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Low-temperature sintering and microwave dielectric properties of $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$ by the glass additions

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Abstract

The system $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$ solid solution containing lithium borosilicate glass were prepared and examined as a low-temperature co-fired ceramics (LTCC). The sintering properties of the low-temperature sintered $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$ with glass frit were investigated using dilatometer, SEM and TEM. The microwave dielectric properties were measured using a network analyzer.

The addition of glass to $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$ significantly lowered the sintering temperature to ~900 °C in comparison to ~1300 °C for samples without glass. The formation of liquid phase present in the low temperature sintered sample was confirmed using TEM. It was found that thermal properties of the added lithium borosilicate glass dominated the sintering properties of $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$ including shrinkage onset temperature and shrinkage rate. The sample of $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ with 10 wt.% glass sintered at 900 °C exhibited a quality factor ($Q \times f$) of 2200 GHz, a ε_r of 68, and a τ_f of 55 ppm/°C.

Keywords: A. Sintering; C. Dielectric properties; D. Glass ceramics; LTCC

1. Introduction

Microwave dielectric materials have been used for wireless applications. Several types of dielectric materials have been developed and put into practical use for microwave filters, resonators and mobile-communications technology [1]. Tungsten-bronze type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Nd, Sm and La) ceramics and their Bi-substituted systems were widely studied, due to their high dielectric constants (>80) and low dielectric losses [2,3]. These systems require a sintering temperature up to 1300 °C.

More recently, low-temperature co-fired ceramics (LTCC) has demonstrated that it meets the performance and cost requirements for portable wireless application. In order to be co-fired with high conductivity electrode such as silver, it is necessary to lower the sintering temperature of the dielectrics to 900 °C. For this purpose, oxide dopants (B_2O_3, CuO, ZnO, etc.) and glasses (low-temperature melting glasses) are widely used as the sintering aids. The performance of ceramics with glass additions strongly depends on the densification behavior, microstructure, and interaction between glass and ceramics. Dernovsek et al. [4] reported that $BaNd_2Ti_4O_{12}$ ceramic with reactive BBSZ (B_2O_3, Bi_2O_3, SiO_2, ZnO) glass was sintered at 900 °C and had $\varepsilon_r = 67$, $Q > 1000$, and $\tau_f = 4$ ppm/°C at a frequency of 6 GHz. Cheng et al. [5] reported that $BaNd_2Ti_4O_{12}$ ceramic was sintered at 950 °C by using the BBS (BaO, B_2O_3, SiO_2) glass and had $\varepsilon_r = 67$ and ($Q \times f$) ~5000 GHz.

In our present work, a kind of lithium borosilicate glass Li_2O–B_2O_3–SiO_2–Al_2O_3–CaO (LBSAC) was added in order to lower the sintering temperature of $Ba(Nd_{0.8}Bi_{0.2})_2Ti_4O_{12}$ (BNBT) ceramics to ~900 °C. The effects of LBSAC glass on the sintering microwave dielectric properties were investigated. The phase formation and microstructure variation during the sintering process were also examined.

2. Experimental procedures

Lithium borosilicate glass (LBSAC) was prepared by mixing appropriate amount of Li_2O, B_2O_3, SiO_2, Al_2O_3 and CaO. The glass was melted at 1000 °C in

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air atmosphere using an uncovered Pt crucible. The $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$ ceramic ($x = 0$, 0.05, 0.1, 0.2, 0.3) were prepared by conventional solid state reaction method. $BaCO_3$, Nd_2O_3, Bi_2O_3 and TiO_2 of 99.9% purity were used as raw material. The powders were ball-milled in a polyethylene bottle with ZrO_2 media for 24 h using ethanol, and then the mixtures were rapidly dried and calcined at 1200–1300 °C for 2 h in air.

The calcined powders were subsequently mixed with the LBSAC glass in wt.% ranging from 3 to 10, and all mixtures were ball-milled for 48 h. The milled powders were then dried, granulated (with PVA) and pressed at 1000 kg/cm^2 to form pellets. The pellets were sintered at 900–1000 °C for 2 h in air with a heating rate of 5 °C/min.

The bulk density of the sintered samples was evaluated by the Archimedes method. Temperature and time-controlled sintering behaviors were investigated using dilatometer (Model DIL 402PC, Netzsch Instruments, Germany). Phase and composition of the samples are examined by X-ray powder diffraction (Model M18XHF, Macscience Instruments, Japan) and EPMA (Electron Probe X-ray Micro Analyzer, Model JXA-8900R, JEOL, Japan). Microstructures of the sintered and quenched samples were examined by using scanning electron microscope (Model JSM-5600, JEOL, Japan). Using a network analyzer (Model HP8720C, Hewlett Packard, USA), the quality factor (unloaded Q) was measured by the transmission cavity method and the relative dielectric constant (ε_r) was measured by Hakki and Colleman's method [6]. The temperature coefficient of the resonant frequency (τ_f) was measured by using an invar cavity in the temperature range of 20–80 °C [7].

3. Results and discussion

3.1. The microwave dielectric properties of $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$

The microwave dielectric properties of $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$ ceramics are shown in Table 1. The dielectric constant of the specimens increased while the $Q \times f$ value decreased with increasing Bi content. Okawa et al. [8] reported the similar tendency with Bi content at the system of $Ba_4(Nd_{1-y}Bi_y)_{9+1/3}Ti_{18}O_{54}$ ($y = 0$–0.3). The composition $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ was chosen for further study because it have the smallest τ_f value among the compositions in Table 1.

Table 1
Microwave dielectric properties of $BaO{\cdot}(Nd_{1-x}Bi_x)_2O_3{\cdot}4TiO_2$ ceramics

Composition	Sintering temperature (°C)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
$x = 0.05$	1300	90	7600	33
$x = 0.1$	1300	93	5900	15
$x = 0.2$	1300	106	4200	8
$x = 0.3$	1275	115	2100	26

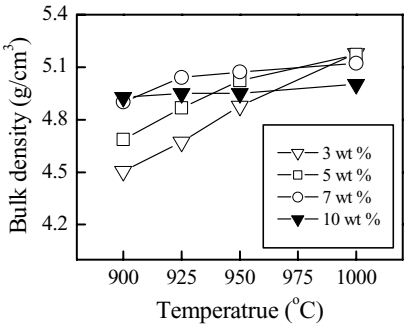

Fig. 1. Bulk density of $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ samples having various amounts of LBSAC glass as a function of sintering temperature.

3.2. The sintering behavior of $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ (BNBT) with LBSAC glass (BNBT)

Fig. 1 shows the bulk densities of the BNBT samples having various amount of LBSAC glass as a function of sintering temperature. The density of samples increased with increasing sintering temperature and well-sintered ceramics

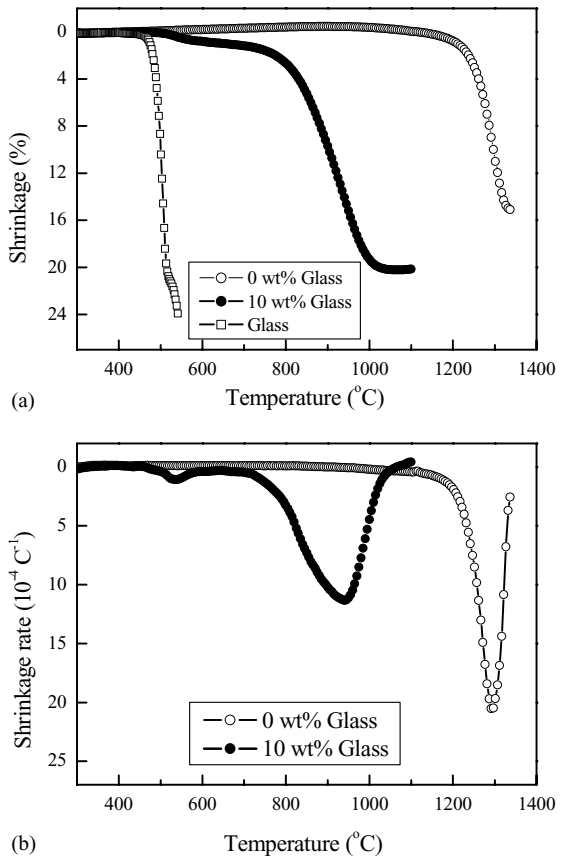

Fig. 2. Shrinkage curves of the green compacts of LBSAC glass and $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ samples with 0 and 10 wt.% LBSAC glass: (a) shrinkage and (b) shrinkage rate.

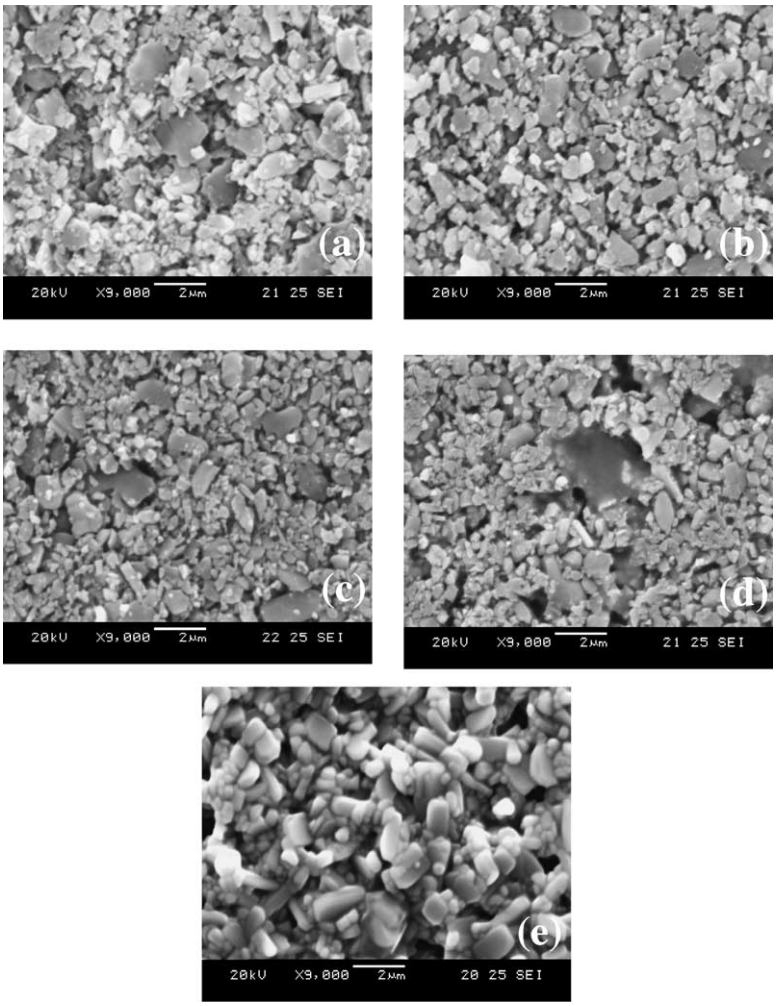

Fig. 3. Scanning electron micrographs of $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ samples with 10 wt.% LBSAC glass quenched at (a) 500 °C, (b) 525 °C, (c) 550 °C, (d) 575 °C and (e) 900 °C.

were obtained at the amount of 10 wt.% glass at 900 °C. Further increase of the sintering temperature did not change the sintered densities of 10 wt.% glass added BNBT system. These results show that LBSAC additions are effective in lowering the sintering temperature of BNBT.

To investigate the role of LBSAC glass on sintering, shrinkage variations during heating were investigated using dilatometer. Fig. 2 shows shrinkage curves and shrinkage rates of the green compact of pure BNBT, 10 wt.% LBSAC added BNBT (10BNBTG), and LBSAC glass. As can be seen in the Fig. 2(a), a rapid shrinkage occurred near 500 °C in the case of LBSAC glass, which means the glass started to melt. Shrinkage was initiated at approximately 1200 °C for pure BNBT sample. By the way, in Fig. 2(b), the shrinkage of the 10BNBTG sample was occurred about 550 °C and large shrinkage was observed about 950 °C. In order to investigate the densification behavior near 550 °C, four 10BNBTG samples were quenched during sintering and Fig. 3 shows scanning electron micrographs of specimens quenched from 500 to 900 °C. In the case of 500 and 550 °C quenched sample, the mixture of relatively small BNBT powder and large LBSAC glass frit were found. The melted LBSAC frit was found at 575 °C quenched sample. By the way, the grain growth between BNBT powders did not occur at 575 °C and large BNBT grains were found

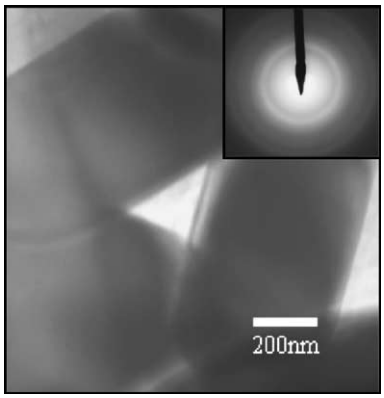

Fig. 4. Transmission electron microscope image of $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ sample with 10 wt.% LBSAC glass sintered at 900 °C for 2 h. (The insets show SAD patterns of the intergranular phase.)

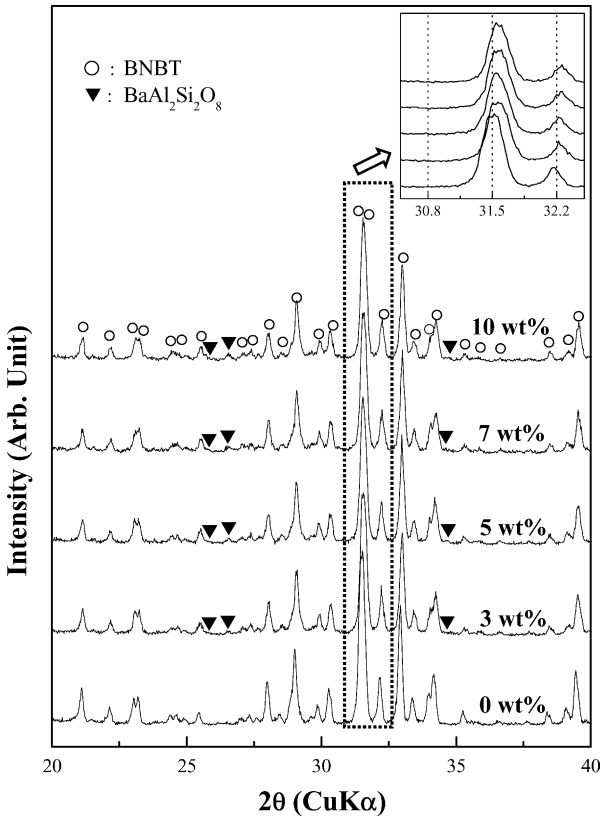

Fig. 5. X-ray diffraction patterns for $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ samples having different amount of LBSAC glass sintered at 900 °C.

at 900 °C quenched sample. It can be said that melting of LBSAC glass frit resulted in the initial shrinkage near 550 °C and the grain growth of BNBT resulted in the main shrinkage near 900 °C.

Fig. 4 shows the TEM image of 10BNBTG sample sintered at 900 °C for 2 h. Liquid phase was found at the junction of BNBT grains. (SAD pattern in the figure indicated that the second phase was amorphous phase.)

Table 2
Microwave dielectric properties of LBSAC glass and $BaAl_2Si_2O_8$ ceramics

Composition	Sintering temperature (°C)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
LBSAC	550	8	2400	−48
$BaAl_2Si_2O_8$	1450	7	56200	−50

3.3. Phase analysis of BNBTG samples

Fig. 5 is the XRD patterns of the pure and LBSAC-added BNBT samples sintered at 900 °C. Additional phases were not detected in the XRD pattern of pure BNBT, while a second phase reflection, due to $BaAl_2Si_2O_8$, was found near 26° in the case of 10BNBTG sample. The reflections of BNBT were shifted to higher angles with the addition of LBSAC glass, in other words, the lattice parameter of BNBT decreased.

Fig. 6 is the compositional mapping data using EPMA of the sintered sample of 10BNBTG. The bright color means high intensity of the element. Two kinds of second phase were found in the figure (A and B region). As can be seen in the figure, main compositions of A phase was Ti and those of B phase was $BaAl_2Si_2O_8$, found in the XRD. We could not identify the A phase because most of the possible Ti-based compounds from BNBT have X-ray reflections almost same location with those of BNBT in the XRD patterns.

3.4. The microwave dielectric properties of BNBTG samples

Fig. 7 shows microwave dielectric properties of the BNBTG, as a function of sintering temperature. Generally, the density and the amount of glass influenced the dielectric constant and $Q \times f$ value of LTCC [9]. The specimen having low LBSAC content exhibited high $Q \times f$ values because LBSAC glass had lower $Q \times f$ value (2400) than BNBT (4200), as can be seen in Table 2. At fixed LBSAC

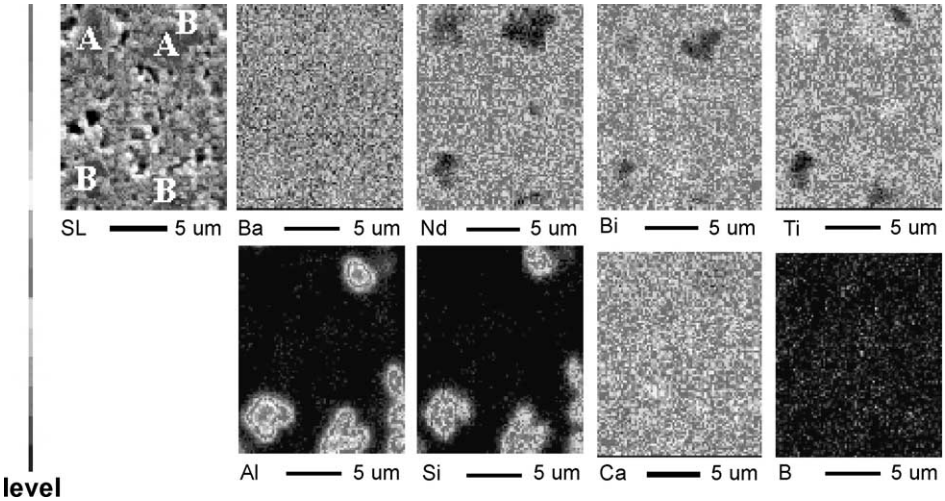

Fig. 6. EPMA analysis of $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ sample with 10 wt.% of glass sintered at 900 °C.

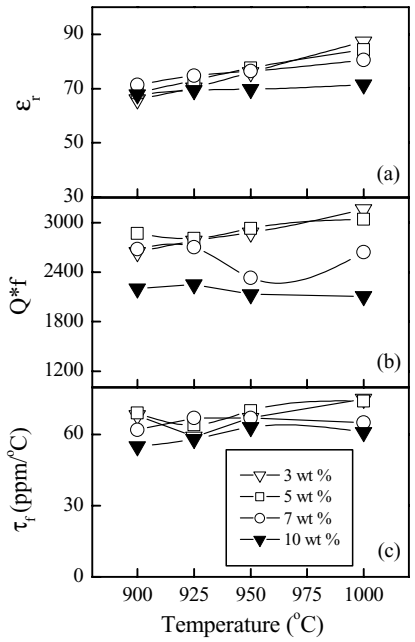

Fig. 7. The microwave dielectric properties of $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ samples with LBSAC glass as a function of sintering temperature.

content, variation of density and dielectric properties over sintering temperature exhibited similar tendency.

In the case of τ_f, large increase (from 8 to 68 ppm/°C) was found with the small amount (3 wt.%) of LBSAC addition. It might be related to Ti-rich second phase (A phase in Fig. 6) since the LBSAC glass and $BaAl_2Si_2O_8$ have negative τ_f value (Table 2).

4. Conclusions

The $BaO{\cdot}(Nd_{0.8}Bi_{0.2})_2O_3{\cdot}4TiO_2$ ceramics with lithium borosilicate glass were prepared and their sintering and dielectric properties were evaluated. It was found that the addition of 10 wt.% LBSAC glass to BNBT lowered the sintering temperature from 1300 to 900 °C. The melting of LBSAC glass occurred near 450 °C, which initiated the initial shrinkage of BNBTG samples. Liquid phases were found at the grain boundary junction of 10BNBT samples sintered at 900 °C. This result indicated that the reduced sintering temperature was attributed to the formation of liquid phase. The 10 wt.% LBSAC glass added BNBT samples was sintered at 900 °C and exhibited the dielectric properties of $\varepsilon_r = 68$, $Q \times f = 2200$ GHz, $\tau_f = 55$ ppm/°C, which indicates this composition can be one of the candidates for high-*k* LTCC materials.

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