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Temperature coefficient-adjustable dielectric ceramics near the nominal composition $Ba_2Ti_3Nb_4O_{18}$

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Abstract

Dense dielectric ceramics with the nominal composition $Ba_2Ti_3Nb_4O_{18}$ were obtained by solid-state reaction. Although the XRD results showed the single phase in $Ba_2Ti_3Nb_4O_{18}$, the micro-structural analysis confirmed the existence of the secondary phase $Ba_3Ti_4Nb_4O_{21}$. Excellent temperature-stable dielectric ceramics were obtained with the nominal composition $Ba_2Ti_3Nb_4O_{18}$, where $\varepsilon_r = 38$, $\tan\delta \sim 0.0003$, and $\tau_\varepsilon \sim 2$ ppm/°C (all measured at 1 MHz). The τ_ε value can be adjusted from −6 to 17 ppm/°C near the vicinity of nominal composition $Ba_2Ti_3Nb_4O_{18}$ by changing the Ti content. The microwave dielectric properties of the nominal composition $Ba_2Ti_3Nb_4O_{18}$ were as follows: $\varepsilon_r = 38.1$, Qf = 14,227 GHz, and $\tau_f = -11$ ppm/°C.

Keywords: C. Dielectric properties; Dielectric ceramic; $BaO–TiO_2–Nb_2O_5$ system

1. Introduction

With the increasing development of microelectronic and communication technologies, the requirement of bulk dielectric ceramics for using in microwave frequency components is steadily increasing. To meet the requirements for use in microwave resonators and filters, dielectric materials must satisfy three properties: high relative permittivity (ε_r) to permit miniaturization, low dissipation factor ($\tan\delta$) for selectivity and noise reduction, and moderate temperature coefficient of resonant frequency (τ_f) for stability [1,2]. Temperature-stable electronic devices require the use of microwave resonators which have τ_f as near zero as possible. Microwave circuits will normally have some low characteristic τ_f, so the resonator components which go into them are required to compensate for the inherent drift. It is imperative that a microwave material has a τ_f close to zero and preferably tunable with composition and processing so that changes in the surrounding circuit can be balanced (temperature compensated).

Recently, dielectric properties of eight compounds in the $BaO–TiO_2–Nb_2O_5$ system were reported by Roberts and Cava in 1997 [3] and several compounds such as $BaTiNb_4O_{13}$, $BaTi_3Nb_4O_{17}$ and $Ba_3Ti_5Nb_6O_{28}$ were reported to have the potential application in the microwave dielectric resonator [4,5]. The structure of another composition in the $BaO–TiO_2–Nb_2O_5$ system, $Ba_2Ti_3Nb_4O_{18}$, has been studied by Gasperin [6], and the composition of $Ba_2Ti_3Nb_4O_{18}$ was presumed to be the same with the composition of $Ba_3Ti_5Nb_6O_{28}$ by Millet and Roth [7]. However, no further dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ have been reported yet. In present work, the samples near the vicinity of the nominal composition $Ba_2Ti_3Nb_4O_{18}$ were prepared by a solid-state reaction method, and the dielectric properties were investigated together with the microstructures.

2. Experimental

All ceramic samples were prepared by the conventional solid-state reaction route: $BaCO_3$, TiO_2 and Nb_2O_5 (High Purity Chemical >99.9%, <1 μm) were weighed and mixed using distilled water and mechanically milled for 4 h. The mixture were dried and calcined in air at 1200 °C for 4 h. The calcined powders were then thoroughly milled for another 4 h. The powders were pressed into cylindrical disks of 15 mm in

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diameter and 2 mm in thickness under a pressure of 25 MPa. The green compacts were sintered in air at 1230–1290 °C for 2 h and furnace cooled.

The bulk densities of the samples were measured by the Archimedean principle. Phase constitutions were identified by X-ray diffraction (XRD) of powders using Cu Kα radiation (Riguka D/max-IIIA). The polished and thermo-etched surfaces of sintered ceramics were observed and analyzed using a LEO1530VP scanning electron microscope (SEM). The constituent phases of grains were determined using scanning electron microscopy (SEM) coupled with an Energy Dispersive X-ray Detector Oxford Inca-300X (EDX). Surfaces of the ceramics were polished and Ag solder was applied as the electrode. Measurements of the dielectric constants and dissipation factors were made at 1 MHz using an Agilent 4288 A Capacitance Meter. The temperature coefficients of capacitance were measured in the GZ-ESPEC MC710P environment temperature chamber (−55 to 125 °C). The temperature coefficient of dielectric constant (τ_ε) is calculated from the equation as follows:

$$\tau_\varepsilon = [(\varepsilon_r\ (125\,^\circ\mathrm{C}) - \varepsilon_r\ (-55\,^\circ\mathrm{C})]/[\varepsilon_r\ (25\,^\circ\mathrm{C}) \times 180] \qquad (1)$$

The microwave dielectric properties were measured using an HP8753E network analyzer. The τ_f value is calculated from the equation as follows [8]:

$$\tau_f = -1/2\tau_\varepsilon - \alpha \qquad (2)$$

where α is the linear expansion coefficient, and the α value of most ceramics is around 10 ppm/°C.

3. Results and discussion

As shown in Fig. 1, dense ceramics of nominal composition $Ba_2Ti_3Nb_4O_{18}$ were obtained by sintering from 1250 to 1290 °C for 2 h. Fig. 2 shows the XRD patterns of $Ba_2Ti_3Nb_4O_{18}$ ceramics sintered at different temperatures. All the reflections shown in Fig. 2 can be attributed to $Ba_2Ti_3Nb_4O_{18}$ phase (JCPDS 77-1205) or $Ba_3Ti_5Nb_6O_{28}$ phase (JCPDS 34-1477). $Ba_2Ti_3Nb_4O_{18}$ and $Ba_3Ti_5Nb_6O_{28}$ have the same monoclinic symmetry with space group *P21/c* (14) and similar unit cell parameters.

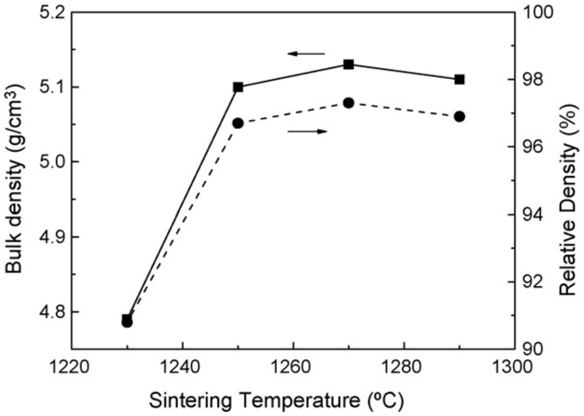


Fig. 1. Bulk density and relative density of $Ba_2Ti_3Nb_4O_{18}$ ceramics sintered at 1230–1290 °C for 2 h.

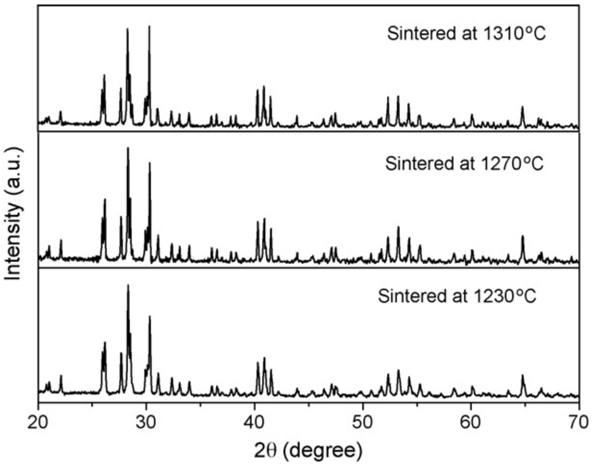


Fig. 2. XRD patterns of $Ba_2Ti_3Nb_4O_{18}$ ceramics at different sintering temperatures.

Though the XRD results showed the single phase in $Ba_2Ti_3Nb_4O_{18}$, the micro-structural analysis confirmed the existence of the secondary phase as shown in Fig. 3, where the trace of bar shape grains dispersed in the matrix-phase which showed ∼3 μm spherical grains. The amount of the secondary phase increased with increasing sintering temperature from 1250 to 1270 °C. As shown in Fig. 4, the composition of the

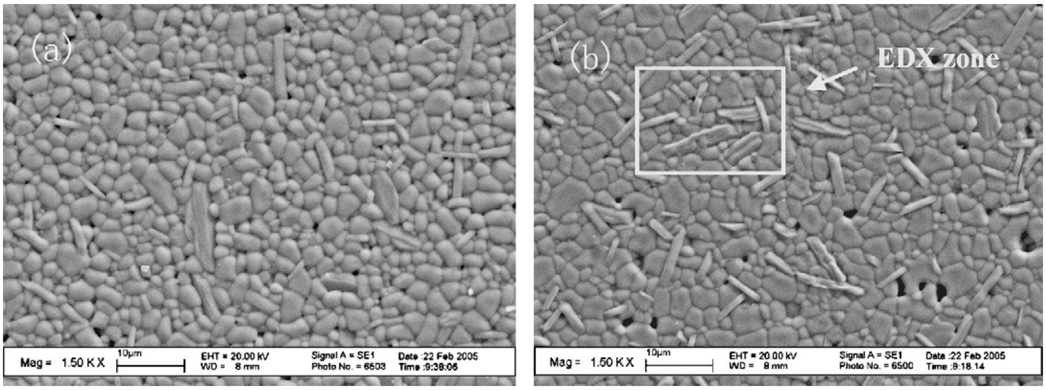
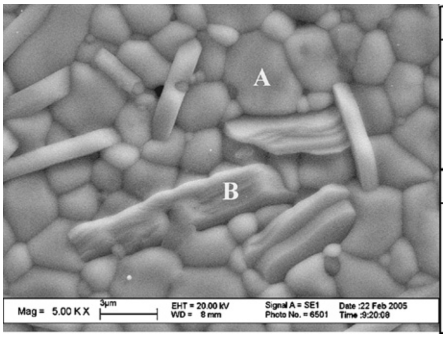


Fig. 3. SEM images of $Ba_2Ti_3Nb_4O_{18}$ ceramics sintered at 1250 °C (a) and 1270 °C (b) for 2 h.



Grain A	Atomic %
Ba	7.78
Ti	11.28
Nb	14.26
O	66.68
Grain B	**Atomic%**
Ba	9.30
Ti	12.08
Nb	12.23
O	66.42

Fig. 4. EDX analysis of different shape grains in $Ba_2Ti_3Nb_4O_{18}$ ceramics sintered at 1250 °C.

matrix phase was analyzed to consist of a compound with the following compositions: 0.297BaO–0.431TiO_2–0.272Nb_2O_5, which closely corresponds to $Ba_2Ti_3Nb_4O_{18}$. The secondary phase was analyzed to be 0.338BaO–0.44TiO_2–0.222Nb_2O_5, which closely corresponds to $Ba_3Ti_4Nb_4O_{21}$. As reported by Millet and Roth [7], the compound of $Ba_2Ti_3Nb_4O_{18}$ is always slightly non-stoichiometric, resulting in a dominant phase of $Ba_3Ti_5Nb_6O_{28}$ and a small amount of both $Ba_3Ti_4Nb_4O_{21}$ and $Ba_6Nb_{14}O_{41}$ phases. In the present study, there is no evidence of the $Ba_6Nb_{14}O_{41}$ phase and the XRD results of $Ba_6Nb_{14}O_{41}$ showed the $BaNb_2O_6$ phase (not given). The exact analyses of the phase relationship are beyond the scope of this paper.

The dielectric properties of the $Ba_2Ti_3Nb_4O_{18}$ ceramic sintered from 1230 to 1290 °C are shown in Fig. 5. Excellent temperature-stable dielectric ceramics were obtained when sintered at 1250 °C, where $\varepsilon_r \sim 38$, $\tan\delta \sim 0.0003$, $\tau_\varepsilon \sim 2$ ppm/°C (at 1 MHz). With the increasing of sintering temperature, ε_r slightly increased and τ_ε became more negative. As mentioned above, the amount of the secondary phase of $Ba_3Ti_4Nb_4O_{21}$ increased with the increasing of sintering temperature. The variety of dielectric properties at different sintering temperatures can be related to the variety of the content of the $Ba_3Ti_4Nb_4O_{21}$ phase. The dielectric properties of the $Ba_3Ti_4Nb_4O_{21}$ phase are described as follows: $\varepsilon_r = 56.8$, $\tau_\varepsilon = -179$ ppm/°C (at 1 MHz) [3].

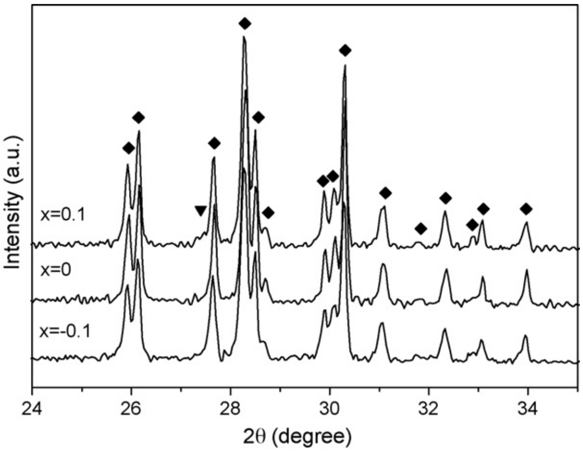


Fig. 6. XRD patterns of $Ba_2Ti_{3+x}Nb_4O_{18+2x}$ ((◆) $Ba_2Ti_3Nb_4O_{18}$ phase; (▼) TiO_2 phase).

The compositions with a non-stoichiometry formula of $Ba_2Ti_{3+x}Nb_4O_{18+2x}$ near the vicinity of $Ba_2Ti_3Nb_4O_{18}$ were also investigated. Fig. 6 shows the XRD patterns of the compositions near the vicinity of $Ba_2Ti_3Nb_4O_{18}$. There was no significant shift of the reflections and a very weak peak of $2\theta \sim 27.45°$ which was related to the TiO_2 phase was found in the Ti-rich phase ($x = 0.1$). Actually, the composition of $Ba_3Ti_5Nb_6O_{28}$ can be written as the formula $Ba_2Ti_{3+x}Nb_4O_{18+2x}$ when x equals to 1/3. Millet and Roth [7] also found the presence of TiO_2 phase in the synthesis of the $Ba_3Ti_5Nb_6O_{28}$ phase. A more detailed microstructure study should be performed to precisely determine the phase constitution in the future research work.

The temperature dependence of the dielectric properties of $Ba_2Ti_{3+x}Nb_4O_{18+2x}$ measured at 1 MHz are shown in Table 1 and Fig. 7. It is noticeable that ε_r and $\tan\delta$ are relatively steady from −55 to 125 °C and τ_ε is tunable with the adjustment of the Ti content. Compared with the τ_ε of $Ba_2Ti_3Nb_4O_{18}$ ($x = 0$), the τ_ε value decreased in the Ti-rich phase ($x > 0$) and increased in the Ti-poor phase ($x < 0$). A series of τ_ε values ranged from −6 to 17 ppm/°C were obtained when x changed from 0.1 to −0.1.

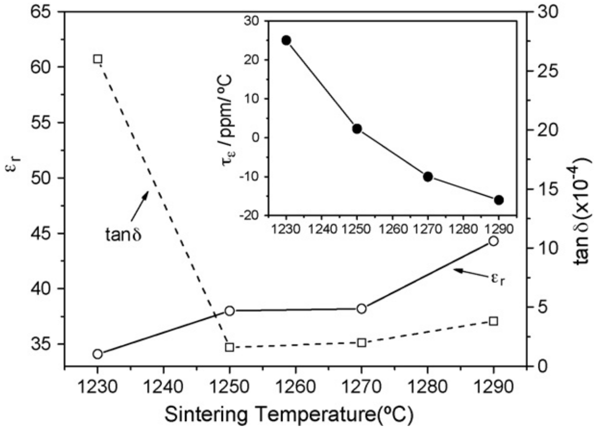


Fig. 5. Dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ ceramics sintered at 1230–1290 °C for 2 h.

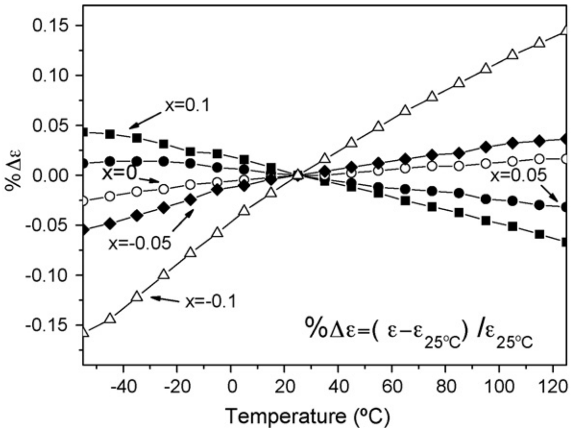


Fig. 7. Temperature dependence of the dielectric constant as a function of x in $Ba_2Ti_{3+x}Nb_4O_{18+2x}$ (sintered at 1250 °C, measured at 1 MHz).

Table 1
Temperature dependences of dielectric properties of $Ba_2Ti_{3+x}Nb_4O_{18+2x}$ at 1 MHz

Compound	X value	Sintering temperature (°C)	ε_r, 125 °C	tan δ, 125 °C	ε_r, 25 °C	tan δ, 25 °C	ε_r, −55 °C	tan δ, −55 °C	τ_ε (ppm/ °C)
$Ba_2Ti_{3.1}Nb_4O_{18}$	+0.1	1250	38.56	0.0003	38.59	0.0003	38.61	0.0003	−6.1
$Ba_2Ti_{3.05}Nb_4O_{18}$	+0.05	1250	38.48	0.0003	38.49	0.0002	38.49	0.0002	−2.4
$Ba_2Ti_3Nb_4O_{18}$	0	1250	38.15	0.0003	38.15	0.0002	38.14	0.0002	2.3
$Ba_2Ti_{2.95}Nb_4O_{18}$	−0.05	1250	38.41	0.0002	38.40	0.0003	38.39	0.0004	3.9
$Ba_2Ti_{2.9}Nb_4O_{18}$	−0.1	1250	39.40	0.0005	39.33	0.0006	39.27	0.0007	17.7

As mentioned above, traces of TiO_2 phase were observed in the Ti-rich phase, so the increase of ε_r and tan δ with the decrease of τ_ε in the Ti-rich phase may be interpreted in terms of the formation of TiO_2 phase considering the dielectric properties of TiO_2 phase ($\varepsilon_r \sim 85$, tan $\delta \sim 0.0005$, $\tau_\varepsilon \sim -700$ ppm/°C). The increase of ε_r and τ_ε in the Ti-poor phase may be attributed to the formation of hexagonal $BaNb_2O_6$ phase which was reported to form near the composition of $Ba_6Nb_{14}O_{41}$ [9]. And the dielectric properties of hexagonal $BaNb_2O_6$ phase are as follows: $\varepsilon_r \sim 42$, Qf ~ 4000, $\tau_f \sim -800$ ppm/°C [10].

The microwave dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ ceramic sintered at 1250 °C were as follows: the ε_r calculated from the TE_{011} (5.938 GHz) resonance is 38.1; the unloaded Q factor for the TE_{011} mode is 2396 (Qf = 14,227 GHz). Although τ_f is not straightly measured, the τ_f value calculated from τ_ε is around −11 ppm/°C and tunable from −7 to −18 ppm/°C. Compared with the microwave dielectric properties of the similar composition $Ba_3Ti_5Nb_6O_{28}$ reported by Sebastian ($\varepsilon_r \sim 41$, Qf $\sim$ 4500 GHz, $TE_{011} \sim 5.4$ GHz, $\tau_f \sim 8$ ppm/°C)[5], the ε_r value of the composition $Ba_2Ti_3Nb_4O_{18}$ is similar while the Qf value is much higher and the τ_f value could be tunable.

4. Conclusions

New low-loss dielectrics near the vicinity of $Ba_2Ti_3Nb_4O_{18}$ have been prepared, characterized and the dielectric properties at 1 MHz have been measured. $Ba_2Ti_3Nb_4O_{18}$ has high dielectric constant ($\varepsilon_r \sim 38$), low dissipation factor (tan $\delta \sim 0.0003$) and low temperature coefficient of dielectric constant ($\tau_\varepsilon \sim 2$ ppm/°C) when sintered at 1250 °C. The presence of a secondary phase of $Ba_3Ti_4Nb_4O_{21}$ was confirmed and had an influence on the dielectric properties. The τ_ε value could be adjusted from −6 to 17 ppm/°C by slightly changing the content of Ti element. Further study of the properties of $Ba_2Ti_3Nb_4O_{18}$ in the microwave frequency range is necessary to determine whether this material has possible applicability for advanced microelectronic components such as dielectric resonator.

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