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Journal of the European Ceramic Society 26 (2006) 2081–2085

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Improvement on the characteristic of $Ba_2Ti_9O_{20}$ microwave dielectric materials prepared by modified co-precipitation method

Li-Wen Chu[a], Ging-Ho Hsiue[a,*], I-Nan Lin[b,c]

[a] Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, Taiwan 300, ROC
[b] Materials Science Center, National Tsing-Hua University, Hsinchu, Taiwan 300, ROC
[c] Department of Physics, Tamkang University, Tamsui, Taiwan 251, ROC

Abstract

Modified co-precipitation process (MCP), which combines the automatic pH value control system and supersonic spraying of co-precipitants, was used to synthesize nano-sized $Ba_2Ti_9O_{20}$ precursors (48.8 nm). Kinetics for crystallization process is markedly enhanced when the O_2 atmosphere was used to replace for air atmosphere in the calcinations and sintering processes. High-density $Ba_2Ti_9O_{20}$ materials (>94% T.D.), possessing good microwave properties ($K = 38.7$ and $Q \times f = 30{,}502$ GHz), can be obtained by sintering the sample at 1200 °C for 4 h in O_2 atmosphere, which is lower than the sintering temperature needed when the materials were processed in air or N_2 atmosphere (i.e., 1250 °C for 4 h).

Keywords: Powder-chemical preparation; Calcination; $Ba_2Ti_9O_{20}$; Dielectric properties

1. Introduction

$Ba_2Ti_9O_{20}$ phase was first reported by Jonker and Kwestroo in $BaO–TiO_2–SnO_2$ ternary system[1] 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] was widely investigated. However, the reported results are quite controversial, which is mainly due to the difficultly in forming single-phase Hollandite-like structured $Ba_2Ti_9O_{20}$ materials. Secondary phases, such as $BaTi_4O_9$ or $BaTi_5O_{11}$, were observed to form preferentially in the calcinations of $BaO–TiO_2$ mixture[8] that hinder the formation of Hollandite-like structured $Ba_2Ti_9O_{20}$ phase. Co-precipitation process, which mixed the cations in atomic scale, can produce multiple-metallic-oxides with better homogeneity and higher activity.[9–13]

However, the conventional co-precipitation process always results in highly agglomerated powders, which hindered the reactivity of the powders. In this paper, the supersonic spray instrument was used to reduce the reaction volume during precipitation process. Moreover, the pH value of the reactor was controlled in a small range (±0.01 pH) by an automatic feedback system. It is expected that careful control of co-precipitation process will ensure the atomic scaled mixing of the cations in proper proportion, i.e., Ba:Ti = 2:9. Which, in turn, will circumvent the formation of undesired intermediate phases and facilitate the formation of Hollandite-like structured $BaTi_9O_{20}$ phase. The effect of processing parameters on the characteristics of $Ba_2Ti_9O_{20}$ and the related microwave dielectric properties can thus be investigated.

2. Experimental

The main procedure in modified co-precipitation process (MCP) is the preparation of cations containing aqueous solution and precipitation agents containing aqueous solution. Schematics of the block diagram of the modified co-precipitation process (MCP) for preparing the $Ba_2Ti_9O_{20}$ materials has shown previously.[14] The $BaCl_2{\cdot}2H_2O_2$ and $TiCl_4$ were first dissolved in water with the cationic ratio of Ba^{2+}:Ti^{4+} = 2:9 to form cationic solutions, whereas the $(NH_4)_2CO_3$: NH_4OH = 2:9 with pH 12.5 was thoroughly mixed to form precipitant solution. The cationic solution was then supersonically sprayed into the reactor containing precipitant. While the solution was thoroughly agitated to ensure the homogeneity of the reaction, proper amount of the alkaline precipitation agent solution was delivered to the reactor by using an automatic pH value control system to maintain the pH value of the reactor at 9.5. Thus, formed co-precipitants

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[*] Corresponding author.
E-mail address: ghhsiue@mx.nthu.edu.tw (G.-H. Hsiue).

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doi:10.1016/j.jeurceramsoc.2005.09.100

were then collected by centrifugal process, washed, dried and then calcined at 900–1100 °C for 4 h, followed by pulverization, pelletization and the sintering at 1150–1300 °C for 4 h, in air, N_2- or O_2-atmosphere.

The morphology of the as-prepared $Ba_2Ti_9O_{20}$ powders and microstructure of the sintered $Ba_2Ti_9O_{20}$ samples were examined using scanning electron microscopy (Jeol 6700F). The crystal structure of the calcined powders and sintered sample were 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 $Q \times f$ value of the $Ba_2Ti_9O_{20}$ samples were measured using a cavity method at 7–8 GHz.

3. Results and discussion

Conventional mixed oxide route for synthesizing pure Hollandite-like structured $Ba_2Ti_9O_{20}$ via calcination of $BaCO_3$ and TiO_2 mixture with micron particulate size requires high reaction temperature (1235 °C) and long soaking time (192 h) to form Hollandite-like phase.[4] It is practically not possible to completely eliminate the preferentially occurred secondary phases. Using nano-sized $BaTiO_3$ powders (∼50 nm) as starting materials markedly facilitates the phase transformation kinetics,[14] but the as-prepared powders are still predominated by $BaTi_4O_9$ phase when calcined at 950–1000 °C for 6 h (spectra I & II, Fig. 1(a)). It required around 1050–1100 °C for 6 h heat treatment process to convert the nano-$BaTiO_3$ and TiO_2 mixtures into Hollandite-like structure (spectra III & IV, Fig. 1(a)). However, all of the samples made from these powders can be transformed completely into Hollandite-like structure, and, at the same time, be effectively densified by sintering the materials at 1300 °C for 4 h, regardless the phase constituents of the sintering powders (not shown).

It is quite interesting to observe that the materials prepared by modified co-precipitation process transform through a different route from those prepared by calcining the mixture of nano-sized $BaTiO_3$ and TiO_2 powders. Fig. 1(b) shows that the MCP-derived powders are predominated with the $BaTi_5O_{11}$ intermediate phase, when they were calcined at 900 °C. Hollandite-like $Ba_2Ti_9O_{20}$ phase already start to form for the powders calcined at 1000 °C for 4 h and the materials can be fully converted into Hollandite-like phase, when they were calcined at 1100 °C for 4 h in air. The as-calcined powders are about 100 nm in size, irregular shaped and moderately agglomerated.

Even though the samples prepared from 1000 °C for 4 h calcined powders are only partially converted into $Ba_2Ti_9O_{20}$ phase and still contain large proportion of $BaTi_5O_{11}$ phase, they can be converted into Hollandite-like phase by sintering at 1150 °C for 4 h and higher temperature, as shown in Fig. 2(a). Moreover, thus obtained powders are of high activity, such that the samples made of these powders can be densified to a very high-density (>94% T.D.) by sintering them at a temperature higher than 1250 °C for 4 h, as shown in Fig. 3(a) (open squares). All the high-density samples are of pure Hollandite-like phase, containing rod-shaped grains, about 7 × 3 μm in size, which is shown as typical SEM micrograph in Fig. 2(b). The grains are rod-shaped, but the rods are roundish instead of faceted. The significance of such geometry on the dielectric properties of the materials will be discussed shortly. It should be noted that the formation of $BaTi_5O_{11}$-phased powders is possible only when they were prepared via MCP process, which is apparently due to the atomically scale mixing of the cations. The $BaTi_5O_{11}$-phased powders can be transformed into Hollandite-like structured materials more easily, as compared to the $BaTi_4O_9$ phase prepared from the calcination of the $BaTiO_3$–TiO_2 mixtures.

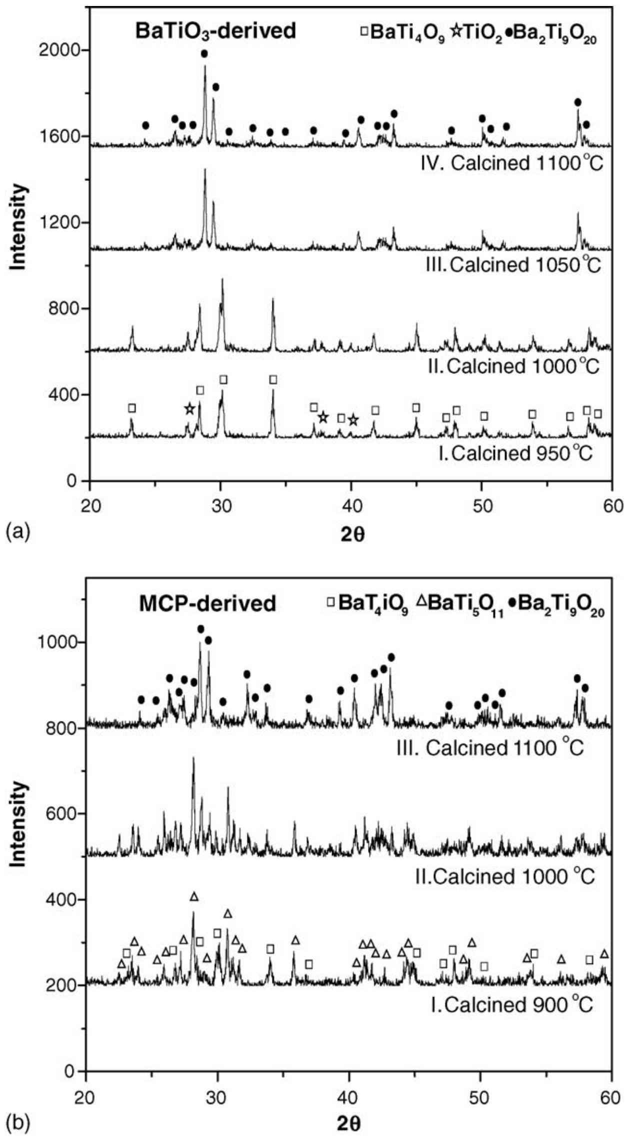

Fig. 1. The X-ray diffraction of the powders prepared from: (a) the nano-sized $BaTiO_3$–TiO_2 mixture, which were calcined at 950–1100 °C for 6 h in air; and (b) the modified co-precipitation (MCP) process, which were calcined at 900–1100 °C for 4 h.

Fig. 3(b) (open squares) indicates that the dielectric constant (K) of the materials increases with the sintered density of the materials and is higher than $K = 38$ for the samples sintered at a temperature higher than 1250 °C for 4 h, which have a density higher than 94% T.D. Interestingly, the quality factor of the samples increases with the materials' density first, reaching largest value ($(Q \times f)_{max} = 31{,}212$ GHz) for 1250 °C-sintered samples,

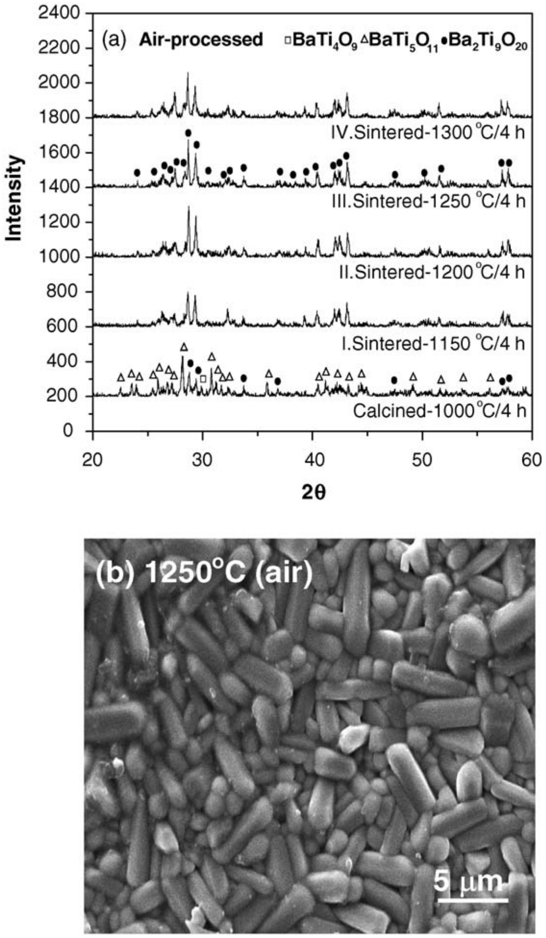

Fig. 2. (a) The X-ray diffraction of the powders calcined at 1000 °C for 4 h or the pellets sintered at 1150–1300 °C for 4 h and (b) the SEM micrographs of the samples sinter at (a) 1250 °C for 4 h. The powders were synthesized by the modified co-precipitation (MCP) technique and were processed in air-atmosphere.

and reverts to lower value when sintered at higher temperature (Fig. 3(c), open squares). Restated, over-firing degrades the quality factor ($Q \times f$) of the samples, although the materials are still of high-density and possess large K-value.

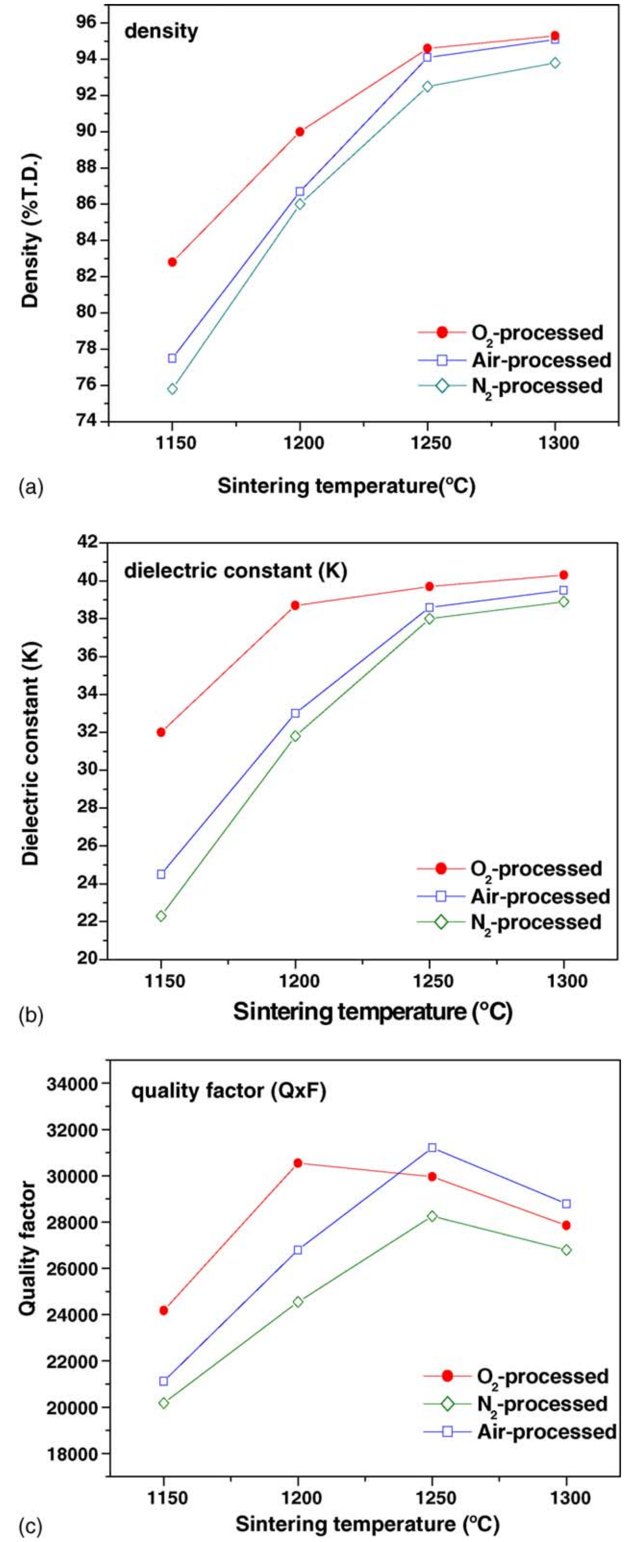

Fig. 3. The variation of: (a) sintered density; (b) dielectric constant, K; and (c) quality factor, $Q \times f$, for the $Ba_2Ti_9O_{20}$ samples with sintering temperature (the samples were sintered in either air-, O_2- or N_2-atmosphere).

For the purpose of improving the characteristics of the $Ba_2Ti_9O_{20}$ materials, the effect of processing atmosphere on the calcinations and sintering behaviour of the materials were then investigated, which are shown in Fig. 4(a) and (b). The as-calcined powders are also of $BaTi_5O_{11}$ phase, rather than $BaTi_4O_9$ phase one, regardless of calcinations atmosphere (O_2 or N_2), which is also ascribed to the atomic scale mixing of the MCP process. It is of great interest to observe that, when calcined at 1000 °C for 4 h, the XRD diffraction peaks of O_2-processed powders are pronouncedly higher than those of air- or N_2-processed ones. The particle size of the O_2-calcined powders is $d_{O_2} = 225$ nm, which is slightly larger than that of the air- or N_2-calcined ones ($d_{air} = 207$ nm and $d_{N_2} = 199$ nm). These results imply clearly that phase transformation kinetics from amorphous to $BaTi_5O_{11}$ phase is facilitated in O_2-environment, as compared with that in air- or N_2-environment. However, when the samples prepared from the O_2-calcined powders were sintered in O_2-atmosphere, it requires 1200 °C for 4 h to completely transform the $BaTi_5O_{11}$ phase into Hollandite-like structure (Fig. 4(a)). In contrast, when the samples prepared from N_2-calcined powders were sintered in N_2-atmosphere, they were already fully converted into Hollandite-like structure

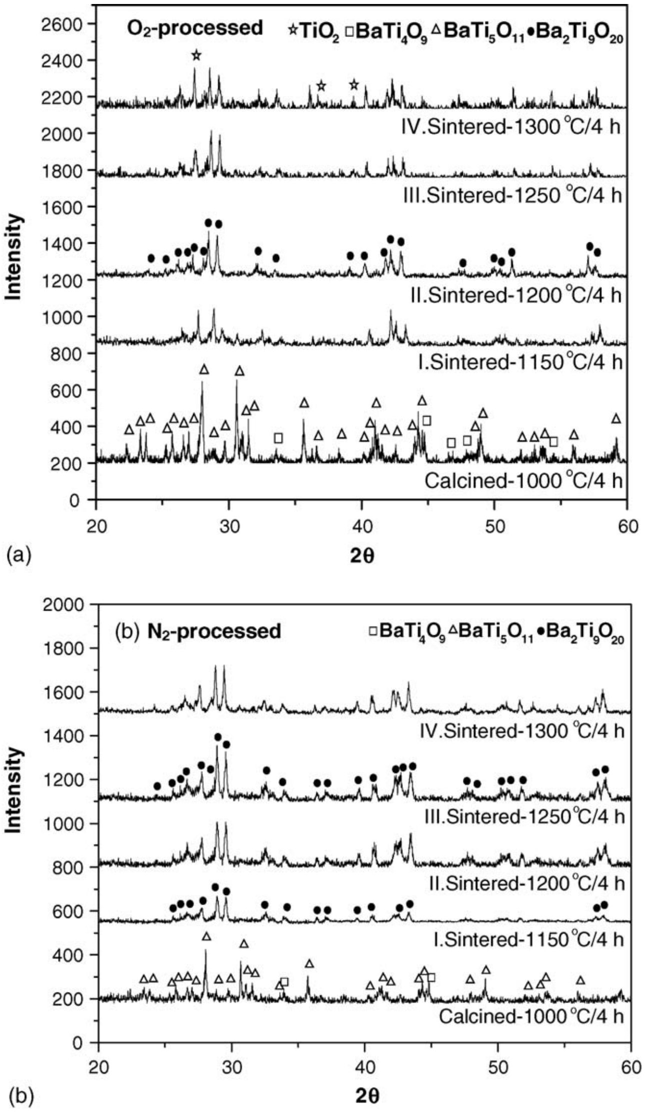

Fig. 4. The X-ray diffraction of the powders calcined at 1000 °C for 4 h or the pellets sintered at 1150–1300 °C for 4 h. The powders were synthesized by the modified co-precipitation (MCP) technique and were processed in: (a) O_2-atmosphere or (b) N_2-atmosphere.

when fired at 1150 °C for 4 h (Fig. 4(b)), which is similar with the behavior of the materials processed in air.

Presumably, it is the nature of chemical reaction, which alters the phase transformation kinetics for the MCP-derived powders due to the difference in processing atmosphere. The conversion of $BaTi_5O_{11}$ phase into $Ba_2Ti_9O_{20}$ phase involves the substraction of one TiO_2 formula from every two $BaTi_5O_{11}$ formula. That is,

$$2BaTi_5O_{11} \rightarrow Ba_2Ti_9O_{20} + TiO_2 \qquad (1)$$

The size of the O_2-calcined powders is about 10% larger than that of air- or N_2-calcined ones. Therefore, although the O_2-atmosphere facilitates the phase transformation from the amorphous to $BaTi_5O_{11}$ phase, the transformation process from $BaTi_5O_{11}$ phase to $Ba_2Ti_9O_{20}$ one is slightly retarded due to larger particulate size of the powders, as compared with those of air- or N_2-atmosphere.

Moreover, XRD patterns in Figs. 2(a) and 4(a) are similar to each other, indicating that 20% oxygen contained in air does not lead to significantly different phase transformation kinetics from the N_2-atmosphere, which contains only residue O_2 (<1%). In fact, in separated experiments (not shown), we observed that when the materials were calcined and sintered in a reduced atmosphere (N_2/1% H_2) at 1000 °C for 4 h, the amorphous phase can still be converted into $BaTi_5O_{11}$ phase but contain large proportion of unreacted phase. Thus, obtained $BaTi_5O_{11}$ phase-predominated powders can never be further transformed into $Ba_2Ti_9O_{20}$ one by sintering at high temperature, ∼1300 °C for 4 h, in the same reducing atmosphere. Restated, phase transformation process is markedly retarded in O_2-deficit environment.

Fig. 3(a) reveals that the density of the materials increases monotonously with the sintering temperature. The O_2-atmosphere densify the materials much more efficiently, whereas the N_2-atmosphere sinter the materials less efficiently, than the air-atmosphere. Restated, the O_2-sintered samples possess pronouncedly higher density, whereas the N_2-sintered possess slightly smaller density, than the air-processed ones for all sintering temperature (solid circles and open diamonds, Fig. 3(a)), which leads to lager dielectric constant value (K) for O_2-sintered samples and smaller K-value for N_2-sintered ones, as compared with those of the air-processed materials (solid circles and open diamonds, Fig. 3(b)). Generally, the quality factor ($Q \times f$) of the materials increases with sintering temperature, reaching a maximum value, and degrades again when over-fired (solid circles and open diamonds, Fig. 3(c)). The samples sintered in O_2-atmosphere reach maximum quality factor when sintered at 1200 °C for 4 h, that is, $(Q \times f)_{\max,O_2} = 30{,}520$ GHz, whereas those sintered in air- or N_2-atmosphere reach $(Q \times f)_{\max}$-value when sintered at 1250 °C for 4 h, that is, $(Q \times f)_{\max,\mathrm{air}} = 31{,}212$ GHz and $(Q \times f)_{\max,N_2} = 28{,}255$ GHz, The $(Q \times f)_{\max,O_2}$-value for O_2-sintered materials is comparable with $(Q \times f)_{\max,\mathrm{air}}$-value for air-sintered ones and is pronouncedly larger than to those for N_2-sintered ones ($(Q \times f)_{\max,N_2}$). The phenomenon that the O_2-sintered materials possess superior microwave dielectric properties to the air- or N_2-sintered materials can partially be ascribed to the large density of the materials. However, better microstructure of the materials is one of the important factors resulting in better microwave properties for the materials, which will be discussed shortly. The temperature coefficient of the resonant frequency, measured at 20–80 °C, does not vary appreciably with samples, i.e., $\tau_f = 2$–3 ppm/°C, which is in accord with the literature reported values.

SEM micrographs for the high-density samples, which were sintered in O_2- and N_2-atmosphere, are shown in Fig. 5(a) and (b), respectively, indicating that the samples contain very little porosity. Fig. 5(a) reveals that the grains are of faceted-rod geometry, 1.5–2 μm in size, when sintered at 1200 °C for 4 h in O_2-atmosphere. The inset in Fig. 5(a) indicates that the grains grow abnormally when the materials were sintered at too high temperature (1250 °C for 4 h), which, in accompanying with the appearance of noisy background signal in the X-ray diffraction patterns (cf. Fig. 4(a)), infers that the formation of secondary phase is due to the dissociation of the Hollandite-like phase

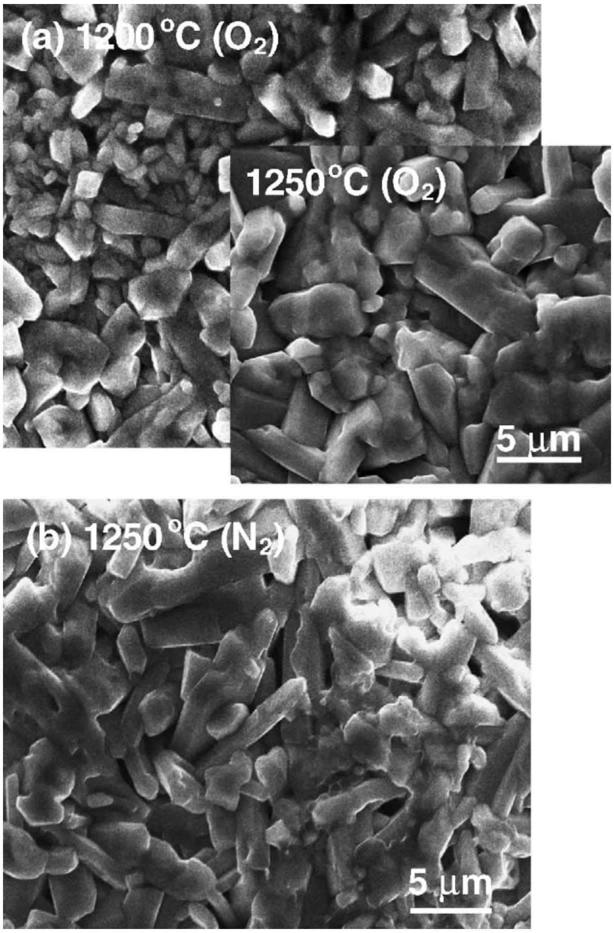

Fig. 5. The SEM micrographs of the samples sinter at: (a) 1200 °C for 4 h or 1250 °C for 4 h (inset) in O_2-atmosphere; and (b) 1250 °C for 4 h in N_2-atmosphere. The powders were synthesized by the modified co-precipitation (MCP) technique and were processed in the corresponding atmosphere.

when the samples were over-fired. The presence of the secondary phase is presumed to be the main cause of the degradation of the quality factor for the over-fired materials.

While the chemical composition of these samples is the same, as the EDAX patterns of these samples are similar with one another, it is interesting to notice the marked difference in microstructure between the air-sintered (1250 °C for 4 h, Fig. 2(b)) and O_2-sintered (1200 °C for 4 h, Fig. 5(a)) samples. The air-sintered materials contain roundish-rod grains, whereas the O_2-sintered ones contain faceted-rod grains. The roundish-rod geometry of the grains for air-sintered samples implies that they are still not fully-grown. In contrast, the faceted-rod geometry of the grains for O_2-sintered materials infers that they are fully developed. In separated experiments, we observed that the Raman and FTIR spectra of the O_2-sintered samples are much sharper than those of the air-sintered ones (not shown), which indicates that the lattice vibration of the O_2-sintered samples is more coherent, as compared with that of the air-sintered ones. It is known that sharper lattice vibration modes for the materials usually lead to higher ($Q \times f$)-value.[15,16] Meanwhile, the inferior lattice vibration characteristics for the air-sintered samples can be ascribed to the incompletely developed grains for the materials, which is implied by the roundish-rod geometry of the grains in these materials.

4. Conclusion

The modified co-precipitation process was observed to be capable of synthesizing single-phase $Ba_2Ti_9O_{20}$ materials free of secondary phases. The prime factor facilitating the formation of Hollandite-like phases is presumably the atomic scale mixing of cationic species. Dielectric constant and $Q \times f$ value increase with the density of the samples. The optimized sintering temperature for the $Ba_2Ti_9O_{20}$ material is significantly lower than the temperature required in mixed oxide process. The sintering temperature needed to achieve the high-density (i.e., >94% T.D.) and microwave properties ($K = 38.7$ and $Q \times f = 30{,}502$ GHz) for the $Ba_2Ti_9O_{20}$ materials at 1200 °C for 4 h when processed in O_2-environment, which is lower than the sintering temperature when processed in air- or N_2-environment (1250 °C for 4 h).

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