Microwave Sintering and Microwave Dielectric Properties of (1-\(x\))Ca\(_{0.61}\)La\(_{0.26}\)TiO\(_3\)-\(x\)Nd(Mg\(_{0.5}\)Ti\(_{0.5}\))O\(_3\) Ceramics

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Abstract: The (1-\(x\))Ca\(_{0.61}\)La\(_{0.26}\)TiO\(_3\)-\(x\)Nd(Mg\(_{0.5}\)Ti\(_{0.5}\))O\(_3\) [(1-\(x\))CLT-xNMT, \(x = 0.35–0.60\)] ceramics were prepared via microwave sintering. The effects of sintering temperature and composition on the phase formation, microstructure, and microwave dielectric properties were investigated. The results show that the microwave sintering process requires a lower sintering temperature and shorter sintering time of (1-\(x\))CLT-xNMT ceramics than conventional heating methods. All of the (1-\(x\))CLT-xNMT ceramics possess a single perovskite structure. With the increase of \(x\), the dielectric constant (\(\varepsilon\)) shows a downward trend; the quality factor (\(Q_f\)) drops first and then rises significantly; the resonance frequency temperature coefficient (\(\tau_f\)) keeps decreasing. With excellent microwave dielectric properties (\(\varepsilon = 51.3, Q_f = 13,852 \text{ GHz}, \tau_f = -1.9 \times 10^{-6}/\text{°C}\)), the 0.65CLT-0.35NMT ceramic can be applied to the field of mobile communications.

Keywords: (1-\(x\))CLT-xNMT ceramics; microwave sintering; microwave dielectric properties; lattice constant

1. Introduction

With the advent of the 5G era, microwave dielectric ceramics attract more and more attention [1]. Microwave dielectric ceramics can not only be used as insulating substrates material in microwave circuits, also as the key basic material to fabricate dielectric resonators, dielectric filters, dielectric oscillators, phase shifters, microwave capacitors, etc., for microwave communication technology [2]. Therefore, microwave components play an increasingly important role in miniaturization, integration, and cost reduction of modern communication tools [3]. The dielectric materials with high dielectric constant, high \(Q_f\) value, near-zero temperature coefficient of resonance frequency, and low sintering temperature are strong candidates for 5G technology [4].

The Ca\(_{0.61}\)La\(_{0.26}\)TiO\(_3\) (CLT) ceramic, with typical perovskite structure, is characterized by a high dielectric constant (\(\varepsilon = 120\)) and a high quality factor (\(Q_f = 10,700 \text{ GHz}\)), but a very high positive resonant frequency temperature coefficient (\(\tau_f = 304 \times 10^{-6}/\text{°C}\)) [5]. The Nd(Mg\(_{0.5}\)Ti\(_{0.5}\))O\(_3\) (NMT) ceramic also has a perovskite structure with \(Q_f\) value of 36,900~151,000 GHz, the \(\varepsilon\) value is only 25~26, and the \(\tau_f\) is a large negative value (\(-72 \times 10^{-6}~47 \times 10^{-6}/\text{°C}\)) [6,7]. The microwave dielectric ceramics with moderate \(\varepsilon\), high \(Q_f\), and \(\tau_f\) of close to zero can be obtained, by combining Ca\(_{0.6\text{Sr}0.4}\)TiO\(_3\) or CLT with NMT ceramics [8,9]. However, preparing the CLT-NMT dielectric ceramics by conventional sintering requires excessively high sintering temperature and long sintering time (1650 °C, 3 h; according to our previous work). A small amount of CuO, ZnO and other sintering aids can be added to reduce the sintering temperature [10,11], but it is difficult to avoid the introduction of the second phase and reduction of the microwave dielectric properties.

As an efficient sintering method for materials, microwave sintering can effectively reduce the sintering temperature, increase the sintering rate, and promote the grain re-
finement of ceramics, thus improving the microwave dielectric properties \cite{12,13}. Up to now, there have been no reports on the preparation of the (1−x)CLT-xNMT ceramics by microwave sintering. In this work, the (1−x)Ca0.61La0.26TiO3-xNd(Mg0.5Ti0.5)O3[(1−x)CLT-xNMT, x = 0.35–0.60] ceramics were prepared by microwave sintering and an in-depth study was conducted of the effects of sintering process and component ratio on its phase composition, microstructure, and microwave dielectric properties.

2. Materials and Methods

The (1−x)Ca0.61La0.26TiO3-xNd(Mg0.5Ti0.5)O3[(1−x)CLT-xNMT, x = 0.35–0.60] ceramics were prepared by the solid-state reaction method. The ingredients were proportioned according to the stoichiometric ratio. High-purity CaCO3 (99.8%, Langfang Pengcai Fine Chemical, Langfang, China), La2O3 (99.9%, Jiangxi Golden Century Advanced Materials Co., Ltd., Nanchang, China), Nd2O3 (99.9%, Jiangxi Golden Century Advanced Materials Co., Ltd., Nanchang, China), MgO (99.99%, Jiangxi Golden Century Advanced Materials Co., Ltd., Nanchang, China), and TiO2 (99.5%, Shanghai Jianglu Titanium Dioxide Chemical, Shanghai, China) powders were mixed by ball mill for 8 h and then dried for 24 h, ground, sieved (200 mesh), and calcined (CLT at 1200 °C for 3 h, NMT at 1400 °C for 3 h, respectively). Then, the calcined CLT and NMT powders were mixed by ball mill for 8 h, dried for 24 h, and sieved (200 mesh). After added 10 wt % of polyvinyl alcohol solution (PVA, 10%) as a binder, the mixed powders were pressed into columns with a diameter of 13 mm and a thickness of 2–6 mm and then these specimens were heated at 600 °C for 1 h to remove the PVA. Finally, these specimens were sintered in air in a microwave sintering furnace (Changsha Longtai Technology Co., Ltd., Changsha, China) (1475–1575 °C, 30 min).

The density was measured by the Archimedes method. After crushed and ground, the phase analysis of (1−x)CLT-xNMT samples was conducted by X-ray diffraction (XRD, Bruker, Bremen, Germany). After the samples were polished and cleaned with ultrasonic cleaner, etched at 50 °C lower than sintering temperature for 30 min, their microstructures were observed by a scanning electron microscope (SEM, FEI, Hillsboro, OR, USA).

To measure the dielectric properties, polished (1−x)CLT-xNMT ceramic cylindric specimen was put in a metal cavity of vector network analyzer (N5230A, Agilent Technologies, Loveland, CO, USA), in which high-frequency electromagnetic field can keep oscillating without radiation loss. The dielectric constant (ε) and quality factor (Q) were measured at 25 °C. The temperature coefficient of resonant frequency (τf) was calculated by using the Equation (1):

\[
\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}
\]

where \(f_1\) and \(f_2\) represent the resonant frequency at \(T_1\) (25 °C) and \(T_2\) (85 °C), respectively.

3. Results and Discussion

3.1. Sintering Characteristics

The influence of sintering temperature on the density (\(\rho\)) of (1−x)CLT-xNMT ceramics is shown in Figure 1. With the increase of sintering temperature (\(T\)), the \(\rho\) presents the tendency of increasing first. However, with the further increase of \(T\), the \(\rho\) tends to decrease. It may be attributed to oversintering.

The relationship between the \(\rho\) and relative density (\(\rho_r\)) of the (1−x)CLT-xNMT ceramic with x is shown in Figure 2. It can be seen intuitively that the \(\rho\) increases with the increase of x, up to 5.457 (x = 0.60), mainly because the density of NMT ceramic (6.16 g/cm³) is higher than that of CLT ceramic (4.51 g/cm³). The \(\rho_r\) is all higher 95.5% with slightly floating and reaches 96.9% when x = 0.50.
Figure 1. Bulk density of the (1–x)CLT-xNMT ceramics.

Figure 2. The curves of bulk density and relative density with the composition of (1–x)CLT-xNMT ceramics.

3.2. Phase and Microstructure

The XRD patterns of the (1–x)CLT-xNMT ceramics are illustrated in Figure 3. The diffraction peak positions are almost completely overlapped in the composition range of x = 0.35–0.60, indicating a perovskite structure without second phase. It should be pointed out that superlattice diffraction peaks were observed when x = 0.40 and 0.45. The enlarged part of 32.1–33.3°, as shown in the upper right corner of Figure 3, indicates that the main diffraction peaks of (1–x)CLT-xNMT ceramics shift toward low angle with the increase of x. It suggests the increasing lattice constant of the identified perovskite structure.

Figure 3. XRD patterns of the (1–x)CLT-xNMT ceramics.
The lattice constant \((a, b, c)\) and unit cell volume \(V_u\) of \((1-x)\)CLT-xNMT ceramics are shown in Figure 4. Both lattice constant and unit cell volume gradually increase with the increasing \(x\), which is in accordance with the XRD analysis. This trend depends on two factors: the decreasing vacancy concentration in \(A\)-site, the increasing \(Mg^{2+}\) content \((r(Mg^{2+}) > r(Ti^{4+}), r(Mg^{2+}) = 0.072\ \text{nm}, r(Ti^{4+}) = 0.061\ \text{nm when CN} = 6)\) in \(B\)-site [14], with the increase of NMT content in \((1-x)\)CLT-xNMT ceramics.

![Figure 4. Lattice constant and unit cell volume of the \((1-x)\)CLT – xNMT ceramics.](image)

SEM images of the \((1-x)\)CLT-xNMT ceramics \((1550\ \text{°C}, 30\ \text{min})\) are presented in Figure 5. When \(x \leq 0.55\), the grain size \((10-30\ \mu m)\) is relatively uniform and change slightly with the increase of NMT content. When \(x = 0.60\), the grain size \((20-50\ \mu m)\) is significantly larger than that of the rest composition. When \(x < 0.60\), strip-shaped grains can be observed, which is similar to the CaTiO\(_3\)-La\((Mg_{0.5}Ti_{0.5})\) ceramics [15].

![Figure 5. SEM images of the \((1-x)\)CLT-xNMT ceramics \((1550\ \text{°C}, 30\ \text{min})\): (a) \(x = 0.35\), (b) \(x = 0.40\), (c) \(x = 0.45\), (d) \(x = 0.50\), (e) \(x = 0.55\), (f) \(x = 0.60\).](image)
3.3. Microwave Dielectric Properties

The relationship between dielectric constant ($\varepsilon$) and composition of the (1–x)CLT-xNMT ceramics is illustrated in Figure 6. With the increase of $x$, the $\varepsilon$ gradually decreases from 51.3 to 36.4 because the $\varepsilon$ of NMT (~24) is much lower than that of CLT (~120). To evaluate the influence of porosity ($p$) on the $\varepsilon$, the theoretical dielectric constant ($\varepsilon_{th}$) of (1–x)CLT-xNMT ceramics can be calculated according to the following equation [16,17]:

$$\varepsilon_{th} = \frac{\varepsilon}{(1 - \frac{3p(\varepsilon - 1)}{2\varepsilon + 1})}$$

(2)

where $\varepsilon_{th}$ is the dielectric constant of a theoretically fully dense ceramic, $\varepsilon$ is the measured dielectric constant, $p$ is the porosity ($p = 100\% - \rho_r$). Furthermore, Equation (2) can be simplified as follows due to $\varepsilon \gg 1$:

$$\varepsilon_{th} = \frac{\varepsilon}{1 - 1.5p}$$

(3)

As shown in Figure 6, the $\varepsilon_{th}$ of (1–x)CLT-xNMT ceramics decreases from 54.2 to 38.3 with the increase of $x$. It indicates an improvement space of 4.9~6.4%.

The $Qf$ value of the (1–x)CLT-xNMT ceramics is presented in Figure 7. It ascends from 13,852 GHz ($x = 0.35$) to 17,148 GHz ($x = 0.40$) and then drops to 8482 GHz ($x = 0.45$) and finally climbs to 32,637 GHz ($x = 0.60$). Generally, the appearance of superlattice diffraction peaks is related to the 1:1 ordering of Mg$^{2+}$ and Ti$^{4+}$ [15], which often affects the dielectric loss and then $Qf$. The dielectric loss decreases with increasing of ions’ degree of order, but increases with attenuation of ions’ phonon mode. As $x$ increases to 0.40, the ions’ degree of order constantly deepens and the phonon mode attenuates slightly, which results in an increase of $Qf$. When $x$ climbs to 0.45, the ions’ degree of order continues to deepen, but the phonon mode attenuates intensively, which leads to a decrease in $Qf$. Later, the further increase of $x$ transforms the (1–x)CLT-xNMT ceramics from a CLT-based ordered solid solution to an NMT-based ordered solid solution, decreasing dielectric loss, and increasing the $Qf$ value to 32,637 GHz ($x = 0.60$).
As shown in Figure 6, the ε and εth of the (1–x)CLT-xNMT ceramics. 

Similarly, the effect of porosity (p) on the Qf value (with 10^3–10^4 GHz order of magnitude) can be evaluated by the following equation [18]:

\[ Q = Q_0(1 - 1.5p) \]  

where \( Q_0 \) is the intrinsic quality factor, and \( p \) is the porosity. The results suggest that an improvement space of 503–1741 GHz.

The temperature coefficient of resonance frequency (\( \tau_f \)) and tolerance factor (\( t \)) of the (1–x)CLT-xNMT ceramics are shown in Figure 8. The relationship between the \( \tau_f \) and temperature coefficient of dielectric constant (\( \tau_c \)) and linear expansion coefficient (\( \alpha_L \)) can be identified as follows [19,20]:

\[ \tau_f = -\frac{1}{2} \tau_c - \alpha_L \]  

where the \( \alpha_L \) of ceramics is 6–10 × 10^{-6}/°C [21]. Therefore, the value of the \( \tau_f \) depends on the \( \tau_c \).

In 1926, Goldschmidt [22] initially proposed the tolerance factor (\( t \)) to evaluate the stability of crystal structure. As to perovskite structure (ABO₃), the \( t \) can be calculated according to the following equation [23]:

\[ t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \]  

where \( R_A, R_B \) and \( R_O \) are the radius of A-site ions, B-site ions and O^{2-}, respectively. The effective ionic radius from Shannon [14] were used to calculate the \( t \) of (1–x)CLT-
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1 means greater tilt degree [23]. The work, microwave sintered 0.65CLT-0.35NMT ceramics (without sintering additive, 1550 ◦C) and shorter sintering time (30 min). Chen et al. [9] prepared 0.40Nd(Mg0.5Ti0.5)O3-0.60Ca0.6La0.8/3TiO3 (with 1 wt % B2O3 as sintering additive) ceramics via conventional sintering (1375 ◦C, 3 h) with excellent microwave dielectric properties: ε = 49, Qf = 13,000 GHz, τf = 1 × 10−6/◦C. As compared to Chen’s work, microwave sintered 0.65CLT-0.35NMT ceramics (without sintering additive, 1550 ◦C, 30 min) also possesses similar microwave dielectric properties: ε = 51.3, Qf = 13,852 GHz, τf = −1.9 × 10−6/◦C.

4. Conclusions

The (1−x)Ca0.61La0.26TiO3−xNd(Mg0.5Ti0.5)O3[x = 0.35–0.60, (1−x)CLT-xNMT] ceramics were prepared by microwave sintering. The effects of sintering process and component distribution compare on its phase composition, microstructure, and microwave dielectric properties were investigated. Microwave sintering can effectively reduce the sintering temperature and the sintering time. The (1−x)CLT-xNMT ceramics have formed a perovskite structure. As x increases, the ε shows a downward trend, the Qf first drops to 8482 GHz and then rises to 32,637 GHz, and the τf keeps decreasing. When x = 0.35, the comprehensive microwave dielectric performance is: ε = 51.3, Qf = 13,852 GHz, τf = −1.9 × 10−6/◦C (1550 ◦C, 30 min). The (1−x)CLT-xNMT ceramics can be applied to the field of mobile communications.

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