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Effect of reaction sintering process on the microwave dielectric properties of $Ba_2Ti_9O_{20}$ materials

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Abstract

The pre-reaction step, which is the holding time at 1000 °C in reaction-sintering process, was observed to influence the characteristics of the $Ba_2Ti_9O_{20}$ materials profoundly. For the materials possessing high sintered density and of pure Hollandite-like structure, the uniformity of granular structure is the prime factor, altering the microwave dielectric properties of the samples. Utilizing the $BaTi_4O_9 + BaTi_5O_{11}$ mixtures to replace for the $2BaTiO_3 + 7TiO_2$ ones pronouncedly improved the uniformity of the microstructure and thus markedly increased the $Q \times f$-value for the $Ba_2Ti_9O_{20}$ materials. The possible explanation for such a phenomenon is that the B-series mixture forms the $Ba_2Ti_9O_{20}$ Hollandite-like phase in a simpler way and results in more uniform microstructure then the A-series mixture. The microwave properties of B-series materials are superior to those of A-series ones, achieving $K = 38.2$ and $Q \times f\text{-value} = 36{,}000$ GHz for the samples, which were pre-reacted at 1000 °C for 6 h and were sintered at 1410 °C for 4 h by reaction-sintering processes.

Keywords: Reaction sintering; Microwave dielectric properties; $Ba_2Ti_9O_{20}$ materials

1. Introduction

$Ba_2Ti_9O_{20}$ phase was first reported by Jonker and Kwestroo[1] in $BaO–TiO_2–SnO_2$ ternary system and was observed to possess marvelous microwave dielectric properties, including high dielectric constant and large quality factor, by O'Bryan et al.[2] Since then the modification on microwave properties of $Ba_2Ti_9O_{20}$ materials via the addition of dopants[3–7] has been widely investigated. However, the reported results are quite controversial, which is mainly due to the difficulty in forming single phase Hollandite-like structured $Ba_2Ti_9O_{20}$ material. Secondary phases, such as $BaTi_4O_9$ or $BaTi_5O_{11}$, are observed to form preferentially in the calcinations of $BaCO_3–TiO_2$ mixture[8–10] that hinder the formation of Hollandite-like phase for the $Ba_2Ti_9O_{20}$ phase. Therefore, the occurrence of reactions among the phases during the sintering process is inevitable, which degrades the reliability of the processing for preparing the $Ba_2Ti_9O_{20}$ materials.

In this paper, reaction-sintering process, which densifies the powder mixture directly without experiencing the calcination process, was employed for preparing the $Ba_2Ti_9O_{20}$ materials. How the processing parameters in such a non-conventional densification process influences the characteristics of the $Ba_2Ti_9O_{20}$ materials will be described and the possible mechanism will be discussed.

2. Experimental procedure

The $Ba_2Ti_9O_{20}$ materials were synthesized via the conventional mixed oxide process, using nano-sized $BaTiO_3$ (~50 nm) and anatase TiO_2 (~50 nm) powders as starting materials. Two types of mixture were used for preparing the $Ba_2Ti_9O_{20}$ samples. In A-series materials, $2BaTiO_3$ and $7TiO_2$ powders were mixed thoroughly using three-dimensional milling technique (3DM). In the B-series materials, the $BaTi_4O_9$ and $BaTi_5O_{11}$ mixtures were used as starting materials, which were prepared by calcining the $BaTiO_3 + 3TiO_2$ and $BaTiO_3 + 4TiO_2$ mixture at 1000 °C/4 h, respectively. The $2BaTiO_3 + 7TiO_2$ (A-series) or $BaTi_4O_9 + BaTi_5O_{11}$ (B-series) powder mixtures were pelletized and then reaction-sintered directly. In this process, the temperature was increased slowly (3 °C/min) to 1000 °C, held

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at that temperature for 0–6 h, and was then increased again to 1300–1410 °C (3 °C/min), soaked for 4 h, followed by slow cooling (2 °C/min). The process, which holds the samples at 1000 °C for 0–6 h, is designated as "pre-reaction process". The microstructure of the sintered samples was examined using scanning electron microscopy (Joel 6700F). The crystal structure of the calcined powders and sintered samples was examined using X-ray diffractometry (Rigaku D/max-II). The density of the sintered materials was measured using Archimedes method. The microwave dielectric constant (*K*) and quality factor ($Q \times f$) of the $Ba_2Ti_9O_{20}$ samples were measured using a cavity method at 3–4 GHz.[11]

3. Results and discussion

Fig. 1 shows the variation of sintered density (*D*), microwave dielectric constant (*K*) and quality factor ($Q \times f$) for the A-series materials, indicating that the characteristics of $Ba_2Ti_9O_{20}$ materials vary markedly with the processing parameters. For the samples pre-reacted at 1000 °C for very short period ($t_r = 0$ h, A_0-samples), the sintered density and the microwave dielectric properties (*K* and $Q \times f$) of the samples increased monotonically with sintering temperature, reaching a density higher than 96% T.D. (theoretical density) with $K = 38.2$ and $Q \times f = 29{,}000$ for 1350 °C/4 h sintered samples (open squares, Fig. 1(a)–(c)). But over-firing these $Ba_2Ti_9O_{20}$ materials at 1400 °C/4 h lowered the sintered density (*D*) and dielectric constant (*K*) and markedly degraded the microwave quality factor ($Q \times f$) for the samples, from $(Q \times f)_A{}^{1350} = 29{,}000$ GHz to $(Q \times f)_A{}^{1400} = 18{,}000$ GHz. In contrast, the samples pre-reacted at 1000 °C for very sufficient long period ($t_r = 6$ h, A_6-samples) can withstand higher sintering temperature (1400 °C/4 h) without inducing the degradation on their characteristics (open circles, Fig. 1(a)–(c)). The microwave properties achieved are dielectric constant $K = 38$ and qualify factor $(Q \times f)_B{}^{1400} = 29{,}200$ GHz for the samples pre-reacted at 1000 °C/6 h and sintered at 1400 °C/4 h. Restated, the pre-reaction process at 1000 °C significantly influences the stability of the characteristics of the A-series materials.

To understand the cause resulting in the pronounced variation of the materials properties with the pre-reaction time interval, the microstructure and crystal structure of the samples were examined. Fig. 2(a) shows that although the pure Hollandite-like phase was obtained for the samples experiencing no pre-reaction process ($t_r = 0$ h), the diffraction peaks of these XRD patterns are very broad. It is suspected that there even appears some residual $BaTi_4O_9$ phase and possibly some residual TiO_2 phase, which is too few to be detected. In contrast, for those pre-reacted at 1000 °C for sufficient long period ($t_r = 6$ h), pure Hollandite-like phase with very sharp diffraction peaks was obtained, regardless of the sintering temperature experienced by the samples (Fig. 2(b)). Such a result implies that sufficient long pre-reaction process is required to complete the phase transformation process for the formation of Hollandite-like phase.

SEM micrographs in Fig. 3(a) reveals that, when sintered at 1400 °C/4 h, the microstructure is extremely complicated for the samples, which experienced no pre-reacting process ($t_s = 0$ h, A_0-samples). There exists abnormally grown extra-large rod-shaped grains about hundreds of micron in size, in addition to the small rod-shaped grains (30 μm × 5 μm) and equi-axed grains (2 μm). The occurrence of abnormally large grains is probably due to the chemical inhomogeneity induced in the heat treatment process, which will be discussed shortly. The number density and

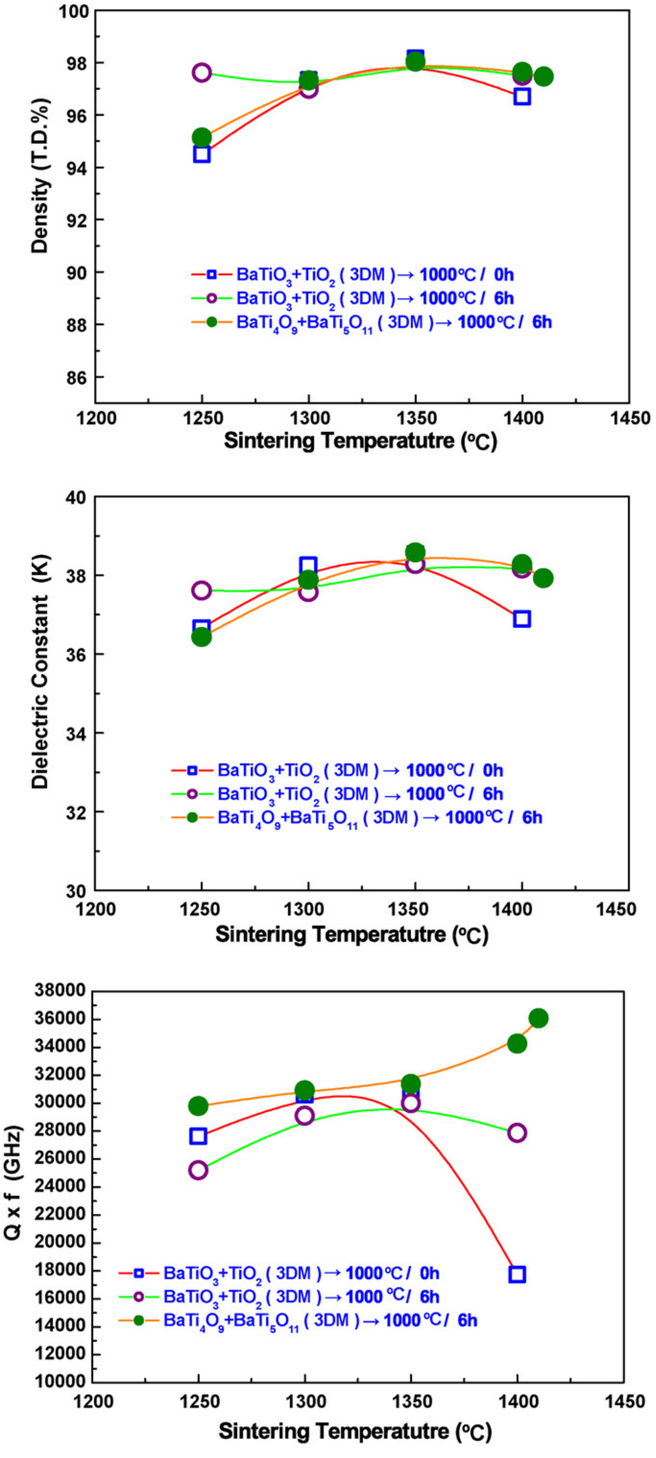
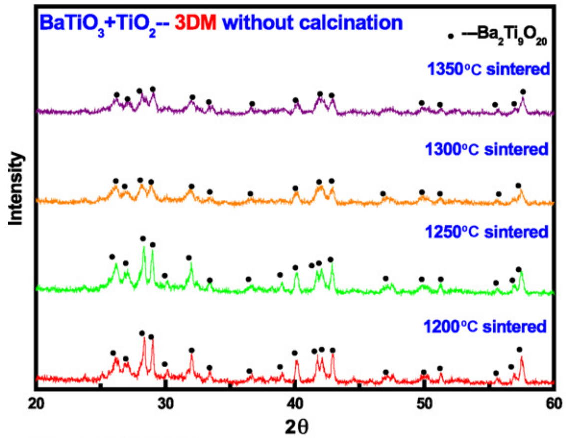


Fig. 1. The effect of powder mixture type on the (a) sintered density, *D*, (b) microwave dielectric constant, *K*, and (c) microwave dielectric quality factor, *Q*, of $Ba_2Ti_9O_{20}$, materials sintered at 1250–1410 °C/4 h by reaction-sintering process. The A-series, samples were made of $2BaTiO_3 + 7TiO_2$ mixture and the B-series samples were made, of $BaTi_4O_9 + BaTi_5O_{11}$ mixture, with the pre-reaction conditions shown in the figure.

(a) A (1000°C/0 h)



(b) A (1000°C/6 h)

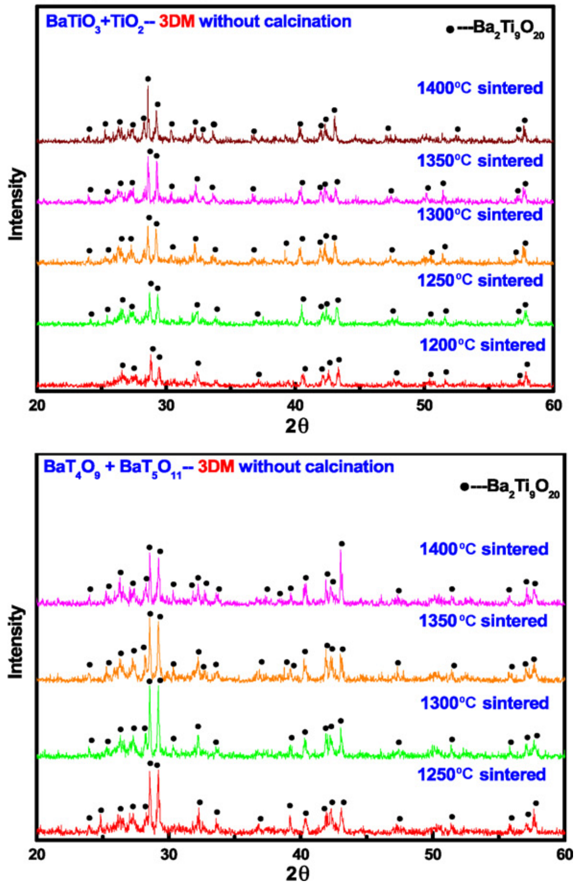


Fig. 2. X-ray diffraction patterns of the $Ba_2Ti_9O_{20}$ materials sintered by reaction-sintering, process at 1250–1400 °C/4 h, where (a) and (b) are XRD of the A-series pellets, pre-reacted at 1000 °C for 0 or 6 h, respectively, and (c) are those of B-series pellets, pre-reacted at 1000 °C for 6 h.

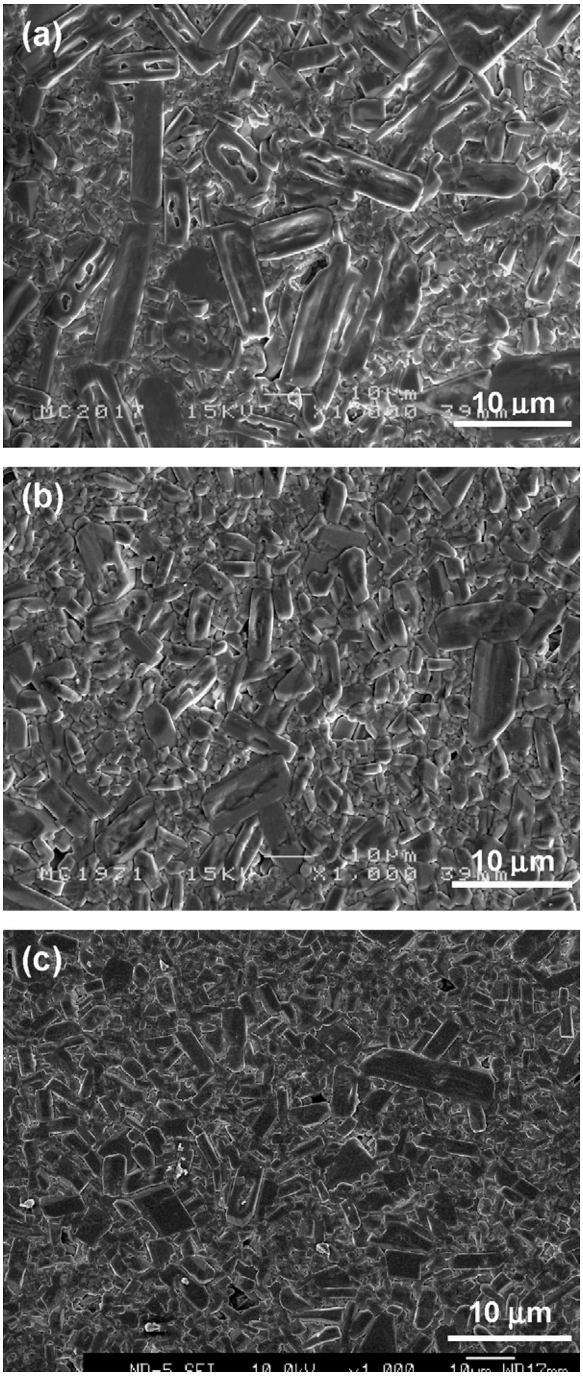


Fig. 3. SEM micrographs of the $Ba_2Ti_9O_{20}$ materials sintered at 1400 °C for 4 h by, reaction-sintering process; where the pellets made of (a) A-series, $2BaTiO_3 + 7TiO_2$ mixture were pre-reacted at 1000 °C for 0 h, (b) A-series, $2BaTiO_3 + 7TiO_2$ mixture were pre-reacted at 1000 °C for 6 h and (c) B-series, $2BaTiO_3 + 7TiO_2$ mixture were pre-reacted at 1000 °C for 6 h.

size of the abnormally grown grains decrease as the pre-reacting period increases. Fig. 3(b) shows that only the small rod-shaped grains about 10 µm × 5 µm in size co-exist with the equi-axed grains (~2 µm in size) for the samples experienced 1000 °C/6 h pre-reacting process. There is no extra-large rod-shaped grains observable. The uniformity of granular structure for A_6 samples is markedly better than that for the other A_0 samples. Both rod-shaped and equi-axed grains grow larger with sintering temperature. The geometry of the grains, which are roundish when sintered at 1350 °C/4 h, are of faceted geometry when sintered at 1400 °C/4 h, indicating that the higher the sintering temperature is, the better the granular structure developed.

The complex microstructure for these materials is apparently due to the complicated reactions of the $2BaTiO_3 + 7TiO_2$ mixture. Previous studies[9] indicated that in the heat treatment of $2BaTiO_3 + 7TiO_2$ mixture, the perovskite $BaTiO_3$

first reacted with anatase TiO_2 to form $BaTi_4O_9$ phase at 950 °C. The $BaTi_4O_9$ phase partially reacted with TiO_2 to form $BaTi_5O_{11}$ phase at 1050 °C, instead of directly transformed into $Ba_2Ti_9O_{20}$ Hollandite-like phase. It takes 1100 °C to complete the phase transformation process for the formation of $Ba_2Ti_9O_{20}$ Hollandite-like phase. The proposed reaction sequence of the A-series materials during reaction sintering process is depicted in Fig. 4. The reaction of $BaTiO_3$ and TiO_2 mixture preferentially formed the $BaTi_4O_9$ phase, which reacts with the residual TiO_2 phase to form $BaTi_5O_{11}$ phase (Fig. 4(a)). The $BaTi_5O_{11}$ phase reacted instantaneously with the $BaTi_4O_9$ phase to form the $Ba_2Ti_9O_{20}$ Hollandite-like phase (Fig. 4(b)). Both intermediate phases $BaTi_4O_9$ and $BaTi_5O_{11}$ preferentially formed grow anisotropically, resulting in rod-shaped grains with high-aspect-ratio. The "bridging effect" of the elongated grains usually hinders the densification of the materials. Moreover, the reaction of $BaTi_4O_9$ (or $BaTi_5O_{11}$) with the TiO_2 phase to form the $Ba_2Ti_9O_{20}$ phase usually leads to the shrinkage in specific volume,[10] which induces the formation of the voids and further retards the densification process. Both factors are the probable causes lowering the sintered density for A-series materials. Moreover, the complicated reaction process occurred in A-series materials usually induces the non-uniformity in chemical composition and possibly resulted in residual TiO_2 and $BaTi_4O_9$ aggregates. When the samples were heated at 1400 °C directly, the residual TiO_2 phase will react with the $Ba_2Ti_9O_{11}$ phase peritectically, which results in the dissociation of $Ba_2Ti_9O_{11}$ phase and induces the degradation of the microwave properties of the materials.[12,13]

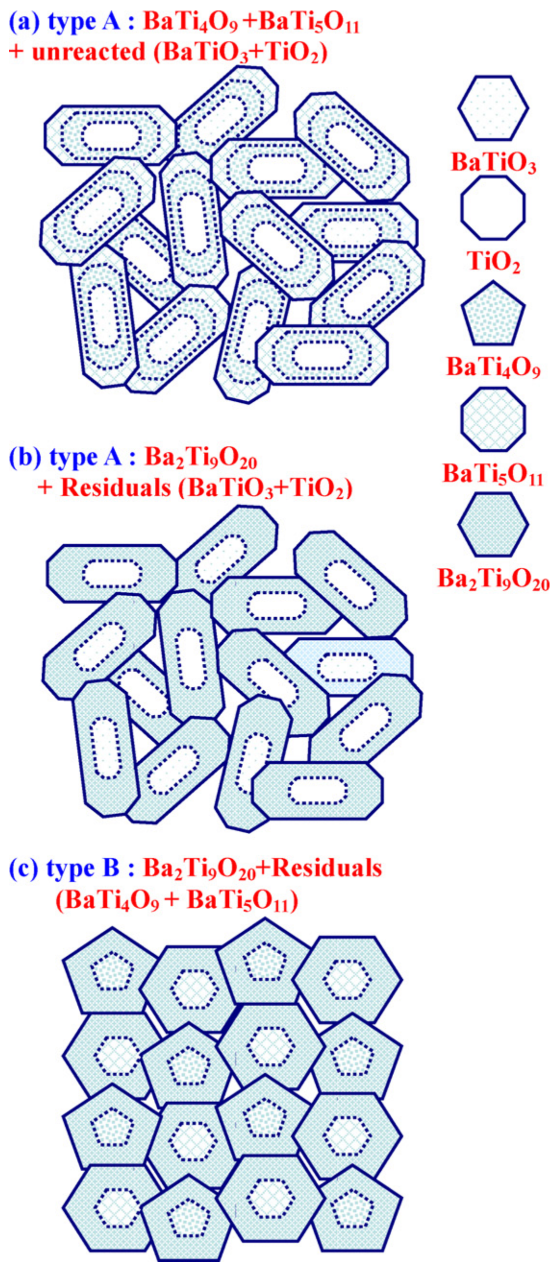


Fig. 4. Schematics showing the reaction sequence of the constituents for the materials, prepared from (a) series-A mixture, $2BaTiO_3$ and $7TiO_2$, at intermediate stage of, sintering, (b) series-A mixture, $2BaTiO_3$ and $7TiO_2$, at final stage of sintering, and (c) series-B mixture, $BaTi_4O_9 + BaTi_5O_{11}$, at final stage of sintering.

The above-described results indicate clearly that uniformity of the granular structure are the most important factor altering the microwave dielectric properties of the $Ba_2Ti_9O_{20}$ materials, besides the high purity of the Hollandite-like phase and high sintered density for the samples. It is apparent that for the purpose of improving the homogeneity of the granular structure for the $Ba_2Ti_9O_{20}$ materials, it is necessary to simplifying the reaction among the constituents in the mixture during sintering process. For this purpose, $BaTi_4O_9 + BaTi_5O_{11}$ mixture (B-series) was used to replace for the $2BaTiO_3 + 2TiO_2$ mixture (A-series) as starting materials for preparing the $Ba_2Ti_9O_{20}$ materials. Such a material is designated as B-series materials.

Fig. 1(a) and (b) (solid symbols) shows that the sintered density (D) and microwave dielectric constant (K) of B_6-samples, which were also pre-reacted for 6 h at 1000 °C/6 h, also increase monotonously with sintering temperature (solid diamonds, Fig. 1(a) and (b)) and are comparable with those of A_6-samples. Although the utilization of type B mixture does not pronouncedly alter the sintered density (D) and dielectric constant (K) characteristics of the B-series materials, it does markedly improve the microwave dielectric quality factor ($Q \times f$) of the materials (solid diamonds, Fig. 1(c)). Moreover, the B-series materials can be sintered to higher temperature without inducing the abnormal grain growth phenomenon such that they can reach higher quality factor, viz. $(Q \times f)_B{}^{1400} = 34{,}000$ GHz for B-series materials sintered at 1400 °C/4 h and $(Q \times f)_B{}^{1410} = 36{,}000$ GHz for those sintered at 1410 °C/4 h, which is markedly higher than the $Q \times f$-value attainable for A-series materials. The factor resulting in better microwave dielectric properties for B-series materials is apparently owing to the overwhelmingly better granular structure of these materials, as compared with the microstructure for the A-series materials, which will be discussed shortly.

XRD patterns in Fig. 2(c) illustrates that, for the B-series materials sintered at 1250–1400 °C for 4 h, the diffraction peaks are all very sharp, indicating that all of them are of pure Hollandite-like structure and containing no secondary phase. Such a result indicates that the phase transformation kinetics for the materials is pronouncedly improved due to the utilization of $BaTi_4O_9 + BaTi_5O_{11}$ mixture (B-series) as starting materials. SEM micrographs shown in Fig. 3(c) reveal that the microstructure of the B_6-materials is much more uniform than that for the A-series materials. For the samples pre-reacted at 1000 °C/6 h and sintered at 1400 °C/4 h, the grains are of short rod-shaped with small aspect ratio and are about 8 μm × 2 μm. All the B-series samples pre-reacted for sufficient long period contain grains of uniform size. No abnormal grain growth phenomenon is observable for these samples.

The above-described results imply that the microwave dielectric constant (K) is more closely related with density of the samples and is insensitive to the detailed microstructure of the samples. In contrast, the quality factor ($Q \times f$) of the samples is very sensitive to the microstructure of the materials. Samples with the microstructure pre-dominated by large grains of small-aspect-ratio usually exhibit superior $Q \times f$-value to the ones with microstructure mainly consisting of small-grains of large-aspect-ratio. The B-series materials own better granular structure and, therefore, possess better microwave properties then A-series samples, which, in turn, is resulted from the simplicity in phase transformation process involved for the B-series materials, since the formation of $Ba_2Ti_9O_{20}$ Hollandite-like phase from $BaTi_4O_9 + BaTi_5O_{11}$ mixture is pronouncedly simpler than that from the $2BaTiO_3 + TiO_2$ mixture.

Previous studies[9] indicated that there is no marked reaction occurred the series-B mixture ($BaTi_4O_9 + BaTi_5O_{11}$) calcined at a temperature lower than 1000 °C, but the phase transformation process is completed at 1025 °C, forming Hollandite-like phase. The chemical composition for B-series materials is thus much more uniform then the A-series materials and there is no peritectic reaction occurred between the $BaTi_4O_9$ (or $BaTi_5O_{11}$) and $Ba_2Ti_9O_{20}$ phases. Therefore, these materials can withstand higher sintering temperature without inducing the abnormal grain growth phenomenon. The reaction sequence in the heat treatment of B-series materials is depicted in Fig. 4(c). The reaction of $BaTi_4O_9$ and $BaTi_5O_{11}$ phases powders in B-series materials directly formed $Ba_2Ti_9O_{20}$ Hollandite-like phase. There is no intermediate phase formed. Moreover, the reaction of $BaTi_4O_9 + BaTi_5O_{11}$ to form $Ba_2Ti_9O_{20}$ Hollandite-like phase leads to the increase in specific volume.[13] No void will be resulted due to such a reaction. Therefore, reaction sintering of these materials is beneficial for achieving high sintered density.

4. Conclusion

Effect of starting materials and densification routes on the characteristics of $Ba_2Ti_9O_{20}$ materials were systematically investigated. Both the materials prepared from the $2BaTiO_3 + 7TiO_2$ (A-series) and $BaTi_4O_9 + BaTi_5O_{11}$ (B-series) mixtures can be densified to a high density (≧96%), possessing high microwave dielectric constant (K = 35–38), regardless of the pre-reaction process the materials experienced. The K-value of the $Ba_2Ti_9O_{20}$ materials is related closely to the density of the samples and is insensitive to the granular structure of the samples, whereas the $Q \times f$-value of the materials varies markedly with the microstructure, which, in turn, is determined by the processing details. The B-series materials, which were prepared from B-series mixture and pre-reacted at 1000 °C for 6 h or longer, show most uniform microstructure and exhibit the highest $Q \times f$-value ($Q \times f$ = 36,000 GHz). It is ascribed to the simplicity in reaction routes for the formation of the $Ba_2Ti_9O_{20}$ Hollandite-like phase from $BaTi_4O_9 + BaTi_5O_{11}$ mixture, which results in better granular structure for the materials.

Acknowledgments

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