Influence of CuO and B_2O_3 on sintering and dielectric properties of tungsten bronze type microwave ceramics: a case study in $Ba_4Nd_{9.3}Ti_{18}O_{54}$

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Abstract The effect of CuO and B_2O_3 co-doping on the sintering behavior, microstructure and microwave dielectric properties of tungsten bronze type $Ba_4Nd_{9.3}Ti_{18}O_{54}$ (BNT) ceramics has been investigated by means of a traditional solid-state mixed oxide route. On the one hand, it was indicated that the mixture of CuO and B_2O_3 is an effective sintering aid for BNT matrix compositions owing to the existence of a low-temperature eutectic reaction. On the other hand, it was found that the addition of CuO and B_2O_3 has an obvious effect on microwave dielectric properties of BNT ceramics, depending on the amount of sintering aids, the sample density and microstructure. The liquid phases from sintering aids can promote densification, but simultaneously induce grain growth which tends to decrease the sintering driving force. BNT ceramics doped with 3 wt% CuO–B_2O_3 mixture can be well sintered at 950°C for 4 h and still exhibit relatively good microwave dielectric properties.

1 Introduction

With rapid development of modern telecommunication technology, extensive attempts have been made to reduce the size of resonating circuits in order to satisfy the requirement for the portability, lightweight and miniaturization of communication terminals. Microwave dielectric ceramic resonator having such advantages over metal cavity resonators, as small size, low weight, good thermal stability, low cost and so on, has been one of the main driving forces for the miniaturization and integration of communications equipments. The size of dielectric resonators is inversely proportional to the square root of dielectric constant ε_r and thus larger ε_r leads to a reduction of the device size. In recent years more and more research has been focused on pursuing super low dielectric loss at a high frequency above 10 GHz, or an increased quality factor $Q \times f$ for a material system with a high ε_r, or a low-temperature sinterable technique for a few known microwave dielectric material systems with a high sintering temperature (above 1,300°C) [1–5]. Particularly, a low-temperature firable microwave ceramic has become more and more interesting since it offers a low-cost processing by using cheap inner electrodes in multilayer microwave devices.

As a typical candidate of microwave dielectric ceramics with a high ε_r, tungsten bronze type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (BRT, R = rare earth) solid solution ceramics have been widely investigated in last few years, exhibiting optimum microwave dielectric properties at $x = 2/3$, such as high ε_r (80–85), high $Q \times f$ value (9,000–10,000 GHz) and a tunable temperature coefficient of resonance frequency τ_f [6–8]. However, a sintering temperature as high as 1,350°C is usually needed for those un-doped solid solution ceramics. Except for the compositions with low sintering temperatures in nature [9], the addition of oxides with a low melting point or glass frit with a low softening point was considered as an effective way to improve the densification behavior [10–17]. B_2O_3 or CuO are often used as a sintering aid to promote the sintering for a couple of material systems [10, 14–17],

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because each of them has low melting points or can form new phases with low melting points with matrix compositions. It was reported that the addition of CuO and B_2O_3 and their co-doping were successfully used in $Ba_3Ti_4Nb_4O_{21}$ ceramics with a hexagonal structure, lowering the sintering temperature till 900°C [10]. It is thus anticipated that these dopants would be also interesting for aiding the densification of tungsten bronze type like BRT ceramics, although they were never used in this system. The use of sintering aids will not only improve sintering behavior due to the formation of liquid phases, but also alter the microstructure and even crystal structure.

The purpose of this study is to investigate low-temperature sintering behavior, microstructure and microwave dielectric properties of a typical composition $Ba_4Nd_{9.3}Ti_{18}O_{54}$ (BNT) belonging to the BRT family as a case study. Pure BNT ceramics need a sintering temperature up to 1,350°C, exhibiting interesting microwave dielectric properties of $\varepsilon_r = 80$, $Q \times f = 10,000$ GHz, $\tau_f = 68$ ppm/°C [6]. In order to realize the cofirability with pure silver electrodes, the sintering temperature should be at least reduced below 960°C (melting point of silver). The mixture of CuO and B_2O_3 in an appropriate ratio was added, considering eutectic reactions in the phase diagram of CuO–B_2O_3 [18]. The influence of the densification behavior and microstructure on electrical properties will be discussed.

2 Experimental

BNT powders were prepared via a conventional mixed oxide method. High purity oxides and carbonates of $BaCO_3$ ($\geq$99%), Nd_2O_3 ($\geq$99.9%) and TiO_2 ($\geq$99%) were used as raw materials. The as-weighed powders were mixed homogeneously in deionized water using a planetary ball mill. After drying, the powder mixture was calcined at 1,200°C for 4 h. The as-calcined BNT powder was added with different amounts of CuO and B_2O_3 mixture (CuO: B_2O_3 = 4 mol: 6 mol, abbreviated as C4B6) and 0.5 wt% PVA powder, and then milled for 24 h (BNT+xC4B6, x = 0, 1, 2, 3, 4, 5, 6 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 910°C to 1,010°C with an interval of 20°C.

The Archimedes method was applied to estimate the bulk density of the sintered samples. The phase structure of the sintered samples was determined by a powder X-ray diffractormeter using Cu $K\alpha$ radiation (XRD, D/Max-II, Rigaku, Japan). The grain morphology was observed by scanning electron microscopy (SEM, SSX-550, Shimadzu, Japan). An HP8720ES network analyzer (Hewlett-Packard, Santa Rosa, CA, USA) was used for the measurement of

microwave dielectric properties. The method for measuring the dielectric constant ε_r and the unloaded quality factor $Q \times f$ can be referred elsewhere [13]. The temperature coefficient of the resonant frequency (τ_f) was measured in the temperature range of 20–80°C. The τ_f value can be obtained by using the following equation: $\tau_f = (f_{80}–f_{20})/[f_{20}(80–20)]$ where f_{20} and f_{80} represent the resonant frequencies at room temperature and 80°C, respectively.

3 Results and discussion

The bulk density of BNT+xC4B6 ceramics is plotted as function of sintering temperature and the content of the additive, as shown in Fig. 1. It can be seen that the sample doped with only 1 wt% C4B6 can be poorly densified within the studied temperature range, exhibiting a maximum density below 80%. With further increase of x, the densification is significantly improved. Samples with x more than 3 wt% can be well densified at 950°C, reaching a density of >95%. The results indicate that the mixture of CuO and B_2O_3 proves an effective sintering aid for BNT compositions since un-doped BNT needs to be densified at 1,350°C [7]. For each sample, the density reaches a maximum value at an appropriate temperature (for example, 950°C for BNT doped with 3 wt% C_4B_6), and then starts to decrease slightly with further increasing sintering temperature, probably because the grain growth counteracts the sintering driving force for densification with increasing temperature. This will be discussed later. The role of CuO and B_2O_3 co-addition can be attributed to the formation of liquid phases as sintering aids caused by eutectic reactions between CuO and B_2O_3 and also an incongruently melting compound CuB_8O_{13} at 750°C [18]. The mechanism of liquid phase sintering is based on that the liquid phase
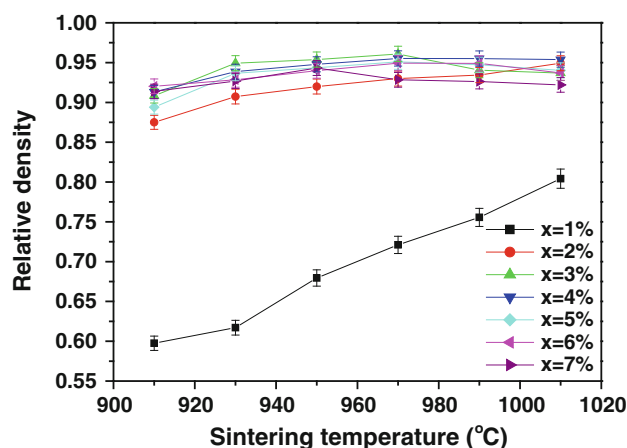
**Fig. 1** Relative densities of BNT+xC4B6 ceramics as a function of sintering temperature

promotes the arrangement of particles at the early stage of sintering and speeds up the mass transportation in the middle of sintering, depending on the quantity of the liquid phase. However, too much liquid phase tends to deteriorate the densification owing to an increase in the distance of mass diffusion and a rapid grain growth. As a result, the 3 wt% C4B6 doped BNT ceramics exhibit the best densification behavior and further increase of x was found to degrade the densification to a certain degree.

The SEM micrographs of BNT samples doped with various contents of C4B6 sintered at 950°C are shown in Fig. 2. It is clear that the BNT sample doped with 2 wt% C4B6 is still porous, keeping consistent with the measurement of bulk densities, although its densification behavior is relatively improved compared to pure BNT [7, 8]. As the content of C4B6 increases up to 3 wt%, the samples become significantly dense although their sintering temperature is reduced by 400°C. Furthermore, it can be seen that all samples exhibit column-like grain morphology. The grain size increases with increasing the content of C4B6. The grain growth with increasing the content of C4B6 would be responsible for the reduction of densification rate for samples with more than 3 wt% C4B6. Moreover, it can be seen that the sintering temperature will influence not only the densification behavior (Fig. 1), but also the grain growth as shown in Fig. 3. The rapid grain growth could be the reason for the degraded densification at a high sintering temperature.

Figure 4 shows XRD patterns of BNT samples with various contents of C4B6 sintered at 950°C. It is evident that all compositions mainly consist of tungsten bronze type like phase (JCPDS card No. 44-0061). As a little amount of C4B6 was added, the liquid phase, which promotes the densification as discussed above, could be completely absorbed back into the lattice of BNT. However, with further increase of x, the liquid phase formed during heating tends to be redundant and cannot be fully absorbed by grains, possibly existing as glass phases at the grain boundary. Therefore, the low-temperature fired $Ba_4Nd_{9.3}Ti_{18}O_{54}$ samples with C4B6 could be a mixture of $Ba_4Nd_{9.3}Ti_{18}O_{54}$ and a small amount of glass phases formed from redundant liquid phases. A small amount of glass phases cannot be observed by SEM or detected by XRD.

Generally speaking, the dielectric properties are correlated to the density, microstructural evolution and composition of ceramics. It was previously reported that pure BNT ceramics sintered at 1,350°C have good microwave dielectric properties of $\varepsilon_r = 80$, $Q \times f = 10,000$ GHz and $\tau_f = 68$ ppm/°C. The similar result for pure BNT can be achieved in our study. Figure 5 shows the relative dielectric constant ε_r of C4B6 doped BNT samples sintered at different temperatures. It can be seen that ε_r generally decreases with increasing C4B6 content, although sintering temperature is significantly reduced. Samples can be well densified at 950°C as the C4B6 content is above 2 wt%.

Fig. 2 SEM micrographs of BNT+xC4B6 ceramics sintered at 950C: **a** $x = 2$ wt% **b** 3 wt%, **c** 5 wt% and **d** 6 wt%
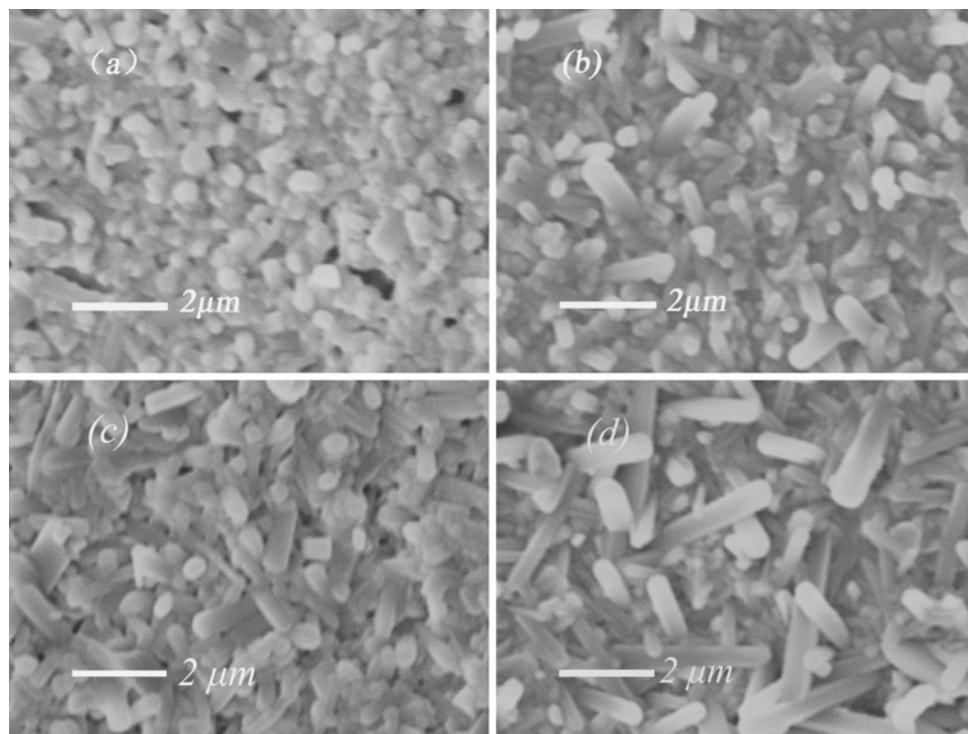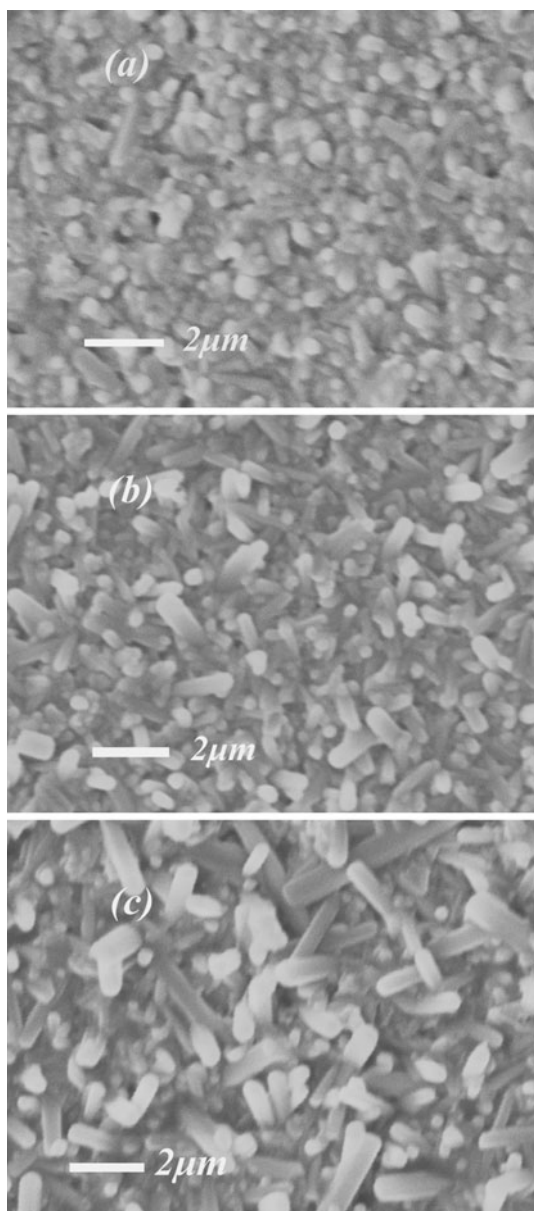
Fig. 3 SEM micrographs of BNT + 3 wt% C4B6 ceramics sintered at different temperatures: **a** 910°C, **b** 950°C and **c** 1,010°C

Fig. 4 X-ray diffraction patterns of BNT+xC4B6 ceramics compared to a standard pattern of a typical tungsten bronze structure

Fig. 5 Dielectric constant of BNT+xC4B6 ceramics as a function of sintering temperature

Therefore, the reduction of ε_r is mainly attributed to the change of microstructure such as grain size, crystal structure and so on, as the C4B6 content is low (2–4 wt%). With an increase of C4B6 content ($\geq$4 wt%), glass phases or porosity with low ε_r may further degrade the dielectric property based on the mixing rule of dielectrics as expressed by the Maxwell–Wagner's equation, although decreased grain boundary volume owing to the increase in grain size may slightly increase it. Moreover, it can be seen that ε_r slightly changes with sintering temperature and exhibits a maximum value for each sample, which should be mainly ascribed to the variation of bulk density.
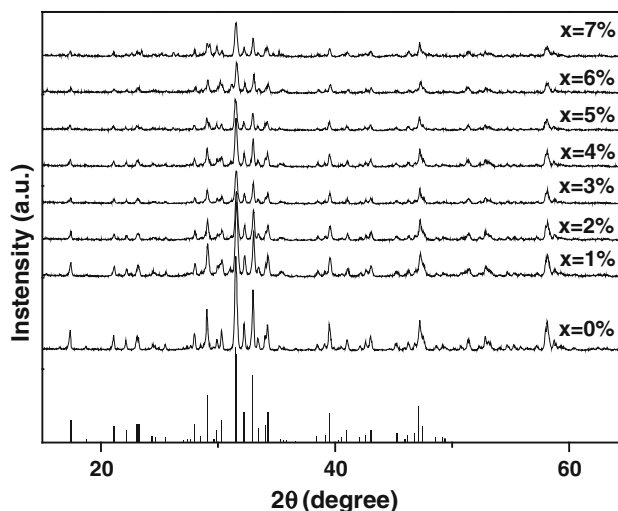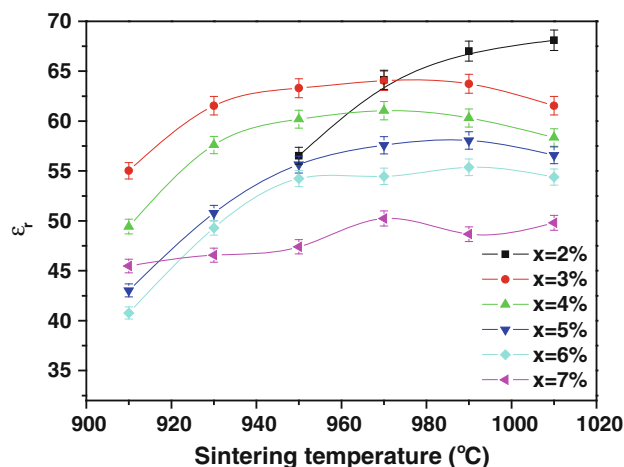
Figure 6 shows the variation of $Q \times f$ values of BNT samples as function of sintering temperature and C4B6 content. The $Q \times f$ value of each composition reaches the maximum at the optimum temperature of the corresponding sample. Moreover, it generally decreases with increasing C4B6 content. The variation of $Q \times f$ values with additive content and sintering temperature can be explained by similar mechanisms as those for the variation of ε_r discussed above. The increased density leads to a reduction of extrinsic losses, thereby increasing $Q \times f$ value. However, with increasing sintering temperature, the grain growth (Fig. 3) tends to decrease the sintering driving force, leading to a relatively low densification (Fig. 1). Thus, the $Q \times f$ value starts to decrease. The influence of sintering aids (C4B6 in this study) on $Q \times f$ value would finally depend on the lattice defects owing to the replacement of ions from sintering aids, glass phases at the grain boundary,
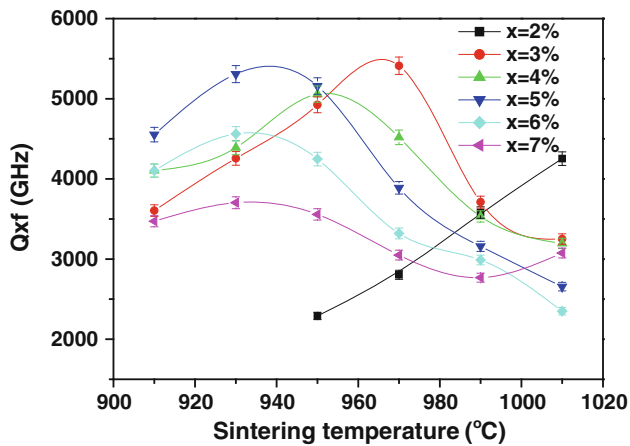
Fig. 6 The $Q \times f$ values of BNT+xC4B6 ceramics as a function of sintering temperature

Table 1 The τ_f values of BNT+xC4B6 ceramics sintered at optimum sintering temperatures

Content of Sintering aid, $100\times$	1	2	3	4	5	6	7
τ_f (ppm/°C)	58.5	52.9	40.4	34.6	30.5	16.3	12.6

in addition to the density. A small amount of lattice defects will contribute to the increase of extrinsic losses.

In addition, the temperature coefficient of the resonant frequency τ_f of C4B6 doped BNT ceramics sintered optimum sintering temperatures was found to change with the C4B6 content as well, as shown in Table 1. The BNT matrix composition has a high positive τ_f (~ 68 ppm/°C) [7]. It was found that the τ_f value decreases with increasing the amount of C4B6. It was generally thought that the τ_f change of BRT system was attributed to the kind of A1-site ions [7]. According to this, a value of τ_f = zero ppm/°C could be achieved by means of additive rule through making solid solutions between two compositions with positive and negative τ_f. However, the τ_f value for C4B6 doped BNT ceramics decreases from 58.5 to 12.6 ppm/°C for 1 wt% C4B6 and 7 wt% C4B6 doped ones, respectively. The reduction of τ_f values can be attributed to the decrease of the corresponding dielectric constant due to the percolation effect. As a case study, this study is of interest to develop BNT based microwave dielectric ceramics with τ_f = zero by incorporating an appropriate amount of sintering aids and other A1-site ions such as Sm [7, 13].

4 Conclusion

Low-temperature firable tungsten bronze-type like microwave dielectric ceramics have been manufactured by using $CuO–B_2O_3$ mixture as a sintering aid and BNT as a case study. It was indicated that $CuO–B_2O_3$ co-doping has an obvious effect on the densification behavior, microstructure and microwave dielectric properties of BNT ceramics. As the content of $CuO–B_2O_3$ mixture is more than 3 wt%, it tends to degrade the sintering behavior and electrical properties considering the grain growth and grain boundary glass phases. BNT ceramics doped with 3 wt% $CuO–B_2O_3$ mixture can be well sintered at 950°C for 4 h and still exhibit good microwave dielectric properties.

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