

Low Temperature Sintering and Microwave Dielectric Properties of Ba₄Nd_{9.33}Ti₁₈O₅₄ Ceramics Doped with Crystallizable Glass

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Keywords: Dielectric properties; Microstructure; Low temperature sintering

Abstract. The effect of CaO-B₂O₃-SiO₂ glass on the densification, microstructure and microwave dielectric properties of Ba₄Nd_{9.33}Ti₁₈O₅₄ ceramics was investigated in this work. It was found that the addition of a few amount of glass ($\leq 2\%$) could effectively decrease the sintering temperature owing to the viscous sintering. However, locally porous structures were formed when overmuch glass was added because of enwrapped air bubbles and rapid grain growth. In addition, the amount of remaining glass after sintering could be decreased due to the re-crystallization of CaO-B₂O₃-SiO₂ glass. Sol-gel derived Ba₄Nd_{9.33}Ti₁₈O₅₄ ceramics containing 2 wt% glass can be well densified at 950°C and exhibit good microwave dielectric properties of $\epsilon_r=68$ and $Q \times f=7400$ GHz.

Introduction

Microwave dielectric ceramics have been actively investigated in recent years mainly because of the rapid progress of mobile and satellite communication system. Rather high sintering temperatures for most of known microwave dielectric material systems made them difficult to cofire with such base metal electrodes as Ag and Cu. 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, the ability of passive integration and low cost [1-3]. How to design a material composition with a sintering temperature lower than the melting point of silver electrode has become an important research direction in the field of microwave ceramics. Few material compositions were found to have low sintering temperatures in nature [4] and good microwave dielectric properties simultaneously. Therefore, one more applicable way might be to reduce the sintering temperature of currently available dielectric ceramics through processing measures.

Ba_{6-3x}R_{8+2x}Ti₁₈O₅₄ (R=rare earth elements) ceramics were reported to have good microwave dielectric properties [5-9]. The high dielectric constant ϵ_r (80~85) and high $Q \times f$ value (9000~10000 GHz) were obtained in Ba_{6-3x}Nd_{8+2x}Ti₁₈O₅₄ ($x=2/3$, BNT) ceramics sintered at 1350°C. The high dielectric constant can help obviously reduce the size of microwave devices. However, the high sintering temperature has restricted their application in multilayer microwave devices because cofiring with Ag electrode is required. Usual ways to improve the densification of BNT ceramics have been so far involved in the use of sintering aids with low-melting points or glass frit with low softening points [10-17]. Although chemical routes were tried to prepare BNT ceramic powders [6,7,18], their sintering temperatures were still too high for the application of LTCC technology. Most of sintering aids are usually single or mixed oxides with low melting points, which could improve the densification behavior because of a liquid phase sintering mechanism [10-15]. However, this kind of sintering aids tends to degrade the dielectric properties at the same time mainly because cations in the sintering aids would enter into the lattice of BNT ceramics during sintering [16, 17].

The CaO-B₂O₃-SiO₂ (CBS) ternary system is one typical crystallizable glass which owns a softening point at ~600°C and can partially transform to the crystal after sintering below 900°C. The commercially available Ferro A6 powder (Ferro Corporation, Ohio, USA) composed of CBS has been

one successful substrate material for multilayer ceramic technology. It has relatively low sintering temperature and excellent dielectric properties (low dielectric loss) based on the viscous sintering mechanism of glass phases and the re-crystallization ability during densification. As far as both densification behavior and electrical properties of microwave ceramics are concerned, it seems that crystallizable glass should be advantageous over oxides with low-melting points in achieving LTCC microwave ceramics. The purpose of this work is thus to study on the effect of the addition of a few amount of CBS glass on the densification, microstructure and dielectric properties of BNT ceramics which were derived by a citrate sol-gel method for better sintering activity.

Experimental Procedures

The BNT powder was first synthesized by a citrate sol-gel method by using high-purity $\text{Ba}(\text{CH}_3\text{COOH})_2$, $\text{Nd}(\text{CH}_3\text{COOH})_3$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ as raw materials. The detailed experimental procedure could be referred to elsewhere [18]. The as-calcined BNT powder was then mixed with different amounts of CBS powder through a wet milling process for 24 h (BNT+yCBS, $y=0\%$, 2%, 3%, 5%, 10% and 15 wt%). The CBS powder used in this study was prepared in our lab [19]. The dried powder mixture 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 925°C to 1300°C with an interval of 25°C.

The bulk density of the sintered samples was estimated by the Archimedes method. The crystal structure of the sintered samples was determined by a powder X-ray diffractometer (XRD) using $\text{Cu } K\alpha$ radiation (Rigaku D/Max-II). The grain morphology was observed by a scanning electron microscope (SEM, Field-emission Sirion200, FEI, Netherlands). An HP8720ES 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

The bulk density of BNT+yCBS ceramics was plotted as function of sintering temperature and the content of glass phase, as shown in Fig. 1. Compared to the solid-state reaction method, the sol-gel method used in this study has reduced the sintering temperature of BNT ceramics by almost 150°C. Moreover, it can be seen that the sintering behavior of sol-gel derived BNT ceramics was obviously improved by adding a few amount of CBS glass. BNT ceramics doped with 2 wt% CBS could be well densified at 950~975°C. However, a more CBS glass was added, the sintering temperature was not evidently reduced any more. It can be understood that the viscous flow of CBS glass during heating would speed up the rearrangement of BNT particles. It seems that the role of CBS glass in the densification of BNT ceramics more depends on its softening point than on the amount of CBS glass. In other words, 2 wt% CBS is much enough to induce viscous flow of BNT particles. In addition, one can see that the addition of the CBS content obviously decreased the absolute density of BNT samples, probably because the glass phase itself has a low molecular weight.

Fig. 2 shows the SEM micrographs of BNT + yCBS samples sintered at 950°C. It can be seen that BNT samples without CBS glass is still porous, which keeps consistent with the measurement of bulk densities (Fig. 1). However, the sample density could be obviously improved as only 2 wt% CBS glass was added. This effect was continued till 5 wt% CBS glass was added.

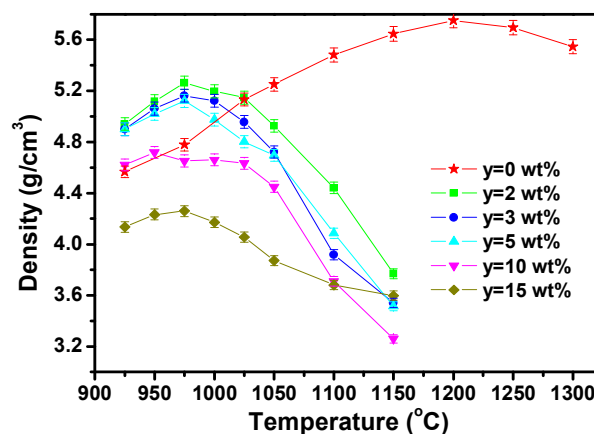


Fig. 1. Influence of sintering temperature and content of CBS on the densification behavior of BNT ceramics

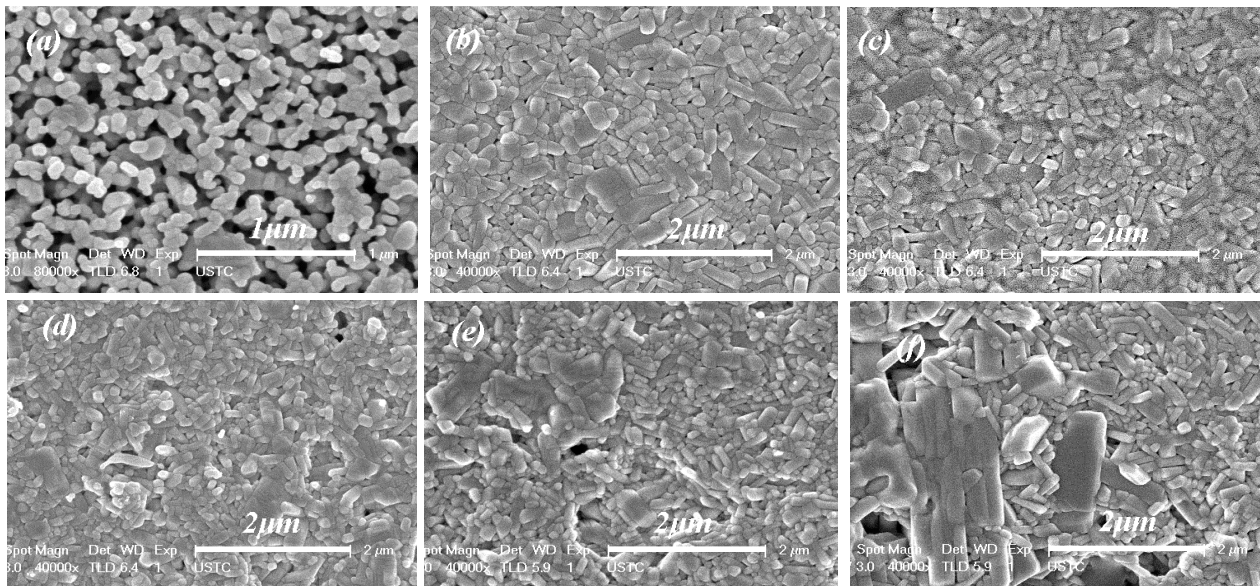


Fig. 2. SEM images of CBS modified BNT ceramics sintered at 950°C: (a) $y=0$, (b) $y=2$ wt%, (c) $y=3$ wt%, (d) $y=5$ wt%, (e) $y=10$ wt%, (f) $y=15$ wt%.

With a further increase of CBS glass content ($>5\%$), one could find that redundant CBS glass tends to unevenly distribute or agglomerate in the sample, such that the local grains grow much faster and the microstructure becomes more porous (for example, BNT samples with 15 wt% CBS). An appropriate amount of CBS glass can well wet BNT grains when it becomes viscous during heating, so that the sintering driving force would be enhanced due to the role of capillary. Overmuch CBS glass tends to enwrap air bubbles inside the sample owing to its high viscosity at the early stage of sintering, leading to locally porous structures. In addition, the fast grain growth was induced at the place rich in CBS glass, meaning that CBS glass probably reacted with BNT ceramics.

The XRD patterns of CBS glass doped BNT samples sintered at 950°C are shown in Fig. 3. It seems that all compositions mainly consist of tungsten bronze type like phase. No secondary phases can be seen even for BNT samples doped with CBS glass. As known, CBS glass is crystallizable and its main crystal phase is CaSiO_3 (CS) [17, 18]. However, the CS phase was not detected by XRD. The possible reasons could be as follows: The formed CS phase may have entered into the lattice of BNT ceramics during sintering or the amount of CS phase is too low to be detected for samples with low

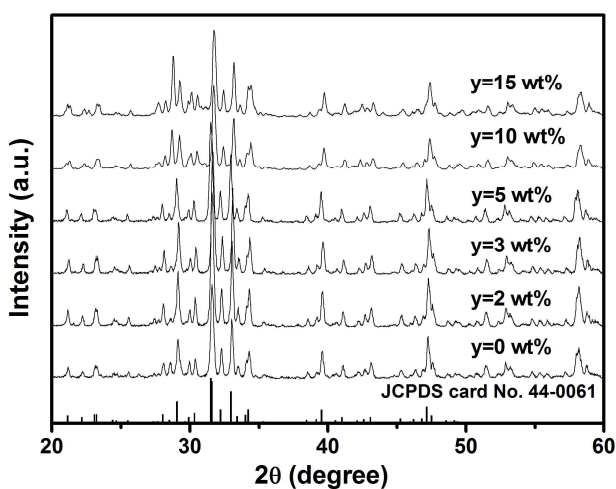


Fig. 3. XRD patterns of BNT ceramics modified by different contents of CBS as indicated compared to a standard pattern of a typical tungsten bronze structure.

CBS content. As the CBS glass content was more than 10 wt% or 15 wt% CBS, all diffraction peaks were found to shift to higher angles, meaning that the unit cells shrink (Ionic radii: 1.34 Å and 1.61 Å for Ca^{2+} and Ba^{2+} , respectively, Coordination number (CN)=12); 0.40 Å and 0.61 Å for Si^{4+} and Ti^{4+} (CN=6) [20]). This would mean that the CS crystalline phase enters into the BNT lattice. From the SEM picture, one can clearly see the remaining glass phase, particularly for samples containing higher CBS glass content, meaning that only a small part of glass phase could transform into crystals. The fast grain growth occurred in the sample with high glass content may indicate that chemical reactions happened between CBS glass and BNT matrix. As a result, the mass transportation could be promoted during

reaction. Interestingly, the expected CS crystal did not exist as a separate phase in the final microstructure but might form a solid solution with BNT matrix composition. This could make extra contribution to the increase of dielectric constant because CS has rather lower dielectric constant than BNT ceramics, but much higher values than pure glass phase. Moreover, the crystallization of CBS glass helps decrease the amount of the remaining glass phase, contributing to the reduction of loss values.

The dielectric constant ϵ_r and quality factor $Q \times f$ values of CBS glass doped BNT ceramics as a function of sintering temperature and glass content are shown in Fig. 4 and Fig. 5, respectively. It can be seen from Fig. 4 that ϵ_r exhibits similar variation to the densification with the change of sintering temperature and glass content. The addition of a small amount of CBS glass could effectively improve the densification, but did not significantly deteriorate the dielectric property. This is because the amount of glass phase (~2 wt%) has been enough to promote the densification by viscous sintering. Also, the amount of the remaining glass phase after sintering becomes very low owing to the re-crystallization of CBS glass. With increasing the CBS glass content, the ϵ_r value obviously decreases mainly due to an increase in the amount of remaining glass phase and a decrease of the sample density. It is a pity that the effect of CS phase on the dielectric property was difficult to distinguish in this study mainly because it did not exist as a separate phase (see Fig. 3). When the sintering temperature is below 1020°C, the $Q \times f$ values are mainly determined by the relative density of the samples. The $Q \times f$ value exhibits a maximum value at the optimal sintering temperature of each sample with different glass content, mainly because the increase of density reduces the extrinsic dielectric loss. However, as the sintering temperature is higher than 1020°C, a slight increase of $Q \times f$ values can be seen. This is because the grain growth at higher sintering temperature tends to decrease the intrinsic dielectric loss. By comparison, sol-gel derived BNT ceramics doped with 2 wt% CBS glass phase sintered at 950°C can own better dielectric properties of $\epsilon_r=68$ and $Q \times f=7400$ GHz, than BNT ceramics doped with CuO-B₂O₃ ($\epsilon_r=63$ and $Q \times f=5200$ GHz) [18]. It was believed that the latter is based on a liquid phase sintering because of the eutectic reactions between CuO and B₂O₃. The results in this study could benefit from both the improved densification owing to the addition of a small amount of CBS glass and the re-crystallization behavior of CBS glass.

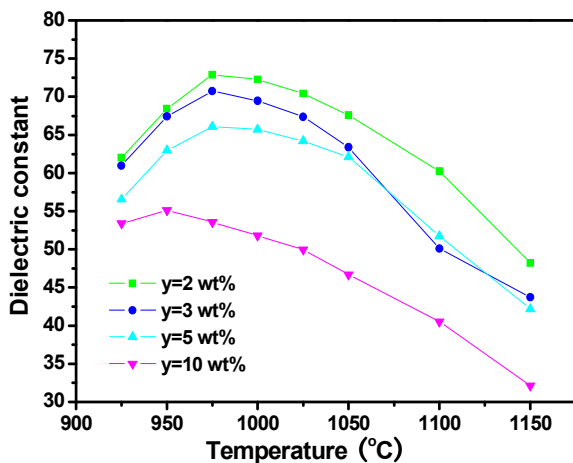


Fig. 4. Dielectric constant of BNT ceramics modified by different contents of CBS as indicated.

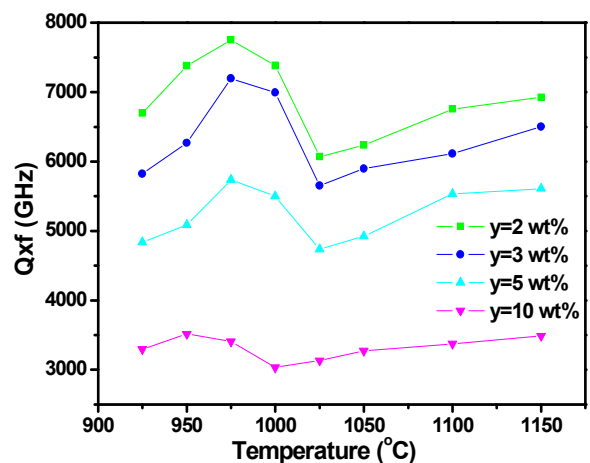


Fig. 5. Quality factor $Q \times f$ of BNT ceramics modified by different contents of CBS as indicated.

Conclusions

Low-temperature cofirable BNT microwave dielectric ceramics were manufactured by using sol-gel powder processing and adding CBS glass powder. An improved densification behavior of BNT ceramics can be achieved as a few amount of CBS glass is added. However, superfluous CBS glass tends to degrade the densification behavior because air bubbles can be enwrapped by high-viscosity

CBS glass in the early stage of sintering. The viscous flow of CBS glass was considered as a main mechanism for the improved densification of BNT ceramics. Compared to those synthesized by solid-state reaction method ($\epsilon_r=80\sim 85$ and $Q\times f=9000\sim 10000$ GHz as sintered at 1350°C), sol-gel derived BNT ceramics doped with 2 wt% CBS glass phase can be well densified at 950°C and exhibit good microwave dielectric properties of $\epsilon_r=68$ and $Q\times f=7400$ GHz.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of Anhui Province (1108085J14) and of China (50972035) and a Program for New Century Excellent Talents in University, State Education Ministry (NCET-08-0766).

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Chinese Ceramics Communications II

10.4028/www.scientific.net/AMR.412

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10.4028/www.scientific.net/AMR.412.280