factor (Q) and very low temperature coefficients of the resonant frequency (τ_f). However, these materials need very high sintering temperature, ranging from about 1,200 °C to 1,400 °C, in order to get superior dielectric properties. If these dielectric materials are intended to be co-fired with silver-based conductors, the sintering temperature of the dielectric materials should be reduced to lower than the melting point of silver (961 °C). The mostly common approach to reducing the sintering temperature of

the microwave dielectric ceramic is adding sintering aids or glasses with low softening temperatures [6-8]. For example, $\text{BaO}(\text{Nd}_{0.8}\text{Bi}_{0.2})_2\text{O}_3\text{Ti}_4\text{O}_{12}$ added with 10 wt.% $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{CaO}$ glass could be sintered at 900 °C, yielding a composite structure having a quality factor ($Q \times f$) of 2,200 GHz, a ϵ_r of 68, and a τ_f of 55 ppm/°C [9]. Similar trends were observed in the $\text{BaNd}_2\text{Ti}_4\text{O}_{12}$ microwave ceramic, in which $\text{B}_2\text{O}_3-\text{Bi}_2\text{O}_3-\text{SiO}_2-\text{ZnO}$ or $\text{La}_2\text{O}_3-\text{B}_2\text{O}_3-\text{TiO}_2$ glass was added to reduce the sintering temperature [2, 10]. It was also shown that alumina and silica based glasses were more effective in improving the dielectric properties of $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ ceramics, whereas borate glasses are more preferred for lowering the sintering temperature [11]. On the other hand, although a glass phase addition could reduce the sintering temperature, it was shown that a larger amount of glass phase addition to $\text{Ca}_5\text{Nb}_2\text{TiO}_{12}$ resulted in increased porosity, in addition to reduced microwave dielectric properties [11].

The dielectric performances of microwave ceramics with glass additions are related with the densification behavior, microstructural evolution, and phase reaction between the glass and ceramics. Lee et al. [12] indicated adding B_2O_3 into a BaTi_4O_9 microwave ceramic decreased the sintered density and deteriorated the dielectric characteristics of BaTi_4O_9 . In addition, a B_2O_3 addition induced complex reactions with BaTi_4O_9 and resulted in the development of secondary phases such as $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and $\text{BaTi}(\text{BO}_3)_2$. Liu and Lin [13] reported $\text{La}_4\text{Ti}_9\text{O}_{24}$ ceramics with 30 vol.% $\text{PbO}-\text{B}_2\text{O}_3-\text{SiO}_2$ added could be sintered to 95% theoretical. In this report, the reaction

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between $\text{ZnO-B}_2\text{O}_3\text{-SiO}_2$ and $\text{La}_4\text{Ti}_9\text{O}_{24}$ resulted in the formation of a secondary phase, $\text{La}_{2/3}\text{TiO}_3$, which had a strong influence on the microwave dielectric properties. The addition of a glass phase not only could cause the precipitation of new phases, but also a change in grain morphology. Chang et al. [14] reported that, sintered at 1250°C , a density of 96% theoretical was obtained for $\text{BaO-Nd}_2\text{O}_3\text{-Sm}_2\text{O}_3\text{-TiO}_2$ ceramics with aluminosilicate glass added. Without a glass addition, the microstructure of $\text{BaO-Nd}_2\text{O}_3\text{-Sm}_2\text{O}_3\text{-TiO}_2$ was predominantly equiaxed fine grains at sintering temperatures lower than $1,250^\circ\text{C}$, but a columnar structure at temperatures higher than $1,350^\circ\text{C}$. On the other hand, with glass additions, exaggerated columnar grains dominated the microstructure of $\text{BaO-Nd}_2\text{O}_3\text{-Sm}_2\text{O}_3\text{-TiO}_2$ at a sintering temperature of $1,150^\circ\text{C}$.

Alkali borosilicate glasses typically exhibit lower softening temperatures than those glass additives shown previously, and can possibly reduce the sintering temperature of the dielectric ceramics more effectively. Nevertheless, such a belief has not been justified. It is thus the goal of this study to investigate the effects of alkali borosilicate glass ($\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-CaO-Na}_2\text{O-K}_2\text{O-BaO}$) additions on the sintering parameters, microstructural evolution and dielectric properties of $\text{Ba}_{0.88}(\text{Nd}_{1.40}\text{Bi}_{0.42}\text{La}_{0.30})\text{Ti}_4\text{O}_{12}$ microwave ceramics. The effects of the glass addition content on the densification kinetics and the microwave dielectric properties of $\text{Ba}_{0.88}(\text{Nd}_{1.40}\text{Bi}_{0.42}\text{La}_{0.30})\text{Ti}_4\text{O}_{12}$ -glass composite were characterized.

Experimental procedure

The materials used in this study are $\text{Ba}_{0.88}(\text{Nd}_{1.40}\text{Bi}_{0.42}\text{La}_{0.30})\text{Ti}_4\text{O}_{12}$ (abbreviated as B(NBL)T, NPO-110; Prosperity Dielectric Co., Ltd.) and alkali-borosilicate glass (CS-9609; China Glaze Co., Ltd.) powders. Fig. 1 shows SEM images of original B(NBL)T ceramic powder and glass powder. The average particle sizes of B(NBL)T ceramic powder and glass powder are about $3.2\text{ }\mu\text{m}$, $4.6\text{ }\mu\text{m}$, respectively. The physical properties and compositions of these materials are listed in Table 1.

B(NBL)T and the glass powders of various volumetric ratios (50/50, 45/55, and 40/60) were ball-milled in isopropyl alcohol (IPA) solvent with zirconia balls 3 mm in diameter for 24 hours in a polyethylene bottle. A solution composed of an acrylic resin (Lucite, Elvacite, 2046) and IPA were then mixed with the milled powder, which subsequently was spray-dried into spherical granules, and sieved to obtain granules having a mean

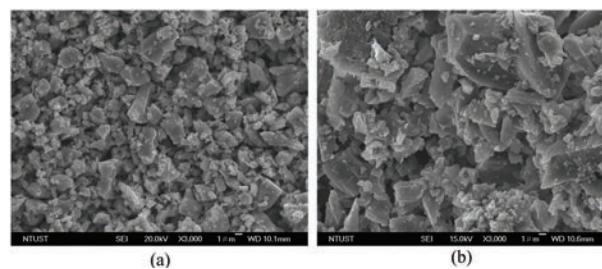


Fig. 1. The morphologies of (a) B(NBL)T powder, and (b) alkali-borosilicate glass powder.

particle size of about $70\text{ }\mu\text{m}$. Pellets of 15 mm in diameter and either 8 mm or 4 mm in thickness were prepared by uniaxially pressing the powder with a pressure of 90 MPa. Sintering was carried out in air. The thermal profile included heating at a rate of 2 K minute^{-1} to 350°C , held for 30 minutes, followed by heating at a rate of 2 K minute^{-1} to 500°C , held for 30 minutes, and finally heating at a rate of 3 K minute^{-1} to a sintering temperature ranging between 750°C and 950°C , held for a period ranging from 30 to 120 minutes. Dilatometric study of the sintering behavior of the powder composite was carried at a ramp of 5 K minute^{-1} to 350°C held for 30 minutes, followed by 5 K minute^{-1} to 500°C held for 30 minutes, and then 5 K minute^{-1} to 950°C in air. The weight loss of glass powder was investigated using a thermal analyzer (SETARAM, SETSYS-TGA, TG/DSC) at a heating rate of 10 K minute^{-1} from room temperature to $1,200^\circ\text{C}$ in air.

The bulk densities of all sintered samples were evaluated using Archimedes method. The crystal structure of the sintered specimens were analyzed using an X-ray diffractometer (XRD, REGAKU, DMAX-VB) at 40 kV and 100 mA, using $\text{CuK}\alpha$ ($\lambda = 0.15418\text{ nm}$) radiation. In a scanning range (2θ) of $10^\circ\text{-}50^\circ$, the scanning rate was $3^\circ\text{ minute}^{-1}$ and the scanning interval was 0.05° . The microstructures of sintered compacts were taken from polished and fractured surfaces using a field emission scanning electron microscope (FESEM, JEOL, JSM-6500F). Both secondary electron imaging (SEI) and back-scattered electron imaging (BEI) were recorded. The dielectric properties were measured using an RF impedance analyzer (HP-4291B) at 1GHz, while the resonant frequency were measured via a parallel plate dielectric resonator by the method of Hakki and Coleman using a network analyzer (Agilent 8722ES). The ratios of diameter to height of all specimens were maintained between 1.8 and 2.3.

Table 1. Physical properties and compositions of B(NBL)T powder and alkali-borosilicate glass powder

Material	Density (g/cm^3)	Mean particle Size (m)	Composition (wt.%)						
			TiO_2	Nd_2O_3	BaO	Bi_2O_3	La_2O_3		
B(NBL)T	5.64	3.2	37.6	28.4	16.2	11.9	5.9		
glass	2.45	4.6	SiO_2	Al_2O_3	B_2O_3	CaO	K_2O	Na_2O	BaO
			38.1	17.3	16.9	12.1	6.8	4.7	4.1

Results and discussions

Shrinkage behavior

Fig. 2 shows the variation of sintered shrinkage percentage with sintering temperature for the B(NBL)/T/glass composites with 50, 55, and 60 vol.% glass in dilatometric tests. It can be observed that the shrinkage percentage of the B(NBL)/T/glass composites with 50 vol.% glass was about 9% and the shrinkage phenomenon diminished substantially at about 900 °C. Such a result was possibly caused by the fact that a phase reaction took place between B(NBL)/T and glass, resulting in a decrease in the amount of liquid phase. With an increase in the volumetric percentage of the liquid phase, the shrinkage percentage for B(NBL)/T/glass composites were about 16% and 22%, respectively for the composites having 55, and 60 vol.% glass additions. A close to full density could be achieved at a sintering temperature slightly higher than 900 °C for the composites with 55 and 60 volume percentage of glass additions.

Sintered density

Fig. 3 shows the variation of density with sintering temperature for B(NBL)/T/glass composites with 50, 55, and 60 vol.% glass additions. The isothermal holding time at the sintering temperature was 120 minutes. The theoretical densities of B(NBL)/T/glass composites, calculated based on the rule of mixtures, are 4.04, 3.88, and 3.73 g/cm³ for 50, 55, and 60 vol.% glass additions, respectively. The sintered densities of the composites with 50 and 55 vol.% glass additions increased with an increase in the sintering temperature from 750 °C to 950 °C. On the other hand, the sintered density of the composite with 60 vol.% glass addition reached a peak value at 800 °C. The results found in this group of specimens seemed to be contrary to those observed in the dilatometric test. However, in the dilatometric test, the heating rate was larger (5 K minute⁻¹ versus 3 K minute⁻¹) and there was not an isothermal hold at the sintering temperature (0 minute versus 120 minutes). The vaporization of some components of high vapor

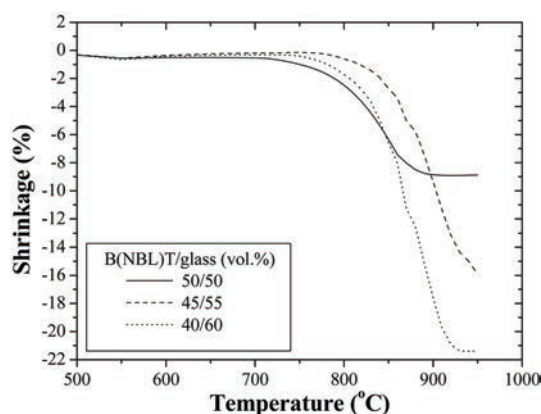


Fig. 2. Temperature-shrinkage curves of the B(NBL)/T/glass composites with 50 vol.%, 55 vol.%, and 60 vol.% glass additions.

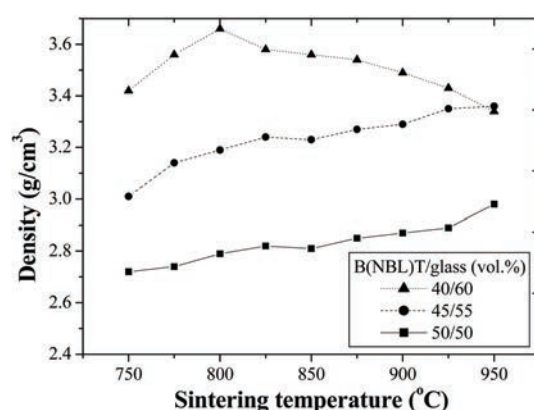


Fig. 3. Variation of the sintered density of B(NBL)/T/glass composites with sintering temperature.

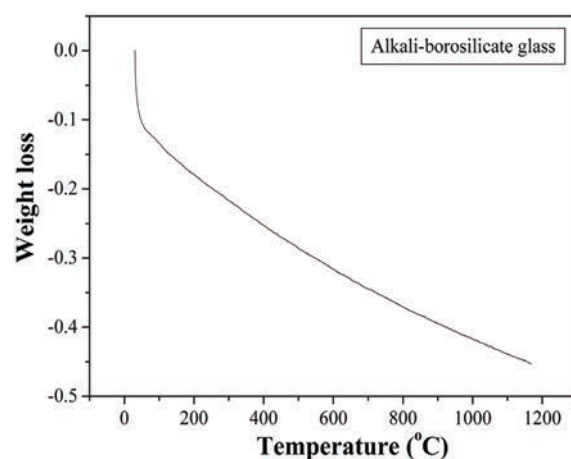


Fig. 4. TGA result of alkali-borosilicate glass powder.

pressure in the glass could have caused blistering in the highly dense structure.

Fig. 4 shows TGA pattern of the glass powder. A continuous weight loss was recorded with an increase in the testing temperature, indicating the continuous vaporization of the glass phase. Such a result was thus responsible for the decrease in density at higher sintering temperatures for the composite with a 60 vol.% glass addition. For the composites with 50 vol.% and 55 vol.% glass additions, the phase reaction between B(NBL)/T and glass in a slow heating and a long isothermal hold at the sintering temperature could have reduced the amount of liquid phase during sintering, which consequently resulted in a lower sintered density. In a structure with a low sintered density and a low amount of vaporizable liquid phase, the blistering phenomenon was less prone to occur, and vice versa.

Microstructural analysis

Fig. 5 show the SEM images of B(NBL)/T sintered at 950 °C, 1,260 °C, 1,360 °C and 1,460 °C for 1 hour. Agglomerated particles without neck growth could still be observed at a sintering temperature of 950 °C. At a

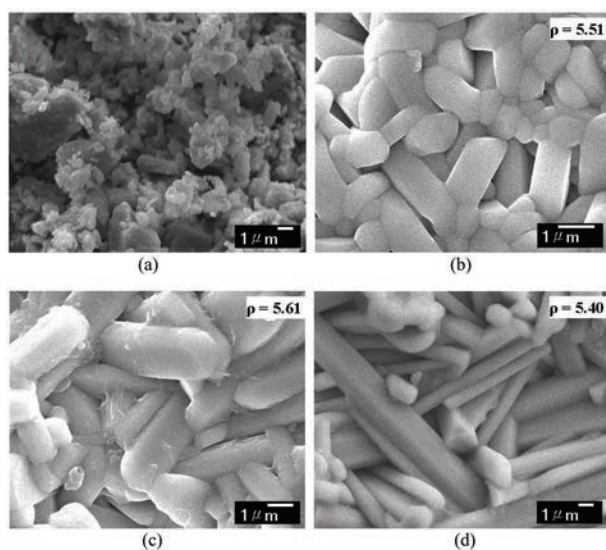


Fig. 5. SEM micrographs of B(NBL)T sintered at (a) 950 °C, (b) 1,260 °C, (c) 1,360 °C and (d) 1,460 °C for 1 hour.

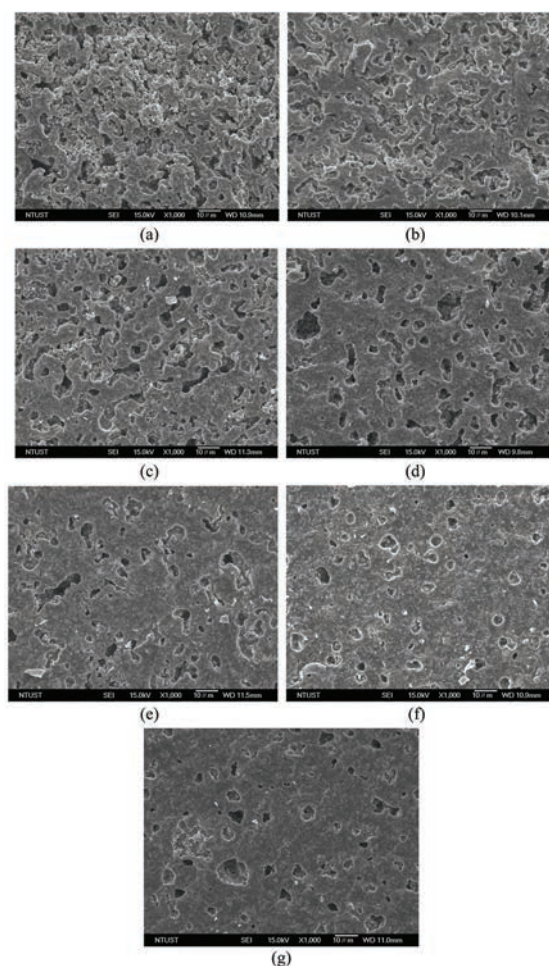


Fig. 6. SEM micrographs of a B(NBL)T/glass composite with 50 vol.% glass addition sintered at (a) 750 °C and (b) 950 °C, a B(NBL)T/glass composite with 55 vol.% glass addition sintered at (c) 750 °C and (d) 950 °C, and a B(NBL)T/glass composite with 60 vol.% glass addition sintered at (e) 750 °C, (f) 800 °C and (g) 850 °C for 2 hours.

sintering temperature of 1,260 °C, an increase in the density could be seen but pores could still be observed in the sintered bulk while a preferred orientation gradually developed. The sample sintered at 1,360 °C had a highly dense structure with highly prefer-oriented grains. Finally, the sample sintered at 1,460 °C exhibited large and elongated grains. Faceting of the grains as a result of preferred growth of certain crystal planes dominated the high-temperature-sintered microstructure of B(NBL)T, indicating the full development of the B(NBL)T phase at 1,460 °C.

When a B(NBL)T/glass composite with 50 vol.% glass addition was sintered at temperatures ranging from 750 °C to 950 °C for 2 hours, continuous pores could still be observed (Fig. 6(a) and (b)). As a result, the relative fraction of liquid was not high enough to cause full rearrangement of B(NBL)T grains, or the viscosity of the glass phase was too high at the sintering temperature. Such a result associated with a high initial glass addition could thus be ascribed to the phase reaction between B(NBL)T and glass during sintering. With a 55 vol.% glass addition, the pore size as well as the porosity apparently decreased with an increase in the sintering temperature, but pores greater than 10 μm were still observed (Fig. 6(c) and (d)). On the other hand, the porosity obviously was very low at a sintering temperature of 750 °C for the composite with a 60 vol.% glass addition. At a sintering temperature of 800 °C, a close to fully densified structure could be obtained (Fig. 6(f)). However, at higher sintering temperatures, pores seemed to grow again (Fig. 6(g)).

Fig. 7 show the BEI images of the surfaces of specimens sintered at different conditions for the composite with a 55 vol.% glass addition. For the specimen sintered at 800 °C for 2 hours, the original B(NBL)T grains still maintained their original morphology. At a sintering temperature of 850 °C, the grains had gradually changed in morphology, and finally, at a sintering temperature of 950 °C and an isothermal hold of 2 hours, preferred orientation of B(NBL)T grains could be easily found (Fig. 7(e)). Similar results were also observed for the composite with a 60 vol.% glass addition. On the other hand, the effect of isothermal holding time on the development of grain morphology was not as significant as that of sintering temperature.

X-ray diffraction analysis

Fig. 8(a) shows the X-ray diffraction patterns of various samples processed at different conditions. It is noted that the X-ray diffraction patterns of the original B(NBL)T powder sintered at 1,260 °C, 1,360 °C and 1,460 °C for 1 hour are almost the same, and are similar to the that of $BaNd_2Ti_4O_{12}$ reported by Silva et al. [15], exhibiting an orthorhombic crystalline structure. Thus, development of the B(NBL)T phase in the solid state reaction stage of the as-received powder was nearly completed. Fig. 8(b), 8(c) and 8(d) show the X-ray diffraction patterns of B(NBL)T/glass composites with 50 vol.%, 55 vol.%,

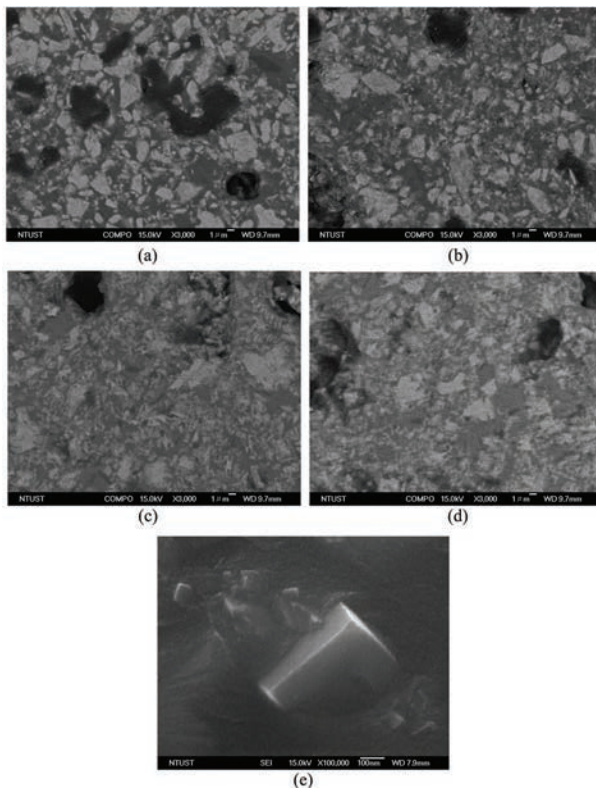


Fig. 7. BEI images of B(NBL)T/glass composite with 55 vol.% glass addition sintered at (a) 800 °C, (b) 850 °C, (c) 900 °C, and (d) 950 °C for 2 hours. (e) an enlarged micrograph of Fig. 7(d), showing a B(NBL) grain with preferred orientation.

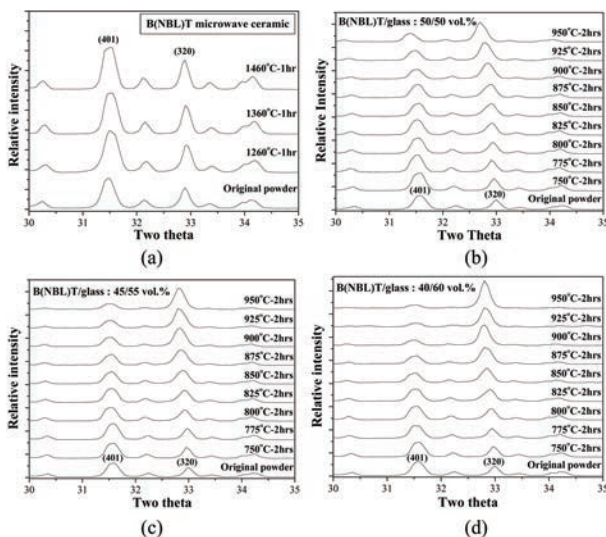


Fig. 8. X-ray diffraction patterns of (a) B(NBL)T, (b) B(NBL)T/glass composite with 50 vol.% glass addition, (c) B(NBL)T/glass composite with 55 vol.% glass addition, and (d) B(NBL)T/glass composite with 60 vol.% glass addition, at different sintering temperatures.

and 60 vol.% glass additions, respectively, at different sintering temperatures. It was shown that the peak intensity of the (320) plane of B(NBL)T increased with an

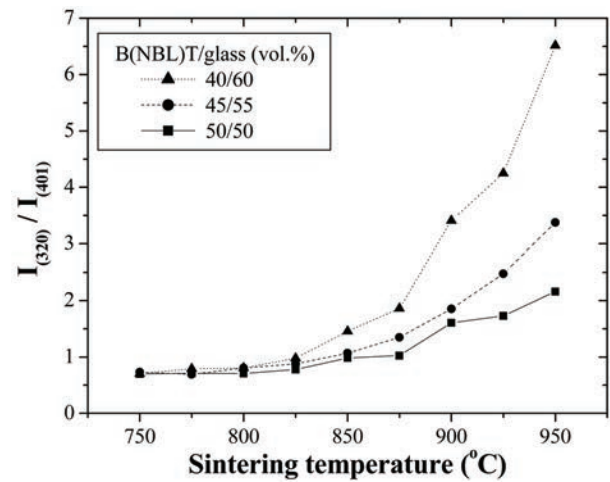


Fig. 9. Intensity ratios of $I_{(320)}/I_{(401)}$ as a function of sintering temperature for the B(NBL)T/glass composites with 50, 55, and 60 vol.% glass sintered for 2 hours in air.

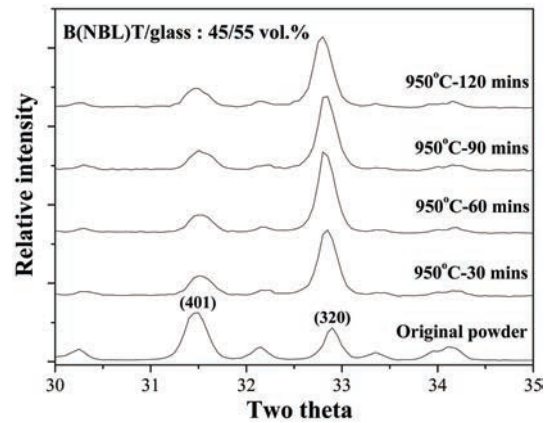


Fig. 10. X-ray diffraction patterns of B(NBL)T/glass composite with a 55 vol.% glass addition sintered at 950 °C for different sintering times.

increase in the sintering temperature, at the expense of (401) plane. Fig. 9 show the variation of the ratio of the peak intensity of (320) to that of (401), $I_{(320)}/I_{(401)}$ with sintering temperature, for B(NBL)T/glass composites with 50, 55, and 60 vol.% glass additions, respectively. It can be observed that the $I_{(320)}/I_{(401)}$ ratio not only increased with the increase in sintering temperature, but also volume percentage of glass phase. Fig. 10 shows the X-ray diffraction patterns of B(NBL)T/glass composites with a 55 vol.% glass addition sintered at 950 °C for different sintering times. It can be observed that the increase in sintering time did not contribute to a significant variation in the relative $I_{(320)}/I_{(401)}$ ratio. Accordingly, sintering temperature, instead of sintering time, dictated the development of preferred orientation.

The diffraction angles of the (320), (401), and (303) planes of the B(NBL)T/glass composite with 60 vol.% glass addition sintered at 950 °C for 2 hours were 32.80°,

31.55° and 29.05°, respectively. The lattice constants of the crystal were calculated by solving the three equations derived from the diffraction angles of these three planes. A least square regression of the three equations yielded lattice constants of $a = 1.154$ nm, $b = 0.776$ nm and $c = 1.536$ nm. Compared with the JCPDS data of $BaNd_2Ti_4O_{12}$ ceramic (No.35-0331, $a = 1.147$ nm, $b = 0.769$ nm, $c = 1.552$ nm), these values were either larger by 0.6% in the a-axis and 0.9% in b-axis, or smaller by 1.0% in c-axis.

The only expected function of the glass phase in the composite is to glue the dielectric particles together at a low temperature, just like the role of the polymer in a dielectric powder-polymer composite [16]. However, in this study, the glass phase did not just play the role of a glue, it also caused a new development in the structure. As can be seen from the X-ray diffraction patterns, the peak of highest intensity in the B(NBL)T crystal belongs to the (401) crystal plane, while that in the B(NBL)T/glass composites belongs to the (320) crystal plane (see in Fig. 8). Such a development could be ascribed to the change of the preferred orientation in B(NBL)T crystals, due to the wetting by the glass phase and, possibly, a phase reaction at the sintering temperature. A similar observation was also reported elsewhere [14], where an aluminosilicate glass addition to $BaO-Nd_2O_3-Sm_2O_3-TiO_2$ promoted the development of columnar grains of (002) preferred orientation. In addition, it was also found that sintering $Ba(Nd_{0.8}Sm_{0.2})_2Ti_4O_{12}$ powder coated with a thin B_2O_3 layer up to 2 wt.% in quantity at 960 °C caused the evolution of elongated grains with a (002) preferred orientation, whose intensity increased with increases of B_2O_3 quantity and sintering temperature [17].

In addition to the change in intensity, it can also be observed that the diffraction angle of the (320) crystal plane shifted to lower angles with an increase in the sintering temperature. This observation indicated that not only a change of preferred orientation but also a change of lattice parameters took place when B(NBL)T was sintered in the presence of the glass phase. Cho et al. [9] reported that two specific planes of $BaO(Nd_{1-x}Bi_x)_2O_3 \cdot 4TiO_2$ shifted to higher angles with the addition of $Li_2O-B_2O_3-SiO_2-Al_2O_3-CaO$ glass when sintered at 900 °C. Chang and Chiou [17] reported that the incorporation of B_2O_3 into the crystal of $Ba(Nd_{2-x}Sm_x)Ti_4O_{12}$ would result in changes of lattice constants of the crystal, due to the diffusion of B atoms to the interstitial sites. Based on these observations, interaction between the B(NBL)T grains and the glass phase could have caused the change of preferred orientation as well as the shifting of diffraction angles in the XRD patterns observed in this study. An increase in the glass phase addition reduced the commenced temperature of which the development of the new preferred orientation.

Dielectric Properties

Fig. 11 shows the dielectric constant and sintered density

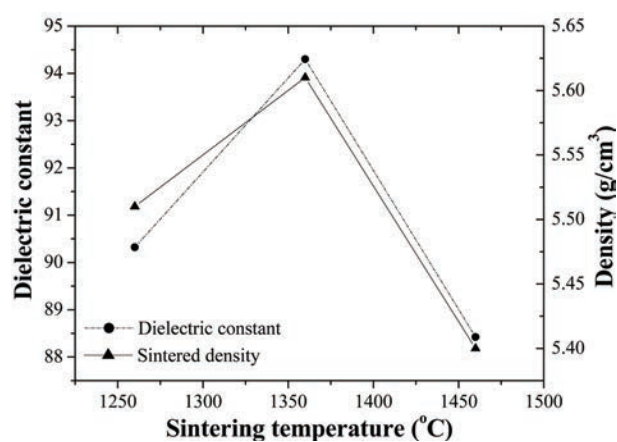


Fig. 11. Variations of dielectric constant and sintered density of B(NBL)T with sintering temperature.

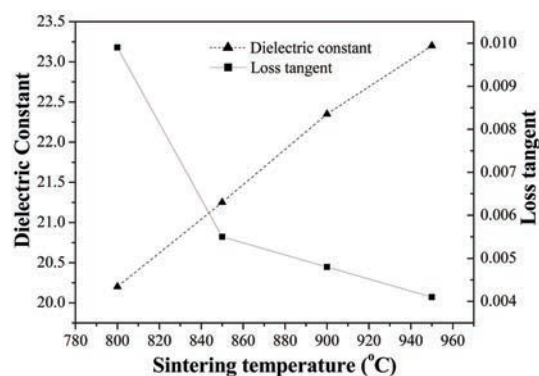


Fig. 12. Dielectric properties as a function of sintering temperature for B(NBL)T/glass composite with a 55 vol.% glass addition sintered in air for 2 hours.

of B(NBL)T as a function of sintering temperature. The dielectric constant increased from 90.3 to 94.3 as the sintering temperature increased from 1,260 °C to 1,360 °C but decreased to 88.4 at a sintering temperature 1,460 °C. The trend was similar to that of the sintered density. A preferred orientation of B(NBL)T grains took places at sintering temperatures higher than 1,360 °C (Fig 5(d)), which resulted in the formation of a loosely packed sintered structure, and, accordingly, decreases in sintered density and dielectric constant.

Fig. 12 shows the variation of dielectric properties with sintering temperature for the B(NBL)T/glass composite with 55 vol.% glass addition. The dielectric constant increased but the loss tangent decreased with an increase in the sintering temperature. An increase in the sintered density generally only resulted in an increase of the dielectric constant but not a decrease in the dielectric loss. Thus, the observation of a decrease in the dielectric loss with an increase in the sintering temperature must have been caused by the phase reaction between the B(NBL)T and the glass phase [18]

Table 2 shows the sintered density and dielectric properties of B(NBL)T, glass, and B(NBL)T/glass

Table 2. Sintered density and dielectric properties of glass, B(NBL)T, and B(NBL)T/glass composites at different sintering parameters

Specimens	(g/cm ³)	ϵ_r	$\tan\delta$	f (GHz)	$Q \times f$ (GHz)
Glass at 700 °C (at 1 GHz)	2.45	6.8*	2×10^{-3} *	—*	—*
B(NBL)T at 1,260 °C	5.51	90.3	1.3×10^{-3}	3.46	2586
B(NBL)T at 1,360 °C	5.61	94.3	1.3×10^{-3}	3.42	2547
B(NBL)T at 1,460 °C	5.40	88.4	1.9×10^{-3}	3.50	1878
50B(NBL)T/50 glass at 950 °C	2.98	20.5	4.9×10^{-3}	6.67	1354
45B(NBL)T/55glass at 950 °C	3.36	23.2	4.1×10^{-3}	6.67	1620
40B(NBL)T/60glass at 950 °C	3.34	20.3	5.2×10^{-3}	7.11	1372

*The dielectric constant (ϵ_r) and loss tangent are reported for a test frequency of 1 GHz, due to the fact that the resonance frequency of glass is higher than the limit of the test equipment, which is 12 GHz. ($Q=1/\tan\delta$)

composites that were processed under different conditions. The best dielectric properties of the B(NBL)T/glass composites were achieved for the composite with a 55 vol.% glass addition. A lower sintered density was responsible for the lower dielectric constant for the B(NBL)T/glass composite with a 50 vol.% glass addition. On the other hand, the existence of an excessive amount of glass phase, whose dielectric constant is smaller but its dielectric loss is larger than those of B(NBL)T, was responsible for the lower dielectric constant and higher dielectric loss for the B(NBL)T/glass composite with a 60 vol.% glass addition. The B(NBL)T/glass composites did not achieve dielectric constant values estimated from the rule of mixtures, but exhibited high dielectric losses, which arose from the motion of the alkali ions in the glass phase [19]. The substantial deviation of the measured dielectric constant from that estimated by the rule of mixtures is a percolation phenomenon, and is believed to arise from the high threshold volume percentage of the B(NBL)T phase that is required to induce a dielectric response in the composite structure [20]. Consequently, in order to further increase the dielectric constant of the composites, a higher volume percentage of B(NBL)T and a better sintering aid are required.

Conclusions

An alkali borosilicate glass ($\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-CaO-Na}_2\text{O-K}_2\text{O-BaO}$) of low softening temperature could reduce the sintering temperature of $\text{Ba}_{0.88}(\text{Nd}_{1.40}\text{Bi}_{0.42}\text{La}_{0.30})\text{Ti}_4\text{O}_{12}$ powder from 1,360 °C to temperatures lower than 950 °C, only at a volumetric percentage higher than 55 vol.%. A phase reaction between B(NBL)T and the glass caused a change in grain morphology and lattice constants of the B(NBL)T phase. Such a phase reaction between B(NBL)T and glass was responsible for the retarded densification for the B(NBL)T/glass composite with a glass phase addition as high as 50 vol.%. On the other hand, due to the vaporization of the glass phase at high temperatures, internal blistering of sintered compacts could take place for the B(NBL)T/glass composite with a 60 vol.% glass addition sintered at a low heating rate and/or with a long isothermal hold at the sintering

temperature. For the B(NBL)T/glass composite with a 55 vol.% glass addition, appropriate dielectric characteristics at high frequencies ($\epsilon_r = 23.2$, $\tan\delta = 4.1 \times 10^{-3}$, and $Q \times f = 1620$ GHz, $f = 6.67$ GHz) could be attained.

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