New high permittivity and low loss ceramics in the BaO–TiO$_2$–Nb$_2$O$_5$ composition

R. RATHEESH[1], H. SREEMOOLANADHAN[2], S. SUMA, M. T. SEBASTIAN
Regional Research Laboratory (CSIR), Trivandrum-695 019, India.
E-mail: mts@csrrltrd.ren.nic.in

K. A. JOSE, P. MOHANAN
Dept. of Electronics, Cochin Univ. Sci. Tech. Cochin-682 022, India

New dielectric ceramics with formula BaTi$_3$Nb$_4$O$_{17}$ and Ba$_6$Ti$_{14}$Nb$_2$O$_{39}$ have been prepared and characterized. BaTi$_3$Nb$_4$O$_{17}$ was densified to 92% of TD after firing at 1310 °C for 4 h. However, Ba$_6$Ti$_{14}$Nb$_2$O$_{39}$ fired under optimized conditions (1260 °C for 4 h) showed only 85% TD together with secondary phase. The crystal system of both of the compositions is orthorhombic. The BaTi$_3$Nb$_4$O$_{17}$ has $\varepsilon_r \sim 56$, $Q_u \sim 2100$ (at 4.402 GHz), $\tau_f \sim +86$ p.p.m. K^{-1} and Ba$_6$Ti$_{14}$Nb$_2$O$_{39}$ as $\varepsilon_r \sim 50$, $Q_u \sim 650$ (4.359 GHz) and $\tau_f \sim +165$ p.p.m. K^{-1}. © 1998 Kluwer Academic Publishers

1. Introduction

Richtmyer [1] showed that dielectric waveguides can confine electromagnetic waves, when they are suitably bent. A dielectric resonator (DR), because of its high permittivity, confines electromagnetic energy through multiple total internal reflections. Since DRs permit miniaturization of microwave devices, they are widely used for a number of applications in microwave communication particularly in microwave integrated circuits. As a result, the demand for temperature-stable and high Q resonators is increasing. It is well established [2] that a DR should possess the following properties for communication applications:

1) $\varepsilon_r > 20$ to permit miniaturization at microwave frequencies.
2) $Q_r > 2000$ for a better selectivity and noise reduction.
3) Temperature-coefficeint of resonant frequency, $\tau_f < 20$ p.p.m. K^{-1} for stability.

The τ_f has to be nearly zero for stringent applications. However, for general applications, τ_f is not critical. Okaya [3] showed that TiO$_2$ (rutile) possessed very good ε_r (~ 100) and Q-factor ($\sim 10\,000$ at 4 GHz) values. However, its high τ_f (~ 400 p.p.m. K^{-1}) precluded its use in circuits requiring high stability. Following rutile, a number of ceramics such as (Zr, Sn)TiO$_4$, Ba$_2$Ti$_9$O$_{20}$, Ba$_5$Nb$_4$O$_{15}$, Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ have been investigated in attempts to find new materials for practical applications [4–12]. These materials have ε_r in the range 24 to 104 and are useful in different frequency bands. The frequency of application of a DR is decided by the

combination of its dielectric properties. The higher the ε_r, the lower the size of the device. The selection of ceramics for applications below 1 GHz is mainly carried out by considering miniaturization, and hence, the ε_r of the DR puts limits on the available materials. However, for applications above 13 GHz, it is the loss factor that limits the number of materials available. Hence, the search for new ceramics is still in progress. It can be seen from the literature that the ceramics used as dielectric resonators are either titanates or niobates/tantalates. However, very little data are available on the microwave dielectric properties of materials in the BaO–TiO$_2$–Nb$_2$O$_5$ system. This paper presents the preparation, characterization and dielectric properties of two ceramics in this system, namely BaTi$_3$Nb$_4$O$_{17}$ (T3N4) and Ba$_6$Ti$_{14}$Nb$_2$O$_{39}$ (T14N2). The microwave dielectric properties are reported for the first time.

2. Experimental

The materials were prepared by the conventional ceramic preparation route. BaCO$_3$ (SD Fine Chemicals, India 99.9%), TiO$_2$ (Autocmeric, U.S.A. Electronic Grade) and Nb$_2$O$_3$ (SD Fine Chemicals, India 99%) were weighed accurately in stoichiometric proportions to obtain a total of 15 g. The powders were mixed using distilled water in the mortar for about 30 min. The mixtures were dried and calcined in air at 1250 °C for 4 h. The calcined powders were then thoroughly ground for about 1 h. A 5% PVA solution was added to the powder and the slurry was dried. The powders were then pressed uniaxially in tungsten carbide (WC)

die of 11 mm diameter. Cylindrical compacts of different thickness were made under a pressure of 175 MPa. These compacts were sintered in air for 4 h, T3N4 at 1310 °C and T14N2 at 1260 °C. The densities of the compacts were measured by the Archimedes method. The phase constitution and the crystal structure of the compounds were obtained using X-ray diffraction (XRD) of powders using CuK$_a$ radiation (Rigaku diffractometer). The sintered bodies were polished and thermally etched. The surface microstructures were obtained by recording the secondary electron images of these specimen using a JEOL 35-C scanning electron microscope (SEM).

Thin discs of about 1 mm thickness were used as a capacitor to determine the ε_r at low frequencies (<10 MHz). Silver powder dispersed in amyl acetate solution was applied to the surfaces of these discs along with tiny copper wires which served as connecting leads. This paste was dried by heating the specimen at about 100 °C for 1 h. The capacitance and loss factor were determined in the range 100 Hz to 10 MHz using an HP 4192 impedance analyser.

The ε_r of the DR was measured by the "post resonator" method proposed by Hakki and Coleman [13] and modified by Courtney [14]. The unloaded quality factor (Q_u) was measured by the stripline method proposed by Khanna and Garault [15]. The Q value thus obtained is very close to that of a DR used in a practical circuit. The measurement of the ε_r and Q_u were carried out automatically by an HP 9000, 300 series instrumentation computer, which controlled the HP 8510 B network analyser with a synthesiser (HP 8341 B) and reflection-transmission test unit (HP 8514 B). The DR was slowly heated in the range 25–80 °C and the coefficient of thermal variation of resonant frequency (τ_f) was obtained.

3. Results and discussion

The T3N4 and T14N2 compositions sintered into dense ceramics without the use of any additive. They showed a bulk density of 4.469 g cm^{-3} (92%) and 4.12 g cm^{-3} (85%) respectively. The XRD patterns obtained using CuK$_a$ radiation are shown in Fig. 1a and b. The patterns are in agreement with earlier reports (JCPDS 38-1482 and 38-1431). The crystal structure of T3N4 has been reported as orthorhombic with space group Bbmm (63). Fig. 2a shows the SEM photograph of T3N4. It shows a monophase constitution with uniformly packed polygonal grains of 12 μm size. The T14N2 has been reported as having orthorhombic crystal structure with space group Bm21b (36). The XRD pattern (see Fig. 1b) shows additional weak peaks due to the presence of a secondary phase. The SEM photograph of Fig. 2b also shows two types of grains. The low percentage density of T14N2 may be due to the presence of a secondary phase.

The dielectric properties (ε_r) in the 10^3–10^7 Hz region measured using an impedance analyser are shown in Fig. 3a and b as a function of frequency. The steep rise in the dielectric constant of T14N2 in the low frequency (<1 kHz) region may be due to the presence of the secondary phase. Moreover, this ce-
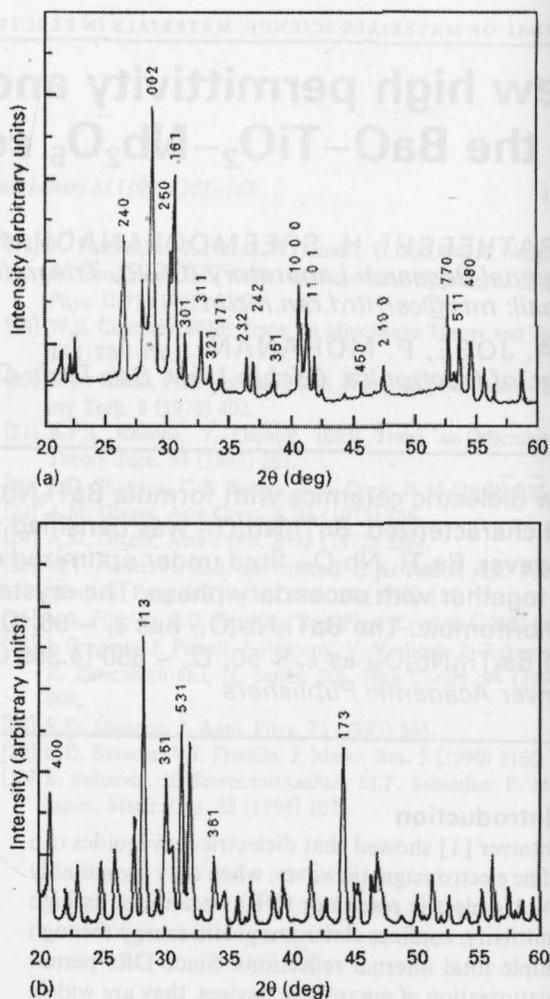

(a)

(b)

Figure 1 Powder XRD pattern of (a) BaTi$_3$Nb$_4$O$_{17}$ and (b) Ba$_6$Nb$_2$Ti$_{14}$O$_{39}$.

ramic also has a higher loss factor at 13 MHz compared to T3N4, probably due to the multiphase nature of the ceramics.

The ε_r calculated from the TE$_{01\delta}$ resonance are 56.44 (5.589 GHz) for T3N4 and 49.72 (5.157 GHz) for T14N2. The ε_r values are in good agreement with the values obtained at 13 MHz.

The unloaded Q factor of T3N4 and T14N2 near 4 GHz for the TE$_{011}$ mode are 2100 and 650, respectively. The normalized Q factors are $(2100 \times 4.402) \times 10^9$ and $(650 \times 4.359) \times 10^9$, respectively. The obtained Q factors are greater than the corresponding Q factors at 13 MHz in accordance with classical dispersion theory [16]. The presence of secondary phase in T14N2 also affects the Q-factors at microwave frequencies.

Fig. 4a and b respectively show the variation of TE$_{011}$ mode of T3N4 and T14N2 ceramic with temperature. The τ_f is calculated using the equation

$$\tau_f = \frac{1}{f} \frac{\Delta f}{\Delta T} \qquad (1)$$

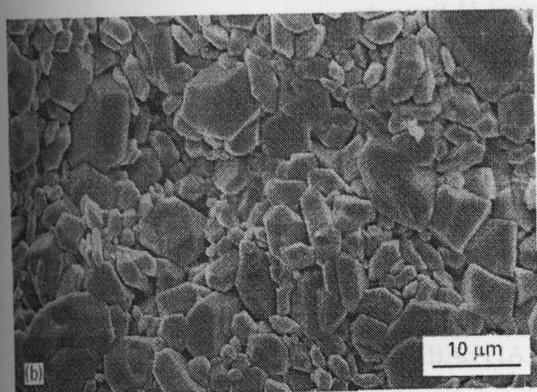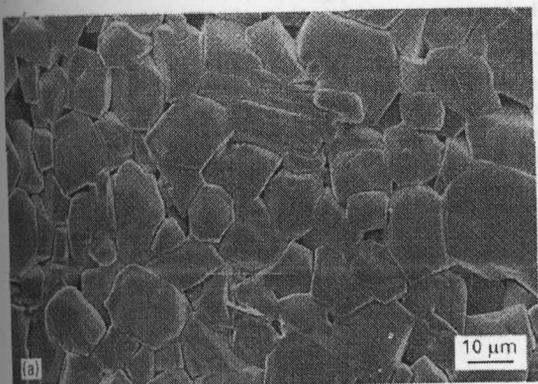The temperature variation of the resonant frequency of T3N4 ceramic is +86 p.p.m. K^{-1} which is

Figure 2 Typical SEM photograph of (a) $BaTi_3Nb_4O_{17}$ at $1000\times$, and (b) $Ba_6Nb_2Ti_{14}O_{39}$ at $2000\times$.

Figure 3 Variation of dielectric constant with frequency of $BaTi_3Nb_4O_{17}$ (●) and $Ba_6Ti_{14}Nb_2O_{39}$ (○).

(a)

(b)
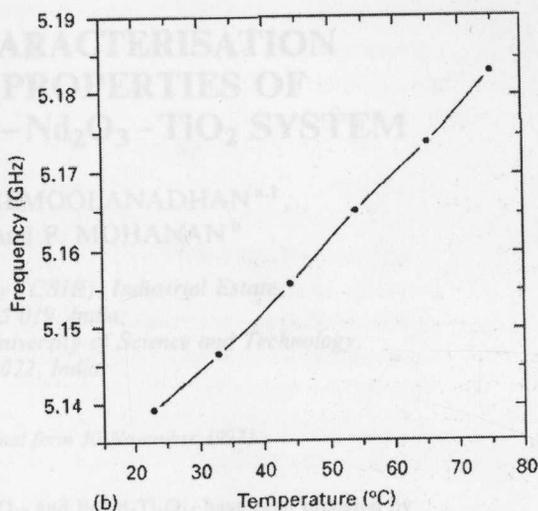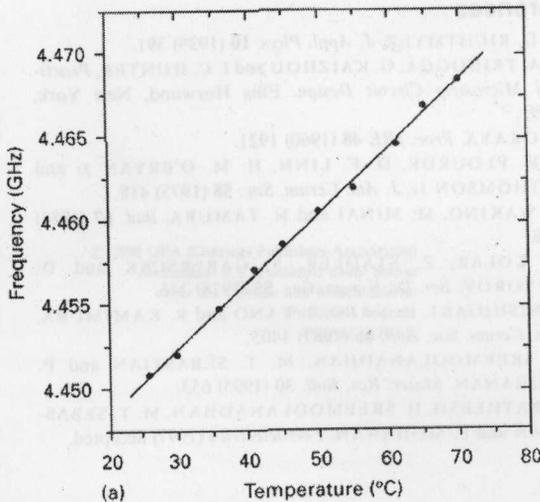
Figure 4 Variation of resonant frequency of (a) $BaTi_3Nb_4O_{17}$ and (b) $Ba_6Nb_2Ti_{14}O_{39}$ with respect to temperature.

less than that of T14N2 ($+165$ p.p.m. K^{-1}). Although the ε_r and Q_u of these ceramics are encouraging, their relatively high τ_f precludes their use as dielectric resonators for practical applications. However, through appropriate substitution or the use of additives. it may be possible to obtain a nearly temperature compensated dielectric.

4. Conclusion

New dielectric resonator ceramics, $BaTi_3Nb_4O_{17}$ and $Ba_6Ti_{14}Nb_2O_{39}$ have been prepared, characterized and the dielectric resonator properties in the microwave frequency range have been measured in the C-band. Both of these ceramics showed high ε_r (56 and 50, respectively) in the microwave frequency region. However, due to the presence of a secondary phase, the $Ba_6Ti_{14}Nb_2O_{39}$ had a lower Q value (650 at 4 GHz) and higher τ_f (165 p.p.m. K^{-1}) compared to $BaTi_3Nb_4O_{17}$ ($Q \sim 2100$ at 4 GHz and $\tau_f \sim +86$ p.p.m. K^{-1}).

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