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Ultra-fine $Ba_2Ti_9O_{20}$ microwave dielectric materials synthesized by chemical process

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Abstract

Co-precipitation process was observed to be able to synthesize the Hollandite $Ba_2Ti_9O_{20}$ phase without the necessity of doping the SnO_2 additives. The $BaTi_5O_{11}$ and $BaTi_4O_9$ phases, which still form preferentially during the calcinations of the co-precipitants, can be converted into Hollandite phase by heat treatment at 1250 °C and higher temperature. The reactivity of the powders can be further improved by using ultrasonic spraying process to improve the co-precipitation process. The heat treatment temperature necessary to fully transform the co-precipitants into Hollandite phase decreased from 1250 °C for conventional–coprecipitation-derived powders to 1150 °C for spraying–coprecipitation-derived ones. The sinterability of the powders and microwave dielectric properties of the sintered $Ba_2Ti_9O_{20}$ materials were also pronouncedly improved. High density $Ba_2Ti_9O_{20}$ ceramic materials possessing good microwave dielectric properties can be obtained by sintering the 1000 °C-calcined powders at 1300 °C (4 h) or higher temperature. The best properties obtained are $K = 39$ and $Q \times F = 21{,}450$, for a 1300 °C sintered samples.

Keywords: $Ba_2Ti_9O_{20}$ materials; Hollandite phase; Spraying–coprecipitation

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1. Introduction

$Ba_2Ti_9O_{20}$ phase was first reported by Jerker and Kwestroo in $BaO–TiO_2–SnO_2$ ternary system[1] and was observer to possess marvelous microwave dielectric properties, including high dielectric constant and large quality factor, by Plovide et al.[2] Since then the modification on microwave properties of $Ba_2Ti_9O_{20}$ materials via the addition of allio-valence or iso-valence dopants[3–6] was widely investigated. However, the reported results are quite controversial, which is mainly due to the difficult in forming single phase Hollandite 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[7] that hinder the formation of Hollandite structured $Ba_2Ti_9O_{20}$ phase.

In this paper, co-precipitation process was adopted for the preparation of nano-sized $BaO–TiO_2$ powder mixture.[8–10] It is expected that the atomic scaled mixing of the cations in proper proportion ($Ba/Ti = 2/9$) will facilitate the formation of Hollandite 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

For preparing the $Ba_2Ti_9O_{20}$ materials by co-precipitation process, $BaCl_2 \cdot 2H_2O$ and $TiCl_4$ with the cationic ratio of $Ba^{2+}:Ti^{4+} = 2:9$ were dissolved in water and then thoroughly mixed by agitation. Meanwhile the precipitation agent containing $(NH_4)_2CO_3$: $NH_4OH = 2:9$ with $PH = 9.5$ was prepared separately. Thus, prepared solutions containing either cationic species or precipitation agents were then mixed to induce the co-precipitation process. Thus formed co-precipitants were then collected by centrifugal process, washed, dried and then calcined at 800–1000 °C for 4 h, followed by pulverization, pelletization and sintering at 1200–1300 °C for 4 h in air.

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 average particle size of the powders was measured by dynamic laser scattering

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apparatuses (DLS, NICOMP™ 380ZLS, 1 nm resolution). 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, which were cylindrical posts with 8 mm in diameter and 3.2 mm height, were measured by a cavity method at 7–8 GHz using H.P. 8722ES network analyzer.

3. Results and discussion

The as-coprecipitated powders are very fine, about 30–50 nm, but are highly agglomerated. SEM micrograph shown in Fig. 1 a indicates that the size of agglomerates varies from a few tens to a few hundreds of nanometer. The average size of the agglomerates is measured by dynamic laser scattering (DLS) to be about 255 nm (Fig. 1b), which is consistent with SEM observation. The heat-treated powders contain mainly the $BaTi_4O_9$ phase and small proportion of $BaTi_5O_{11}$ phase, even when they were calcined at a temperature as high as 1000 °C for 4 h (XRD pattern I, Fig. 2). Such a phenomenon is similar with the crystallization process for the $BaCO_3$ and TiO_2 powder mixture prepared by mixed oxide method, in which, the $BaTi_5O_{11}$ phase formed preferentially when $BaCO_3$ reacted with TiO_2. This result implies that, in co-precipitation process, although the mixing of cations is much more homogeneous, the cations still form individual clusters, probably the $Ba(OH)_2$ and $Ti(OH)_4$ clusters, such that the interaction started at the boundaries between the clusters, forming metastable intermediate phase preferentially.

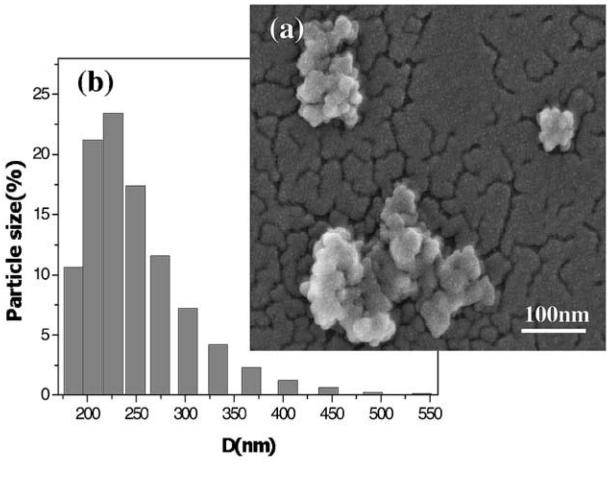

Fig. 1. (a) SEM micrograph and (b) dynamic laser scattering, DLS, measurement for the $Ba_2Ti_9O_{20}$ powder prepared by conventional co-precipitation process.

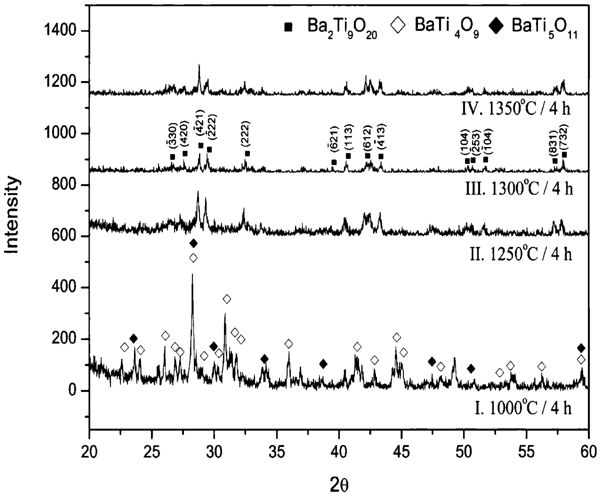

Fig. 2. X-ray diffraction patterns of heat treated $Ba_2Ti_9O_{20}$ materials prepared by conventional co-precipitation process: (I)1000 °C/4 h calcined powders and (II). 1250 °C/4 h, (III)1300 °C/4 h and (IV)1350/4 h sintered pellets, which were pressed from the 1000 °C/4 h-calcined $Ba_2Ti_9O_{20}$ powders.

The powders derived from co-precipitation process is much more reactive than those prepared by mixed oxide (MO) process. The co-precipitants of the $BaTi_5O_{11}$/$BaTi_4O_9$ mixture can be fully converted into Hollandite structure when sintered at a temperature higher than 1250 °C, which are shown as XRD patterns II–IV in Fig. 2. In contrast, the Hollandite phase can never be obtained by MO-process, no matter how high the processing temperature is. To confirm the phase purity of the thus derived materials, the XRD patterns of these samples were compared with those of commercial $Ba_2Ti_9O_{20}$ materials (Fujitsu, MBT-40) sintered at 1350 °C/4 h. As shown in Fig. 3 the XRD pattern for conventionally co-precipitated (ccp) materials (pattern II) is exact the same as that for commercial MBT-40

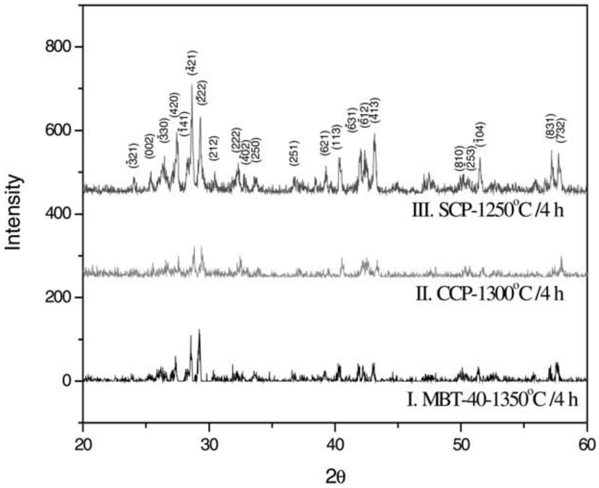

Fig. 3. Comparison on X-ray diffraction patterns of sintered $Ba_2Ti_9O_{20}$ sample; which were prepared from (I) commercial MBT-40 powders, (II) conventionally co-precipitated powders and (III) spraying co-precipitated powders.

materials (pattern I), revealing that the ccp-materials contain the same phase as the commercial MBT-40 materials.

Moreover, the co-precipitation derived powders possess much better sinterability, such that the samples pelletized from these powders can achieve a high density (≧96% T.D.) by sintering the samples at 1300 °C (4 h) or higher temperature (Fig. 4a). In contrast, for the materials prepared from mixed oxide powders, pure Hollandite-structured samples can be achieved only when 2 mol% SnO_2 additives were included in the composition to facilitate the formation of Hollandite phase and it needs at least 1350 °C (4 h) to reach the same high density. Inset in Fig. 4a shows that the high density samples contain equi-axed grains about 2 μm in size. Fig. 4b reveals that the microwave dielectric properties of the $Ba_2Ti_9O_{20}$ samples increase with the sintered density, possessing high dielectric constant, $K=39$, and large quality factor, $Q\times F=19{,}500$, for the samples possessing sintered density higher than 96% T.D.

Apparently, the tendency for the formation of agglomeration in conventional co-precipitation process may result retards the densification process. Suppressing the agglomeration phenomenon is thus necessary for further improving the characteristics of the $Ba_2Ti_9O_{20}$ materials. A modified co-precipitation process is thus developed. In which, the cationic solution was diluted and was sprayed using an ultrasonic nozzle into co-precipitants, which was controlled at pH = 9.5. Such a modified process is designated as spraying-cppt process. Fig. 5 shows that the agglomeration phenomenon is greatly suppressed and the DLS measurements reveals that the average agglomeration size is about 45 nm, which is much smaller than the powders derived from conventional co-precipitations process (225 nm, cf. Fig. 1a). Apparently, the advantage of such a spraying-cppt process is that the sprayed droplets are small, which tends to form fine particles. Moreover, the pH-value of the co-precipitant can be better controlled, which ensures the completeness of the co-precipitation process.

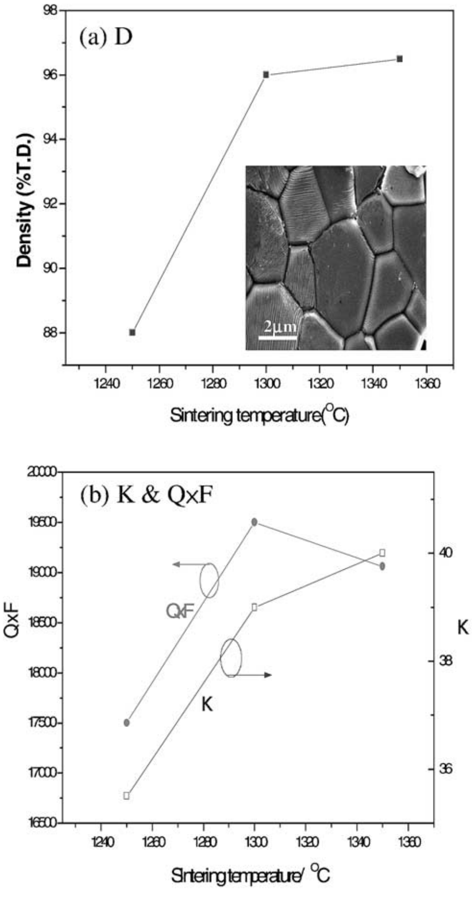

Fig. 4. Variation of (a) sintered density and (b) microwave dielectric properties, K and $Q\times F$, with the sintering temperature for $Ba_2Ti_9O_{20}$ material derived from conventional co-precipitation process (inset of (a) shows the typical microstructure of the sintered samples).

$BaTi_4O_9$ phase, with small amount of $BaTi_5O_{11}$ phase, still predominates the 1000 °C (4 h) calcined powders prepared by spraying-cppt process, shown as XRD pattern I in Fig. 6. However, the powders derived from the spraying-cppt process are much more reactive than the conventional co-precipitants process. XRD pattern II in Fig. 6 indicates that Hollandite phase already presents when the spraying-cppt derived powders were calcined at 1100 °C (4 h) and XRD pattern III in this fig. shows that all the intermediate phase was converted into Hollandite phase for the 1150 °C-calcined powders. In contrast, the powders prepared by conventional co-precipitation process need at least 1250 °C (4 h) to convert all the phases into Hollandite structure (cf. XRD pattern II, Fig. 2). Thus formed Hollandite phase will not be transformed into other structure when sintered at 1200–1300 °C (XRD patterns IV to VI, Fig. 6).

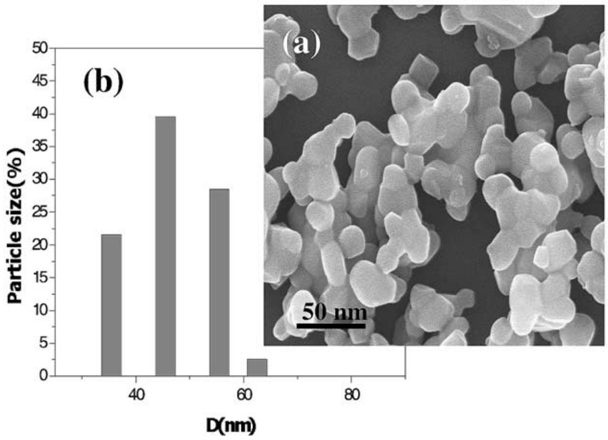

Fig. 5. (a) SEM micrograph and (b) dynamic laser scattering, DLS, measurement for the $Ba_2Ti_9O_{20}$ powder prepared by modified spaying co-precipitation process.

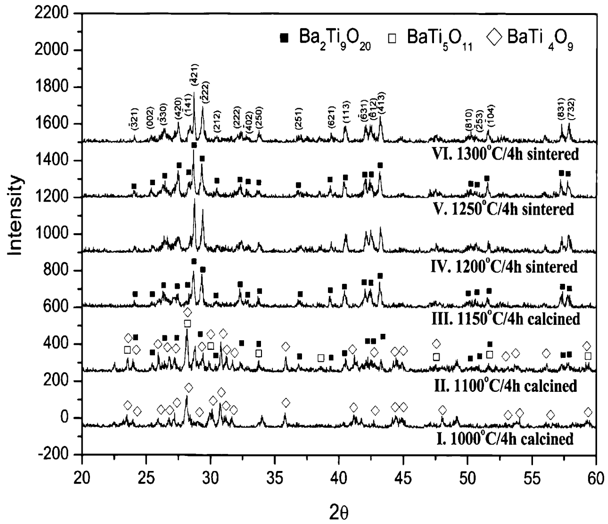

Fig. 6. X-ray diffraction patterns of heat treated $Ba_2Ti_9O_{20}$ powders prepared by modified spaying co-precipitation process and calcined at (I) 1000 °C/4 h, (II) 1100 °C/4 h and (III) 1150 °C/4 h ; those of sintered materials, which were pressed from the 1000 °C/4 h-calcined $Ba_2Ti_9O_{20}$ powders and sintered at (IV) 1200 °C/4 h, (V) 1250 °C/4 h and (VI) 1300 °C/4 h.

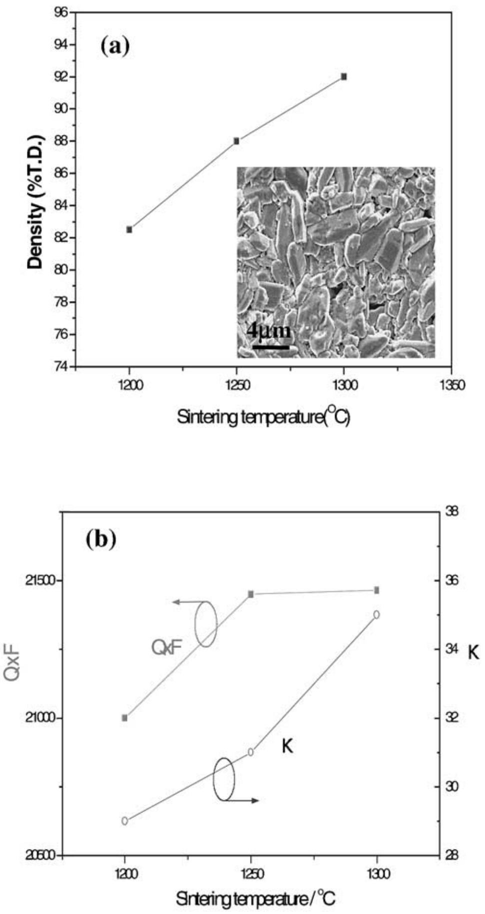

Fig. 7. Variation of (a) sintered density and (b) microwave dielectric properties, K and $Q\times F$, with the sintering temperature for $Ba_2Ti_9O_{20}$ material derived from modified spraying co-precipitation process (inset of (a) shows the typical microstructure of the sintered samples).

The XRD pattern of the 1250 °C-sintered $Ba_2Ti_9O_{20}$ samples, which were prepared by spraying-cppt process, was compared with those of cpp-derived or commercial $Ba_2Ti_9O_{20}$ samples in Fig. 3 (XRD pattern III). These figures indicate that the spraying-cppt prepared samples not only possess the same Hollandite structure as conventional co-precipitation process, but also are of better crystallinity, which is inferred by the larger peak intensity for the corresponding XRD patterns.

The sintered density for the $Ba_2Ti_9O_{20}$ materials prepared form spraying-cppt process also increases with the sintering temperature, approaching a high density (≧92% T.D.) when sintered at 1300 °C (Fig. 7a). Grains are of rod-shape and of submicron size (inset, Fig. 7a). Fig. 7b indicates that the dielectric constant (K) also increases with sintering temperature, reaching $K=35$ for 1300 °C-sintered samples. The quality factor already achieves a large value when sintered at 1250 °C ($Q\times F=21{,}450$), which is markedly larger than that attainable for the materials prepared by conventional co-precipitation (ccp) routes. It should be noted that, although the powders prepared by spraying co-precipitated process are of smaller size and possess higher reactivity, the resulted ceramic samples are of smaller density. The true mechanism for such a phenomenon is not clear yet. One of the possible reasons is that these grains grow easily, forming rod-shaped geometry, which hinder the densification process.

4. Conclusion

Conventional and ultrasonic spraying co-precipitation processes were used to synthesize the Hollandite phase $Ba_2Ti_9O_{20}$ powders without the necessity of doping the SnO_2 additives. The powders prepared by using ultrasonic spraying process posses better reactivity such that the Hollandite phase can be formed at markedly lower temperature (1150 °C), which, in turn, results in better sinterability of the powders. The microwave dielectric properties for the sintered $Ba_2Ti_9O_{20}$ materials were also vastly improved ($K=39$ and $Q\times F=21{,}450$).

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