Effects of Nd_2O_3 and TiO_2 Addition on the Microstructures and Microwave Dielectric Properties of BaO-Nd_2O_3-TiO_2 System

Tae-Hong Kim, Jung-Rae Park, Suk-Jin Lee, Hee-Kyung Sung, Sang-Seok Lee and Tae-Goo Choy

CONTENTS

ABSTRACT

The effects of Nd_2O_3 and TiO_2 addition on the microstructures and microwave dielectic properties of BaO-Nd_2O_3-TiO_2 system were investigated. $BaNd_2Ti_4O_{12}$ or $BaNd_2Ti_5O_{14}$ phases were observed for compositions based on $BaO/Nd_2O_3 = 1$ ratio. The compositions deviated from $BaO/Nd_2O_3 = 1$ ratio were composed of major phases of $BaNd_2Ti_4O_{12}$ or $BaNd_2Ti_5O_{14}$, and the compound of Nd_2O_3 and TiO_2 ($Nd_2Ti_2O_7$) or that of BaO and TiO_2 ($BaTi_4O_9$). The microstructure of ceramic with $BaO \cdot Nd_2O_3 \cdot 4TiO_2$ composition varied from spherical grains to needlelike grains with increasing sintering temperature. With increasing Nd_2O_3, the optimum sintering temperature with maximum density increased, and the dielectric constant(ε_r) and quality factor(Q) decreased due to the formation of secondary phases. With increasing TiO_2, the optimum sintering temperature and the dielectric constant decreased with increased Q value. And the temperature coefficient of resonant frequency, τ_f shifted toward positive direction. The dielectric ceramics with $BaO/Nd_2O_3 = 1$ showed Q values of above 2000 and dielectric constants of above 80 at 3GHz.

I. INTRODUCTION

With recent progress of microwave telecommunication and satellite broadcasting, many kinds of microwave components such as band pass filters (BPFs), duplexers and oscillators using dielectric resonators have been developed [1]. Microwave dielectric ceramics have been used in miniaturized filters and resonators because of their excellent frequency stability, reliability and low dielectric loss [1].

Since 1970's, microwave dielectric ceramics with dielectric constants ranging from 20 to above 100, such as BaO-PbO-Nd_2O_3-TiO_2 [2] and PbO-CaO-ZrO_2 [3] systems have been developed. Future works on high dielectric constant ceramics will be focused on reducing the size of components [4].

Although Kolar *et al.* [5] reported high dielectric BaO-Nd_2O_3-TiO_2 systems in 1978, their microwave properties such as dielectric constant, quality factor and the temperature coefficient of resonant frequency (τ_f) at microwave frequencies were not characterized at that time. A later work on this system by Takahashi *et al.* [6] reported the existence of the phases of $BaNd_2Ti_4O_{12}$ or $BaNd_2Ti_5O_{14}$, which is still debated in literatures [7]. Although microwave dielectric properties of $BaO{\cdot}Nd_2O_3{\cdot}5TiO_2$ and $BaO{\cdot}Nd_2O_3{\cdot}4TiO_2$ ceramics have been reported [4],[6], the microwave dielectric properties of BaO-Nd_2O_3-TiO_2 ceramics with varying Nd_2O_3 and TiO_2 addition amounts have not been reported yet. The microwave dielectric properties of this system depend on the fabrication procedures and compositions. To develop the high quality dielectric ceramics, it is necessary to perform studies about the effects of compositional changes upon the microwave dielectric properties. In the present study, we have investigated the effects of Nd_2O_3 and TiO_2 additions on dielectric constant, Q value and τ_f variations at microwave frequencies and the microstructural changes of BaO-Nd_2O_3-TiO_2 ceramics.

II. EXPERIMENTAL PROCEDURE

Samples were prepared by conventional mixing ceramic processes using $BaCO_3$, Nd_2O_3 and TiO_2 oxide powders of high purity above 99.9% (High Purity Chemicals Laboratory, Saitama, Japan). The compositions investigated in this study are summarized in Table 1. In the first 4 compositions the amount of Nd_2O_3 was varied from 0.5 mole to 1.5 mole with 1.0 mole BaO and 4.0 mole TiO_2 remaining fixed. For the next 3 compositions in Table 1, the amount of TiO_2 was varied from 4.0 mole to 5.0 mole while both BaO and Nd_2O_3 were fixed at 1.0 mole. Mixing was carried out in a polyethylene bottle containing zirconia balls and deionized water. The mixture was calcined at 1150° for 2 hours, crushed, mixed with poly vinyl alcohol (PVA), and then pressed with a cylindrical mold of

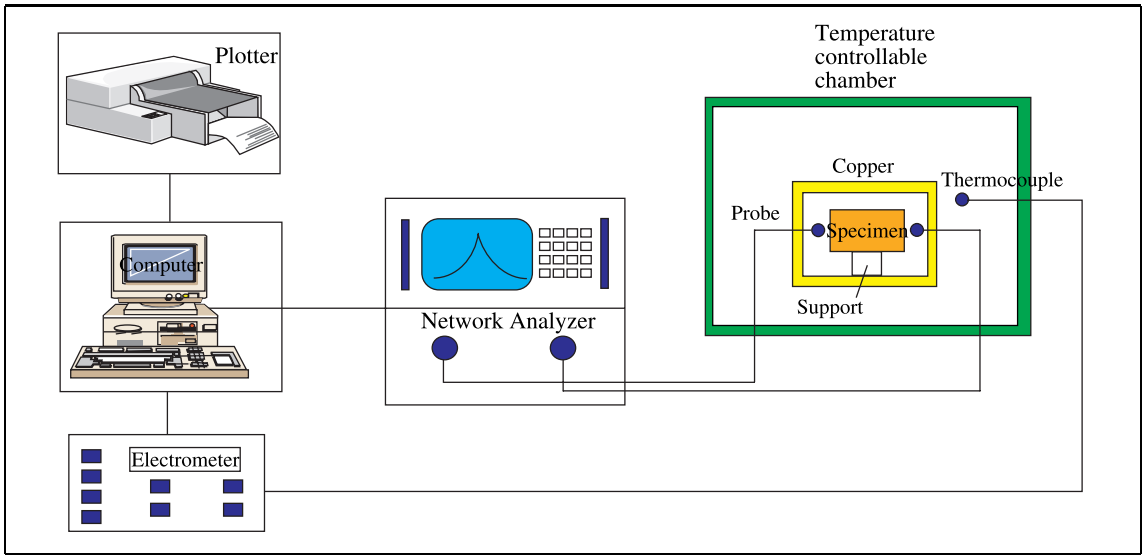

Fig. 1. Open cavity resonator method for τ_f and Q measurement.

15 mm diameter under pressure of 1 ton/cm^2 to yield cylindrical sample pellets. The specimens were sintered at temperature ranging from 1200°C to 1500°C with 50°C steps for 2 hours in the air. The relative densities of the sintered samples were measured using a water immersion technique. Structural analysis was performed by X-ray diffraction (XRD). Microstructures and composition analyses of sintered samples were examined using a scanning electron microscope (SEM) and wavelength dispersive spectrometer (WDS).

Samples for microwave dielectric measurements were prepared from sintered pellets by polishing both faces of cylinderical specimens (7 mm height and 10 mm diameter) with grinding paper(#1000) followed by 0.5 μm Al_2O_3 paste. The microwave dielectric constant was measured by the parallel plate method proposed by Hakki and Coleman using the $TE_{01\delta}$ resonant mode [9]. The qual-

Table 1. Compositions of the specimens of BaO-xNd$_2$O$_3$ – yTiO$_2$ system (B:BaO, N:Nd$_2$O$_3$, T:TiO$_2$).

Specimens	Powders		
	BaO	$Nd_2O_3(x)$	$TiO_2(y)$
BN0.5T4	1. 0	0. 5	4. 0
BN0.8T4	1. 0	0. 8	4. 0
BN1.2T4	1. 0	1. 2	4. 0
BN1.5T4	1. 0	1. 5	4. 0
BNT4	1. 0	1. 0	4. 0
BNT4.5	1. 0	1. 0	4. 5
BNT5	1. 0	1. 0	5. 0

ity factor and τ_f were measured by the open cavity resonator method using the $TE_{01\delta}$ mode [10] at 3 GHz with an HP8720C network analyzer connected with a computer and a temperature controllable chamber as shown in Fig. 1. The τ_f values were measured over the temperature range $0 \sim 100$°C according to the relation $\tau_f = \triangle f/(f_0 \triangle T)$, where f_0 is the resonant frequency at 25°C.

III. RESULTS AND DISCUSSION

1. Sintered Density

It is well known in dielectric materials that high density generally means good dielectric properties. A series of sintering experiments was performed to find the optimum sintering condition. Figure 2(a) shows the density changes as a function of sintering temperature for 5 compositions, which are described in Table 1 and have the different addition amounts of Nd_2O_3. Compositions containing more Nd_2O_3 than BNT4 show maximum densities above 1350°C. Compositions containing less Nd_2O_3 than BNT4 such as BN0.5T4 and BN0.8T4 show maximum densities below 1300°C. At a given sintering temperature and time, the more Nd_2O_3 added, the higher sintered density is obtained and the higher sintering temperature for maximum density is required. From this behavior, it can be interpreted by the fact that the rare-earth oxides like Nd_2O_3 usually have higher melting temperatures than any other oxide in the BNT system.

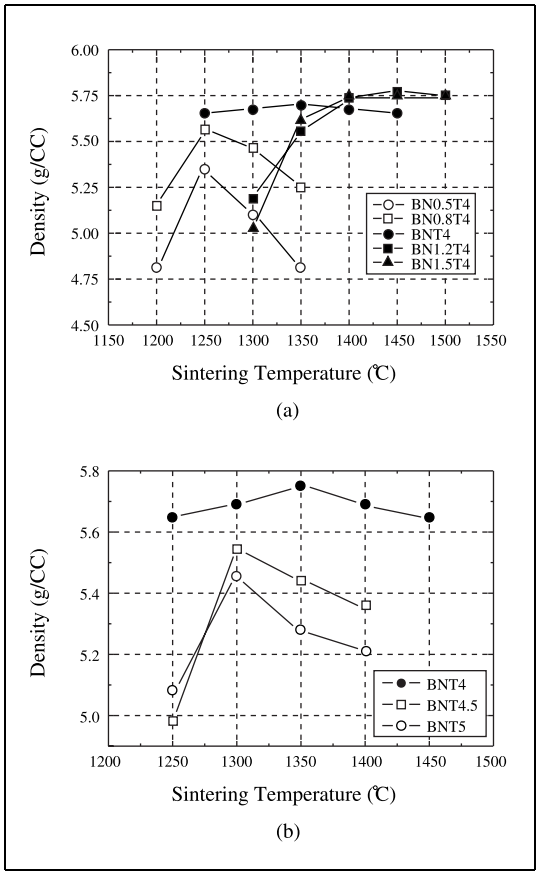

Fig. 2. Sintered density change as a function of sintering temperature for 2 hours (a) with Nd_2O_3 variation and (b) with TiO_2 variation.

Figure 2(b) shows the density changes as a function of sintering temperature of 3 compositions with the different amounts of TiO_2 in Table 1. The sintered density decreased with increasing TiO_2 amounts at a given sintering temperature and time. The compositions containing more TiO_2 than BNT4 show the maximum density below 1300°C, the optimum sin-

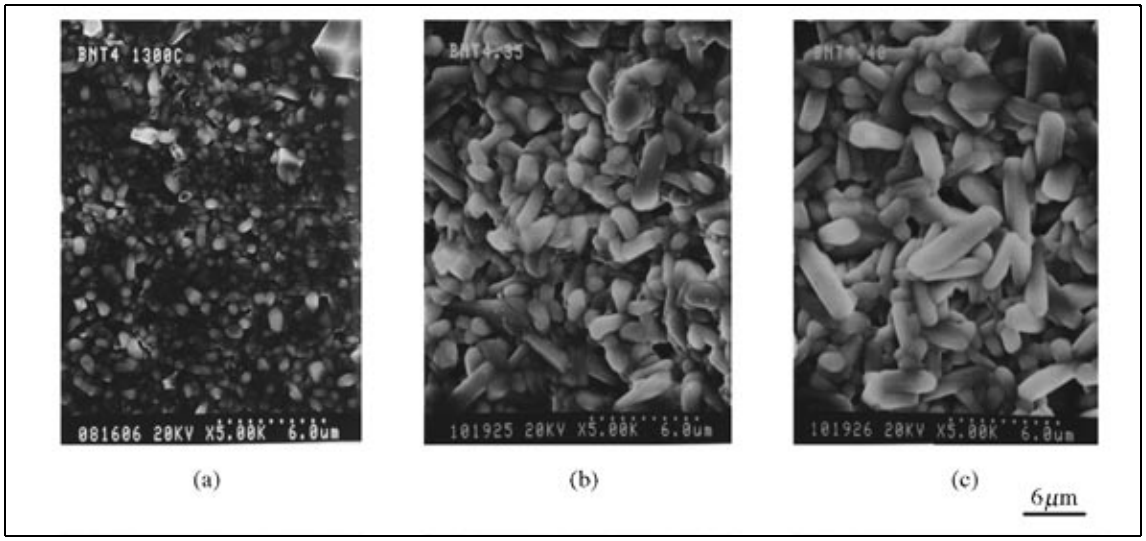

Fig. 3. SEM micrographs of BNT4 specimens at various sintering temperatures for 2 hours. (a) 1300°C, (b) 1350°C, and (c) 1400°C

tering temperature. This behavior can be interpreted as follows: TiO_2 , with a lower melting temperature than that of any other oxide in the BNT system, promotes the sintering effect. Finally it can be concluded that the Nd_2O_3-rich compositions require a higher sintering temperature for maximum density than the TiO_2-rich compositions require.

2. Microstructural Change and Phase Relation

Figure 3 shows the microstructures of sintered samples with the BNT4 composition at the sintering temperatures of 1300°C, 1350°C and 1400°C. Both spherical and needlelike grains are observed in the samples sintered at 1350°C and more needlelike shaped grains are observed in sample sintered at 1400°C. Sung *et al.* [11] reported that the grain shape of $BaO{\cdot}(Sm_{0.85}La_{0.15})_2O_3 \cdot 4TiO_2$ system was changed from spherical to needlelike as the sintering temperature increased. It is suggested that preferred grain growth occurs along orthorhombic a or b axes because a or b axes are longer than c axis in the orthorhombic structure, where estimated lattice parameters by Sung *et al.* using XRD were $a = 22.20$ Å, $b = 12.14$ Å and $c = 3.86$ Å respectively [11].

Figure 4 shows the microstructures of various compositions having maximum sintered densities. The grains of a Nd_2O_3-poor BN0.5T4 compositional sample are nearly spherical in shape, and in the samples of Nd_2O_3-rich BN1.5T4 composition, both spherical and needlelike grains are observed. The shapes of grains observed in the TiO_2-rich BNT5 composition are mostly needlelike.

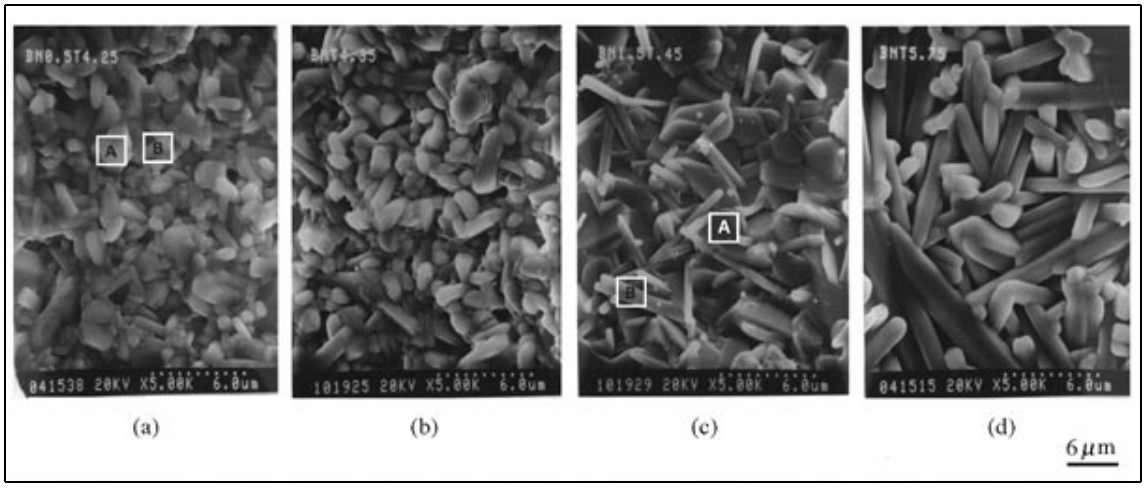

Fig. 4. SEM micrographs of specimens for various compositions at sintering temperatures with maximum density for 2 hours. (a) BN0.5T4 (at 1250°C), (b) BNT4 (at 1350°C), (c) BN1.5T4 (at 1450°C), and (d) BNT5 (at 1300°C)

Figure 5 shows the XRD patterns of 4 compositions. The peaks of the major phase of orthorhombic $BaNd_2Ti_4O_{12}$ reported by Takahashi *et al.* [6] are observed; however, $Nd_2Ti_2O_7$ phases in the Nd_2O_3-rich BN1.5T4 composition and $BaTi_4O_9$ phase in the Nd_2O_3-poor BN0.5T4 composition are also observed. This indicates that since the Nd_2O_3 stoichiometry is deviated from $BaO/Nd_2O_3 = 1.0$ in the compositions of BN1.5T4 and BN0.5T4, the mixed phases of Nd_2O_3 and TiO_2, or BaO and TiO_2 also exist in the two compositions.

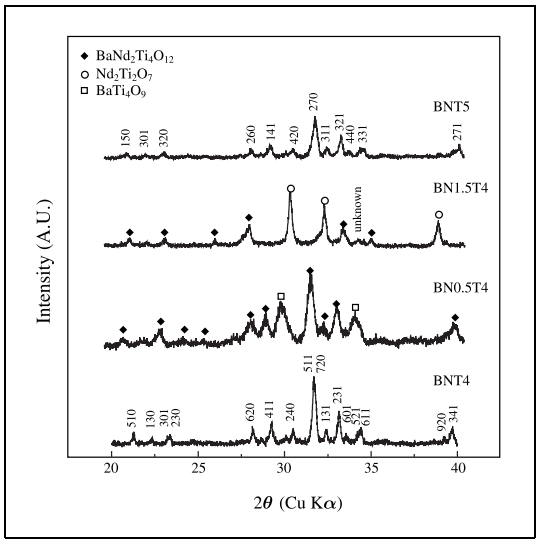

Fig. 5. XRD patterns of specimens for various compositions at sintering temperature with maximum density.

To confirm the above XRD results, composition analyses were carried out using SEM and WDS. Figure 6 shows the SEM image and WDS analysis results of the BNT4 specimen sintered at 1350°C. The SEM image shows various grain shapes. WDS analysis tells us that the spherical (A grain), elliptic (B grain) and needlelike shaped grain (C grain) are confirmed to have the same composition, $BaNd_2Ti_4O_{12}$ reported by Takahashi

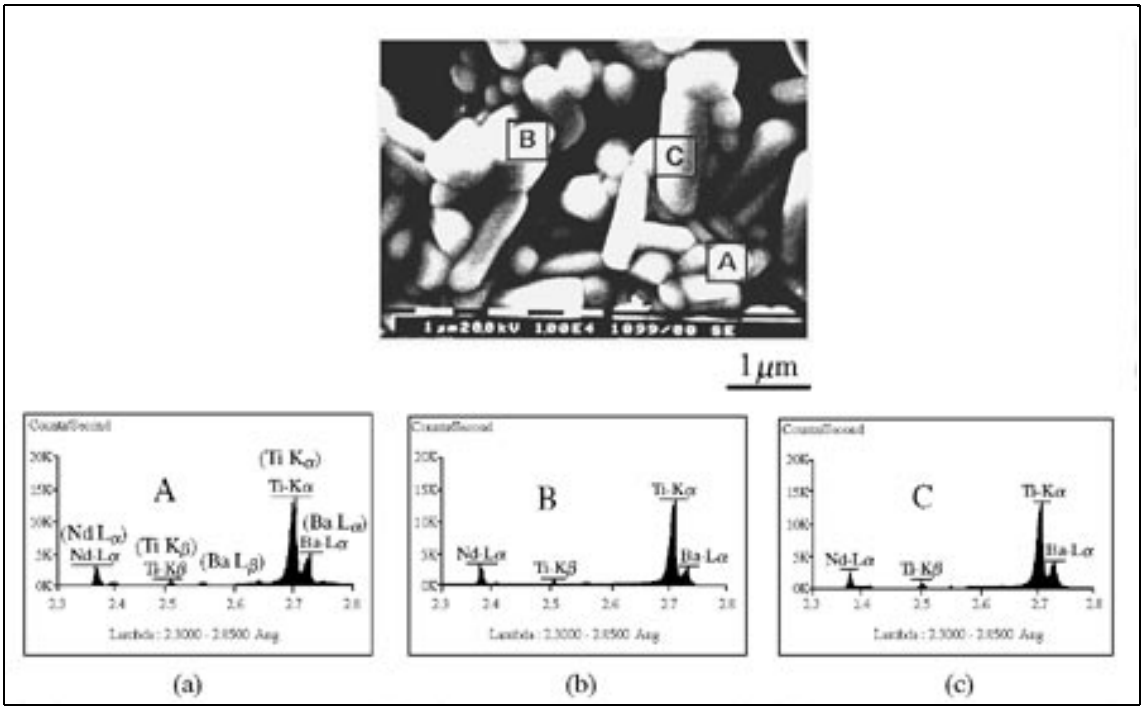

Fig. 6. SEM micrograph and WDS analysis results of BNT4 at 1350°C for 2 hours with various grain shapes. (a) round, (b) elliptic, and (c) needlelike

et al. [6]. Figure 7 shows the WDS analysis results for Nd_2O_3-poor BN0.5T4 and Nd_2O_3-rich BN1.5T4 specimens with a maximum density. The composition element peaks indicate that the large spherical grain (A grain) is the mixed compositions of Ba and Ti, and the needlelike grain (B grain) contains Ba, Nd and Ti elements in Fig. 4(a) of the BN0.5T4 specimen. Combining the WDS and XRD results, it seems that large spherical grain phase (A grain in Fig. 4(a)) is $BaTi_4O_9$, and the phase of needlelike grain (B grain) is the major phase of $BaNd_2Ti_4O_{12}$. The WDS analysis results of the large spherical grain (A grain) and the needlelike grain (B grain) in Fig. 4(c) of BN1.5T4 specimen are shown in Fig. 7(b). The large spherical grain (A grain) shows Nd and Ti compositional element peaks, and Ba, Nd and Ti elements peaks are observed in the needlelike grain (B grain). Comparing the WDS and XRD results, the phase of the large spherical grain (A grain) is $Nd_2Ti_2O_7$, and the phase of the needlelike grain (B grain) appears to be $BaNd_2Ti_4O_{12}$.

All the above results suggest that the compositions deviating from the $BaO/Nd_2O_3 = 1.0$ ratio are composed of phases of $BaNd_2Ti_4O_{12}$

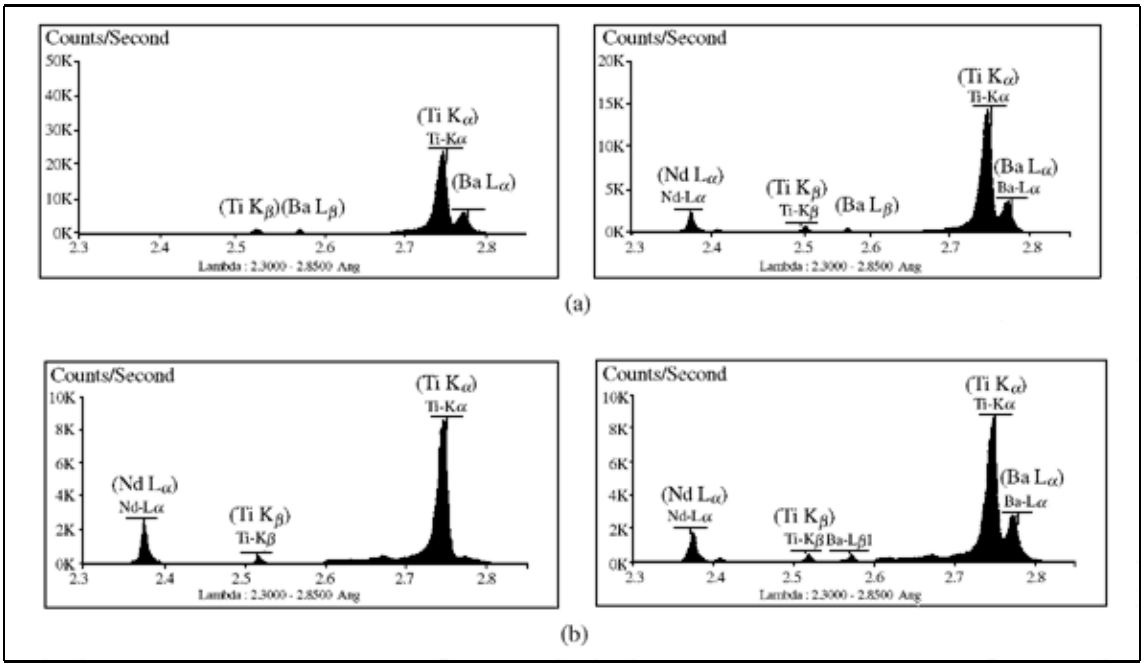

Fig. 7. WDS analysis results of (a) BN0.5T4 and (b) BN1.5T4 from Fig. 4.

and the compound of Nd_2O_3 and TiO_2 ($Nd_2Ti_2O_7$) or that of BaO and TiO_2 ($BaTi_4O_9$).

3. Microwave Dielectric Properties

Figure 8(a) shows the change in dielectric constant at 3GHz as a function of sintering temperature with Nd_2O_3 variation. In the case of BNT4, the sample sintered at 1350°C shows the maximum dielectric constant of 82.6. The compositions containing less Nd_2O_3 than BNT4 show lower dielectric constants than that of the BNT4, and the sintering temperature with maximum dielectric constant decreases. The compositions having more Nd_2O_3 than BNT4 show dielectric constants below 65, which are lower than that of BNT4, and poor-Nd_2O_3 compositions while the sintering temperature of the maximum dielectric constant increases. This can be explained by considering that the low dielectric constants are caused by the formation of secondary phases such as $Nd_2Ti_2O_7$ compound and $BaTi_4O_9$ compound observed by WDS and XRD. Figure 8(b) shows the dielectric constant changes with TiO_2 variation. As TiO_2 increases, the dielectric constant decreases and the sintering temperature of the maximum dielectric constant decreases. The variations in dielectric constant are in good agreement with sintered density changes as shown in Fig. 2. This result indicates that the processing conditions for high density are the same as the con-

ditions for high dielectric constant.

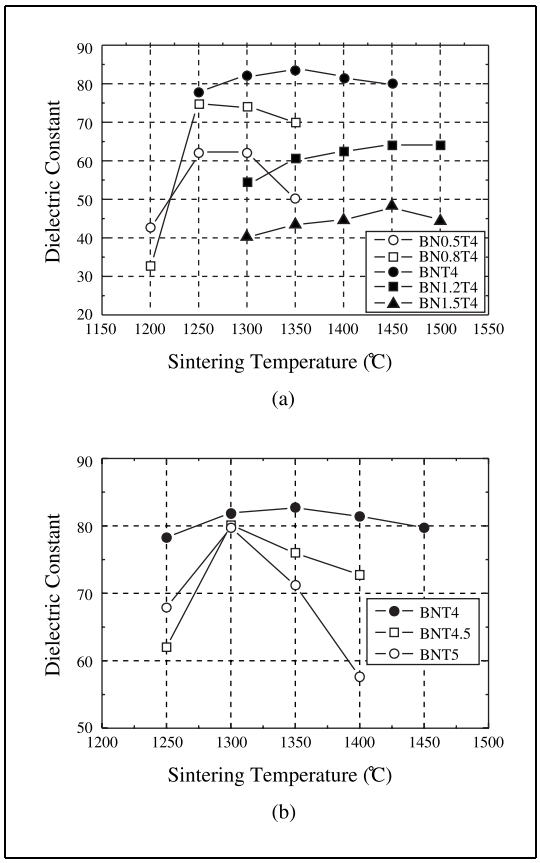

Fig. 8. Sintering temperature dependence of dielectric constant at 3 GHz (a) with Nd_2O_3 variation and (b) with TiO_2 variation.

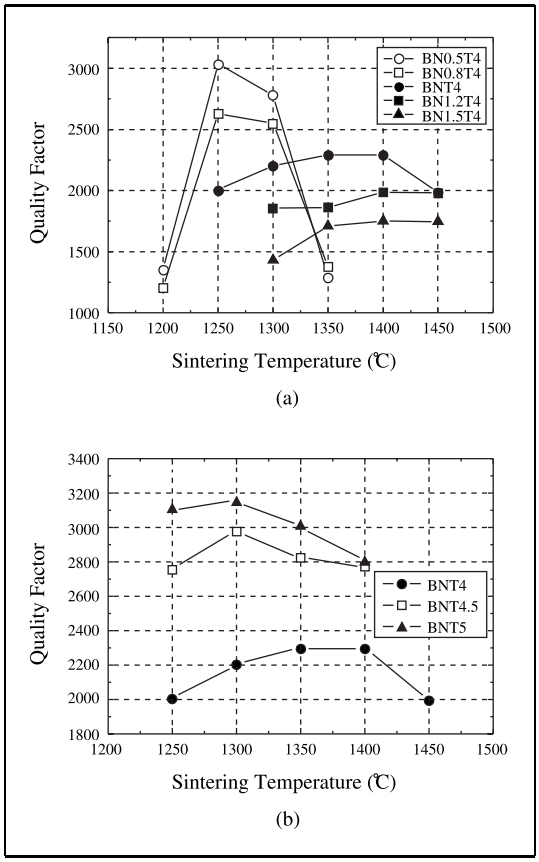

Fig. 9. Sintering temperature dependence of Q at 3 GHz for various compositions (a) with Nd_2O_3 variation and (b) with TiO_2 variation.

Figure 9(a) shows the Q values of the compositions with Nd_2O_3 variation at 3 GHz as sintering temperatures are varied. By comparing Fig. 9(a) with Fig. 2(a) showing the density changes with respect to Nd_2O_3 amounts and sintering temperatures, we can obtain 2 facts: First, for each individual composition the behavior of both density and Q value is very closely related, i.e., high density corresponds to high Q value just like the relation between density and dielectric constant. Second, as Nd_2O_3 increases, the maximum Q value decreases. This fact can be explained by the existence of $Nd_2Ti_2O_7$ compound which are known to have poor Q values [2]. The Q value of the BNT4 composition increases gradually up to 1350°C and decreases slowly at a higher sintering temperature. Compositions containing more Nd_2O_3 than BNT4 show Q values

below 2000. On the other hand, the compositions containing less Nd_2O_3 than BNT4 show higher Q values due to the existence of $BaTi_4O_9$ compound which is known to have high Q values [12], and the sintering temperature for maximum Q values becomes lower than for BNT4. Figure 9(b) shows Q value changes with TiO_2 variation, and we also find very close relations between Q value and density shown in Fig. 2(b). With increasing TiO_2, Q values increase and the sintering temperatures for the maximum Q values decrease compared to BNT4 because TiO_2 has high Q value (14,000 at 3 GHz) [2] and plays the role of sintering aid. Thus it can be concluded that the behavior of both the microwave dielectric constants and Q values are very closely related to the sintered density changes with respect to sintering temperature for all compositions. A high sintered density corresponds to a high microwave dielectric constant and Q value in $BaO\text{-}Nd_2O_3\text{-}TiO_2$ ceramics.

For microwave device applications, τ_f of microwave materials should be nearly 0 ppm/°C because the center frequency of microwave devices should be stable at considerable temperature changes. We can also figure out the effects of Nd_2O_3 and TiO_2 variations on τ_f changes which is shown in Fig. 10. The τ_f values of compositions with Nd_2O_3 variations at the sintering temperature of maximum density show maximum value(+54.6 ppm/°C) for BNT4 specimen. The τ_f of the compositions with more or less Nd_2O_3 than BNT4 are lower than τ_f of BNT4, because of the formations of secondary phases with low τ_f. τ_f values of the compositions with more TiO_2 than BNT4 are higher than that of the BNT4 specimen because of TiO_2 rutile with high positive τ_f(+427 ppm/°C) [2] by the mixture rule.

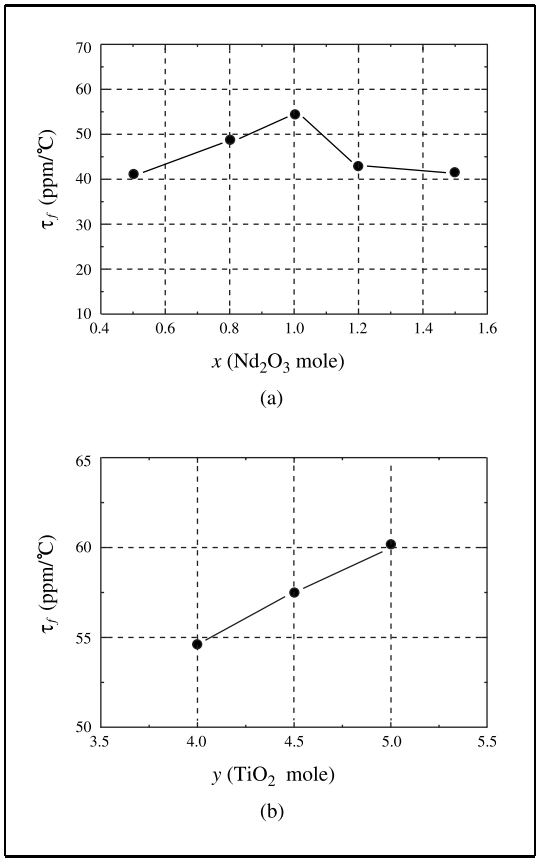

Fig. 10. τ_f changes for various compositions at sintering temperatures with maximum density (a) with Nd_2O_3 variation and (b) with TiO_2 variation

IV. CONCLUSIONS

The effects of Nd_2O_3 and TiO_2 stoichiometric control on dielectric constant, Q value and τ_f at microwave frequency, and the microstructures of $BaO\text{-}Nd_2O_3\text{-}TiO_2$ ceramics were investigated. As Nd_2O_3 amount increases, the sintering temperature for maximum sintered density increases, and as the TiO_2 amount increases, the optimum sintering temperatures decrease. In the $BaO\text{-}Nd_2O_3\text{-}TiO_2$ system the dielectric constant is the highest with $BaO/Nd_2O_3 = 1$ compositions. When the ratio is different from 1, the dielectric constants were deteriorated because of the formations of the secondary phases with low dielectric constants, such as the compound of Nd_2O_3 and TiO_2 ($Nd_2Ti_2O_7$) or the compound of BaO and TiO_2 ($BaTi_4O_9$). The dielectric constant decreased as the amounts of TiO_2 increased.

As the amount of Nd_2O_3 increases, the maximum Q value decreases. With increasing TiO_2, the Q value increases and the sintering temperature for the maximum Q value decreases. The τ_f values of the $BaO\text{-}Nd_2O_3\text{-}TiO_2$ ceramics with BaO/Nd_2O_3 ratio deviated from 1 decrease because of the formation of secondary phases with low τ_f. τ_f of the compositions with TiO_2 variations increase as the amount of TiO_2 increases.

The behaviors of microwave dielectric constant and Q values are very closely related to the sintered densities for all compositions in the $BaO\text{-}Nd_2O_3\text{-}TiO_2$ system. High sintered density corresponds to high microwave dielectric constant and Q value.

For the practical use of this material, the τ_f should be controlled to nearly 0 ppm/°C. In order to improve microwave properties further, we will carry out studies on the influence of other additives with the basis of this work on $BaO\text{-}Nd_2O_3\text{-}TiO_2$ system.

REFERENCES

[1] Takano Katsuyoshi, Abe Masaaki, Miyoshi Satoru, and Toda Takahumi, "The applications of microwave dielectric materials for telecommunication components," *Electronic Ceramics (Japan)*, vol. 24, no. 124, pp. 45-53, 1993.

[2] K. Wakino, K. Minai, and H. Tamura, "Microwave characteristics of (Zr,Sn) TiO_4 and $BaO\text{-}PbO\text{-}Nd_2O_3\text{-}TiO_2$ dielectric resonators," *J. Am. Cer. Soc*., vol. 67, no. 4, pp. 278-281, 1984.

[3] J. Kato, H. Kagata, and K. Nishimoto, "Dielectric properties of lead alkaline-earth zirconate at microwave frequencies," *Jap. J of Appl. Phys.*, vol. 30, no. 9B, pp. 2343-2346, 1991.

[4] S. Kawashima, "The trends of microwave dielectric materials," *Electronic Ceramics* (Japan), vol. 24, no. 124, pp. 4-10, 1993.

[5] D. Kolar, Z. Stadler, S. Gaberscek, and D. Survorov, "Ceramic and dielectric properties of selected compositions in $BaO\text{-}TiO_2\text{-}Nd_2O_3$ system," *Ber. Dt. Keram. Ges*, vol. 55, no. 7, pp. 346-348, 1978.

[6] J. Takahashi and T. Ikegami, "Occurrence of dielectric 1:1:4 compound in the ternary system $BaO\text{-}Ln_2O_3\text{-}TiO_2$ (Ln=La, Nd, and Sm): II, reexamination of formation of isostructural ternary compounds in identical systems," *J. Am. Cer. Soc.*, vol. 74, pp. 1873-1879, 1991.

[7] H. D. Kim, J. H. Kim, and S. H. Jo, "Phase relation

and microwave dielectric properties of BaO-$(Nd_{1-x}Sm_x)_2O_3$-TiO_2 Ceramic system," *J. Kor. Cer. Soc.*, vol. 31, no. 9, pp. 995-1004, 1994.

[8] X. M. Chen, Y. Suzuki, and N. Sato, "Microstructures and microwave dielectric characteristics of ceramics with the composition BaO-Nd_2O_3-$5TiO_2$," *J. Mat. Sci: Mat. in. Electro*. vol. 6, pp. 10-16, 1995.

[9] J. W. Hakki and P. D. Coleman, "A dielectric resonator method of measuring inductive capacities in the millimeter range," *IEEE. Trans. MTT.*, vol. 16, pp. 402-407, 1960.

[10] Y. Jing and Y. Kobayashi, "Calculation of resonant frequency and unloaded Q for dielectric loaded cavity resonator used in permittivity measurement in UHF band," *IEICE Japan*, MW 93-57, pp. 161-166, 1993.

[11] H. K. Sung, T. H. Kim, J. S. Lee, and T. G. Choy, "Microwave dielectric properties of BaO-$(Sm_{1-x}La_x)_2O_3$-TiO_2 Ceramics," *ETRI Journal*, vol. 14, no. 4, pp. 217-227, 1993.

[12] S. G. Mhaisalkar, D. W. Readey, and S. A. Akbar, "Microwave dielectric properties of doped $baTi_4O_9$," *J. Am. Cer. Soc.*, vol. 74, pp. 1894-1988, 1991.

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