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# Effects of additives on the phase formation and microstructural evolution of $Ba_2Ti_9O_{20}$ microwave ceramic

Sea-Fue Wang[a,*], Thomas C.K. Yang[b], Chuang-Chung Chiang[a], Stanley H.Y. Tsai[c]

[a]*Department of Materials and Minerals Resources Engineering, National Taipei University of Technology,*
*1, Sec. 3, Chung-Hsiao E. Road, Taipei, Taiwan, ROC*
[b]*Department of Chemical Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC*
[c]*Union Chemical Laboratory, Industrial Technology Research Institute, Hsin-Chu, Taiwan, ROC*

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## Abstract

Preparation of dense and phase-pure $Ba_2Ti_9O_{20}$ is generally difficult using solid state reaction, since there are several thermodynamically stable compounds in the vicinity of the desired composition and a curvature of $Ba_2Ti_9O_{20}$ equilibrium phase boundary in the BaO–$TiO_2$ system at high temperatures. It was reported that a small amount of solid solution additives is essential for the formation of a pure $Ba_2Ti_9O_{20}$ phase, however, contradictory results were also addressed in the literature. In this study, $TiO_2$, MnO, and $ZrO_2$, were used to investigate the effects of additives on the densification, microstructural evolution and phase stability of $Ba_2Ti_9O_{20}$. With the addition of 2.8 wt.% $TiO_2$ and sintering at 1200 °C, ceramic yielded a pure $Ba_2Ti_9O_{20}$ phase. It indicates that $Ba_2Ti_9O_{20}$ is a nonstoichiometric compound, which can accommodate an excess amount of $TiO_2$. With the addition of 4 wt.% $ZrO_2$, phase pure $Ba_2Ti_9O_{20}$ was obtained in the sintering temperatures of 1200 °C and 1300 °C. Results also indicated that MnO addition could promote the formation of $Ba_2Ti_9O_{20}$, compared with that of pure host material, though pure $Ba_2Ti_9O_{20}$ was not obtained. SEM microstructures are consistent with the observations in XRD patterns.

*Keywords:* B. Microstructure; Microwave materials; Phase stability; $Ba_2Ti_9O_{20}$

## 1. Introduction

Commercial wireless communication has been a rapid growth market in the past decade. This technology advancement has been made possible in part with recent revolution in miniaturization of microwave circuits by using low-loss and temperature stable dielectric resonators. Functioning as important components in communication circuits, dielectric resonators can create, filter, and select frequencies in oscillators, amplifiers and tuners.

Several ceramic materials have been developed for using as microwave resonators. Among the various candidates, $Ba_2Ti_9O_{20}$, which contains 81.8 mol% of $TiO_2$ and 18.2 mol% of BaO, has received much attention for its good microwave properties [1,2].It has a good quality factor (8000 at a frequency of 4 GHz), a high dielectric constant (39.8), and a low temperature coefficient ($\tau_f = 2$ ppm/°C) [3]. The crystal structure of $Ba_2Ti_9O_{20}$ is layered; it has a hexagonal, close-packed arrangement of Ba and O, with Ti occupying the appropriate octahedra sites, and containing a primitive triclinic cell made up of six crystal-structure layers [4].

For the preparation of phase pure $Ba_2Ti_9O_{20}$ from $BaCO_3$ and $TiO_2$ by solid state reaction [5], the stoichiometry and fabrication parameters must be precisely controlled, since there are various thermodynamically stable compounds in the vicinity of the desired composition of $TiO_2$-rich BaO–$TiO_2$ system: $Ba_6Ti_{17}O_{40}$, $BaTi_3O_7$, $BaTi_4O_9$, $BaTi_5O_{11}$, and $Ba_4Ti_{13}O_{30}$.[4,6] Furthermore, studies revealed a curvature of $Ba_2Ti_9O_{20}$ equilibrium phase boundary in the BaO-$TiO_2$ system at high temperature [7], which creates an additional complication in forming monophase $Ba_2Ti_9O_{20}$. O'Bryan and Thomson reported that the formation of some $Ba_2Ti_9O_{20}$ on calcination is required for the complete transform of mixed powders into pure $Ba_2Ti_9O_{20}$ during

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* Corresponding author.

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sintering [8]. Jaakola et al. [9] noted that a reaction temperature of 1150 °C or higher is necessary for the crystallization of $Ba_2Ti_9O_{20}$ phase within a reasonable time span in a mixture of $BaCO_3$–$TiO_2$. Wu and Wang gave a phase development sequence of $BaTi_5O_{11} \rightarrow BaTi_4O_9 \rightarrow Ba_2Ti_9O_{20}$ and proposed that in addition to diffusion, the nucleation barrier is another important factor in the formation of $Ba_2Ti_9O_{20}$ [10].

It was reported that a small amount of solid solution additives, such as $SnO_2$, $ZrO_2$, SrO, $Al_2O_3$, or $Bi_2O_3$, is essential for the formation of a pure $Ba_2Ti_9O_{20}$ phase [5,11–17]. Nevertheless, contradiction results were also addressed in the literature. O'Brayn showed that these substitutions are not required to stabilize the $Ba_2Ti_9O_{20}$ phase [3]. In order to clarify the role of additives on the stabilization of $Ba_2Ti_9O_{20}$ phase, investigation on the effects of additives on the densification, microstructural evolution and phase stability of $Ba_2Ti_9O_{20}$ was performed in this study. Three additives, including $TiO_2$, MnO, and $ZrO_2$, were used throughout the experiments. Excess $TiO_2$ was added to explore the effect of nonstoichiometry on the $Ba_2Ti_9O_{20}$ formation. MnO and $ZrO_2$ were chosen due to the difference in their solubility and chemical nature.

## 2. Experimental procedure

A host material, containing 81.8 mol% of $TiO_2$ and 18.2 mol% of BaO, was prepared using the solid-state reaction. $BaCO_3$ and $TiO_2$ powders (Fisher Scientific, reagent grade) were mixed using polyethylene jars and zirconia media with methyl alcohol for 8 h. They were then mixed with different amount of $TiO_2$, MnO, or $ZrO_2$ (Fisher Scientific, reagent grade), in methyl alcohol using ball mill for 24 h. The powders have particle size of ≈0.73 μm measured by light scattering (Zeta 1000) and surface area of ≈7.60 $m^2/g$ from B.E.T. method.

After drying, the powders were mixed with a 4.0 wt.% of 15%-PVA solution and pelletized into disc-shapes using uniaxial pressure of 2 $tons/cm^2$. The samples were then heat treated at 550 °C for 2 h to eliminate the PVA, followed by sintering at different temperatures for 4 h (heating rate = 10 °C /min) on $ZrO_2$ setter. Densities of specimens were measured using geometrical method. X-ray diffraction (XRD, Rigaku D/max-B), scanning electron microscopy (SEM, Jeol JSM-T330A), and energy dispersive spectroscopy (EDS) on the sintered surfaces were used to confirm the formation of the phases and characterize the microstructures.

## 3. Results and discussion

The effects of excess $TiO_2$, MnO, and $ZrO_2$ on the microstructural evolution and phase stability of $Ba_2Ti_9O_{20}$ ceramic are discussed based on the results of densifications, X-ray diffraction patterns and SEM microstructures. These additives were selected due to the dissimilarity in their chemical nature. MnO has little solubility in $Ba_2Ti_9O_{20}$ [18,19]. However, it is reported that substitution of $Ti^{4+}$ by $Zr^{4+}$ could reach as much as 5 mol% [20]. Excessive $TiO_2$ was added to explore the effect of nonstoichiometry on the $Ba_2Ti_9O_{20}$ formation.

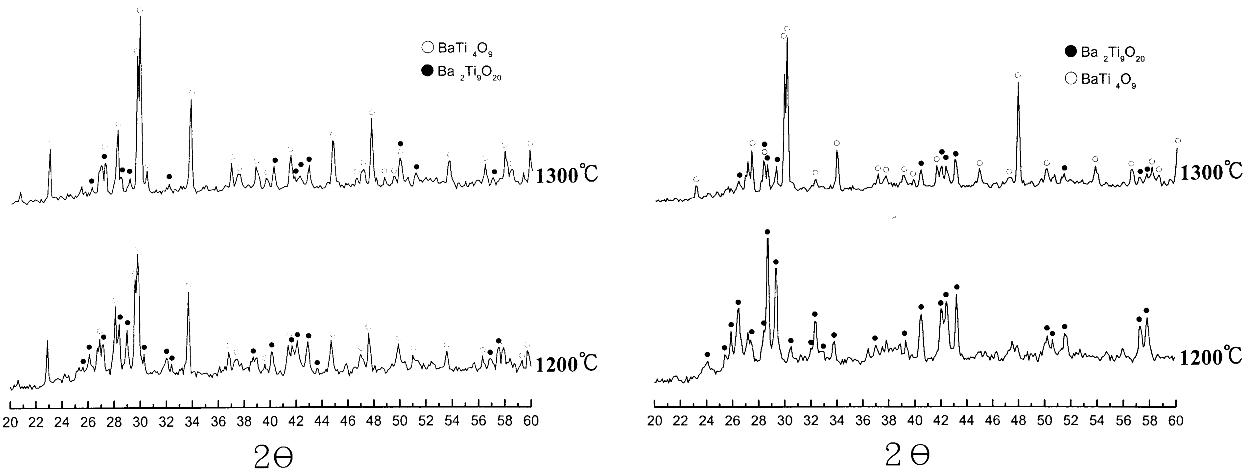
Fig. 1 shows the X-ray diffraction (XRD) patterns for pure host materials ($BaO/TiO_2 = 18.18/81.82$) and those with 0.5 wt.% MnO, 4 wt.% $ZrO_2$, or 2.8 wt.% $TiO_2$ additives sintered at 1200 and 1300 °C for 4 h. The corresponding apparent density and the existing phases identified from XRD patterns are summarized in Table 1. Similar to those reported in the literature, significant densification does not occur until 1300 °C, which is due to the high surface energy and interfacial energy of $Ba_2Ti_9O_{20}$ particles [10,21,22]. Maximum density of ≈95% was achieved in most cases after sintering at 1300 °C.

The XRD results display that the phase stability of $Ba_2Ti_9O_{20}$ is dependent on the sintering condition as well as the constituents of additives. It indicates that the pure host material sintered at 1200 °C would produce a mixture of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$, with $BaTi_4O_9$ as the major phase (Fig. 1a). This is generally agreed with the results shown in the literature, except that $BaTi_5O_{11}$ was detected in some studies [22,23]. Depending on the precursor and thermal history of the powders, $BaTi_5O_{11}$ was reported to decompose into $Ba_2Ti_9O_{20}$ and $TiO_2$ or $BaTi_4O_9$ as the soaking time proceeds at 1200 °C [24]. It is generally agreed in the literature that the nominal content in $Ba_2Ti_9O_{20}$ corresponds to 81.82% $TiO_2$ [8]. However, it is difficult to obtain pure $Ba_2Ti_2O_9$ phase using solid-state reaction from $BaCO_3$ and $TiO_2$ precursors, due to the limitation in homogeneity [21,25] It is suggested that the diffusion was the rate-limited factor in controlling the formation of $Ba_2Ti_9O_{20}$ [10,26]. As the sintering temperature increased to 1300 °C, ceramic with structure of $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, and a trace amount of $TiO_2$, was obtained (Table 1). The fraction of $Ba_2Ti_9O_{20}$ phase is less than that sintered at 1200 °C. This reflects the difficulty of obtaining pure $Ba_2Ti_9O_{20}$ at temperature above 1300 °C. This is consistent with Negas et al. studies on subsolidus phase relations in the $BaTiO_3$–$TiO_2$ system [4]. They revealed that the upper temperature at which $Ba_2Ti_9O_{20}$ was stable was close to 1300 °C. Nevertheless, O'Bryan and Thomason reported that it was near to 1400 °C and that above 1420 °C the phase underwent a peritectoid decomposition [12,27].

Fig. 1b shows the XRD patterns for material with 2.8 wt.% $TiO_2$ (i.e. $BaO/TiO_2 = 17.56/82.44$) sintered at 1200 and 1300 °C for 4 h. It is interesting to notice that sintering of this material at 1200 °C yielded a pure

(a) Pure Host Material

(b) Host Material + 2.8wt % $TiO_2$



(c) Host Material + 4.0wt % $ZrO_2$

(d) Host Material + 0.5wt % MnO

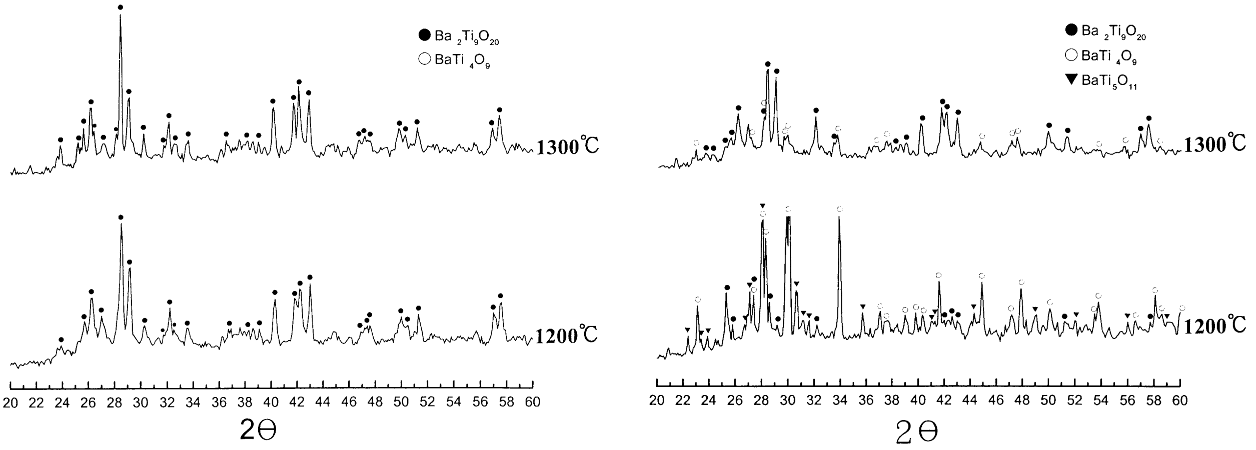


Fig. 1. X-ray diffraction (XRD) patterns for (a) pure host materials ($BaO/TiO_2 = 18.18/81.82$), and those with (b) 2.8 wt.% $TiO_2$, (c) 4 wt.% $ZrO_2$, or (d) 0.5 wt.% MnO additions, sintered at 1200 and 1300 °C for 4 h.

Table 1
The apparent density and the existing phases observed in XRD patterns for (a) pure host materials ($BaO/TiO_2 = 18.18/81.82$), and those with (b) 0.5 wt.% MnO, (c) 4 wt.% $ZrO_2$, or (d) 2.8 wt.% $TiO_2$ additions, sintered at 1200 and 1300 °C for 4 h

| Sample | Sintering profile | Density (g/cm$^3$) | Major phases | Minor phases |
|---|---|---|---|---|
| Host material (HM) | 1200 °C/4 h | 3.98 | $BaTi_4O_9$ | $Ba_2Ti_9O_{20}$ |
| | 1300 °C/4 h | 4.25 | $BaTi_4O_9$ | $Ba_2Ti_9O_{20}$, $TiO_2$ |
| HM + 2.8 wt.%$TiO_2$ | 1200 °C/4 h | 3.47 | $Ba_2Ti_9O_{20}$ | – |
| | 1300 °C/4 h | 4.33 | $BaTi_4O_9$ | $Ba_2Ti_9O_{20}$ |
| HM + 4 wt.%$ZrO_2$ | 1200 °C/4 h | 3.23 | $Ba_2Ti_9O_{20}$ | – |
| | 1300 °C/4 h | 4.55 | $Ba_2Ti_9O_{20}$ | – |
| HM + 0.5 wt.%MnO | 1200 °C/4 h | 4.00 | $BaTi_4O_9$, $BaTi_5O_{11}$ | $Ba_2Ti_9O_{20}$ |
| | 1300 °C/4 h | 4.03 | $Ba_2Ti_9O_{20}$ | $BaTi_4O_9$ |

$Ba_2Ti_9O_{20}$ phase. As the sintering temperature increased to 1300 °C, it resulted in $BaTi_4O_9$ with a minor amount of $Ba_2Ti_9O_{20}$, as well as a higher densification. It not only reflects the difficulty of obtaining a pure $Ba_2Ti_9O_{20}$ at temperature above 1300 °C, but also shows the enhancement of $Ba_2Ti_9O_{20}$ formation by the existed excessive $TiO_2$. It seems that $TiO_2$ excess is accommodated in the form of nonstoichiometric $Ba_2Ti_9O_{20}$. This is similar to what O'Bryan and Thomson observed in their quenching experiments from the melts [7], yet in contrast to the results presented by Lin et al. [13]. O'Bryan and Thomson reported that, at 1400 °C, the composition with $TiO_2$ of 81.68% is single phase, whereas at 1300 °C and below the single phase region comprised the composition between 81.80 and 81.86% of $TiO_2$. In this study, results apparently indicate a broadened nonstoichiometric region for $Ba_2Ti_9O_{20}$, though Lin et al. suggested that excessive titanium does not influence the stability of $Ba_2Ti_9O_{20}$.

Fig. 1c indicated the XRD patterns for material with 4 wt.% $ZrO_2$ addition and sintered at 1200 and 1300 °C for 4 h. Pure $Ba_2Ti_9O_{20}$ was obtained in both sintering temperatures. No $TiO_2$, $ZrO_2$, or $ZrTiO_4$ was detectable. The results are consistent with several studies reported in the literature [5,11,13,17,22]. $Ba_2Ti_9O_{20}$ compound could be stabilized by the additions of $ZrO_2$, though the mechanism is still in doubt. It was reported that the addition of $ZrO_2$ resulted in larger unit cell dimensions. It led to a slightly higher value of quality factor and a lower temperature coefficient of $Ba_2Ti_9O_{20}$.

The effect of Mn doping on the phase stability of $Ba_2Ti_9O_{20}$ is shown in Fig. 1d. At the sintering temperature of 1200 °C, a mixture of $BaTi_4O_9$ and $BaTi_5O_{11}$ with $Ba_2Ti_9O_{20}$ as a minor phase was observed. Increasing the sintering temperature to 1300 °C, $Ba_2Ti_9O_{20}$ become a major phase in the mixture of $Ba_2Ti_9O_{20}$ and $BaTi_4O_9$ phases. Nomura et al. suggested that MnO behaved as an oxidizing agent to prevent the formation of $Ti^{3+}$ during the sintering process of $Ba_2Ti_9O_{20}$ [17–19]. Results of this study, apparently, indicate that MnO addition could also facilitate the formation of $Ba_2Ti_9O_{20}$ phase, compared with that of pure host material, even though pure $Ba_2Ti_9O_{12}$ was not obtained.

SEM microstructures for various densified specimens including pure host material, and those with 2.8 wt.% $TiO_2$, 4 wt.% $ZrO_2$, and 0.5 wt.% MnO additives are shown in Fig. 2a–d, respectively. EDS was performed to characterize the compositions of the grains with different morphology. In Fig. 2a and b, a mixture of elongated, columnar $BaTi_4O_9$ and angular $Ba_2Ti_9O_{20}$ was seen. However, in Fig. 2c and d, almost all grains were angular $Ba_2Ti_9O_{20}$. The average grain sizes are somewhat similar in both cases, except Fig. 2c contains some small, granular, or columnar $BaTi_4O_9$ distributed in the matrix of angular $Ba_2Ti_9O_{20}$ grains. No abnormal grain growth was observed in either case. The microstructural evolution confirms the observations in XRD patterns.

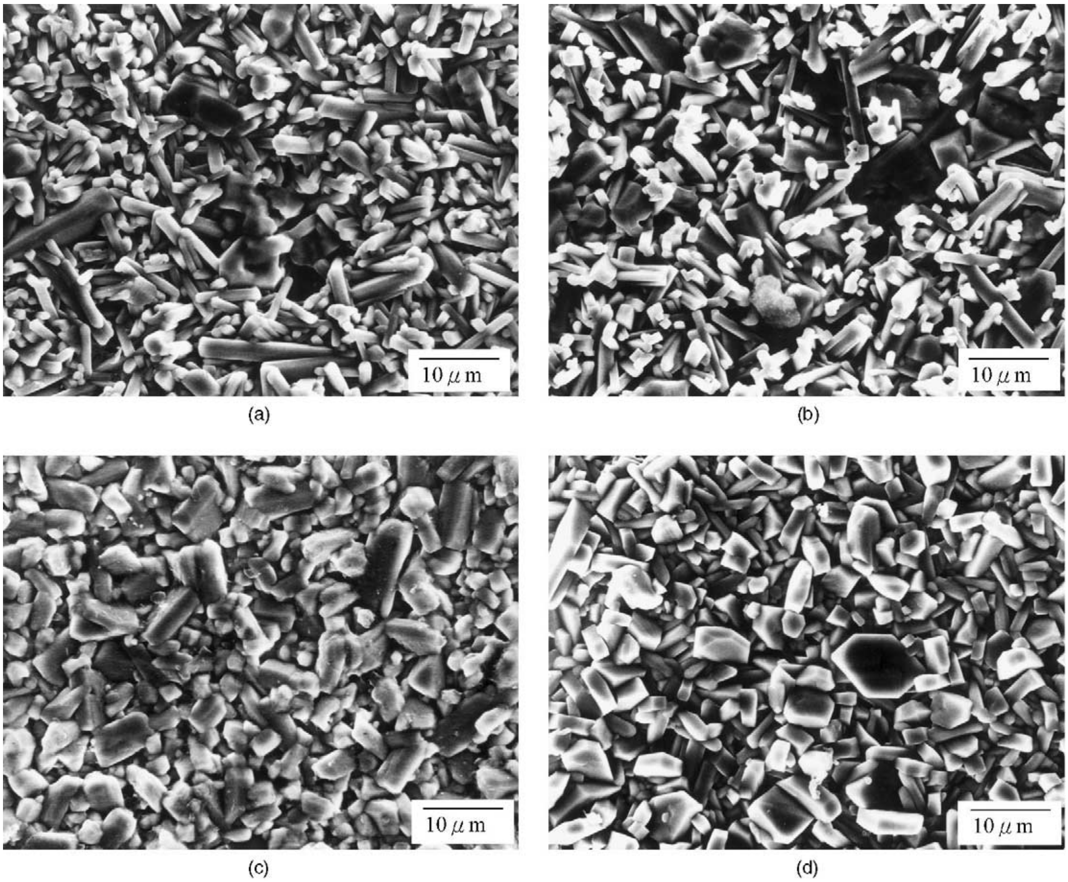


Fig. 2. SEM microstructures for (a) pure host material, and those with (b) 2.8 wt.% $TiO_2$, (c) 4 wt.% $ZrO_2$, and (d) 0.5 wt.% MnO additions, sintered at 1300 °C for 4 h.

## 4. Summary

The effects of excess $TiO_2$, MnO, and $ZrO_2$ on the microstructural evolution and phase stability of $Ba_2Ti_9O_{20}$ ceramic were investigated. Sintering of host material with 2.8 wt.% $TiO_2$ at 1200 °C yielded a pure $Ba_2Ti_9O_{20}$ phase. This indicates that excess titanium is accommodated in the form of nonstoichiometric $Ba_2Ti_9O_{20}$. With 4 wt.% $ZrO_2$ addition, pure $Ba_2Ti_9O_{20}$ was obtained in sintering temperatures of 1200 and 1300 °C. It seems that MnO addition could promote the formation of $Ba_2Ti_9O_{20}$ phase, compared with that of pure host material, though pure $Ba_2Ti_9O_{20}$ was not obtained. The phases identified in XRD patterns were verified by SEM microstructures.

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