The Korean Journal of Ceramics, **2** [2] 111-113 (1996)

Communications

$Ba_5Nb_4O_{15}$ Ceramics with Temperature-Stable High Dielectric Constant and Low Microwave Loss

Woo-Hwan Jung*, Jeong-Ho Sohn, Yoshiyuki Inaguma and Mitsuru Itoh**

Research Laboratory of Engineering Materials, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan

**Materials Science, Department of Mechanical Engineering and Materials Science, Faculty of Engineering, Yokohama National University, Tokiwada, Hodogaya-ku, Yokohama 240, Japan*

***Department of Electronic Ceramics Engineering, School of Engineering, Kaya University, Jisan-ri, Koryong-Kun, Kyungpook 717-800, Korea*

(Received June 15, 1996)

Dielectric properties at microwave frequency region of the five-layered compound $Ba_5Nb_4O_{15}$ prepared by the conventional solid state reaction method were investigated. $Ba_5Nb_4O_{15}$ has excellent microwave dielectric characteristics; ε_r=38, Q=7500 at 10 GHz, and τ_f=+50 ppm/K Since this compound has a high dielectric constant, high Q and sufficiently stable characteristics, it is useful for the applications at microwave frequencies.

Key words : Microwave dielectrics, $Ba_5Nb_4O_{15}$, Layered compound

I. Introduction

Several kinds of dielectric ceramics are used for microwave applications.[1-3] For the microwave dielectric-resonator applications, high dielectric constant (ε_r), low dielectric loss (a high unloaded Q), and a small temperature coefficient of resonance frequency (τ_f) are required. Until now, the microwave dielectric properties were vigorously investigated for the B-site cation ordering complex perovskite with a high Q value[4,5] and for the relation between r and the microstructure of the ceramics.[6,7]

A number of perovskite-related compounds having the general formula $A_5B_4O_{15}$, especially $Ba_5Nb_4O_{15}$, is of interest because these compounds are very attractive for optical studies.[8] Since there are four Nb^{5+} ions on each five-layer sequence, there is an empty octahedra which avoids direct face sharing on the NbO_6 sublattice. This configuration implies strong anharmonicity making these compounds very attractive for optical studies. In fact, a recent far-infrared reflectivity measurement on $Ba_5Nb_4O_{15}$ predicts that this perovskite-related compound is a very attractive material to be applied for microwave dielectric resonators.[8]

Far-infrared reflectance spectra of several materials used for microwave applications have recently been measured and analyzed according to the classical dispersion theory.[9,10] Experimentally, following relation holds between dielectric loss (tanδ) and reflectance data obtained by far-infrared reflectivity measurements.[11]

$$\tan\delta_j = \frac{\Delta\varepsilon_j(\gamma_{jTO}\,\omega)/\Omega_{jTO}^2}{\varepsilon_\infty + \sum_i \Delta\varepsilon_i} \propto \frac{\gamma_{jTO}\,\omega}{\Omega_{jTO}^2} \qquad (1)$$

where $\Delta\varepsilon_j$ is the oscillator strength, Ω_{jTO} and γ_{jTO} are transverse optic (TO) mode frequency and its damping constant, respectively. The dielectric constant ε_∞ is caused by electronic polarization at higher frequencies.

We have calculate the tanδ for $Ba_5Nb_4O_{15}$ at microwave frequencies using far-infrared reflectivity measurement results by Massa *et al.*[8] Then, the values of tanδ calculated from Eq. (1) is found to be 4.443×10^{-5}, this calculating result thus implies that $Ba_5Nb_4O_{15}$ expect to be utilized for the microwave dielectric resonators. In this study, we have investigated the dielectric properties of B-site defect perovskite-related $Ba_5Nb_4O_{15}$ ceramics at microwave frequency.

Polycrystalline sample of $Ba_5Nb_4O_{15}$ was prepared by conventional solid state reaction. The starting materials were $BaCO_3$ and Nb_2O_5 powders with high purity (3N grade). The mixture of powders were calcined in air at 1473 K for 12 h. Ground again, well mixed, and pressed into pellets. Pellets were fired on a platinum foil at 1723 K 12 h in air. The crystal structure was examined using X-ray diffraction and the grains of the ceramics was observed by SEM. The sintered density of the ceramic was measured by water immersion method.

Flat surface of specimen was coated with a sliver for an electrode to measure the low frequency dielectric properties. Using YHP 4192A impedance analyzer, capacitances were obtained as a functions of temperature by four-terminal pair ac impedance measurements with frequency range from 5 kHz to 600 kHz and in the temperature range from 77 K to 700 K. The measured values of capacitances was correlated by calibrating the capacitances of leads as zero. Microwave dielectric properties were measured by means of the dielectric resonator cavity method in the $TE_{01\delta}$ mode.[12,13] The temperature coefficient of resonant frequency, τ_f, was measured in the temperature range from 240 K to 353 K and the resonant frequency was about 10 GHz.

The crystal structure in $Ba_5Nb_4O_{15}$ is hexagonal perovskite-related structure with lattice constant a=5.7943Å and c= 11.783Å, which agree well with data in JCPDS (Code; #14-0028). The grain size was 7 μm and density of the sintered specimen was about 87% of theoretical value.

Low frequency dielectric data for $Ba_5Nb_4O_{15}$ are showed in Fig. 1, dielectric constant (a) and tanδ (b) as a function of temperature are shown at various frequencies. The dielectric constant and tanδ increases smoothly with the increasing temperature at various frequency. There are no dielectric anomalies peaks observed. The room temperature dielectric constant is 41.2 at 600 kHz and the temperature dependence of dielectric constant ($TC\varepsilon_r$) is calculated as about -106 ppm/K in temperature range 250 K≤T≤350 K.

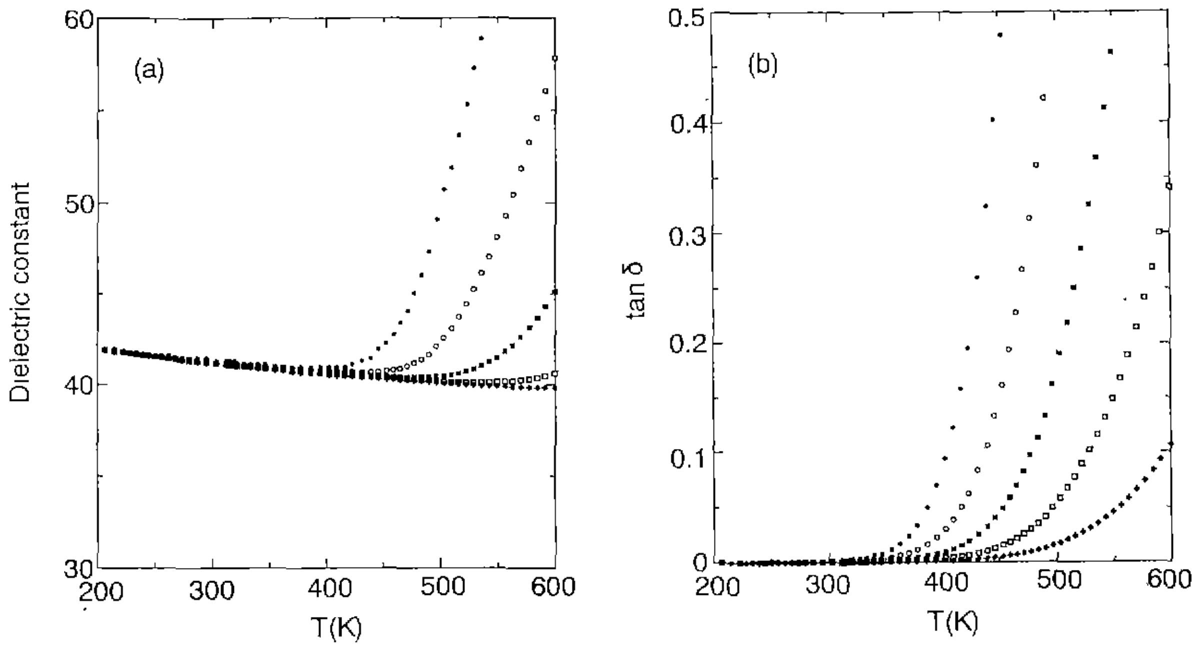
The Q value was 7500, the ε_r was estimated as 38 at 10 GHz, and the τ_f was +50 ppm/K. The microwave dielectric constant are determined by the combination of ionic and electronic polarization. The electronic polarization value of $Ba_5Nb_4O_{15}$ obtained by Massa et al.[8] was about 3.5, however, the contribution of electronic polarization was very small compare to ionic polarization.

The investigation of $TC\varepsilon_r$ at low frequency is important because the $TC\varepsilon_r$ of a specified compounds is closely associated with τ_f of a dielectric resonator at microwave frequency. An outstanding feature in the properties of the dielectrics examined is a considerable deviation of the $TC\varepsilon_r$ from a simple relation which have been observed in many ceramic dielectrics. Based on the differentiated form of the Clausius-Mosotti equation, the variation in dielectric constant with temperature can be related to temperature variations of material's dimensions (linear expansion coefficient, αL), and of the polarizability (α) of the volume (V) containing N polarizable units as follow:[14]

$$TC\ \varepsilon_r = \frac{\varepsilon_r}{3}\left(\frac{1}{\alpha}\frac{\partial\alpha}{\partial T} - 3\,\alpha_L\right) \qquad (2)$$

If $1/\alpha\ (\partial\alpha/\partial T)$ is negligibly small, Eq. (2) gives $TC\varepsilon_r = -\varepsilon_r \cdot \alpha_L$. This simplified relation can hold for a number of dielectrics with $\varepsilon_r \geq 30$.[13] The τ_f is approximately expressed as $\tau_f = -\alpha_L - TC\varepsilon_r/2$. The $TC\varepsilon_r$ for $Ba_5Nb_4O_{15}$ exhibited a considerable deviation from a simple relation of $TC\varepsilon_r = -\varepsilon_r \cdot \alpha_L$. This results suggested that the temperature coefficient of polarizability might be comparable to or considerably exceed the volume expansion coefficient, if the application of the Clausius-Mosotti equation is allowed.

There are many factors to influence the Q value, especially in the high Q ceramics, such as crystal structure, sintered density, impurities and defects. From the viewpoint of the crystal sturcture, it is generally accepted that the characteristics of microwave dielectrics are strongly correlated to crystal symmetry. Dielectric



(a) (b)

Fig. 1. Temperature dependence of dielectric constant (a) and tanδ (b) for $Ba_5Nb_4O_{15}$ measured at various frequencies. Open circles represent the results at the applied frequeccy 5 kHz; solid circles, 16 kHz; solid square, 54 kHz; squares, 180 kHz; and solid triangles, 600 kHz.

Table 1. Comparison with Microwave Dielectric Properties for $Ba_5Nb_4O_{15}$ and Other Dielectric Resonators

Compounds	ε_r	Q	τ_f (ppm/K)	f_r (GHz)	Ref.
$Ba(Mg_{1/3}Ta_{2/3})O_3$	25	16800	2.7	10.5	4
$Ba(Zn_{1/3}Ta_{2/3})O_3$	30	14000	0	12.0	5
$BaTi_4O_9$	36	4900	16	10.3	13
$Ba_2Ti_9O_{20}$	37	5300	-6.0	10.7	13
$Ba_5Nb_4O_{15}$	38	7500	50	10.0	this work

characteristics at microwave frequency of $Ba_5Nb_4O_{15}$ and other resonator reported by several works are summarized in Table 1. $Ba_5Nb_4O_{15}$ shows relatively low Q value compare to 1:2 B-site ordering type perovskite. This result means that the very high Q value for $A(B_{1/3}^{II}B_{2/3}^{I})O_3$ is due to the B-site order arrangement of the cations in the perovskite structure. Although 1:2 B-site ordering perovskites and $Ba_5Nb_4O_{15}$ have a same D_{3d}^3-P_{3m1} crystal space group which is determined by raman-spectra,[16] $Ba_5Nb_4O_{15}$ have a lower symmetry structure due to the empty octahedron.[16] Because these empty octahedron in $Ba_5Nb_4O_{15}$ play a role of the intrinsic defect. However, although it is B-site defect perovskite-related compound, $Ba_5Nb_4O_{15}$ show outstanding microwave unloaded Q value.

It seems that the five layer perovskite-related ceramics containing Nb^{5+} has potential use for dielectric resonators with high Q value and dielectric constant. Using this low loss ceramics, one can design a high quality microwave band pass filter or stabilize a frequency in microwave oscillation.

References

1. R. C. Kell, A. C. Greenham, and G. C. E. Olds, "High-permittivity Temperature-Stable Ceramic Dielectrics with Low Microwave Loss," *J. Am. Ceram. Soc.*, **56**[7], 352-54 (1973).
2. J. K. Ploude, D. F. Linn, H. M. O'Bryan, Jr. and J. T. Thomson, Jr., "$Ba_2Ti_9O_{20}$ as a Microwave Dielectric Resonator," *J. Am. Ceram. Soc.*, **58**[9-10], 418-20 (1975).
3. K. Wakino, K. Minai, and H. Tamura, "Microwave Characteristic of (Zr, Sn)TiO_4 and BaO-PbO-Nd_2O_3-TiO_2 Dielectric Resonators," *J. Am. Ceram. Soc.*, **67**[4], 278-81 (1984).
4. S. Nomura, K. Toyama, and K. Kaneta, "$Ba(Mg_{1/3}Ta_{2/3})O_3$ Ceramics with Low Dielectric Loss at Microwave Frequency," *Jpn. J. Appl. Phys.*, **21**[10], L624-26 (1982).
5. S. Kawashima, M. Nishida, I. Ueda, and H. Ouchi, "Ba$(Zn_{1/3}Ta_{2/3})O_3$ Ceramics with Low Dielectric Loss at Microwave Frequency," *J. Am. Ceram. Soc.*, **66**[6], 421-23 (1983).
6. H. Takahashi, Y. Baba, K. Ezaki, Y. Okamoto, K. Shibata, K. Kuriki, and S. Nakamo, "Dielectric Characterics of $(A^{1+}_{1/2}\ A^{3+}_{1/2})TiO_3$ Ceramics at Microwave Frequencies," *Jpn. J. Appl. Phys.*, **30**[9B], 2339-42 (1991).
7. A. Yamada, Y. Utsumi, and H. Watarai, "The Effect of Mn Addition on Dielectric Properties and Microstructure of BaO-Nd_2O_3-TiO_2 Ceramics," *Jpn. J. Appl. Phys.*, **30**[9B], 2350-53 (1991).
8. N. E Massa, S. Pagola, and R. Carbonio, "Far-Infrared Reflectivity and Raman Spectra of $Ba_5Nb_4O_{15}$," *Phys. Rev. B.*, **53**[13], 8148-50 (1996).
9. K. Wakino, M. Murata, and H. Tamura, "Far-Infrared Reflection Spectra of Ba(Zn, Ta)O_3-$BaZrO_3$ Dielectric Resonator Material,' *J. Am. Ceram. Soc.*, **69**[1], 34-37 (1986).
10. A. Sawata, and T. Kuwabara, "Infrared Study of Ba$(Mg_{1/3}Ta_{2/3})O_3$ Ceramics for Microwave Resonator." *Ferroelectrics.*, **95**, 205-208 (1989).
11. K. Fukuda, R. Kitoh, and I. Awai, "Far-Infrared Reflection Spectra of Dielectric Ceramics for Microwave Applications," *J. Am. Ceram. Soc.*, **77**[1], 149-54 (1994).
12. J.-H. Sohn, Y. Inaguma, S.-O. Yoon, M. Itoh, T. Nakamura, S.-J. Yoon, and H.-J. Kim, "Microwave Dielectric Characteristic of Ilmenite-Type Titanates with High Q Values," *Jpn. J. Appl. Phys* , **33**[9B], 5466-70 (1994).
13. J.-H. Choy, Y.-S. Han, J.-H. Sohn, and M. Itoh, 'Microwave Characteristics of BaO-TiO_2 Ceramics Prepared via a Citrate Route," *J. Am. Ceram. Soc.*, **78**[5], 1169-72 (1995).
14. A. J. Moulson, and J. M. Herbert, Electroceramics -Materials Properties · Applications-, pp 233-36, Chapman & Hall, London, 1990.
15. B. K. Kim, H. Hamaguchi, I. T. Kim, and K. S. Hong, "Probing of 1:2 Ordering in $Ba(Ni_{1/3}Nb_{2/3})O_3$ and Ba$(Zn_{1/3}Nb_{2/3})O_3$ Ceramics by XRD and Raman Spectroscopy," *J. Am. Ceram. Soc.*, **78**[11], 3117 (1995)
16. K. Fukuda, R. Kitoh, and I. Awai, "Far-Infrared Reflection Spectra of Dielectric Ceramics for Microwave Application," *J. Am. Ceram. Soc.*, **77**[1], 149 (1994).