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Sol–gel synthesis, densification, and electrical properties of CuO–B_2O_3 doped $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Nd) microwave dielectric ceramics

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Abstract The low-temperature confirmable $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (BNT, R = Nd, $x = 2/3$) ceramics were prepared by means of a citrate sol–gel soft-chemical method and the addition of sintering aid. Nano-sized BNT crystallite powders (~80 nm) were successfully synthesized as indicated by transmission electron microscopy and X-ray diffractometry. The powder compacts exhibit enhanced sintering activity and can be well densified at 925 °C with the aid of a small amount of CuO and B_2O_3. Compared to pure BNT ceramics prepared by a solid-state reaction method, not only was the sintering temperature significantly decreased, but also the good microwave dielectric properties of dielectric constant $\varepsilon_r = 63$ and quality factor $Q \times f = 5200$ GHz were maintained. Moreover, the relationship between the microstructure, densification, and electrical properties was discussed.

Introduction

The rapid progress in mobile and satellite communication system has accelerated the development of dielectric materials at microwave frequencies. Moreover, the electronic circuit and components are progressing in the direction of miniaturization, lightweight, and high integration [1–4]. However, most of microwave ceramic systems have distinct drawbacks such as high sintering temperature which remarkably limits practical applications of those ceramic systems. The low temperature co-fired ceramic (LTCC) technique has been so far widely used in the modern electronic components because it affords the high integration density, excellent identity at high frequency, ability of passive integration, and low cost [5–7].

In addition to searching for special compositions with low sintering temperature, the common methods to reduce the sintering temperature are involved in adding sintering aids or using chemical routes to prepare nano-powders. On the one hand, the addition of sintering aids with low-melting points was considered to be a useful way; however, the electrical properties were always influenced [8–13]. Among sintering aids, the mixture of CuO and B_2O_3 in a certain ratio has demonstrated to be an effective sintering aid [8–10]. On the other hand, the citrate sol–gel route was taken as a conventional method to synthesize nano-sized powders; however, the role in improving densification seems to be extremely restricted because small particles tend to be easily coarsened during heating.

$Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth elements) ceramics were reported to have good microwave dielectric properties [14–18]. The high dielectric constant ε_r (80–85) and high $Q \times f$ value (9000–10,000 GHz) were obtained in $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$, BNT) solid solutions. However, the sintering temperature of BNT ceramics prepared by a solid-state reaction (SSR) method reaches approximately 1350 °C. Although chemical routes were ever tried to prepare microwave ceramic powders [15, 16], their sintering temperatures were still too high for the application of LTCC technology.

In this work, a citrate sol gel route and the addition of a small amount of CuO and B_2O_3 mixture was combined to

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decrease the sintering temperature. The processing of nano-scaled BNT powders, their low-temperature sintering behavior with the assistance of sintering aids, and relevant microwave dielectric properties were discussed.

Experimental procedure

High-purity $Ba(CH_3COOH)_2$, $Nd(CH_3COOH)_3$, and $Ti(OC_4H_9)_4$ were used to synthesize BNT powder by means of a citrate sol–gel method. The molar ratio of citric acid to metal cations was 1.5:1. The proper amount of citric acid was dissolved into the deionized water and then ammonia was dripped slowly into the solution to adjust the pH value to 7–8. In succession, tetrabutyl titanate diluted in ethanol was added slowly into the citric acid solution and simultaneously stirred at 80 °C for 2 h. A transparent Ti-citric solution was then obtained. After a suitable amount of multi-metal salts was added, the above solution was stirred continuously at 80 °C for 4 h till it became completely clear and transparent. The gel was subsequently obtained with the increase of fluidity. After heat treatment at 900 °C for 3 h, the lilac ceramic powders were finally gained.

The as-calcined BNT powder was mixed with different amounts of CuO and B_2O_3 mixture ($CuO/B_2O_3 = 76$ wt%, abbreviated as CB) and 0.5 wt% polyvinyl alcohol, and then milled for 24 h (BNT + *y*CB, $y = 0$, 2, 3, 5, and 7 wt%). The dried powder was compacted into cylindrical samples with a diameter of 10 mm and a height of 5–6 mm. Sintering was carried out in air for 4 h in the temperature range of 900–1000 °C with an interval of 25 °C.

Thermo-gravitometry (TG) and differential scanning calorimetry (DSC) analysis of the as-prepared gel was carried out by using a simultaneous thermal analyzer (STA409C, Netzsch, Germany). The bulk densities of the sintered samples were measured by the Archimedes method. The crystal structure of the sintered samples was determined by a powder X-ray diffractometer (XRD) using Cu Kα radiation (Rigaku D/Max-II). The grain morphology was observed by a scanning electron microscope (SEM, Field-emission Sirion200, FEI, Netherlands). An HP87 20ES network analyzer (Hewlett-Packard, Santa Rosa, CA, USA) was used for the measurement of microwave dielectric properties by means of a Hakki–Coleman method [13].

Results and discussion

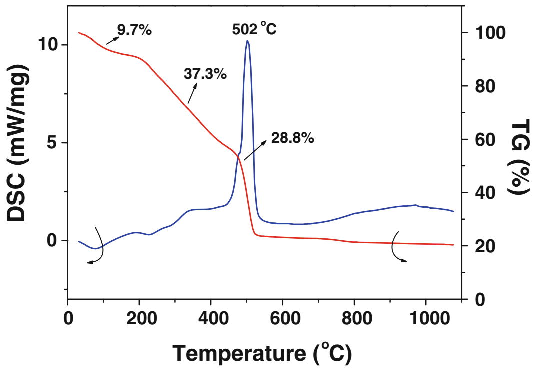

Fig. 1 Thermo-gravitometry and differential scanning calorimetry curves of the BNT gel

The TG–DSC curves of the BNT gel are shown in Fig. 1. It can be seen that the total weight loss is about 75% and can be completed in three stages. First of all, the evaporation of residual water induces initial weight loss (~9.7%) below 200 °C. A remarkable weight loss (~37%) can be then found between 200 and 460 °C, which could be due to the decomposition of the citrate and inorganic carbonic residues. No obvious exothermic peaks in the low temperature range can be found probably because these reactions are relatively weak compared to a strong exothermic reaction at 502 °C. The strong exothermic peak is related to the combustion of residual organic components and the decomposition of acetates, accompanied by a weight loss of 29%. There are no exothermic and endothermic peaks any more after 600 °C, indicating that the oxidation and decomposition of the citrate complexes are finished before 600 °C.

The XRD patterns of BNT gel powders are shown in Fig. 2. It is evident that the gel powders are amorphous in nature. The crystallization starts to occur after heat treatment at 850 °C. The pure tungsten bronze like phase forms at 900 °C, which is much lower than that for an SSR method (~1200 °C). The low calcination temperature

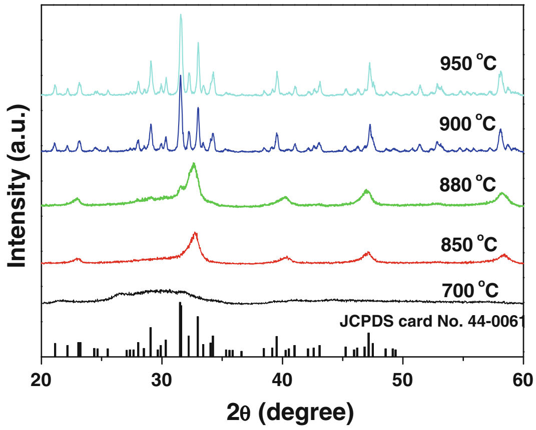

Fig. 2 XRD patterns of sol–gel derived BNT powders calcined at different temperatures compared to a standard pattern of a typical tungsten bronze structure

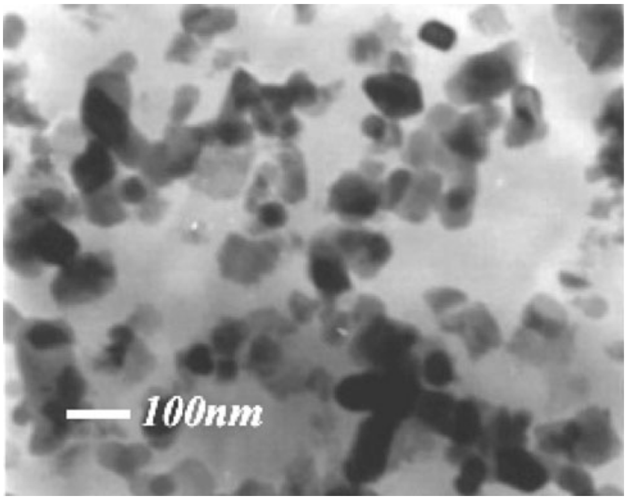

Fig. 3 TEM image of sol–gel derived BNT powder calcined at 900 °C

might afford a relatively high sintering activity of the as-prepared powder. The grain morphology of BNT gel powder calcined at 900 °C for 3 h is shown in Fig. 3. It is shown that the particles have been well-dispersed. All particles exhibit column-like grain morphology with an average particle size of ~80 nm or less. The well-dispersed fine initial powders should be helpful for improving the sintering behavior.

Densities of nano-sized BNT powder compacts as a function of sintering temperature are shown in Fig. 4. Compared to the powder prepared by a conventional SSR method, the sol–gel derived BNT powder shows significantly improved densification behavior and its maximum densification temperature (1150 °C) is reduced by ~150 °C. As stated above, the fine and well-dispersed initial powders provide a high sintering driving force. However, this is still not low enough to allow the material to cofire with pure silver electrode. As a conventionally used sintering aid, an appropriate amount of CuO–B_2O_3 mixture was added. It can be found that the sintering temperature of the samples was further reduced by more than 200 °C. The 5 wt% CB added BNT nano-sized powder compacts can be well densified at 925 °C, with a relative density of >95%. The results indicate that both the sintering temperature and the amount of sintering aids have an effect on the densification. At a relatively low sintering temperature, the amount of sintering aids has a small effect on the densification. At a higher sintering temperature, the increase of the amount of sintering aids will contrarily degrade the densification. Higher sintering temperature and more liquid phases tend to simultaneously speed up the grain growth, apart from the enhancement of mass transfer (higher temperature) and the rearrangement of particles (liquid phase). Therefore, a suitable sintering temperature and an approximate amount of sintering aids are necessary for good densification.

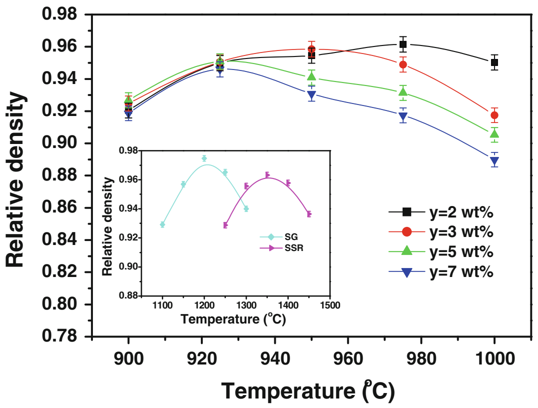

Fig. 4 Densification behavior of sol–gel derived BNT ceramics co-doped with CuO and B_2O_3; Inserted are densification curves for undoped BNT ceramics prepared via sol–gel method and solid-state reaction method, respectively

The microstructure of the CB doped BNT ceramics is shown in Fig. 5. It can be seen that all samples exhibit dense microstructure with relatively uniform grain size as sintered at 925 °C, except for undoped samples. The undoped BNT sample can be well densified 1200 °C (Fig. 5b) but has much bigger grain size. The BNT samples doped with CB need much lower sintering temperature (925 °C here) such that the grain size was significantly reduced. The results indicate that the CuO–B_2O_3 mixture could be an effective sintering aid for this system. Moreover, it can be seen that there is only a slight increase in grain size owing to the increase of the CB content as the sample was sintered at 925 °C. The grain growth of BNT samples seems more sensitive to the sintering temperature than the amount of the liquid phases. A combination of chemical routes and the sintering aid proves to be a successful measure for decreasing the sintering temperature of BNT ceramics.

Microwave dielectric properties and sintering conditions of BNT ceramics prepared by different processing routes were summarized in Table 1. It is clear that pure sol–gel derived BNT ceramics exhibit excellent electrical properties of $\varepsilon_r \sim 82$ and $Q \times f \sim 10{,}200$, comparable to those of BNT ceramics prepared by the SSR method. The addition of sintering aids (CB) was found to effectively reduce the sintering temperature, but to somewhat degrade the microwave dielectric properties simultaneously. The dielectric constant ε_r, quality factor $Q \times f$ and temperature coefficient τ_f decrease with the addition of CB. For 5 wt% CB doped BNT samples derived from the sol–gel route, the overall properties of $\varepsilon_r \sim 63$, $Q \times f \sim 5300$ and density $\rho > 95\%$ can be achieved as the sintering temperature is 925 °C. It should not be a problem that the τ_f value is still high since it

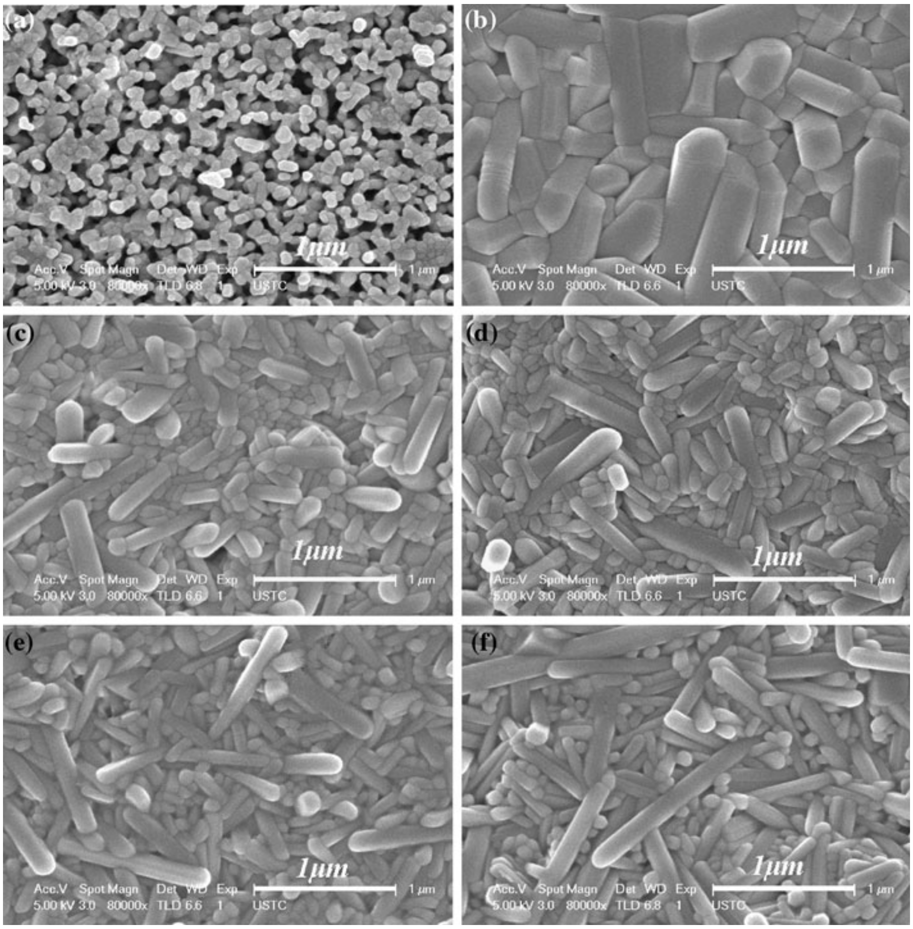

Fig. 5 SEM images of sol–gel derived BNT ceramics co-doped with CuO and B_2O_3 and sintered at different temperatures: **a** $y = 0$, at 925 °C; **b** $y = 0$, at 1200 °C; **c** $y = 2$ wt%, at 925 °C; **d** $y = 3$ wt%, at 925 °C; **e** $y = 5$ wt%, at 925 °C; and **f** $y = 7$ wt%, at 925 °C

Table 1 Microwave dielectric properties and sintering parameters of BNT ceramics prepared via different processing routes

Compositions	Firing temperatures (°C)	Relative density (%)	Dielectric constant	$Q \times f$ (GHz)	τ_f (ppm/°C)
Undoped BNT by SSG	1350	97.0	80	10,000	68
Undoped sol–gel BNT	1200	97.5	82	10,200	60
Sol–gel BNT + 2 wt%CB	975	96.1	69	5800	45
Sol–gel BNT + 3 wt%CB	950	95.8	67	5600	36
Sol–gel BNT + 5 wt%CB	925	95.1	63	5300	28
Sol–gel BNT + 7 wt%CB	925	94.5	55	4100	24

can be tailored to ~zero by substituting Nd with other rare earth elements such as Sm [18].

Conclusions

Tungsten bronze-type like BNT microwave ceramics were prepared by a citrate sol–gel method in combination with the addition of CuO and B_2O_3 and their processing, sintering behavior and microwave dielectric properties were investigated. The sintering temperature was decreased remarkably by using nano-scaled BNT powders (~80 nm) in comparison to a conventional SSR method. Further improvement was realized by incorporating a small amount of CuO and B_2O_3 mixture. The overall properties of sol–gel derived BNT samples doped with 5 wt% CB are as follows: $\varepsilon_r \sim 63$, $Q \times f \sim 5300$, and $\rho > 95\%$ as they were sintered at 925 °C.

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