Crystal Structures and Microwave Dielectric Properties of Novel MgCu$_2$Nb$_2$O$_8$ Ceramics Prepared by Two-Step Sintering Technique

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Abstract: In this work, novel MgCu$_2$Nb$_2$O$_8$ (MCN) ceramics were synthesized by the two-step sintering (TSS) technique, and the phase composition, crystal structures, and microwave dielectric properties were comprehensively studied. X-ray diffraction (XRD) and Raman analysis demonstrated that MCN ceramics are multi-phase ceramics consisting of MgNb$_2$O$_6$ and CuO phases. X-ray photoelectron spectroscopy (XPS) was utilized to investigate the chemical composition and element valence of MgCu$_2$Nb$_2$O$_8$ ceramics. Scanning electron microscopy (SEM) analysis demonstrated dense microstructures in the MCN ceramics prepared at a sintering temperature of 925 °C. The microwave dielectric properties were largely affected by the lattice vibrational modes and densification level of the ceramics. The outstanding microwave dielectric properties of $\varepsilon_r = 17.15$, $Q \times f = 34.355$ GHz, and $\tau_f = -22.5$ ppm/°C were obtained for the MCN ceramics sintered at 925 °C, which are results that hold promise for low temperature co-fired ceramic (LTCC) applications.

Keywords: MgCu$_2$Nb$_2$O$_8$ ceramics; crystal structure; annealing; microwave dielectric property

1. Introduction

Microwave dielectric ceramics (MWDC) are usually used as dielectric materials in the microwave frequency band (including UHF and SHF frequency band, 300 MHz~300 GHz), and they can be used to perform a variety of functions [1,2]. They are new functional ceramic materials developed in the last 20 years and are also the critical material for the production of microwave resonators and dielectric filters [3–5]. Microwave dielectric ceramics have attracted great attention because of their exceptional features, such as their high-quality, low microwave loss, and stable temperature performance [6,7]. Based on the original microwave ferrite, many researchers have greatly improved the formula and manufacturing process of microwave dielectric ceramics [8]. Microwave dielectric ceramics are suitable for manufacturing modern products, including navigation, communication, radar, household satellite TV receivers, and mobile phones. In pursuit of microwave circuits with high integration and reliability, they can also be used to make oscillators, filters, and frequency discriminators [9,10]. Along with the rapid development of microwave technology, much attention has been paid to studying microwave dielectric ceramics, which hold much potential for the future of microwave devices.

Along with the fast-growing development of fifth-generation mobile communication (5G), microwave ceramic filters have come to play a major role in the 5G base station filter due to their superior dielectric properties, which in turn has resulted in higher requirements for microwave dielectric ceramics [11,12]. Niobate ceramics such as RNb$_2$O$_6$ (R = Ca, Co, Cu, et al.) [13], R$_3$Nb$_2$O$_9$ [14], RMNb$_2$O$_8$ (M = Zr, Ti) [2], ATiNbO$_6$ (A = rare earth) [15], and ANbO$_4$ [16], have long been widely and deeply studied because of their excellent
microwave properties. Furthermore, the novel copper–niobate ACu$_2$Nb$_2$O$_8$ (A = Ni, Ca, Mg, Co, or Zn) ceramics have attracted great attention because of their optimal dielectric properties and low sintering temperature (Sr) for LTCC applications [17]. Yang [18] reported CaCu$_2$Nb$_2$O$_8$ ceramics that contained several phases and that showed outstanding microwave dielectric properties of $\varepsilon_r = 15.7, Q \times f = 28.700$ GHz and $\tau_f = –38.4$ ppm/°C, which are promising results for LTCC applications. MgCu$_2$Nb$_2$O$_8$ ceramics are less-studied, especially for their single-phase or multi-phase structure. We proposed the two-step sintering technique to prepare MgCu$_2$Nb$_2$O$_8$ microwave ceramics with optimal dielectric properties and investigated their phase composition, microstructure, and microwave dielectric characteristics. In this paper, the effects of synthesis conditions on phase composition, microstructure, crystal structure and microwave dielectric properties of MCN ceramics were carefully analyzed, and our results provide a valuable reference for MCN ceramics researchers.

2. Experimental

MgCu$_2$Nb$_2$O$_8$ ceramics were synthesized by the solid-phase reaction process with the use of high-purity oxides of MgO (98%), CuO (99%), and Nb$_2$O$_5$ (99.9%) produced by Shanghai Aladdin Biochemical Technology Co., Ltd. (Aladdin, Shanghai, China). First, the raw materials were mixed and ball-milled with deionized water and zirconia balls for 24 h. Then, the mixtures were calcined at 750 °C for 5 h and re-milled for 24 h. After this, the calcined powders were mixed with 6 wt% polyvinyl alcohol as a binder and pressed into cylinders of 15 mm × 7 mm. Finally, the pressed samples were sintered using the two-step sintering technique. The samples were initially sintered at temperatures between 875 °C and 1000 °C for 10 h to obtain an intermediate density, and then they were annealed at 800 °C for 4 h to obtain high density.

The phase composition was checked by X-ray diffraction (Aolong, AL-2700B, Dandong, China) with copper K$_\alpha$ radiation. The microstructure was analyzed via scanning electron microscope (Hitachi, S4800, Tokyo, Japan). The crystal structure of the MgCu$_2$Nb$_2$O$_8$ ceramics was verified through Raman spectroscopy (Renishaw, London, UK, 532 nm). The element valence state in the MgCu$_2$Nb$_2$O$_8$ ceramics was studied via X-ray photoelectron spectroscopy (VG Scientific, ESCALAB 250, Waltham, MA, USA). The apparent density of the ceramic system was acquired using the Archimedes method. The porosity and average grain size (AG) were estimated using ImageJ software (ImageJ.JS). A network analyzer (Agilent, N5230A, Santa Clara, CA, USA) was performed on the MCN ceramics to attain microwave dielectric properties over a temperature range of 25–85 °C [19].

3. Results and Discussion

The XRD patterns of MgCu$_2$Nb$_2$O$_8$ ceramics sintered at 875–1000 °C are shown in Figure 1. The MgNb$_2$O$_6$ phase (JCPDS #88–0708) was observed from the XRD analysis, and its structure was identified as the orthorhombic columbite-type structure in space group Pbcn [20]. Meanwhile, the diffraction peaks of CuO (JCPDS #48–1548) were also detected and identified as the monoclinic structure with space group C2/c [21]. Careful examination of the XRD patterns indicated that no other phases existed except these two phases. Therefore, it could be inferred that the MgCu$_2$Nb$_2$O$_8$ ceramics are multi-phase ceramics consisting of MgNb$_2$O$_6$ and CuO phases.

The Rietveld refinement was performed to further explore the structural characteristics of MgCu$_2$Nb$_2$O$_8$ ceramics, and the refined cell parameters of MgCu$_2$Nb$_2$O$_8$ ceramics sintered at the temperatures from 875 °C to 1000 °C were obtained by the GSAS software. The orthorhombic columbite MgNb$_2$O$_6$ and monoclinic CuO were introduced as individual phases in the refinement model, and their specific crystal structures are exhibited in Figure 2. Figure 3 displays the refinement patterns of MgCu$_2$Nb$_2$O$_8$ ceramics sintered at different temperatures in the range from 875 °C to 1000 °C. The refinement XRD patterns are in good agreement with the measured results, demonstrating that MgCu$_2$Nb$_2$O$_8$ ceramics are the multi-phase ceramics composed of MgNb$_2$O$_6$ and CuO phases. The crystallographic
parameters and reliability factors of MgCu$_2$Nb$_2$O$_8$ ceramics, including profile factors ($R_p$), weighted profile factors ($R_{wp}$), and goodness of fit values ($\chi^2$), are listed in Table 1. The results showed that all $R_p$ and $R_{wp}$ values obtained using GSAS software are below 10% and $R_p$ is less than $R_{wp}$, suggesting that the refinement data obtained by GSAS software are reliable.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of MgCu$_2$Nb$_2$O$_8$ ceramics sintered at different temperatures.

![Figure 2](image2.png)

**Figure 2.** The crystal structures of (a) orthorhombic columbite MgNb$_2$O$_6$ and (b) monoclinic CuO.

**Table 1.** Crystal structure information of the MgNb$_2$O$_6$ (p1) and CuO (p2) after refinement.

| $S_T$ (°C) | $a_{p1}$ (Å) | $b_{p1}$ (Å) | $c_{p1}$ (Å) | $V_{p1}$ (Å$^3$) | $W_{p1}$ | $a_{p2}$ (Å) | $b_{p2}$ (Å) | $c_{p2}$ (Å) | $V_{p2}$ (Å$^3$) | $R_{wp}$ | $R_F$ | $\chi^2$ |
|------------|--------------|--------------|--------------|----------------|----------|--------------|--------------|--------------|----------------|---------|-------|--------|
| 875        | 14.1865      | 5.7032       | 5.0325       | 407.168        | 73.05%   | 4.6889       | 3.4198       | 5.1313       | 81.164         | 5.95%   | 4.57% | 2.676  |
| 900        | 14.1827      | 5.7025       | 5.0306       | 406.855        | 77.43%   | 4.6889       | 3.4197       | 5.1291       | 81.110         | 5.95%   | 4.37% | 3.678  |
| 925        | 14.1857      | 5.7024       | 5.0324       | 407.081        | 77.12%   | 4.6874       | 3.4171       | 5.1266       | 80.991         | 5.5%    | 3.94% | 2.879  |
| 950        | 14.1750      | 5.6975       | 5.0289       | 406.146        | 76.58%   | 4.6880       | 3.4157       | 5.1253       | 80.941         | 5.37%   | 4.16% | 2.679  |
| 975        | 14.1612      | 5.6911       | 5.0232       | 404.835        | 76.43%   | 4.6819       | 3.4068       | 5.1194       | 80.543         | 5.97%   | 4.51% | 3.201  |
| 1000       | 14.1611      | 5.6914       | 5.0241       | 404.929        | 74.82%   | 4.6794       | 3.4087       | 5.1157       | 80.460         | 5.30%   | 4.11% | 2.386  |
Raman phonon modes can be used not only to analyze the crystal structure, but also to obtain the phase composition of the ceramic system. The Raman spectra of MgCu$_2$Nb$_2$O$_8$ ceramics sintered at different temperatures are shown in Figure 4a. Twelve Raman modes, located at 220, 264, 278, 295, 314, 344, 410, 485, 533, 634, 848 and 905 cm$^{-1}$, were detected. As for the MgNb$_2$O$_6$ phase reported by Wu [20], the weak peak at 220 cm$^{-1}$ is attributed to the O-Nb-O bending mode. The bands at 250–400 cm$^{-1}$ are identified as the stretching vibration of Nb-O bonds. For CuO, three Raman active optical phonons (Ag +2Bg) could be observed clearly from the Raman spectra. The peaks of 295, 344 and 634 cm$^{-1}$ are correspondent to the Ag, Bg and Bg modes, respectively, and it is consistent with the previous results [21]. Thus, Raman analysis also proves that Raman phonon modes are sensitive to not only the crystal structures but also to dielectric properties of the ceramics. As presented in Figure 4b for the A$_g$(MgNb$_2$O$_6$ or CuO) modes, the full width at half-maximum (FWHM) displays an opposite changing trend as that in $Q \times f$ value. Notably, the sample sintered at 925 °C possessed the weakest FWHM value, which was completely consistent with the results of ref. [22].

The chemical composition and element valence of MgCu$_2$Nb$_2$O$_8$ ceramics were studied by XPS analysis, and the resulted spectra are given in Figure 5. The survey XPS spectrum, as shown in Figure 5a, displays the presence of Mg 1s, Cu 2p, Nb 3d, O 1s, O KLL, Cu LMM, Mg KLL and C 1s, and it verifies the chemical purity of the MCN ceramics. The XPS data obtained from the sample were all corrected for charging effects with reference to the C1s peak fixed at 284.8 eV. Figure 5b shows the narrow scan XPS spectrum of Mg 1s for MCN ceramics. The peak of Mg 1s was at 1303.24 eV, corresponding to the characteristic spectrum of Mg with a valence of +2 [23]. The Cu 2p spectrum, as shown in Figure 5c, presented spin-orbit components of Cu 2p$_{1/2}$ and Cu 2p$_{3/2}$ at 962.24, 953.49, 943.59 and 933.44 eV, which were assigned to Cu$^{2+}$ [24]. The narrow scan XPS spectrum of Nb 3d for MCN ceramics is exhibited in Figure 5d, consisting of spin-orbit doublet peaks Nb 3d$_{3/2}$ and Nb 3d$_{5/2}$ at 209.34 and 206.59 eV ($\Delta = 2.75$ eV), respectively, which is in good agreement with the reported data [24].
agreement with the characteristic spectra of Nb$^{5+}$ in XPS [25,26]. The peak of O1s (O$_1$) for MCN ceramics shown in Figure 5e was at 529.69 eV, which was indexed to O$^{2-}$ [24,27]. In addition, it could be found that, besides the main peak, a shoulder (O$_2$) at 531–533 eV is evident in the O 1s core level and this component can be attributed to the hydrocarbonates formation at the sample surface [26]. The above analysis proved that the chemical states of Cu, Mg, Nb and O were +2, +2, +5 and −2, respectively.

![Figure 4](image_url)

**Figure 4.** (a) The Raman spectra of MgCu$_2$Nb$_2$O$_8$ ceramics; (b) The correlations between $Q \times f$ values and FWHM values.

![Figure 5](image_url)

**Figure 5.** XPS spectra of MgCu$_2$Nb$_2$O$_8$ ceramics sintered at 925 °C: (a) the survey spectrum, (b) Mg 1s, (c) Cu 2p, (d) Nb 3d, and (e) O 1s.

Figure 6 is the SEM images recorded for the MgCu$_2$Nb$_2$O$_8$ ceramics sintered at different temperatures in the range from 875 °C to 1000 °C. As observed in Figure 6a, the sample possessed a porous microstructure, and the average grain size is about 1.2 µm, indicating low density and insufficient sintering. It could be seen from Figure 6b, the grain growth is obvious, and the average grain size reached 1.59 µm. While, there were also many small grains in dense contact and the pores were eliminated gradually as compared to Figure 6a. As $S_T$ increased gradually to 925 °C, the samples presented compact microstructures with...
clear grain boundaries. In addition, the grain growth was further enhanced and some abnormal grains were obvious, meanwhile, the average grain size was increased to 2.02 µm.

In general, migration and diffusion of ions were beneficial to the grain growth at the proper sintering temperature. It is proved that the densification process of ceramic system by traditional solid-state ceramic route is largely determined by the migration and diffusion of ions, and proper sintering temperature could assist these processes [28]. Thus, the grain growth was enhanced gradually as ST increased. With further increasing ST, the abnormal grains in the samples become more than before, and it yields strong negative effects on the densification.

Figure 6. SEM images and grain size distribution (inset figure) of MgCu2Nb2O8 ceramics sintered at
(a) ST = 875 °C, (b) ST = 900 °C, (c) ST = 925 °C, (d) ST = 950 °C, (e) ST = 975 °C, and (f) ST = 1000 °C.

In order to further determine compositions of the abnormal grains, EDS was developed to explore the large grains (spots A, C and E) and small grains (spots B, D and F), as shown in Table 2. Notably, spots A, C and E in the large grains displayed Mg:Nb:O elemental molar ratios of 11.81:22.38:65.81, 11.93:22.66:65.41 and 12.06:23.71:64.23 respectively, which are close to that in MgNb2O6. And the elemental molar ratios of Cu:O in the small grains (spots B, D and F) were 52.12:47.88, 50.87:49.13 and 51.59:48.41 respectively, similar to that in CuO. Combining with the XRD patterns shown in Figure 1, it turned out that the large grains are MgNb2O6 and the small grains are CuO.

Table 2. The EDS results of MgCu2Nb2O8 ceramics corresponding to the abnormal grains.

| Spot | Atom Fraction(%) |
|------|------------------|
|      | Mg   | Cu   | Nb   | O    |
| A    | 11.81| 22.38| 65.81|
| B    | 52.12| 47.88|
| C    | 11.93| 22.66| 65.41|
| D    | 50.87| 49.13|
| E    | 12.06| 23.71| 64.23|
| F    | 51.59| 48.41|
The relations between the apparent density, relative density and porosity of the MCN ceramics sintered at the temperatures from 875 °C to 1000 °C can be observed in Table 3, which indicates that the apparent density and relative density first increase and then decrease with an increase of sintering temperature, while the porosity shows an opposite varying trend as compared to that of apparent density. Moreover, the sample prepared at the sintering temperature of 925 °C presented the largest apparent density of 5.519 g/cm³, corresponding to the smallest value of 1.13% for porosity. With the increase of S_T, the apparent density firstly increased to the peak value of 5.519 g/cm³ at S_T = 925 °C, which was primarily accused to the improvement of densification caused by the appropriate sintering temperature, as shown in Figure 6c. However, when S_T > 925 °C, with the further increase of S_T, the apparent density showed a downward trend and accompanied by the increase of porosity. Thus, combining with Figure 6d–f, this phenomenon was due to the loose microstructures caused by the formation of abnormal grain. In general, porosity greatly affected the apparent density of MCN ceramics, which might be attributed to the dense and uniform microstructure [29].

Table 3. The apparent density, theory density, relative density and porosity of MgCu_2Nb_2O_8 ceramics sintered at different temperatures.

| S_T (°C) | \( \rho \text{apparent} \) (g/cm³) | \( \rho \text{p1} \) (g/cm³) | \( \rho \text{p2} \) (g/cm³) | \( \rho \text{theory} \) (g/cm³) | \( \rho \text{relative} \) (%) | Porosity (%) |
|---------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-----------------------------|-------------|
| 875     | 5.161                         | 4.994                         | 6.510                         | 5.883                         | 87.73                       | 15.63       |
| 900     | 5.324                         | 5.029                         | 6.481                         | 5.796                         | 91.86                       | 5.42        |
| 925     | 5.519                         | 5.026                         | 6.483                         | 5.803                         | 95.11                       | 1.13        |
| 950     | 5.467                         | 5.022                         | 6.488                         | 5.815                         | 94.02                       | 2.83        |
| 975     | 5.386                         | 5.025                         | 6.506                         | 5.828                         | 92.42                       | 4.12        |
| 1000    | 5.192                         | 5.021                         | 6.517                         | 5.865                         | 88.53                       | 8.67        |

Figure 7 presents the dielectric constant (\( \varepsilon_r \)), quality factor (\( Q \times f \)), temperature coefficient of resonant frequency (\( \tau_f \)), and dielectric loss (\( \tan \delta \)) of the MgCu_2Nb_2O_8 ceramics sintered at the temperatures in the range from 875 °C to 1000 °C. Careful examination of the curves reveals that \( \varepsilon_r \) displays a homologous varying trend as that of apparent density shown in Table 3. Generally speaking, the \( \varepsilon_r \) is mainly dependent on the phase composition and densification of the samples [22]. In this study, \( \varepsilon_r \) starts to increase initially and reaches the peak value of 17.15 at 925 °C, which is attributed to the enhancement of densification caused by the appropriate sintering temperature. To an extent, the densification of sintered ceramics has a dominant role to increase the dielectric constant, which might be ascribed to the dense and uniform microstructure at high densities. At S_T > 925 °C, the dielectric constant starts to decline, and it is due to the decrease of densification caused by the expansion in abnormal grains. Combining the results shown in Figures 6 and 7a, the expansion in abnormal grains should be responsible for the decline in dielectric constant.

Figure 7b,c display the correlations between \( Q \times f \) value and dielectric loss (\( \tan \delta \)) in the sintered MgCu_2Nb_2O_8 ceramics. Analysis on the \( Q \times f \) and \( \tan \delta \) indicated that the \( Q \times f \) value shows an opposite varying trend as that of \( \tan \delta \). As for \( Q \times f \) value, it first increase to the peak value of 34.355 GHz at S_T = 925 °C, and then declines with the increase of S_T. As is well known, the \( Q \times f \) value is influenced by a lot of factors, such as dielectric loss, densification, crystal defects, second phases and the average grain size [28,30]. Moreover, dielectric loss is not only related to intrinsic loss because of the lattice vibration mode, but extrinsic loss, including cation ordering degree, grain size, second phases and defects [31]. When 875 °C ≤ S_T ≤ 925 °C, the \( Q \times f \) value presents an upward trend. For one thing, the increase is derived from the decreased intrinsic loss owing to the deteriorated FWHM value, as shown in Figure 4b. For another, the increased densification caused by the proper sintering temperature is beneficial to the enhancement of \( Q \times f \) value. It was clear that the \( Q \times f \) value increases from 23.230 GHz to 34.355 GHz when the microstructures get improved, and dense microstructure generally corresponds to higher \( Q \times f \) value [32].
While the decline in $Q \times f$ value was attributed to the increased intrinsic loss and poor densification due to the abnormal grain grown. As depicted in Figure 7c, the dielectric loss declined firstly, and acquired the minimum value of $3.436 \times 10^{-4}$ at $S_T = 925 ^\circ C$, then started to increase with increasing $S_T$, showing an opposite varying trend as that of $Q \times f$ value. Combining with Figures 6 and 7, it could be seen that the $Q \times f$ value was primarily determined by the dielectric loss and compactness of sintered ceramics [33,34]. Careful examination of the Figure 7 presented that proper sintering temperature led to the elevation of $Q \times f$ values from 23.230 GHz to 34.355 GHz as well as the decrease of dielectric loss from $4.740 \times 10^{-4}$ to $3.436 \times 10^{-4}$. Therefore, the increased densification had a dominant role to improve $Q \times f$ value and reduce dielectric loss. Furthermore, the two-step sintering technique was conducive to reducing the internal stress during the sintering process, and thus improving the $Q \times f$ value [35]. Moreover, the two-step sintering technology could enable microwave dielectric ceramics to be densified at a temperature lower than the normal sintering temperature, and obtained excellent dielectric properties [11]. Therefore, due to the advantages of two-stage sintering technology, we improved the sintering scheme properly in this work to attenuate the internal stress under the condition of obtaining high-density ceramic samples. In fact, in this work, the two-step sintering technique has greatly improved the microwave dielectric properties of the samples. As presented in Figure 7b, the $Q \times f$ value of the sintered ceramics was significantly improved, reaching the maximum value of 34.355 GHz.

Figure 7. Microwave dielectric properties of MgCu$_2$Nb$_2$O$_8$ ceramics sintered at different temperatures: (a) $\varepsilon_r$, (b) $Q \times f$, (c) $\tau_f$, and (d) $\tan\delta$.

The $\tau_f$ values of MgCu$_2$Nb$_2$O$_8$ ceramics sintered at the temperature range from 875 °C to 1000 °C are ascribed in Figure 7d. It is deserved to note that the $\tau_f$ value initially increases to $-22.5$ ppm/°C at $S_T = 925$ °C, and then declines to $-48.69$ ppm/°C at $S_T = 1000$ °C, which agrees with the varying trend of apparent density. As we know, the $\tau_f$ value is correlated with the phase composition, degree of densification and distortion of oxygen octahedra [36,37]. Thus, associating Figure 7d with Table 3, it is obvious that the increased $\tau_f$ value is primarily determined by the enhancement in densification before $S_T$ increases.
to 925 °C. At further increasing $S_T$ with $S_T > 925$ °C, the low densification contributes to decreasing the $\tau_f$ value. The $\tau_f$ value exhibits an upward tendency owing to the decreased densification, which is due to the abnormal grain growth caused by the higher sintering temperature.

4. Conclusions
In this work, the phase composition, microstructure, crystal structure and microwave dielectric properties of MCN ceramics were investigated as a function of the sintering temperature. MCN ceramics were confirmed to be multi-phase ceramics by XRD and Raman analysis. The SEM analysis showed that the dense microstructures appeared at 925 °C. As $S_T$ increased from 875 °C to 925 °C, the grain growth was obvious, and the $Q \times f$ value, $\epsilon_r$ value and $\tau_f$ value increased from 23.230 GHz to 34.355 GHz, from $-59.01$ ppm/°C to $-22.5$ ppm/°C and from 16.12 to 17.15, respectively, and the dielectric losses and porosity declined form $4.740 \times 10^{-4}$ to $3.436 \times 10^{-4}$ and from 15.63% to 1.13%, respectively. However, when $S_T$ was further increased with $S_T > 925$ °C, the $Q \times f$ value, $\tau_f$ value and $\epsilon_r$ declined gradually, while the dielectric losses and porosity increased accordingly. Thus, the dielectric properties such as $\epsilon_r$, $Q \times f$ and $\tau_f$ depended very strongly on the densification and microstructure of the samples, which was closely related to the sintering temperature. The sample prepared at the sintering temperature of 925 °C presented the largest values of $Q \times f$ value and apparent density, 34.355 GHz and 5.519 g/cm$^3$, respectively. Correspondingly, the porosity decreased from 15.63% to 1.13% as the sintering temperature increased form 875 °C to 925 °C, and then increased with the further increased sintering temperature. The MCN ceramics prepared at the sintering temperature of 925 °C, and then annealed at 800 °C displayed dense microstructures, and possessed outstanding microwave dielectric properties of $\epsilon_r = 17.15$, $Q \times f = 34.355$ GHz, and $\tau_f = -22.5$ ppm/°C. These results imply that the MCN ceramics are suitable candidates for application in LTCC devices.

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