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Mg-substituted $ZnNb_2O_6$–TiO_2 composite ceramics for RF/microwaves ceramic capacitors

Wu Sp*, Luo Jh

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China

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ABSTRACT

Microstructure and microwave dielectric properties of Mg-substituted $ZnNb_2O_6$–TiO_2 microwave ceramics were investigated. Mg acted as a grain refining reagent and columbite phase stabilization reagent. With an increasing Mg content, the amount of ixiolite (Zn, Mg) $TiNb_2O_8$ decreased, and the amount of $(Zn_{0.9}Mg_{0.1})_{0.17}Nb_{0.33}Ti_{0.5}O_2$ and columbite increased. ZnO–Nb_2O_5–1.75TiO_2–5 mol.%MgO exhibited excellent dielectric properties (at 950 °C): ε_r = 35.6, $Q \times f$ = 16,000 GHz (at 5.6 GHz) and τ_f = −10 ppm/°C. The material was applied successfully to make RF/microwaves ceramic capacitor, whose self-resonance frequency was 19 GHz at low capacitance of 0.13 pF.

1. Introduction

With the rapid advancement in mobile communication technology, the application of microwave ceramic components becomes an inevitable trend, leading to the rapid progress in related field [1,2]. To be a useful material for incorporation into multilayer type elements with a high reliability, microwave dielectric materials must be sintered along with low melting point electrodes, which were made from metals with a high conductivity, such as copper, silver or silver palladium powders [3,4].

$ZnNb_2O_6$ ceramics exhibited an excellent quality factor ($Q \times f$ = 83,700 GHz) [5]. Robert C [6] reported that all columbite niobates had ε_r between 17 and 22 and a negative τ_f between −45 and −76 ppm/°C. The best $Q \times f$ values were for $ZnNb_2O_6$ (84,500 GHz), $MgNb_2O_6$ (79,600 GHz), $CaNb_2O_6$ (49,600 GHz), and $CoNb_2O_6$ (41,700 GHz) after being fired to 1200 °C, 1300 °C, 1350 °C, and 1150 °C, respectively, for 2 h. Robert C. [7] reported that the columbite niobates are of great interest as microwave ceramics, particularly $ZnNb_2O_6$ ($Q \times f$ up to 103,730 GHz), $MgNb_2O_6$ ($Q \times f$ up to 104,000 GHz), $CoNb_2O_6$ ($Q \times f$ up to 81,000 GHz), and $CaNb_2O_6$ ($Q \times f$ up to 49,600 GHz). The transition metal columbites are sintered at relatively low temperatures of 1000–1200 °C, and they have relatively simple chemistry, ordering and processing needs compared with the complex perovskites. However, the low dielectric constant (ε_r = 25) and the large negative temperature coefficient of resonant frequency (τ_f = −56 ppm/°C) limited its application in cofired ceramic device. In contrast, ε_r and τ_f of TiO_2 are 100 and 400 ppm/°C respectively. It was a logical speculation that $ZnNb_2O_6$–TiO_2 composite ceramic (ZNT) has an adjustable ε_r and τ_f value. Pullar et al. [8] reported that near-zero τ_f mixtures with good microwave properties for 94% $CoNb_2O_6$/6% TiO_2 sintered at 1150 °C/2 h and 90% $CoNb_2O_6$/10% $CaTiO_3$ sintered at 1150 °C/2 h in a systematic study of columbites. Kim et al. [9,1,10] reported that the $(1-x)$ $ZnNb_2O_6$–$x TiO_2$ system has a near-zero τ_f and a large ε_r (45) at x = 0.58, however, the quality factor was low ($Q \times f$ = 6000 GHz). Kim found that 10 wt.% CuO could reduce the sintering temperature of ZNT ceramics to 900 °C, however, the $Q \times f$ value obviously decreased with an increasing content of CuO. In our previous research [11], we found that $ZnNb_2O_6$–1.75TiO_2 exhibited good dielectric properties (at 975 °C): ε_r = 40, $Q \times f$ = 17,000 GHz (at 5.6 GHz) and τ_f = −12 ppm/°C. Addition of Mg ion gave the Zn–Nb–Ti ceramics a high insulation resistivity because of the electrovalence compensation effect.

In the present work, we discussed further the influence of MgO on $ZnNb_2O_6$–TiO_2 composite microwave ceramics. The microstructure and micro-composition of Mg-substituted $ZnNb_2O_6$–TiO_2 ceramic system were studied with SEM and EDS analysis. The microwave dielectric behavior of materials was also investigated.

2. Experimental

The starting materials were ZnO (>99.7%), Nb_2O_5 (>99.8%), MgO (>99.8%) and TiO_2 (>99.8%). Mg-substituted $ZnNb_2O_6$–TiO_2 composite ceramics were synthesized. Microwave ceramic capacitors were made using a conventional thick film process. The crystalline phases of specimen were analyzed by X-ray diffraction

* Corresponding author. Tel.: +86 20 87112897; fax: +86 20 87112897.
E-mail address: chwsp@scut.edu.cn (W. Sp).

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(XRD) (Rigaku, D/max-A, Japan) with Cu-Ka radiation of 2θ from 20 to 80°. The microstructure observations of the ceramic surfaces were performed under a scanning electron microscope (SEM) (Zeiss, LEO 1530 VP, German). The element analysis of micro domain was carried out with an energy dispersive spectrometer (EDS) (EPMA1600, Japan). Microwave dielectric constants (ε_r) and the quality factor values ($Q \times f$) at microwave frequencies were measured by Hakki-Coleman dielectric resonator method using a Network Analyzer (Agilent, E5071B, U.S.A). Temperature coefficient of resonant frequency (τ_f) was also measured by the same method with a changing temperature from 25 to 75 °C, and calculated by the following Eq. (1):

$$\tau_f = \frac{f_{75} - f_{25}}{f_{25} \times 50} \quad (1)$$

where f_{75} and f_{25} represent the resonant frequencies at 75 °C and 25 °C, respectively. Capacitance (C_p), quality factor (Q), equivalent series resistance (ESR) and self-resonance frequency (SRF) of multilayer ceramic chip capacitors (MLCC) could be tested with radio frequency impedance material analyzer (Agilent, E4991A, U.S.A).

3. Results and discussion

3.1. Phase identification of low-fired $ZnNb_2O_6$–TiO_2–MgO ceramics

The solid solution of the zinc magnesium niobites is easily formed because $ZnNb_2O_6$ and $MgNb_2O_6$ have the same columbite structure and similar lattice parameters. In addition, a smaller ionic radii of Mg (0.66 Å) than that of Zn (0.74 Å) make them easy to substitute the zinc-site of $ZnNb_2O_6$ [12]. Fig. 1 showed the XRD patterns of $ZnNb_2O_6$–1.75TiO_2–yMgO (y = 5–30 mol.%) sintered at 950 °C for 4 h. The super lattice diffraction peak (4 0 0) of columbite $ZnNb_2O_6$ (ICCD/JCPDS PDF# 37-1371) could be employed to identify columbite [9]. As seen from Fig. 1a, the diffraction peaks of ixiolite ($ZnTiNb_2O_8$) and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ coexisted in all samples, regardless of the Mg content. It suggested that they were the main crystalline phases in the material system. However, with an increasing Mg content, peak intensity of ixiolite and $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ varied oppositely. The former decreased while the latter increased. The diffraction peaks of columbite ($ZnNb_2O_6$) and cubic Zn_2TiO_4 appeared when Mg content increased to 20 mol.%.

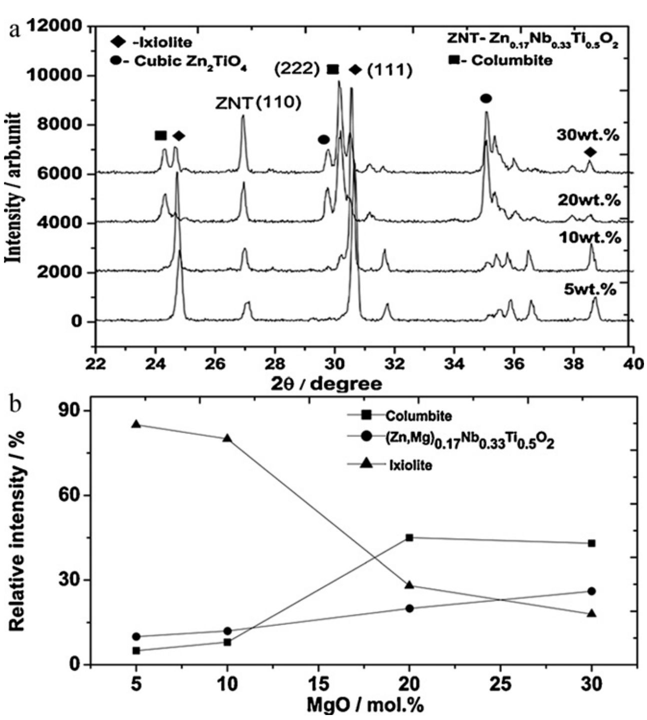

Fig. 1. (a) XRD patterns of ZnO-Nb_2O_5–1.75TiO_2–yMgO(sintered at 950 °C for 4 h)with a varied MgO content; (b) influence of Mg content on phase composition.

The relative integrated intensities of columbite (2 2 2), ixiolite (1 1 1) and ZNT (1 1 0) peaks are plotted in Fig. 1b. The relative integrated intensities demonstrate the difference in amount of each phase more clearly. It can be assumed that the relative intensities represent the amount of each phase present. The Eq. (2) was given as follows (for example ixiolite):

$$\text{Relative intensity of ixiolite} = \frac{I_{\text{ixiolite}(1\,1\,1)}}{I_{\text{ixiolite}(1\,1\,1)} + I_{\text{columbite}(2\,2\,2)} + I_{\text{ZNT}(1\,1\,0)}} \times 100\% \quad (2)$$

With an increasing Mg content, columbite ($ZnNb_2O_6$) content increased from 8 mol.% to 45 mol.%, while ixiolite content decreased greatly from 85 mol.% to 10 mol.%. The content of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ increased linearly as MgO content improved despite its small portion of 10–20 mol.%. The results indicated that MgO could effectively stabilize columbite $ZnNb_2O_6$ phase because of the formation of solid solution (Zn, Mg) Nb_2O_6. In addition, the substitution of Mg^{2+} for Zn^{2+} in $ZnNb_2O_6$ results in dissociated ZnO, which reacted with TiO_2 to form cubic Zn_2TiO_4.

The Mg ion firstly entered Zn sites (A substitution) to stabilize columbite $ZnNb_2O_6$, then parts of Mg-stabilized $ZnNb_2O_6$ reacted with TiO_2 to form $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ solid solutions, which restrained the formation of ixiolite $ZnTiNb_2O_8$.

3.2. SEM and EDS analysis of $ZnNb_2O_6$–TiO_2–yMgO ceramics

SEM and EDS micrographs of Mg-substituted $ZnNb_2O_6$–1.75TiO_2 (sintered at 950 °C) were given in Fig. 2. According to our previous work [11], the $ZnTiNb_2O_8$, $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ and trace cubic Zn_2TiO_4 coexisted in the specimen at 950 °C. As seen in SEM photographs (Fig. 2(1)), the grain shape was not uniform and the grain sizes were ranged from 2 μm to 10 μm. Abnormal grain growth could be observed and some crystal defects appeared when 10 mol. % Mg was employed. Micro domain compositions of crystal grains, assigned as "a, b, c and d" in Fig. 1(1), have been identified by the corresponding EDS spectra. The results showed that those compositions were: (a) $(Zn_{0.80}Mg_{0.20})TiNb_2O_8$ (in Fig. 2(2)), (b) $(Zn_{0.90}Mg_{0.10})Nb_2O_6$ (in Fig. 2(3)), (c) $(Zn_{0.92}Mg_{0.08})_2TiO_4$ and $(Zn_{0.9}Mg_{0.1})_{0.17}Nb_{0.33}Ti_{0.5}O_2$ (in Fig. 2(4)) respectively.

From those EDS patterns, one could find that the Mg ion scattered evenly in those coexisting phases. With an increasing Mg content, the amount of club-shape grain, identified as ixiolite (Zn, Mg)$TiNb_2O_8$, decreased obviously, and the amount of spherical $(Zn_{0.9}Mg_{0.1})_{0.17}Nb_{0.33}Ti_{0.5}O_2$ or columbite grains increased simultaneously. This agreed with the conclusion by XRD observation. The refinement of ixiolite grain could be ascribed to the so-called pinning effect derived from Mg ion, which deposited at grain boundaries and prevented them from moving. Composition of small grain with 1–3um diameter was (Zn, Mg) Nb_2O_6. Several cubic shape grains, which can be easily confirmed to be cubic $(Zn_{92}Mg_8)_2TiO_4$ by EDS micro domain analysis, appeared in Fig. 1(1). According to the report from HSIEH [13], the major crystalline phase of the $(Zn_{1-x}Mg_x)TiO_3$ ceramic sintered at 950 °C was Zn_2TiO_4 when $x \leq 0.1$. This agreed with our observation. The results further confirmed the conclusion from XRD analysis.

XRD and SEM photograph of the specimen containing 30 mol.% Mg showed that the spherical columbite grains became one of main crystal phases. The spherical (Zn, Mg) Nb_2O_6 grain (marked as "b") was light white under back scattering electron probe micro analyzer. Mg content at grain edge was 2.32 at.%, however, that was 1.59% at core. It further suggested that Mg deposited first at grain boundary, then diffused into core of grain owing to the concentration diffusion effect of Mg ion at sintering. Therefore, Mg can act as a colunmite.

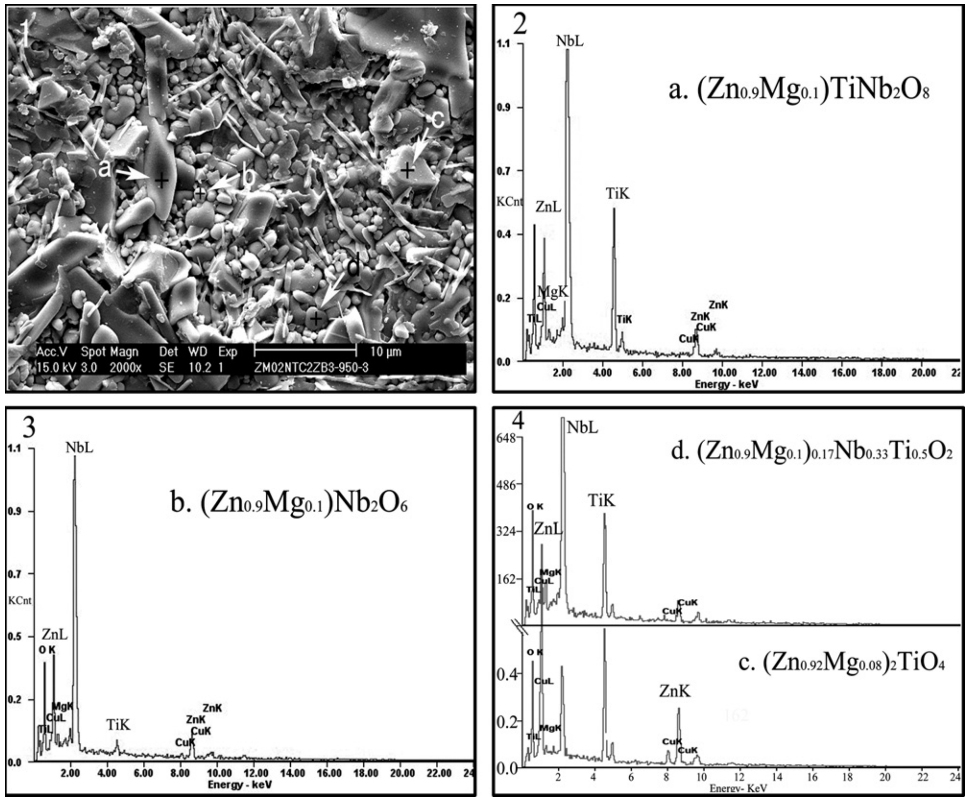

Fig. 2. (1) SEM photograph of $ZnNb_2O_6$–TiO_2 ceramics with 10 mol.% MgO additive; EDS spectra of micro domain marked as "a" (showed in Fig. 1(2)), "b" (in Fig. 1(3)), "c" (in Fig. 1(4))and "d" (in Fig. 1(5)).

3.3. Microwave dielectric properties of $ZnNb_2O_6$–$1.75TiO_2$–yMgO ceramics

Influences of Mg content on the ε_r and τ_f of $ZnNb_2O_6$–$1.75TiO_2$–*y*MgO ceramics (sintered at 950 °C) were shown in Fig. 3a. One could see that the variations of ε_r and τ_f were smoothly as a small quantity of Mg ions were employed. However, when the Mg content changed from 10 mol.% to 20 mol.%, ε_r rapidly increased from 35.8 to 45, and τ_f value greatly promoted from −0.9 ppm/°C to 132 ppm/°C, respectively. It could be ascribed to the dramatically increase in content of $(Zn_{0.9}Mg_{0.1})_{0.17}Nb_{0.33}Ti_{0.5}O_2$ when *y* value was more 10 mol.%. The ε_r and τ_f of $Zn_{0.17}Nb_{0.33}Ti_{0.5}O_2$ should be about 80 and 270 ppm °C^{-1} [11], which contributed to the sharp increase in ε_r and τ_f value of $ZnNb_2O_6$–$1.75TiO_2$–*y*MgO ceramics according to well-known addition theory [14,15].

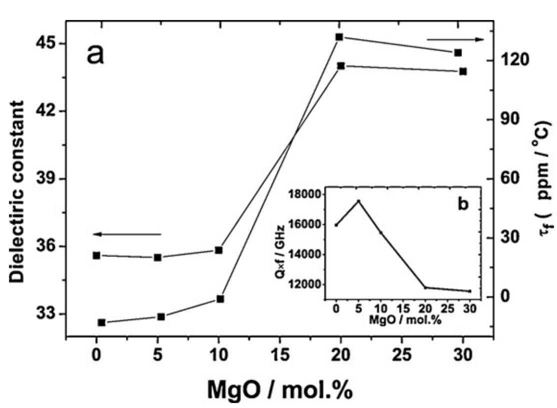

Fig. 3. Influence of Mg content on microwave dielectric properties of ZnO–Nb_2O_5–$1.75TiO_2$–*y*MgO.

As showed in Fig. 3b, $Q \times f$ of ceramics showed a highest value ($Q \times f$ = 16,000 GHz at 5.6 GHz) at 5 mol.% MgO, then it linearly decreased to 11,300 GHz (at 6.56 GHz) as Mg^{2+}content increased to 30 mol.%. Generally speaking, microwave dielectric loss could be ascribed to two fields: the intrinsic loss and extrinsic loss. The intrinsic loss was mainly caused by lattice variation modes while the extrinsic loss was mainly dominated by secondary phase, oxygen vacancies, grains sizes and densification. In this study, the phase transition, which was derived from an increasing Mg content, decreased content of (Zn, Mg)$TiNb_2O_8$ with a high $Q \times f$ value, increased $(Zn, Mg)_{0.17}Nb_{0.33}Ti_{0.5}O_2$ content, forming new cubic $(Zn, Mg)_2TiO_4$ phase. It should seriously deteriorate the quality factor of the material. In addition, the smaller grain produced more grain defects and grain boundary distortion, which further contributed to the low quality factor.

3.4. Microwave properties of MLCC

Mg-substituted $ZnNb_2O_6$–TiO_2 composite ceramics was applied to make multilayer ceramic chip capacitors (MLCCs) according to the process in literature [11]. Fig. 4a showed the SEM micrograph and EDS spectra of cross-section of MLCCs with $Ag_{90}Pd_{10}$ electrode. SEM analysis revealed that the ceramics exhibited a high densification and low porosity. The average thickness of the $Ag_{90}Pd_{10}$ electrode was about 3–4 μm. The electrode was continuous and no obvious crack was found. EDS analysis was carried out on the polished section along the marked line to study element distribution. The line scanning results suggested that Ag and Pd coexisted in inner electrode. The normalized element analysis pattern was given in Fig. 4b, where the atom ratio of silver/palladium was 91%:9%. Delamination between ceramics and $Ag_{90}Pd_{10}$ electrode had not been detected, and diffusion of Ag and Pd to dielectric layer did not

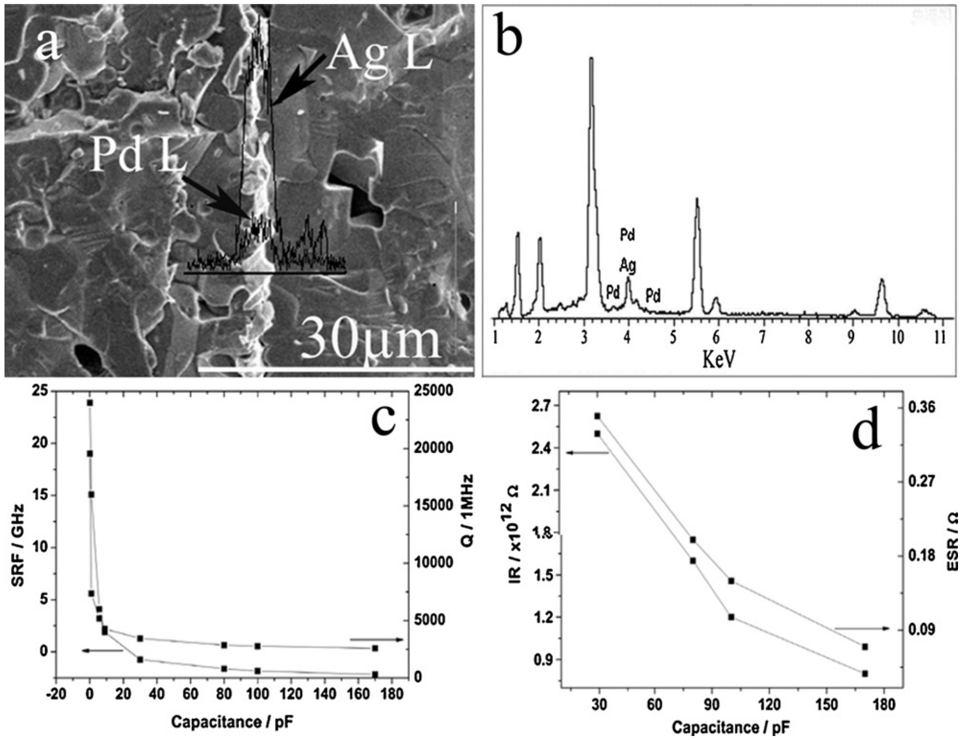

Fig. 4. (a) SEM micrograph and EDS spectrum of cross-section of MLCC, (b) Normalized element analysis pattern; influences of capacitance on (c) SRF and Q, (d) IR and ESR of capacitors.

occur. It showed the dielectric layer had an excellent compatibility with $Ag_{90}Pd_{10}$ electrode.

Mg-substituted $ZnNb_2O_6$–$1.75TiO_2$ could be selected as a suitable candidate for MLCCs. The self-resonance frequency (SRF) and equivalent series resistance (ESR) could be measured with a RF impedance material analyzer or network analyzer (Agilent N5230C). The SRF is the frequency of acceptor resonance arose from capacitance and spurious inductance. From Fig. 4c, the SRF greatly decreased to 2.2 GHz from 19 GHz when capacitance increased to 9 pF from 0.135 pF. The quality factor (Q) values decreased with capacitance increasing. The increased capacitance caused a decreasing capacity reactance, and then led to a low quality factor. From Fig. 4d, the ESR and insulating resistance (IR) of MLCC decreased with capacitance increasing. Because these capacitors were parallel, more capacitance meant more dielectric layer numbers, resulting in a lower ESR and IR values of MLCC.

In recent years, MLCCs have become more important components for radio frequency (RF)/microwave applications. As-prepared MLCCs have low sintering temperature, good temperature stability of capacitance (TCC = −3 to −10 ppm/°C), and exhibited excellent behaviors ($Cp = 0.135$ pF, $Q = 24000/1$ MHz, SRF = 19 GHz, IR = 3.0×10^{13} Ω). They can meet the RF/microwave applications.

4. Conclusion

Mg-substituted $ZnNb_2O_6$–TiO_2 composite ceramics was synthesized. The Mg ion entered Zn situation and produce A-substitution. ZnO–Nb_2O_5–$1.75TiO_2$–5 mol.% MgO sintered at 950 °C exhibited good dielectric properties: $\varepsilon_r = 35.6$, $Q \times f = 16{,}000$ GHz (at 5.6 GHz) and $\tau_f = -10$ ppm/°C.

The refinement of grain could be ascribed to pinning effect. With an increasing Mg content, the amount of ixiolite (Zn, Mg) $TiNb_2O_8$ decreased, however, the amount of $(Zn_{0.9}Mg_{0.1})_{0.17}Nb_{0.33}Ti_{0.5}O_2$ and columbite increased. MLCCs have low sintering temperature, good temperature stability of capacitance, and exhibits excellent behaviors. The capacitor with ultrahigh SRF (19 GHz) can meet the RF/microwaves applications.

Acknowledgments

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