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$BaO–TiO_2$ microwave ceramics

Shunhua Wu*, Guoqing Wang, Yushuang Zhao, Hao Su

College of Electronics and Information Engineering, Tianjin University, Tianjin, PR China

Abstract

In this paper, the structure and dielectric properties of $BaO–TiO_2$ system ceramics were studied. By adding ZnO and Nb_2O_5 as sintering agents to the raw materials, the $BaO–TiO_2$ system ceramics were sintered at a temperature of 1260 °C for 2 h and have superior dielectric properties at 1 GHz: quality factor $Q=12,500$, relative dielectric constant $\varepsilon_r \approx 37$, temperature coefficient of dielectric constant $\alpha_\varepsilon = 0 \pm 30$ ppm/°C. XRD pattern shows that the main crystal phase of the ceramics is $Ba_2Ti_9O_{20}$, accompanied by a small number of additional phases: $BaTi_4O_9$, $Ba_4Ti_{13}Zn_7O_{34}$, $Ba_4Ti_{13}O_{30}$ and $Ti_2Nb_{10}O_{29}$, etc. The initial Ba/Ti ratio has a great effect on the dielectric properties of the ceramics, which can be explained by the variance in the formation of phases due to different Ba/Ti ratios.

Keywords: Dielectric properties; Microwave ceramics; Sintering; X-ray methods; $BaO–TiO_2$

1. Introduction

In the past decades, $Ba_2Ti_9O_{20}$ ceramics has received wide attention for its good microwave properties.[1] Jonker and Kwestroo[2] first reported the existence of $Ba_2Ti_9O_{20}$. O'Bryan et al.[3] deeply studied the $Ba_2Ti_9O_{20}$ ceramics, and indicated that it could work as a kind of superior resonator material. It is well known that the formation of the single phase of $Ba_2Ti_9O_{20}$ is very difficult in that it can only be formed within a very narrow range of Ba/Ti ratio close to 2:9.[4] Several reports have proved that the addition of dopants such as ZrO_2, SnO_2, $BaSnO_3$, etc. can make the formation of $Ba_2Ti_9O_{20}$ easier.[1,5]

In the current work, ZnO and Nb_2O_5 were added to $BaO–TiO_2$ system, which lowered the sintering temperature to 1260 °C without deteriorating the dielectric properties. The dielectric properties as functions of initial Ba/Ti ratios were investigated. We have used this system ceramics to make multilayer ceramic capacitors (MLCCs) with excellent microwave characteristics.

2. Experimental procedure

The starting materials of $BaCO_3$, TiO_2, ZnO and Nb_2O_5 powders were weighed according to the composition of $0.62\ Ba_xTi_yO_{x+2y} + 0.33\ ZnO + 0.05\ Nb_2O_5$ ($x=1$–4, $y=4$–9). The purity of these powders and additives was higher than 99.9%. They were mixed and milled with zirconia balls in distilled water for 1.5 h, then dried and calcined in air at 1110 °C for 2 h. After that, the powders were milled again for 4.5 h and dried. Then they were sieved by No. 80 mesh and pressed isostatically into pellets at 75 MPa. The pellets were sintered in air at 1260 °C for 2 h at a heating rate of 4 °C/min. Finally they were covered with Ag electrodes for measurement.

The capacitance (C) and quality factor (Q) of the samples were measured at 1 GHz with a capacitance meter (Model 4291B, HP Co.). The temperature coefficient of dielectric constant α_ε was calculated using the equation $\alpha_\varepsilon = (C_{85} - C_{25})/(C_{25} \cdot 60\ °C)$, where C_{85} and C_{25} are the capacitances of the samples at 85 and 25 °C, respectively. The phases present were examined with an X-ray diffractometer (Model 2038X, Rigaku Co.) and the surface microstructure was observed with a Scanning Electronic Microscope (SEM).

3. Results and discussion

Figs. 1 and 2 are the SEM micrograph and XRD pattern of the sample ($Ba/Ti = x/y = 2/9$) sintered at 1260 °C for 2 h, respectively.

As shown in Fig. 2, the major crystal phase of the samples is $Ba_2Ti_9O_{20}$, accompanied by additional phases

* Corresponding author.

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$BaTi_4O_9$, $Ba_3Ti_{12}Zn_7O_{34}$, $Ba_4Ti_{13}O_{30}$ and $Ti_2Nb_{10}O_{29}$, *etc*. $Ba_2Ti_9O_{20}$ is triclinic with lattice parameters[6] $a = 0.7471$ nm, $b = 1.4081$ nm, $c = 1.4344$ nm, $\alpha = 89.94°$, $\beta = 79.43°$, $\gamma = 84.45°$. $BaTi_4O_9$ and $Ba_4Ti_{13}O_{30}$ are both orthorhombic with lattice parameters[7] $a = 1.453$ nm, $b = 0.379$ nm, $c = 0.629$ nm, and $a = 1.706$ nm, $b = 0.986$ nm, $c = 1.405$ nm, respectively.

3.1. Dielectric properties of single phases in the BaO–TiO_2 system ceramics

Several single-phase compounds detected via XRD were prepared respectively in the same process as mentioned in the experimental procedure according to the following equations:

$$2BaCO_3 + 9TiO_2 \rightarrow Ba_2Ti_9O_{20} + 2CO_2 \uparrow \quad (1)$$

$$BaCO_3 + 4\,TiO_2 \rightarrow BaTi_4O_9 + CO_2 \uparrow \quad (2)$$

$$4BaCO_3 + 13\,TiO_2 \rightarrow Ba_4Ti_{13}O_{30} + 4CO_2 \uparrow \quad (3)$$

$$2TiO_2 + 5Nb_2O_5 \rightarrow Ti_2Nb_{10}O_{29} \quad (4)$$

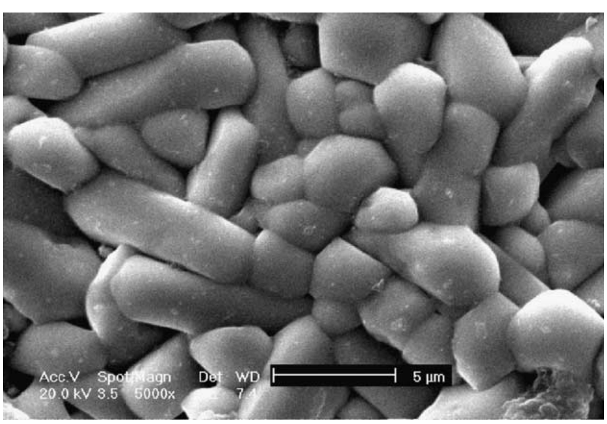

Fig. 1. SEM micrograph of the surface of the sample (Ba/Ti = 2/9) sintered at 1260 °C for 2 h.

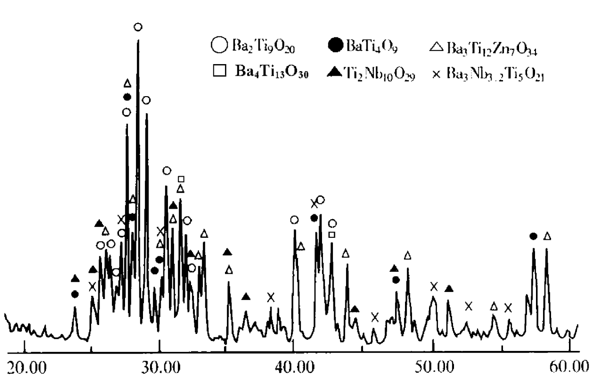

Fig. 2. XRD pattern of the sample (Ba/Ti = 2/9) sintered at 1260 °C for 2 h.

When the compounds above were prepared, we used a small number of sintering agents.

Table 1 shows the dielectric properties of these compounds.

The number of these compounds in the BaO–TiO_2 system ceramics varies with Ba/Ti ratios, which can explain different properties of this system ceramics as functions of different Ba/Ti ratios.

3.2. The structure of $Ba_2Ti_9O_{20}$

The crystal structure of $Ba_2Ti_9O_{20}$ can be described as a hexagonal closest packing of oxygen and barium atoms.[7] Titanium atoms distribute in the octahedral interstices of the closest packing to form TiO_6 octahedra.

Fig. 3 shows a projection of the unit cell along [010] in six layers of TiO_6 octahedra.[7] Chains of four octahedra each at $y \approx 1/6$[Ti(15)–Ti(18)] and $y \approx 1/3$[Ti(7)–Ti(10)] are connected by common edges to form double rutile-type chains. These groups of eight octahedra each are again linked to each other by edge-sharing octahedra [Ti(11)–Ti(14)]. The same structural unit is formed by the TiO_6 octahedra at $y \approx 2/3$ and $y = 5/6$. Groups of six edge-sharing octahedra at $y \approx 0$[Ti(1)–Ti(3)] and $y \approx 1/2$ [Ti(4)–Ti(6)] connect these units via common corners.

3.3. The effects of Ba/Ti ratio on the dielectric properties of BaO–TiO_2 system ceramics

Fig. 4 indicates the relationships between the initial Ba/Ti ratio and ε_r, α_ε, in which we can see that with the increase of the Ba/Ti ratio, ε_r decreases gradually and α_ε shifts negatively. This tendency can be explained by the most well-known empirical equations for the calculation of ε_r and α_ε of a multi-phase compound.

$$\ln\varepsilon_r = \sum_i V_i \cdot \ln\varepsilon_{ri} \quad (5)$$

$$\alpha_\varepsilon = \sum_i V_i \alpha_{\varepsilon i} \quad (6)$$

where V_i, ε_{ri} and $\alpha_{\varepsilon i}$ are the volume fraction, the relative dielectric constant, and the temperature coefficient of dielectric constant of the *i*th phase, respectively.

As shown in Table 1 for $Ba_2Ti_9O_{20}$, $\varepsilon_r = 39$, $\alpha_\varepsilon = -29$ ppm/°C; for $Ti_2Nb_{10}O_{29}$, $\varepsilon_r = 180$, $\alpha_\varepsilon = +1100$ ppm/°C; for $Ba_4Ti_{13}O_{30}$, $\varepsilon_r = 41$, $\alpha_\varepsilon = -135$ ppm/°C.

Table 1
Dielectric properties of the compounds

Samples	Sintering temperature (°C)	ε_r	α_ε (ppm/°C)
$Ba_2Ti_9O_{20}$	1280	39	−29
$BaTi_4O_9$	1260	38	+18
$Ba_4Ti_{13}O_{30}$	1260	41	−135
$Ti_2Nb_{10}O_{29}$	1300	180	+1100

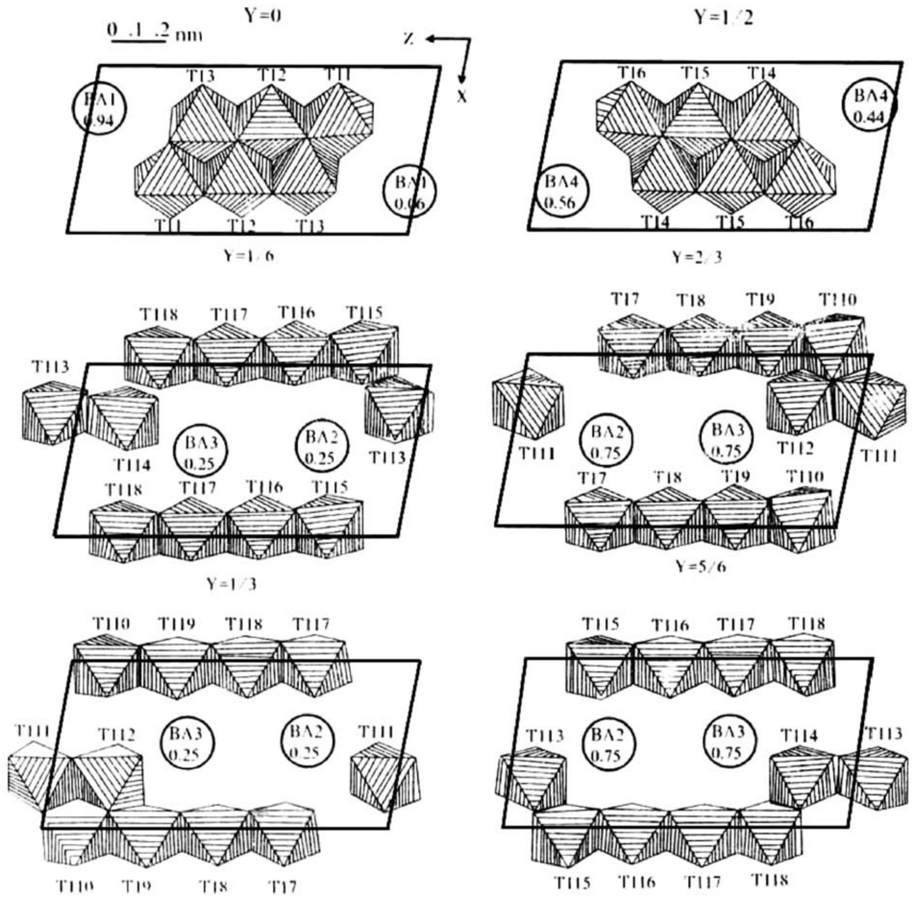

Fig. 3. Six layers of crystal structure of $Ba_2Ti_9O_{20}$ stacked parallel to [010].

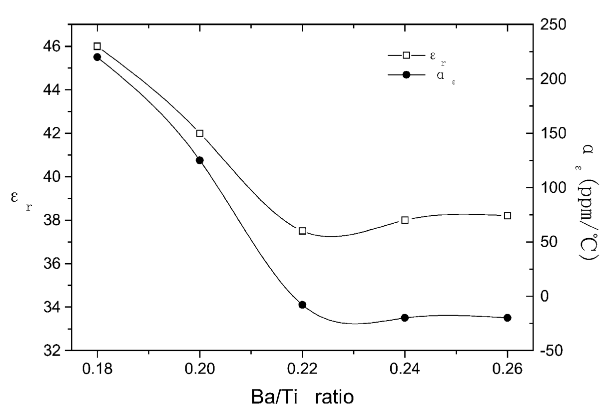

Fig. 4. ε_r and α_ε as functions of the Ba/Ti ratios.

When the Ba/Ti ratio is less than 2/9, more $Ti_2Nb_{10}O_{29}$ maybe exist in the multi-phase samples that were composed of $Ba_2Ti_9O_{20}$, $BaTi_4O_9$, $Ba_3Ti_{12}Zn_7O_{34}$, $Ti_2Nb_{10}O_{29}$ and $Ba_4Ti_{13}O_{30}$ etc. According to Eqs. (5) and (6), ε_r of the samples has a relative larger value and α_ε is positive because of the high ε_r (180) and the positive α_ε (+1100 ppm/°C) of $Ti_2Nb_{10}O_{29}$.

With the increase of Ba/Ti ratio, especially when the ratio exceeds 2/9, probably the amount of $Ti_2Nb_{10}O_{29}$ decreases, while the amount of $Ba_4Ti_{13}O_{30}$ ($\varepsilon_r = 41$, $\alpha_\varepsilon = -135$ ppm/°C) increases. Meanwhile, the formation of $Ba_2Ti_9O_{20}$ ($\varepsilon_r = 39$, $\alpha_\varepsilon = -29$ ppm/°C) was facilitated due to the rise of Ba/Ti ratio. So ε_r of the samples decreases, and α_ε shifts negatively, which can also be attributed to the two equations above.

4. Conclusions

1. BaO–TiO_2 system ceramics were prepared at a sintering temperature of 1260 °C for 2 h and have excellent microwave dielectric properties.
2. The initial Ba/Ti ratio in the raw materials has a great effect on the dielectric properties of the system ceramics. Lower Ba/Ti ratio increases ε_r and shifts α_ε positively, while higher Ba/Ti ratio has an opposite effect.

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