Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 75–79

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Microwave dielectric properties of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ compound ceramic with controlled temperature coefficient

Ching-Fang Tseng*, Ping-Sung Tsai

Department of Electronic Engineering, National United University, No. 1 Lien-Da, Kung-Ching Li, Miao-Li 36003, Taiwan

Received 5 September 2011; received in revised form 21 May 2012; accepted 30 May 2012
Available online 9 June 2012

Abstract

In this study, microwave dielectric properties of $(1-x)ZnAl_2O_4-xCaTiO_3$ samples with controlled temperature coefficient feature are analyzed. The crystal structures of all the compositions were refined by X-ray diffraction. A homogeneous distribution of cations within instrument sensitivity in all the samples was observed using scanning electron microscopy, coupled with energy dispersive X-ray analysis. $ZnAl_2O_4$ and $CaTiO_3$ could coexist when the x content was less than 0.1, whereas Al_2O_3 and $Ca_3Al_2O_6$ phases were observed in composite ceramics. As expected, the dielectric constant (ε_r) of the composite ceramics increased with the increasing x content, and the quality factor (Qf) generally decreased with increasing x-content because of the low Qf of the $CaTiO_3$ phases. The temperature coefficient of resonant frequency (τ_f) could be controlled by varying the $CaTiO_3$ content and could lead to zero τ_f value. The $0.92ZnAl_2O_4-0.08CaTiO_3$ ceramic exhibited ε_r of 10.8, Qf of 32,300 GHz, and τ_f of 0 ppm/°C.

Keywords: A. Sintering; C. Dielectric properties; $(1-x)ZnAl_2O_4-xCaTiO_3$ ceramics

1. Introduction

Recently, much attention has been paid to the development of millimeter-wave devices because large amount of information could be transported rapidly. The dielectric ceramics for millimeter-wave telecommunication devices are required to have a low dielectric constant (ε_r) to reduce the cross-coupling effect with conductors and the delay time of electronic signal transmission, a high quality factor (Qf) for better selectivity and a near-zero temperature coefficient of resonant frequency (τ_f) for stability.

The $ZnAl_2O_4$ ceramics have been reported to have good dielectric properties and have been of great interest as a potential dielectric resonator for millimeter-wave applications in the last decade [1–3]. $ZnAl_2O_4$ is a rare mineral belonging to the spinel group (AB_2O_4), which crystallizes in the cubic crystal system, with the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice. It exhibits a low ε_r of ~8.5, a high Qf of ~57,000 GHz, and a large negative τ_f value of ~−79 ppm/°C [3]. The high negative τ_f value of $ZnAl_2O_4$ ceramics prohibits its use in practical applications. Surendran et al. reported that $ZnAl_2O_4$ with molar addition of TiO_2, sintered at 1500 °C for 4 h, forms mixtures based on $(1-x)ZnAl_2O_4$–$xTiO_2$ ceramics and that zero τ_f value was achieved at $x=0.17$ with $\varepsilon_r=12.67$ and Qf ~100,000 GHz [1]. In addition, Lei et al. also studied the microwave dielectric properties of $(1-x)ZnAl_2O_4$–$xTiO_2$ spinel-base composites sintered at 1500 °C for 3 h [2]. They found that the near-zero τ_f value having a ε_r of 11.4 and Qf of 71,810 GHz was obtained with the composition $x=0.21$. However, till now, we could not control the τ_f value of $ZnAl_2O_4$ ceramics by other materials, except TiO_2. Therefore, in the present study, $(1-x)ZnAl_2O_4$–$xCaTiO_3$ system was investigated to control the τ_f value of $ZnAl_2O_4$-based materials. The microstructures and dielectric properties of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ composite ceramics were studied, and the experimental data were compared with those predicted from the dielectric rules of mixture.

2. Experimental procedure

Samples of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ were synthesized by the conventional solid-state method. The starting

*Corresponding author. Tel.: +886 37 381529; fax: +886 37 362809.
E-mail address: cftseng@nuu.edu.tw (C.-F. Tseng).

0272-8842/$36.00
http://dx.doi.org/10.1016/j.ceramint.2012.05.096

materials were high-purity oxide powders (>99.9%): ZnO, Al_2O_3, TiO_2, and $CaCO_3$, which were separately prepared according to the desired stoichiometry of $ZnAl_2O_4$ and $CaTiO_3$. The powders were ground in distilled water for 12 h in a ball mill with agate balls and then dried at 80 °C in an oven overnight. After drying, the $ZnAl_2O_4$ and $CaTiO_3$ powders were forced through a 200-mesh sieve and calcined at 1150 °C for 3 h and 1100 °C for 4 h, respectively. After calcinations, the calcined powders were mixed according to the molar fraction and then re-milled for 12 h. The fine powder with 3 wt% of a 10% solution of PVA as a binder was pressed into pellets with dimensions of 11 mm in diameter and 5 mm in thickness under a pressure of 150 MPa. These pellets were sintered at temperatures of 1370−1520 °C for 4 h in air. The heating and the cooling rates were both set at 10 °C/min. The X-ray diffraction (XRD; Siemens D5000) data of powder and bulk samples were collected using Cu-Kα radiation and a graphite monochromator in the 2θ range of 20–60°. The microstructural observations and analysis of the sintered surface were performed using a scanning electron microscopy (SEM; Philips XL40FEG, Eindhoven. the Netherlands) and an energy dispersive X-ray spectrometer (EDS). The density of the sintered specimens, as a function of sintering temperature, was measured through the liquid Archimedes method using distilled water as the liquid.

The ε_r and Qf values at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney [4,5]. The dielectric resonator was positioned between two brass plates to form a cavity-like structure. The test cavity was placed over a thermostat, and the temperature range was 25–80 °C with a heating rate of 1 °C/min and the residence time was 10 min for each cycle. The τ_f (ppm/°C) was calculated by noting the change in the resonant frequency, as

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is the resonant frequency at T_1 and f_2 is the resonant frequency at T_2.

3. Results and discussions

The XRD patterns of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ($0.02 \le x \le 0.1$) ceramics are shown in Fig. 1. According to the XRD patterns, the composite ceramics have a two-phased structure with a $GdFeO_3$-type perovskite structure $CaTiO_3$ and a spinel structure $ZnAl_2O_4$ indexed in JCPDS card no. 82-0228 and 82-1043, respectively. This implies that $ZnAl_2O_4$ cannot form solid solution with $CaTiO_3$. The $Ca_3Al_2O_6$ and Al_2O_3 second phase between $ZnAl_2O_4$ and

Table 1
The microwave dielectric properties of $0.92ZnAl_2O_4$–$0.08CaTiO_3$ ceramics for different sintering temperature.

Sintering temperature (°C)	Density (g/cm^3)	ε_r	Qf (GHz)	τ_f (ppm/°C)
1370	4.38	10.6	26,400	−6
1400	4.42	10.8	32,300	0
1430	3.38	10.7	29,000	−4
1460	4.29	10.6	24,000	−1
1490	4.20	10.5	18,800	−1
1520	4.09	10.4	15,000	1

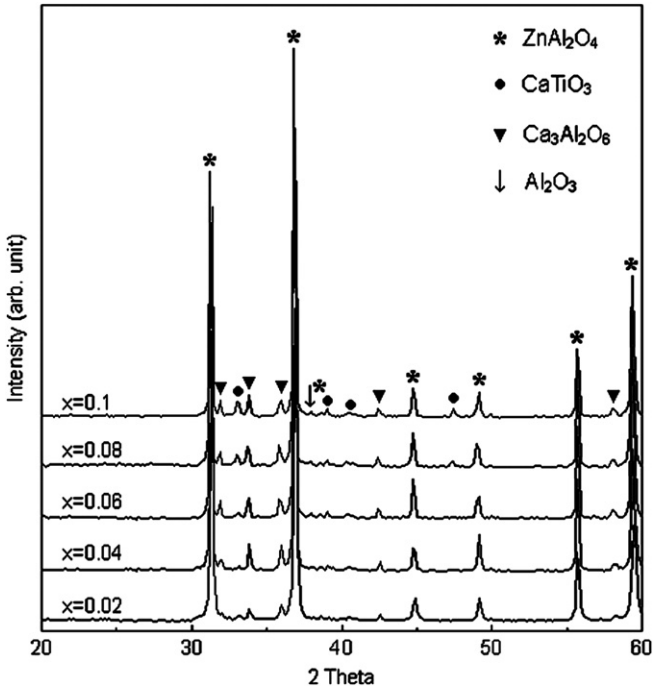

Fig. 1. XRD patterns of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ceramics with different x value.

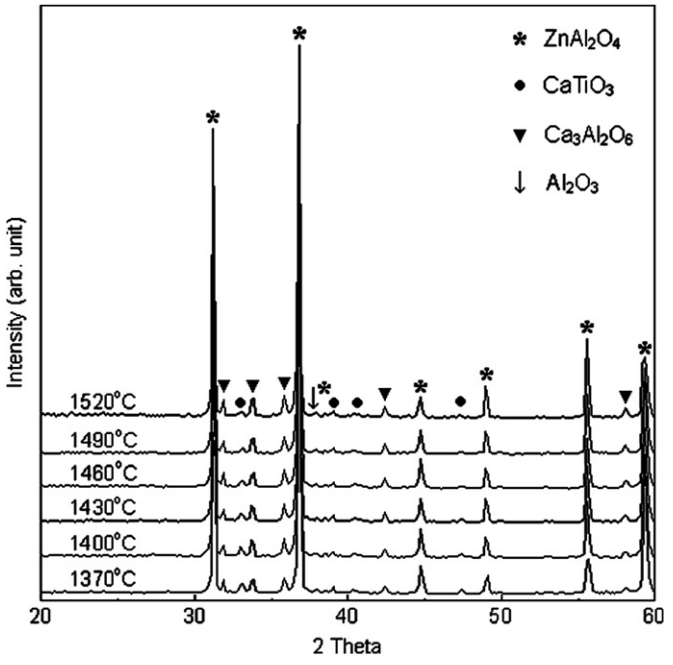

Fig. 2. XRD patterns of $0.92ZnAl_2O_4$–$0.08CaTiO_3$ ceramics sintered at different sintering temperature for 4 h.

$CaTiO_3$ were detected during the composite ceramics preparation process. Furthermore, the relative content of $Ca_3Al_2O_6$ and Al_2O_3 second phases was increased with respect to the $CaTiO_3$ content. The EDS analysis was performed to confirm the secondary phases, as shown in Table 1. It implies that the microwave dielectric properties would be affected by the existence of secondary phases.

Fig. 2 shows the XRD patterns of $0.92ZnAl_2O_4$–$0.08CaTiO_3$ ceramics sintered at different temperatures for 4 h. The diffraction patterns are similar to those of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ceramics with different x and secondary phases. In addition, no significant changes could be observed at sintering temperatures ranging from 1370 to 1520 °C. It can be concluded that $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ceramics could be stabilized at different sintering temperatures.

Table 1 shows the microwave dielectric properties of $0.92ZnAl_2O_4$–$0.08CaTiO_3$ composite ceramics at different temperatures. The ε_r and Qf increased with the increasing density and sintering temperature. As the sintering temperature increased to 1400 °C, the optimal dielectric properties were obtained. Thereafter, the ε_r and Qf values slightly decreased when the sintering temperature increased, which may be related to the existence of secondary phases, small amount of trapped porosity, and the abnormal grain growth caused by the decrease in the grain boundary area. In addition, it was also noted that the variation trend between τ_f values and sintering temperatures of $0.92ZnAl_2O_4$–$0.08CaTiO_3$ composite ceramics did not significantly differed from each other, and the near-zero τ_f value could be achieved.

The microstructural changes in $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ceramics were studied using SEM and EDS to observe the effects of $CaTiO_3$ content on the morphologies of $(1-x)ZnAl_2O_4$–$xCaTiO_3$. The SEM micrographs of

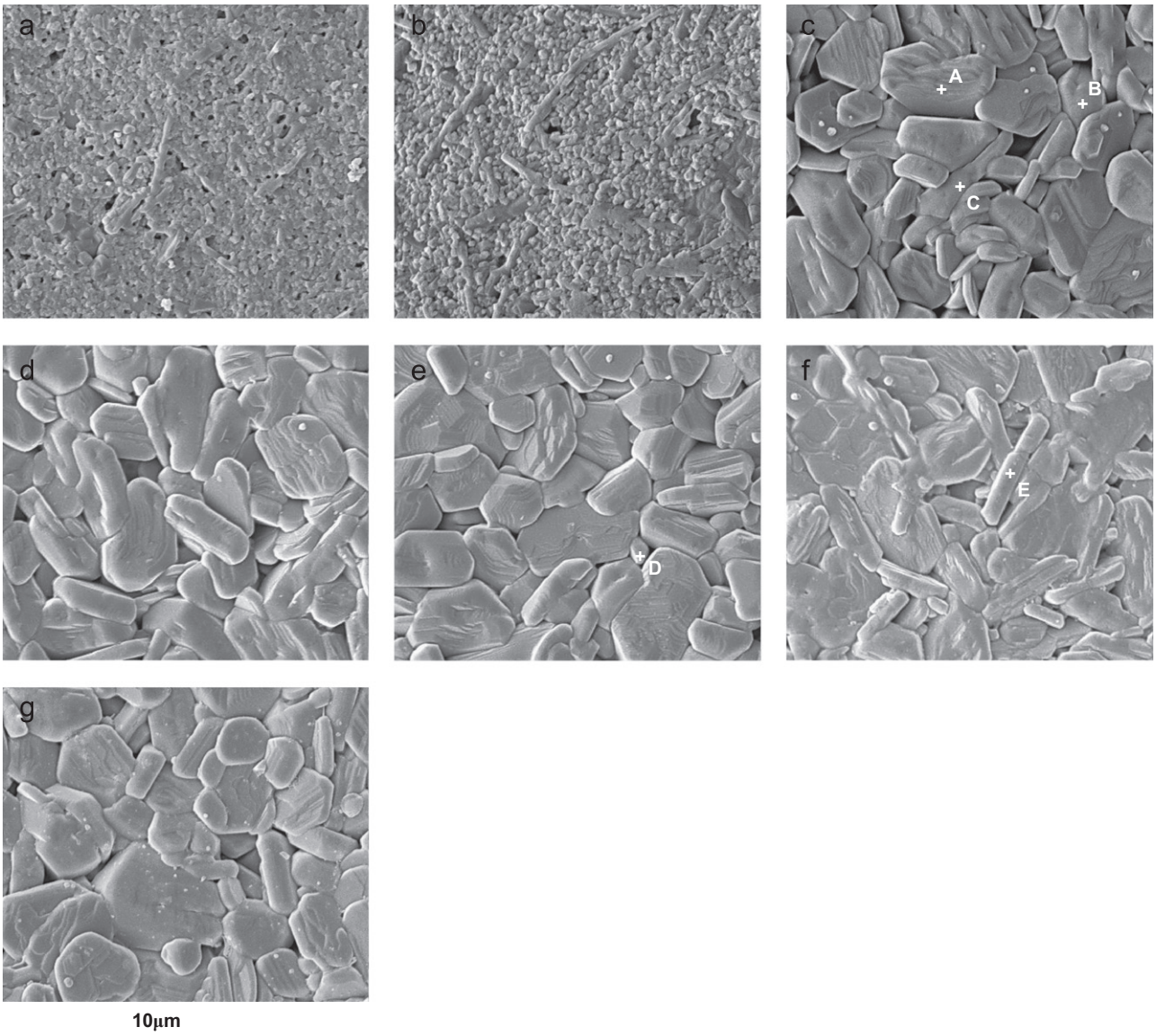

Fig. 3. SEM micrographs of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ composite ceramic samples with (a)–(e) $x=0.02$, 0.04, 0.06, 0.08, 0.1 respectively, sintered at 1400 °C; (f) and (g) $x=0.08$, sintered at 1370 °C and 1430 °C.

$(1-x)ZnAl_2O_4$–$xCaTiO_3$ composite ceramics are shown in Fig. 3. Fig. 3(a)–(e) illustrates the SEM images of sintered samples, with x ranging from 0.02 to 0.1, sintered at 1400 °C. The increase in grain size was observed with the increasing content of $CaTiO_3$. The grain sizes of $0.98ZnAl_2O_4$–$0.02CaTiO_3$ and $0.96ZnAl_2O_4$–$0.04CaTiO_3$ were small (less than 0.5 μm), whereas the grain sizes of $0.9ZnAl_2O_4$–$0.1CaTiO_3$ ceramic were about 5 μm, although both were sintered at the same temperature. Fig. 3 shows that $CaTiO_3$ can contribute to grain growth. Many authors also had reported the same phenomenon by incorporating $CaTiO_3$ into the main phase [6–7]. The SEM images for the samples with $x=0.08$ sintered at 1370, 1400, and 1430 °C are shown in Fig. 3(f), (d), and (g), respectively. From the three photographs, it is evident that more uniform grain size could be obtained when sintered at 1400 °C. The changes in microwave dielectric properties of the $0.92ZnAl_2O_4$–$0.08CaTiO_3$ ceramics at different sintering temperature may be due to grain morphologies, which is in agreement with the results presented in Table 1. To evaluate the evolution of phase constitution associated with microstructures, EDS analysis was used further on the flat grain (A), large circular grain (B), small circular grain (D), and rod-like grains (C, E). As shown in Table 2, the flat grain, large circular grain, small circular grain, and rod-like grain were $ZnAl_2O_4$, $CaTiO_3$, Al_2O_3, and $Ca_3Al_2O_6$, respectively. These results correlate well with the XRD analyses.

The calculated values of density, dielectric constant, and τ_f are defined as ideal values and, therefore, do not have second phases. By comparing calculated values with measured values, the effect of the second phases on the microwave dielectric properties of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ system can be understood. The density ($\rho_{mixture}$) of a mixture of two phases can be computed using the following formula:

$$\rho_{mixture} = V_1\rho_1 + V_2\rho_2 \quad (2)$$

where $\rho_{mixture}$ is the calculated theoretical density of the two phases, and V_i and ρ_i are the volume fraction and density of the two components, respectively [8]. The ε_r of the mixture is obtained as follows:

$$\ln\varepsilon_{r,mixture} = V_1 \ln\varepsilon_{r1} + V_2 \ln\varepsilon_{r2} \quad (3)$$

where ε_{ri} is the dielectric constant of the two components [9].

Table 2
EDS analysis result of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ceramics marked in Fig. 2.

Spot	Atom (%)				
	Zn–K	Al–K	Ca–K	Ti–K	O–K
A	14.28	28.39	0.2	0.1	57.03
B	0.03	0.02	19.84	20.08	60.03
C	0.02	18.28	27.23	0.04	54.43
D	0.01	39.78	0.06	0.03	60.12
E	0.1	18.03	27.32	0.02	54.53

The variations of density and ε_r with x for $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ceramics are shown in Fig. 4 (full symbols). The open symbol values were calculated based on the mixture rule. The trend of density showed good agreement between experimental and calculated values when using mixture rule. A lower experimental value could be obtained, when compared with the calculated one. The existence of Al_2O_3 ($\rho=3.987$ g/cm^3) and $Ca_3Al_2O_6$ ($\rho=3.064$ g/cm^3) secondary phases has been considered to contribute to the decreasing density, as shown in the XRD data. In addition, it can also be observed that the densities decreased with the increasing x content. This behavior can be expected because the density of $CaTiO_3$ ($\rho=4.04$ g/cm^3) is less than that of $ZnAl_2O_4$ ($\rho=4.58$ g/cm^3). The ε_r values of the experimental results agree with those of the calculated results. The difference between the calculated values and the

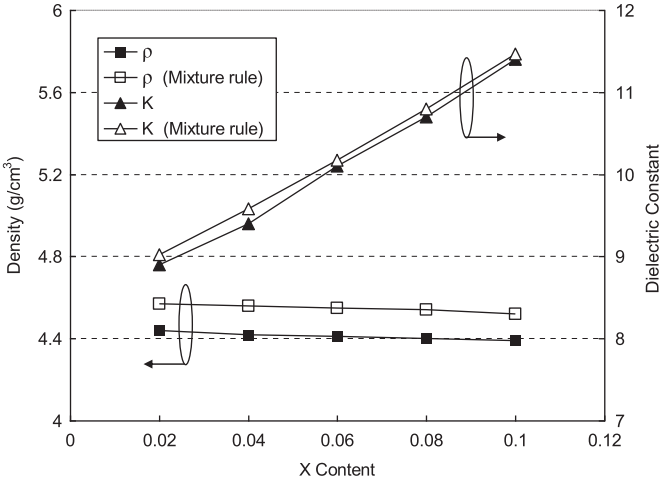

Fig. 4. The variations of experimental (full symbols) and calculated (open symbols) density and dielectric constant of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ceramics as a function of x.

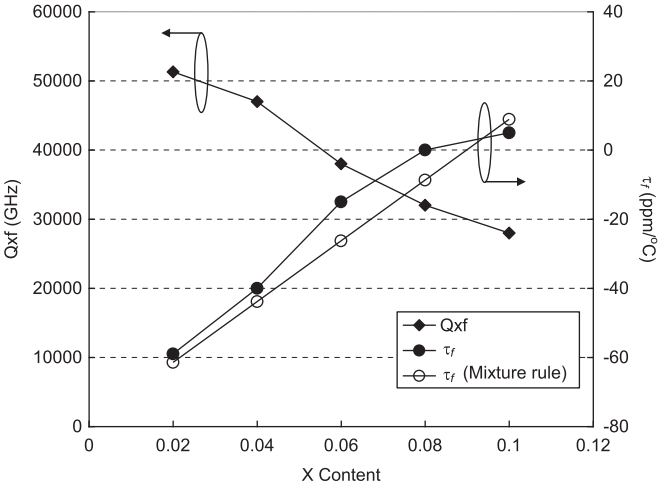

Fig. 5. The variations of experimental (full symbols) and calculated (open symbols) quality factor (Qf) and τ_f of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ ceramics as a function of x.

experimental ones is small, which may be due to the fact that the ε_r of Al_2O_3 is 10 and is close to that of $ZnAl_2O_4$. The ε_r of $ZnAl_2O_4$ and $CaTiO_3$ is 8.5 and 170, respectively. As expected, the ε_r has been found to increase as x varied from 0.02 to 0.1.

The variation of Qf and τ_f values of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ composite ceramics with x content is plotted in Fig. 5. The Qf value of $ZnAl_2O_4$ and $CaTiO_3$ is 56,000 and 12,900 GHz, respectively, whereas their τ_f value is -79 and 800 ppm/°C, respectively. With x increasing from 0.02 to 0.1, the Qf value decreases from 51,300 to 28,000 GHz, and τ_f value increases from -59 to 5 ppm/°C. A zero τ_f value occurs at $x=0.08$ in $0.92ZnAl_2O_4$–$0.08CaTiO_3$ mixture, which can reach a Qf value of 32,000 GHz. In addition, to calculate the τ_f value of a mixture, a general formula has been presented as follows:

$$\ln\tau_{f,mixture} = V_1\tau_{f1} + V_2\tau_{f2} \quad (4)$$

where τ_{fi} is the temperature coefficient of resonant frequency of the two components [10]. It can be noticed that the τ_f values show a reasonably good agreement between the experimental values and those obtained from the mixture rule.

4. Conclusion

In this study, the microwave dielectric properties of $(1-x)ZnAl_2O_4$–$xCaTiO_3$ composite ceramics with controlled temperature coefficient feature were analyzed. The density, ε_r and τ_f value were found to vary near-linearly with the increasing $CaTiO_3$ content; in addition, they also showed good agreement with the calculated results. The τ_f value was found to vary with the $CaTiO_3$ content from negative to positive values, whereas $\tau_f=0$ was obtained for the $0.92ZnAl_2O_4$–$0.08CaTiO_3$ composite ceramics. However, the Qf value decreased steadily because of the lower Qf of $CaTiO_3$. The $0.92ZnAl_2O_4$–$0.08CaTiO_3$ ceramics showed an ε_r of 10.8, a Qf of 32,300 GHz, and a τ_f of 0 ppm/°C.

Acknowledgments

This work was sponsored by the National Science Council of the Republic of China under Grant NSC 99-2221-E-239-018.

References

[1] K.P. Surendran, P.V. Bijumon, P. Mohanan, M.T. Sebastian, $(1-x)MgAl_2O_4-xTiO_2$ dielectrics for microwave and millimeter wave applications, Applied Physics A 81 (2005) 823–826.
[2] W. Lei, W.Z. Lu, J.H. Zhu, X.H. Wang, Microwave dielectric properties of $ZnAl_2O_4$–TiO_2 spinel-based composites, Materials Letters 61 (2007) 4066–4069.
[3] K.P. Surendran, N. Santha, P. Mohanan, M.T. Sebastian, Temperature stable low loss ceramic dielectrics in $(1-x)ZnAl_2O_4$–$xTiO_2$ system for microwave substrate applications, European Physical Journal B—Condensed Matter and Complex Systems 41 (2004) 301–306.
[4] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IEEE Transactions on Microwave Theory and Techniques 8 (1960) 402–410.
[5] W.E. Courtney, Analysis and evaluation of a method of measuring the complex permittivity and permeability microwave insulators, IEEE Transactions on Microwave Theory and Techniques 18 (1970) 476–485.
[6] C.F. Tseng, C.L. Huang, W.R. Yang, Microwave dielectric properties of $xNd(Zn_{1/2}Ti_{1/2})O_3$–$(1-x)CaTiO_3$ ceramics, Materials Letters 61 (2007) 4054–4057.
[7] M.P. Seabra, M. Avdeev, V.M. Ferreira, R.C. Pullar, N.McN. Alford, Structure and microwave dielectric properties of $La(Mg_{0.5}Ti_{0.5})O_3$–$CaTiO_3$ system, Journal of the European Ceramic Society 23 (2003) 2403–2408.
[8] P.S. Anjana, M.T. Sebeatian, A.K. Axelsson, N.M. Alford, Microwave dielectric properties of CeO_2–0.5AO–0.5TiO_2 (A=Ca, Mg, Zn, Mn, Co, Ni, W) ceramics, Journal of the European Ceramic Society 27 (2007) 3445–3452.
[9] D.W. Kim, B. Park, J.H. Chung, K.S. Hong, Mixture behavior and microwave dielectric properties in the low-fired TiO_2–CuO system, Japanese Journal of Applied Physics 39 (2000) 2696–2700.
[10] A.E. Paladino, Temperature-compensated $MgTi_2O_5$–TiO_2 dielectrics, Journal of the American Ceramic Society 54 (1971) 168–169.