ELSEVIER

Ceramics International 31 (2005) 667–670

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

# Effect of $TiO_2$ ratio on $BaO–Nd_2O_3–TiO_2$ microwave ceramics

Yen-Pei Fu*, Chung-Wen Liu, Cheng-Hsiung Lin, Chien-Kuo Hsieh

*Department of Chemical Engineering, Wu-Feng Institute of Technology, Ming-Hsiung, Chiayi 621, Taiwan*

Received 8 May 2004; received in revised form 21 July 2004; accepted 23 August 2004
Available online 9 December 2004

**Abstract**

The dielectric properties of $BaO–Nd_2O_3–TiO_2$ ceramics with various $TiO_2$ contents at microwave frequencies were investigated, by varing the range of composition from 1:1:4 to 1:1:5 ($BaO:Nd_2O_3:TiO_2$). Sintered ceramics were studied by X-ray diffractometer (XRD), scanning electron microscopy (SEM), and dielectric data measured at microwave frequencies. The XRD results revealed that the matrix phase was $BaNd_2Ti_5O_{14}$, and that $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ secondary phases were present. The dielectric constant saturates at 80–83 with various $TiO_2$ content. $Q \times f$ values of 5700–11,560 (at 4 GHz) can be obtained by doping with various the ratio of $TiO_2$, sintering at 1300 °C for 2 h. The temperature coefficient of resonant frequency ranges from 62 to 151 ppm/°C.


*Keywords:* D. $TiO_2$; Dielectric resonator; Microwave dielectric properties

## 1. Introduction

Recently, dielectric resonators with high dielectric constant ($\varepsilon_r$) in the range 25–100, low loss ($\tan\delta < 5 \times 10^{-4}$, where $\tan\delta$ is dielectric loss), and small frequency temperature coefficient ($\tau_f$) within ±20 ppm/°C; have been widely used in microwave integrated circuits and microwave filters [1]. Several materials have been developed as microwave dielectrics, such as $Ba_2Ti_9O_{20}$ [2], $(Zn,Sn)TiO_4$ [3], $Ba(Mg_{1/3}Ta_{2/3})O_3$ [4], $Ba(Zn_{1/3}Ta_{2/3})O_3$ [5] and $BaO–Ln_2O_3–TiO_2$ (Ln = La, Nd, Sm) [6–8]. Among these dielectrics with $BaO:Nd_2O_3:TiO_2$ of around 1:1:4 and a high dielectric constant ($\varepsilon_r$ = 70–90) have been commonly applied in mobile telephone systems. They can be used to miniaturize resonance circuits without degrading the $Q$ value.

Numerous approaches existed for modifying the characteristics of microwave dielectrics including (1) doping with additives of $Bi_2O_3$, $Bi_4Ti_3O_{12}$ [9], PbO [10] and rare-earth oxide [6], and (2) varying the composition. The dielectric characteristics of $BaO–Nd_2O_3–TiO_2$ ceramics strongly depend on their crystal structure, stoichiometry, grain size, additives, and phase composition [11]. Optimizing dielectric properties and ensuring reproducibility are important. This study reports the effect of the proportion of $TiO_2$ in $BaO–Nd_2O_3–TiO_2$ ceramics upon their microwave dielectric properties and microstructures.

## 2. Experiment procedures

### 2.1. Sample preparation

Samples were prepared from reagent-grade $BaCO_3$, $TiO_2$, and $Nd_2O_3$. The resonator was prepared as $BaO–Nd_2O_3–nTiO_2$ with $n$ = 4.0, 4.3, 4.7, and 5.0. Initially, appropriate mixtures of the powders were ground finely by ball mill in a plastic jar using deionized water and zirconia balls. After it had been dried, the powder was calcined from 1000–1200 °C for 2 h. Subsequently, an organic binder was added to produce granulation. Cylindrical specimens were pressed

* Corresponding author. Tel.: +886 5 206 3264; fax: +886 5 206 3264.
*E-mail address:* ypfu@mail.wfc.edu.tw (Y.-P. Fu).

0272-8842/$30.00 
doi:10.1016/j.ceramint.2004.08.005

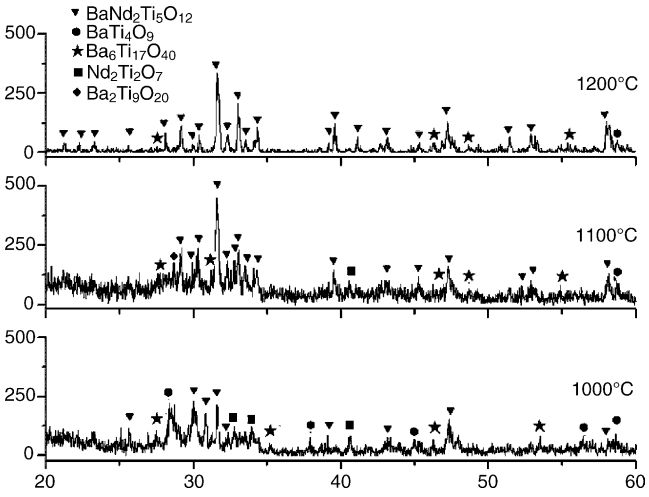


Fig. 1. XRD pattern of $BaO–Nd_2O_3–4.7TiO_2$ ceramic powder calcined at various temperatures for 2 h.

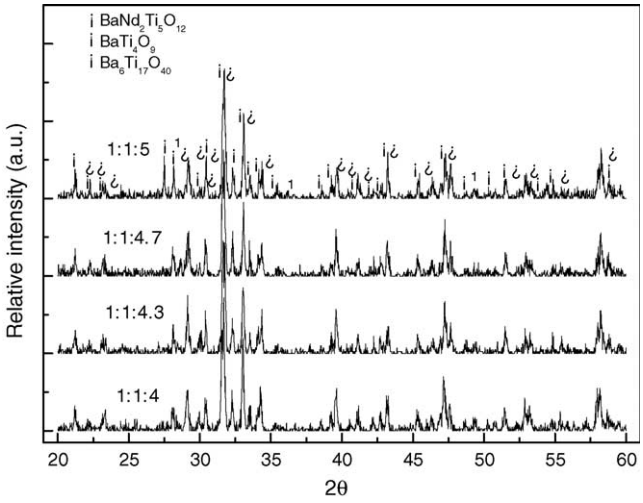


Fig. 2. XRD pattern of $BaO–Nd_2O_3–TiO_2$ ceramics with various $TiO_2$ content, sintered at 1300 °C for 2 h.

under a pressure of 1000 kg/cm$^2$ and sintered in air at 1300 °C for 2 h.

### 2.2. Characterization

The calcined and sintered samples were characterized by X-ray powder diffractiometer (XRD, Rigaku D/Max-II). The microstructure of the sintered specimens was observed by scanning electron microscopy (SEM, JEOL JSM-6330F). The bulk density of the sintered pellets was measured by the Arichimedes method. The dielectric constant ($\varepsilon_r$) and the quality factor ($Q$) at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method [12], as modified and improved by Courtney [13] and Kobayashi [14]. Two dielectric resonators were prepared under the same sintering conditions. They had the same diameter, but one was twice as high as another sample. The temperature coefficient of resonant frequency ($\tau_f$) at microwave frequencies was measured at temperature from 25 to 80 °C, and was defined as follows $\tau_f = \Delta f_o/f_o\Delta T$ (ppm/°C), where $\Delta f_o$ is the shift in the center frequency introduced by the temperature change $\Delta T$. The above-mentioned microwave properties were calculated by the resonant frequency of the $TE_{011}$ and $TE_{012}$ resonant modes.

## 3. Results and discussion

Fig. 1 presents the X-ray diffraction patterns of $BaO–Nd_2O_3–4.7TiO_2$ calcined powder at different temperatures. It reveals that the ceramics powders calcined at 1000 °C for 2 h contains $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $Nd_2Ti_2O_7$, $Ba_6Ti_{17}O_{40}$ and $Nd_2Ti_2O_7$ phases. As the temperature of calcinations was increased, the $BaNd_2Ti_5O_{14}$ gradually became major phase. Calcination conditions are well known to be able to affect greatly the densification behavior. However, the densification process primarily affects characteristics of the particles of the calcined powder. A lower calcination temperature will yield in the presence of more unreacted reagents, whereas a high calcination temperature will result in grain growth during calcination. Both calcination conditions suppress densification. Accordingly, these results indicate that a calcination temperature of 1100 °C is appropriate for $BaO–Nd_2O_3–nTiO_2$ ceramics ($n$ = 3–5).

$BaO–Nd_2O_3–TiO_2$ ceramics with various $TiO_2$, which phase change during heat treatment was examined by X-ray diffraction analyses. Fig. 2 presents the X-ray diffraction patterns of the $BaO–Nd_2O_3–TiO_2$ ceramics with compositions from 1:1:4 to 1:1:5 ($BaO:Nd_2O_3:TiO_2$) after sintering at 1300 °C for 2 h. The patterns are similar for all the compositions and indicate that $BaNd_2Ti_5O_{14}$ is the dominant phase. The patterns in all compositions include additional peaks that correspond to $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$. These impurity phases were present probably due to the solid state reaction generated an inhomogeneous microstructure in

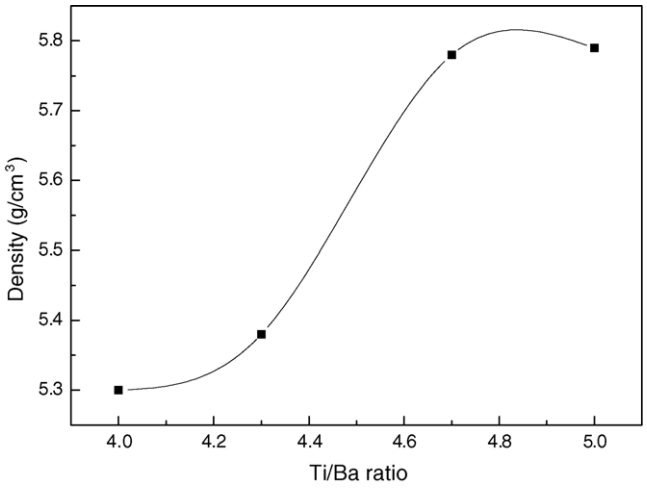


Fig. 3. Densities of $BaO–Nd_2O_3–TiO_2$ ceramics with various $TiO_2$ content, sintered at 1300 °C for 2 h.

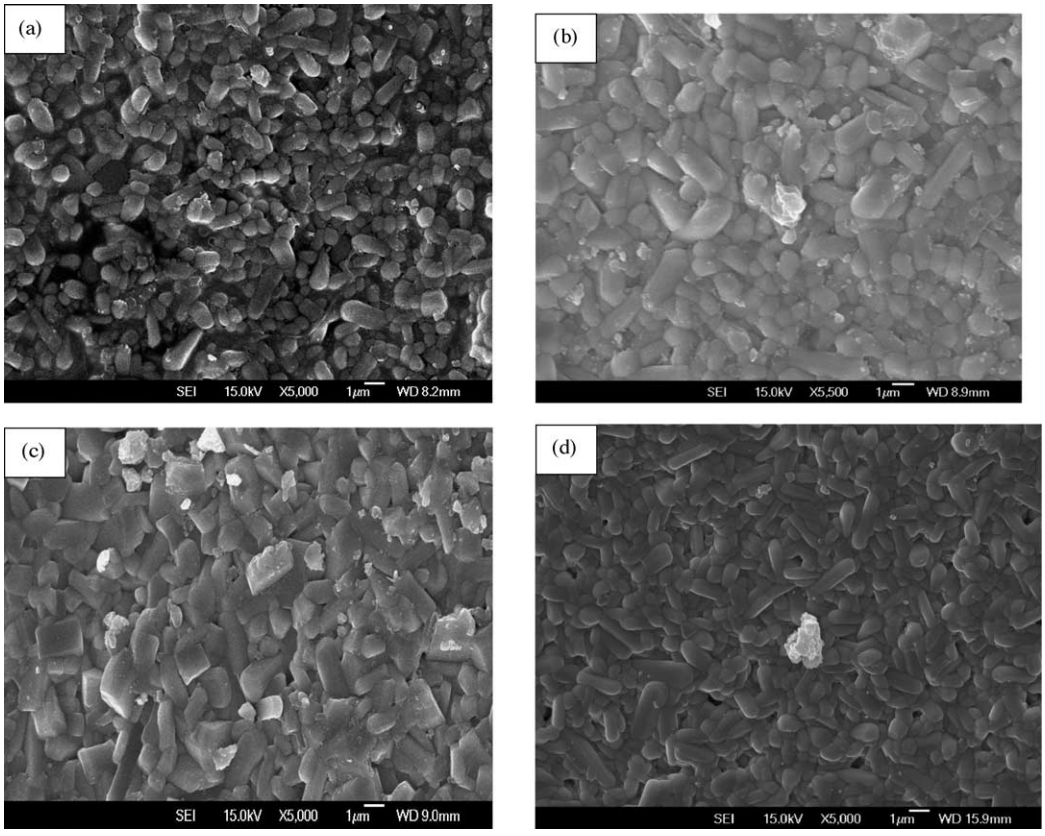


Fig. 4. Microstructures of $BaO–Nd_2O_3–TiO_2$ ceramics with various $TiO_2$ content for (a) 1:1:4, (b) 1:1:4.3, (c) 1:1:4.7, and (d) 1:1:5 samples, sintered at 1300 °C for 2 h.

$BaO–Nd_2O_3–TiO_2$ ceramics. Barium titanates compounds may have formed because the performed $BaTiO_3$ reacted with excess $TiO_2$. Fig. 3 plots the density of $BaO–Nd_2O_3–TiO_2$ ceramics against $TiO_2$ content, sintered at 1300 °C for 2 h. The density of $BaO–Nd_2O_3–TiO_2$ ceramics increases with $TiO_2$ content. The above results imply that the density of $BaO–Nd_2O_3–TiO_2$ ceramics is related to their sintering temperature and the proportion of $TiO_2$. Fig. 4 displays SEM micrographs of $BaO–Nd_2O_3–TiO_2$ ceramics with different amount of $TiO_2$. The microstructures of these ceramics exhibit a uniform grain size of approximately 2–3 μm, with $BaNd_2Ti_5O_{14}$ as the major phase. The presence of second phases such as $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ is very common in these types of compounds [15]. The porosity of $BaO–Nd_2O_3–TiO_2$ ceramics declines as $TiO_2$ content increases. This behavior is associated with the replacement mechanism of $Ba^{2+} + 2Nd^{3+} \leftrightarrow 2Ti^{4+}$ [16]. These results are consistent with the findings concerning density.

Various factors influence the microwave properties of dielectric ceramics materials, including the content of individual crystalline, secondary phases, and the degree of densification. Fig. 5 presents the dielectric constant of $BaO–Nd_2O_3–TiO_2$ ceramics with various$TiO_2$ contents, sintered at 1300 °C for 2 h. The dielectric constant increases gradually with $TiO_2$ content. The relationship between dielectric constant and proportion of $TiO_2$ follow the same trend as that between density and proportion of $TiO_2$ content. Fig. 6 plots $Q \times f$ and $\tau_f$ of $BaO–Nd_2O_3–TiO_2$ ceramics as a function proportion of $TiO_2$, following sintering at 1300 °C for 2 h. As the proportion of $TiO_2$ increase, the $Q \times f$ value initial declines, and then, reaching a minimum (5700 GHz) at the ratio of 1:1:4.7, whereas $BaO–Nd_2O_3–TiO_2$ ceramics in the ratio of 1:1:5 exhibit excellent microwave dielectric properties, which the $Q \times f$ value of 11,560 (at 4 GHz). This behavior may be due to the fact that $BaO–Nd_2O_3–TiO_2$ ceramics in the ratio of 1:1:5

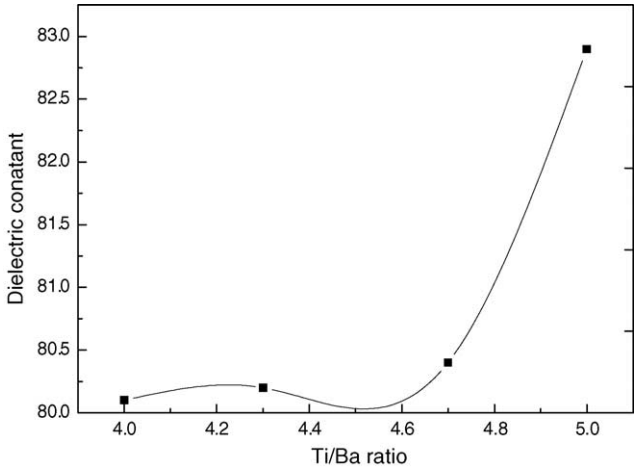


Fig. 5. Dielectric constant of $BaO–Nd_2O_3–TiO_2$ ceramics with various $TiO_2$ content, sintered at 1300 °C for 2 h.

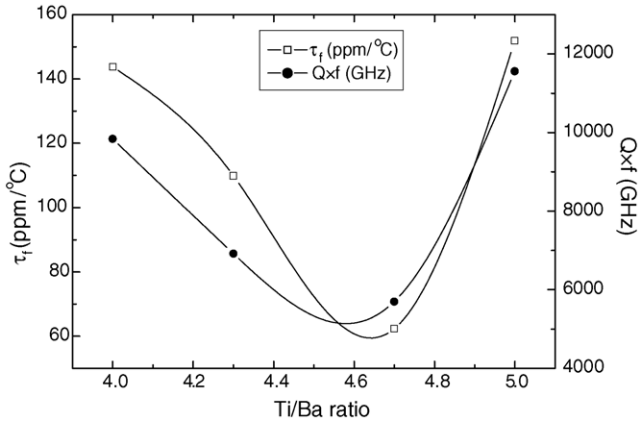


Fig. 6. $Q \times f$ and $\tau_f$ of $BaO–Nd_2O_3–TiO_2$ ceramics with various $TiO_2$ content, sintered at 1300 °C for 2 h.

exhibit more densification. As indicated in Fig. 4(d), the grains were uniformly and the porosities reduced. Moreover, the $\tau_f$ value decreases as the proportion of $TiO_2$, after reaching a minimum (62 ppm/°C) at the ratio 1:1:4.7, $\tau_f$ increases slightly. The relationship between $Q \times f$ value and the proportion of $TiO_2$ follows the same trend as that between $\tau_f$ value and the proportion of $TiO_2$.

## 4. Conclusions

In this study, the microwave dielectric properties of $BaO–Nd_2O_3–TiO_2$ ceramics with various proportion of $TiO_2$ were investigated by the conventional solid-state ceramic route. The composition content of $TiO_2$ was controlled to yield excellent microwave dielectric properties. $BaO–Nd_2O_3–TiO_2$ ceramics with an optimum ratio of 1:1:5 exhibits excellent microwave dielectric properties. Their dielectric constant is 82.9; $Q \times f$ value is 11,560 (at 4 GHz), and $\tau_f$ value is 151.2 ppm/°C. These characteristics are appropriate for many microwave devices such as filters, oscillators, patch antenna, and others.

## Acknowledgement

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. NSC 93-2212-E-274-001.

## References

[1] J.S. Sun, C.C. Wei, L. Wu, J. Mater. Sci. 27 (1992) 5818.
[2] J.K. Pourde, D.F. Linn, H.N. O'Bryan, J. Thomson, J. Am. Ceram. Soc. 58 (1975) 418.
[3] G. Wolfram, H.E. Gobel, Mater. Res. Bull. 16 (1981) 1455.
[4] S. Nomura, K. Toyama, K. Kaweta, Jpn. J. Appl. Phys. 21 (1982) 264.
[5] S. Kawashina, M. Nishada, I. Ueda, H. Ouchi, J. Am. Ceram. Soc. 66 (1983) 421.
[6] P. Laffez, G. Desgardin, B. Raveau, J. Mater. Sci. 27 (1992) 5229.
[7] D. Kolar, Z. Stadler, S. Gaberseck, D. Suvorov, Ferroelectrics 27 (1980) 269.
[8] J.M. Durand, J.P. Boilot, J. Mater. Sci. Lett. 6 (1987) 134.
[9] Y.J. Wu, X.M. Chen, J. Eur. Ceram. Soc. 19 (1999) 1123.
[10] K. Wakino, K. Minai, H. Tamura, J. Am. Ceram. Soc. 67 (1984) 278.
[11] S. Skapin, D. Kolar, D. Suvorov, Z. Samardzija, J. Mater. Res. 13 (5) (1998) 1327.
[12] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theory Tech. 8 (1960) 402.
[13] W.E. Courtney, IEEE Trans. Microwave Theory Tech. 18 (1970) 476.
[14] Y. Kobayashi, M. Katoh, IEEE Trans. Microwave Theory Tech. 33 (1985) 586.
[15] H. Sreemoolanadhan, M.T. Sebastian, P. Mohanan, Br. Ceram. Trans. 95 (2) (1996) 79.
[16] K.M. Cruickshank, X. Jing, G. Wood, E.E. Lachowski, A.R. West, J. Am. Ceram. Soc. 79 (1996) 1605.