

Study on the $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ Microwave Dielectric Ceramics

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Abstract: The microwave dielectric properties of the $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ (MZCNT) system were investigated. The system was prepared using a conventional solid-state ceramic route. The objective of the present work is to compensate for the negative temperature coefficient of resonant frequency (τ_f) of $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ by the addition of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$. The microwave dielectric properties are strongly correlated with the sintering temperature and the composition. Very dense MZCNT ceramics were synthesized by sintering at 1250°C, when sintered at temperatures above 1300°C, the decomposition of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ and evaporation of Zn resulted the decrease in density and degradation in dielectric properties. With increasing $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$, the dielectric constant (ϵ_r) increased and the quality factor $Q \times f$ decreased. For practical application, 0.87 $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - 0.13(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ceramics sintered at 1250°C with a dielectric constant $\epsilon_r \sim 24.3$, a $Q \times f$ value of 34000GHz and a temperature coefficient of resonance frequency (τ_f) of $-9 \times 10^{-6}/^\circ\text{C}$ is proposed in this paper.

Key words: $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ceramics; dielectric constant; quality factor; temperature stable resonant frequency

Microwave dielectric ceramics are important materials used in microwave devices such as resonators, filters and oscillators in microwave communication systems^[1]. For a good microwave dielectric ceramics, three dielectric characteristics should be satisfied, which are high dielectric constant (ϵ_r) to reduce the size of devices, high quality factor ($Q \times f$) for achieving prominent frequency selectivity and stability, and a near zero temperature coefficient of resonance frequency (τ_f)^[2] for temperature stability, respectively.

MgTiO₃-based ceramics is one of the leading dielectric materials for microwave frequency applications. In the past, CaTiO₃ or SrTiO₃ were incorporated to adjust temperature coefficient of resonance frequency of MgTiO₃-based ceramics^[3,4]. Recently, Li *et al*^[5] reported that through partial replacement of Mg by Zn, the $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ ceramics with ilmenite-type structure possesses good dielectric characteristics ($\epsilon_r \sim 18.6$, $Q \times f \sim 90000\text{GHz}$ and $\tau_f \sim -50 \times 10^{-6}/^\circ\text{C}$). Moreover, $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ was another important microwave dielectric ceramic, which shows a positive τ_f value of $213 \times 10^{-6}/^\circ\text{C}$ associated with a high ϵ_r of 109 and a $Q \times f$ value of 17600GHz^[6]. In order to achieve near zero τ_f value, $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ was introduced in $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ and a ceramic system of

$(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ was prepared. The resultant microwave dielectric properties were analyzed based upon the sintering properties, X-ray diffraction (XRD) patterns and microstructures of the ceramics. The correlation between the microstructure and the $Q \times f$ value was also investigated.

1 Experimental

High-purity oxide powders (> 99.9%) MgCO₃, Nd₂O₃, ZnO, TiO₂ and CaCO₃ were weighed and mixed for 6 h with distilled water. These powders were used as raw materials according to the desired stoichiometry of $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ and $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$, respectively. Then the two mixed powders were calcined at 1100°C for 3h to produce $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ and $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ respectively and mixed according to the composition of $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ($x = 0.11 - 0.19$) and re-milled for 6h. After being dried, the resultant mixed powder were pressed into pellets of 11mm in diameter and 5mm in thickness under a pressure of 300MPa, and then were sintered at 1200 - 1350°C for 4h.

The microstructures of the sintered samples were observed by scanning electron microscope (SEM) and

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energy dispersive spectroscopy (EDS). X-ray power diffraction (XRPD) data were collected for phase identification using $\text{CuK}\alpha$ radiation. The bulk density of the samples was measured by the Archimedes method. The dielectric properties of the samples at microwave frequency were measured by the modified Hakki and Coleman's method in the TE011 mode using a network analyzer^[7-8]. τ_f was evaluated in the temperature range from 20 to 80°C.

2 Results and Discussion

2.1 Sintering properties

Figure 1 shows the bulk density of $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ceramics sintered at different temperatures. With the increase of sintering temperature, the bulk density reaches up to a maximum at 1250°C and thereafter slightly decreased. The total porosity was accordingly minimal at 1250°C. Densified ceramics can be obtained when sintered at 1250–1300°C. The decrease of density at 1300°C and

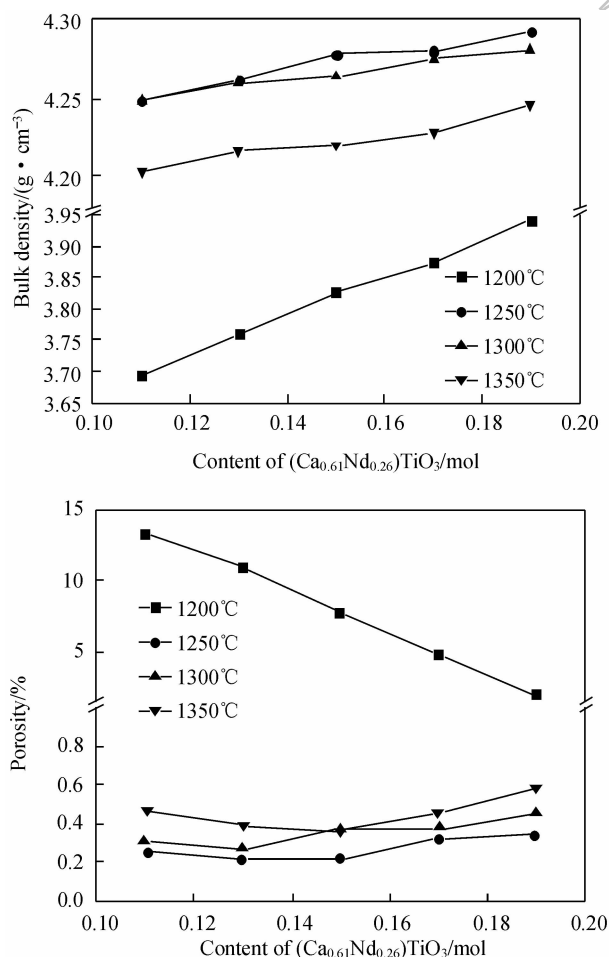


Fig. 1 Bulk density and porosity of $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics system sintered at different temperatures

1350°C as compared to 1250°C may result from the decomposition of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ as observed in Fig. 2 and the evaporation of Zn at high temperatures ($>1300^\circ\text{C}$)^[9]. Bulk density of that materials was also influenced by the composition and increased with the increase of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ content, which possesses a higher density than $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ ^[10].

2.2 Phase composition

XRD patterns of $0.87(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - 0.13(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ceramics sintered at different temperatures for 4h are shown in Fig. 2. It can be seen that when the materials sintered at 1200°C and 1250°C, $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ (can be indexed as MgTiO_3) and $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ are the main phases and small amount of MgTi_2O_5 was also identified when the materials sintered at 1300°C and 1350°C, which is difficult to be completely eliminated in the mixed oxide route. However, when sintered at 1300°C and 1350°C, the phase composition became complicated. Owing to the decomposition of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ into $\text{Ca}_3\text{Ti}_2\text{O}_7$ and NdTiO_3 at temperature above 1300°C, $\text{Ca}_3\text{Ti}_2\text{O}_7$ and NdTiO_3 apart from $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ and $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ also existed in the materials.

2.3 Microstructure characterization

The SEM micrographs of $0.87(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - 0.13(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ceramics sintered at different temperatures are illustrated in Fig. 3. The grain size of the materials slightly increased with arising sintering temperature and very dense materials with uniform grain size and morphology was obtained. The EDS patterns of $0.87(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - 0.13\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics sintered at 1250°C are shown in the Fig. 4. EDS analysis of Fig. 3 (b) indicated that the grain A and B were

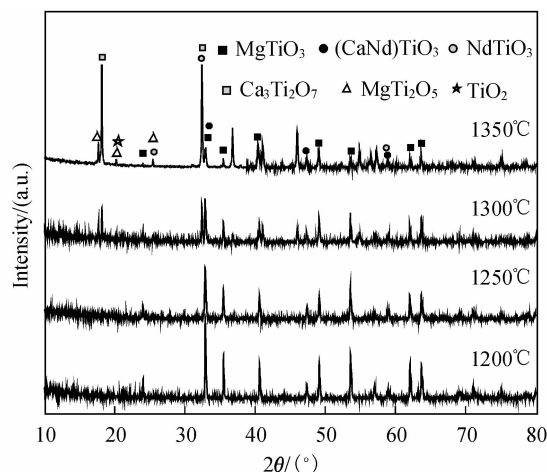


Fig. 2 XRD patterns of $0.87(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - 0.13\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics sintered at different temperatures for 4 h

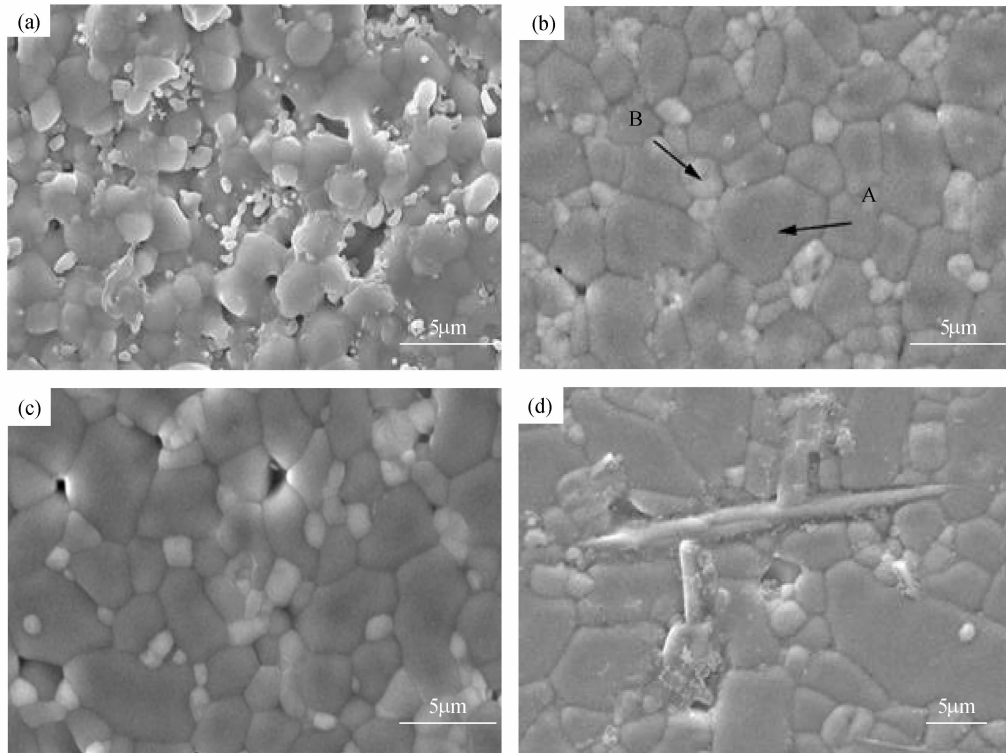


Fig. 3 SEM micrographs of $0.87(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - 0.13\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics sintered at different temperatures (a) 1200°C; (b) 1250°C; (c) 1300°C; (d) 1350°C

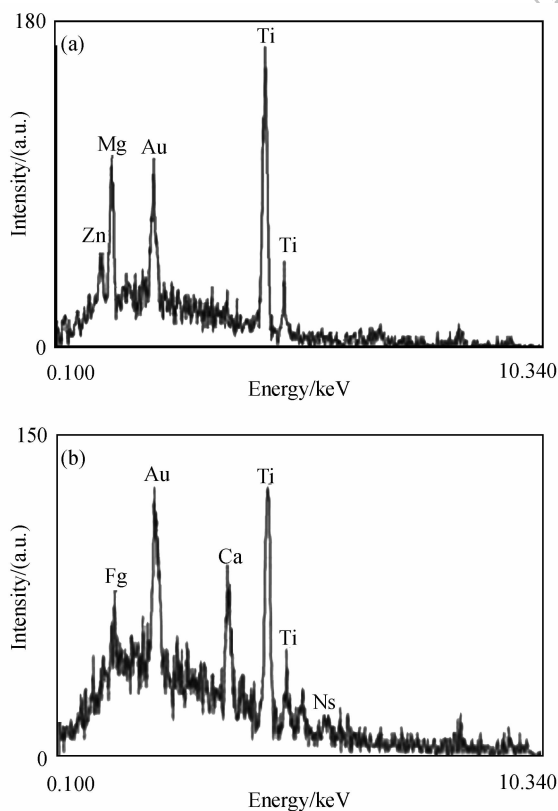


Fig. 4 EDS patterns of $0.87(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - 0.13\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics in Fig. 3 (b) (a) A Point; (b) B Point

$(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ and $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ respectively, which further verified the $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ system. However, rapid grain growth was observed when sintering temperature is higher than 1300°C. Some rod-shaped grains appeared in Fig. 3 (d).

2.4 Microwave dielectric properties

Figure 5 demonstrates the dielectric constant of the $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ceramics sintered at different temperatures. Variation of the ϵ_r value was consistent with that of density and the maximum dielectric constant was obtained for each composition when sintered at 1250 – 1350°C. As can be expected from mixing rule, the dielectric constant increased from 23.6 to 27.5 as the content of $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ increased from 0.11 to 0.19, owing to a much higher ϵ_r value of $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ than $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$. It also suggests an ϵ_r -tunable system through the control of the x value. The quality factor value ($Q \times f$) of $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics sintered at different temperatures are shown in Fig. 6. Many factors are believed to affect the microwave dielectric loss which consists of intrinsic loss and extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by the second phases, oxygen vacancies

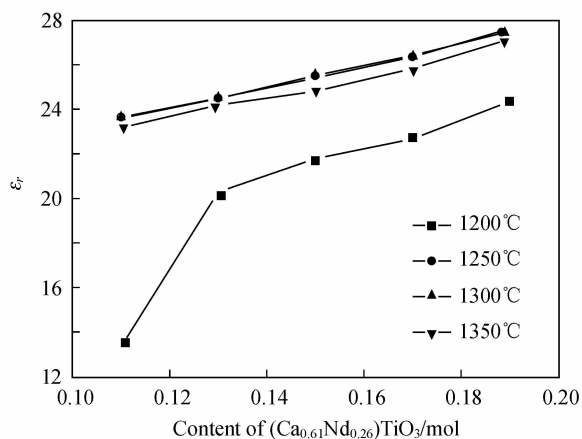


Fig. 5 ε_r value of $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics system sintered at different temperatures

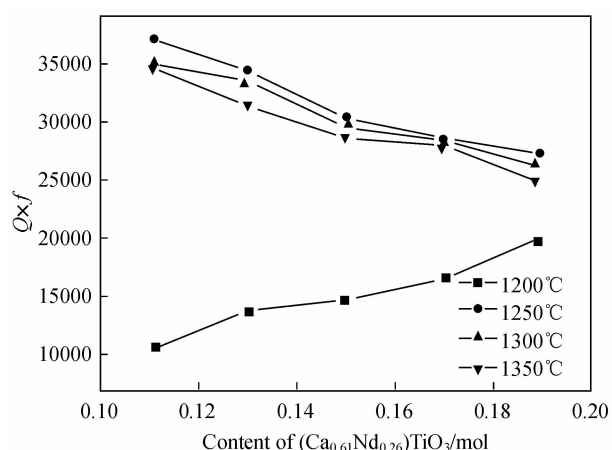


Fig. 6 $Q \times f$ value of $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics system sintered at different temperatures

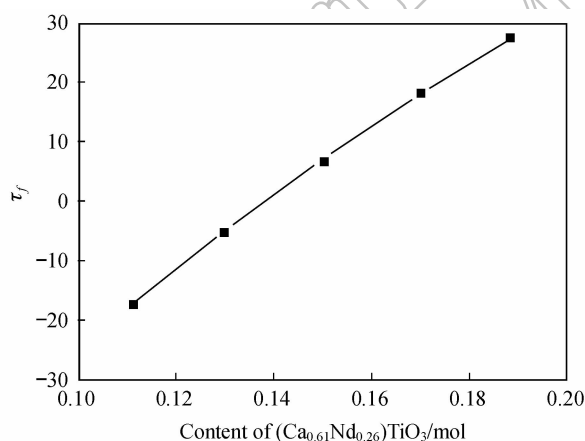


Fig. 7 The τ_f value of $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ ceramics system sintered at 1250°C

and grain size. Meanwhile, relative density also plays an important role in controlling the dielectric loss, and also has been shown in other microwave dielectric materials^[11-12]. With increasing sintering temperature, the $Q \times f$ value increased to a maximum value at 1250°C. It is

consistent with the variation of density, which plays an important role in controlling the dielectric loss. As a low $Q \times f$ value of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ (17600GHz), the dense MZCNT in Fig. 6, ceramics show a gradual decrease in $Q \times f$ value with increasing x and the maximum $Q \times f$ value of 37000GHz was obtained in $0.89(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - 0.11(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ceramics sintered at 1250°C.

Figure 7 illustrates the temperature coefficient of the resonant frequency (τ_f) of $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ ceramics sintered at 1250°C. In general, τ_f is related to the phase composition of the ceramics and insensitive to the sintering temperature. A higher $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ (τ_f about $213 \times 10^{-6}/^\circ\text{C}$) content led to a variation of τ_f toward positive value, which increased from -18 to $28 \times 10^{-6}/^\circ\text{C}$ as the addition of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ increased from 0.11 to 0.19. It gives a cross-zero line which implies that zero τ_f can be achieved through appropriate adjustment of the x value in the system.

3 Conclusions

Very dense MZCNT ceramics were prepared by sintering at 1250°C, which exhibited optimum dielectric properties. When sintered at temperatures above 1300°C, the decomposition of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ and evaporation of Zn resulted the decrease in density and degradation in dielectric properties.

With the molar fraction of $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ in MZCNT ceramics increasing from 0.11 to 0.19, both ε_r and τ_f value increased, whereas $Q \times f$ value decreased gradually. A relatively ideal dielectric properties with a dielectric constant (ε_r) of 24.3, $Q \times f$ value of 34000GHz, and temperature coefficient of resonance frequency (τ_f) of $-9 \times 10^{-6}/^\circ\text{C}$ were obtained when ceramics sintered at 1250°C, which shows a good prospect for practical application.

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$(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ 系微波介质陶瓷介电性能研究

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摘要: 本实验研究了 $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ 体系陶瓷 (MZCNT) 的微波介电性能, 通过 $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ 协调 $(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3$ 陶瓷的谐振频率温度系数. 实验发现, 烧结温度和陶瓷组成对微波介电性能影响显著, 当烧结温度为 1250℃ 时, 可以获得良好的致密度, 当烧结温度超过 1300℃ 时, $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ 的分解和 Zn 的蒸发导致陶瓷致密度和介电性能下降. 此外, 随着 $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ 含量的增大, 材料的介电常数增大, 品质因数减小. 当 $(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ 含量为 13%, 烧结温度为 1250℃, 保温 4h, (MZCNT) 陶瓷具有优良微波介电性能, $\epsilon_r = 24.3$, $Q \cdot f = 34000\text{GHz}$, $\tau_f \sim -9 \times 10^{-6}/^\circ\text{C}$, 从而达到实用要求.

关键词: $(1-x)(\text{Mg}_{0.7}\text{Zn}_{0.3})\text{TiO}_3 - x(\text{Ca}_{0.61}\text{Nd}_{0.26})\text{TiO}_3$ 陶瓷; 介电常数; 品质因数; 谐振频率温度系数

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