Journal of Alloys and Compounds 480 (2009) 820–823

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Structural and dielectric properties of $La(Mg_{1/2}Ti_{1/2})O_3$–$Ca_{0.6}La_{0.8/3}TiO_3$-doped CuO

Yuan-Bin Chen*

Department of Engineering & Management of Advanced Technology, Chang Jung Christian University, 396 Chang Jung Rd., Sec.1, Kway Jen, Tainan 71101, Taiwan, ROC

ARTICLE INFO

Article history:
Received 4 December 2008
Received in revised form 11 February 2009
Accepted 13 February 2009
Available online 4 March 2009

Keywords:
Ceramics
Sintering
Grain size

ABSTRACT

Doping with CuO (1 wt.%) can effectively promote the densification and the dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics. The system was prepared using a conventional solid-state ceramic route. In order to produce a temperature-stable material, $Ca_{0.6}La_{0.8/3}TiO_3$ was added for a near-zero temperature coefficient (τ_f). The microwave dielectric properties are strongly correlated with the sintering temperature and the additions. $0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics with 1 wt.% CuO addition possesses a dielectric constant (ε_r) of 45.5, a $Q\times f$ value of 44,600 GHz (at 8 GHz) and a temperature coefficients of resonant frequency (τ_f) of 2 ppm/°C sintering at 1450 °C. As the content of $La(Mg_{1/2}Ti_{1/2})O_3$ increases, the highest $Q\times f$ value of 55,400 (GHz) for $x=0.8$ is achieved at the sintering temperature 1475 °C.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The development of microwave communication technology has been promoted by microwave dielectric ceramics. A large number of ceramic dielectric materials had been developed over the years. The traditional method for developing new dielectric materials has focused on considering new single-phase solid solutions having a high quality factor ($Q\times f$ value) or a high relative permittivity (ε_r). Candidate materials for microwave dielectric resonators suitable for 3G technology must satisfy three main criteria: high quality factor ($Q>15{,}000$), high dielectric constant (ε_r) > 25, and a near-zero temperature coefficient of resonant frequency ($\tau_f=\pm3$ ppm/°C) [1,2]. Small temperature coefficients of the resonant frequency ensure the stability of the microwave components at different working temperatures. To satisfy the demands of microwave circuit designs, each dielectric property requires precise control. Using two or more compounds with negative and positive temperature coefficients to form a solid solution or mixed phases is the most promising method of obtaining a zero temperature coefficient of the resonant frequency, in our previous reports [1–3].

Although most dielectric ceramics with high dielectric constants have positive τ_f values, material with a high dielectric constant, high Q and negative τ_f are desired to achieve this goal. S.-Y. Cho and co-workers have reported many complex perovskites $A(B_{1/2}^{2+}B_{1/2}^{4+})O_3$ with negative τ_f [4]. Among them, $La(Mg_{1/2}Ti_{1/2})O_3$ has a high dielectric constant ($\varepsilon\sim29$), a high quality factor ($Q\times f$ value ~75,500 GHz) and a negative τ_f value (−65 ppm/°C). The crystal structure of $La(Mg_{1/2}Ti_{1/2})O_3$ was reported to be cubic. $Ca_{0.6}La_{0.8/3}TiO_3$ ($\varepsilon_r=100$, $Q\times f=20{,}000$ GHz, $\tau_f=212$ ppm/°C) [5] with a positive τ_f value was introduced to into the mixture form a solid solution $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ to compensate for the τ_f value.

Many kinds of dielectric ceramics have been developed for microwave applications [6–8]. $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics have suitable dielectric constant and quality factors for application in dielectric resonators and filters [9]. However, pure $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics require a very high sintering temperature (1600 °C). There are three approaches to reducing the sintering temperature of microwave dielectric ceramics: low melting sintering aids addition [10–12], chemical processing, and the use of smaller particles as the starting materials. Of these three, sintering aids addition is the most effective and least expensive. However, no liquid phase sintering of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ with sintering aids addition has been reported yet. Previously, CuO was researched and found to have good dielectric properties. In this paper, CuO was used as a sintering aid for reducing the sintering temperature of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics. The effects of CuO on the sintering and microwave dielectric properties of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics were investigated.

* Fax: +886 6 3359815.
E-mail address: cubnck@yahoo.com.tw.

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.02.089

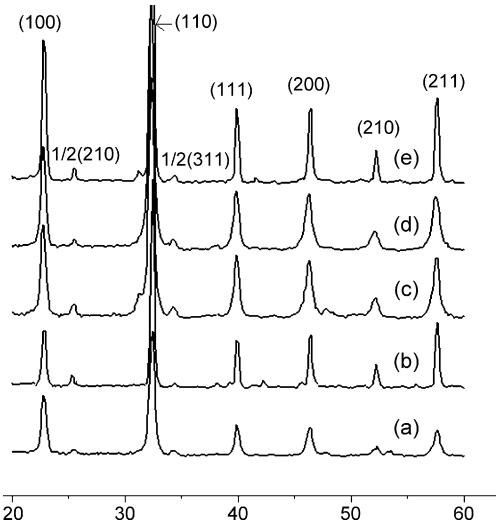

Fig. 1. X-ray diffraction patterns of $0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics with 1 wt.% CuO addition sintered at different temperatures for 5 h. (a) 1400 °C, (b) 1425 °C, (c) 1450 °C, (d) 1475 °C and (e) 1500 °C.

2. Experimental procedure

Samples of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ were synthesized by conventional solid-state method. The starting materials were mixed according to a stoichiometric ratio. A small amount of CuO (1 wt.%) was added as a sintering aid. High purity oxide powders (>99.9%) La_2O_3, MgO, $CaCO_3$, TiO_2 and CuO were weighed and mixed for 24 h with distilled water. The mixture was dried at 100 °C and thoroughly milled before it was calcined at 1200 °C for 4 h. The calcined powder was ground and sieved through 100-mesh screen. Phase formation of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ was confirmed using X-ray diffraction. The calcined powders were then re-milled for 24 h with PVA solution as a binder. Pellets with 11 mm in diameter and 5 mm in thickness were pressed using uniaxial pressing. A pressing pressure of 2000 kg/cm^2 was used for all samples. After debinding, these pellets were sintered at temperatures 1400–1500 °C for 5 h in air. The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) spectra were collected using Cu Kα radiation (at 30 kV and 20 mA) and a graphite monochrometer in the 2θ range of 20–60°. The microstructural observations and analysis of sintered surface were performed by a scanning electron microscopy (SEM, Philips XL-40FEG).

The bulk densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman [13] dielectric resonator method as modified and improved by Courtney [14]. The dielectric resonator was positioned between two brass plates. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. Identical technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from +25 °C to +80 °C. The τ_f value (ppm/°C) can be calculated by noting the change

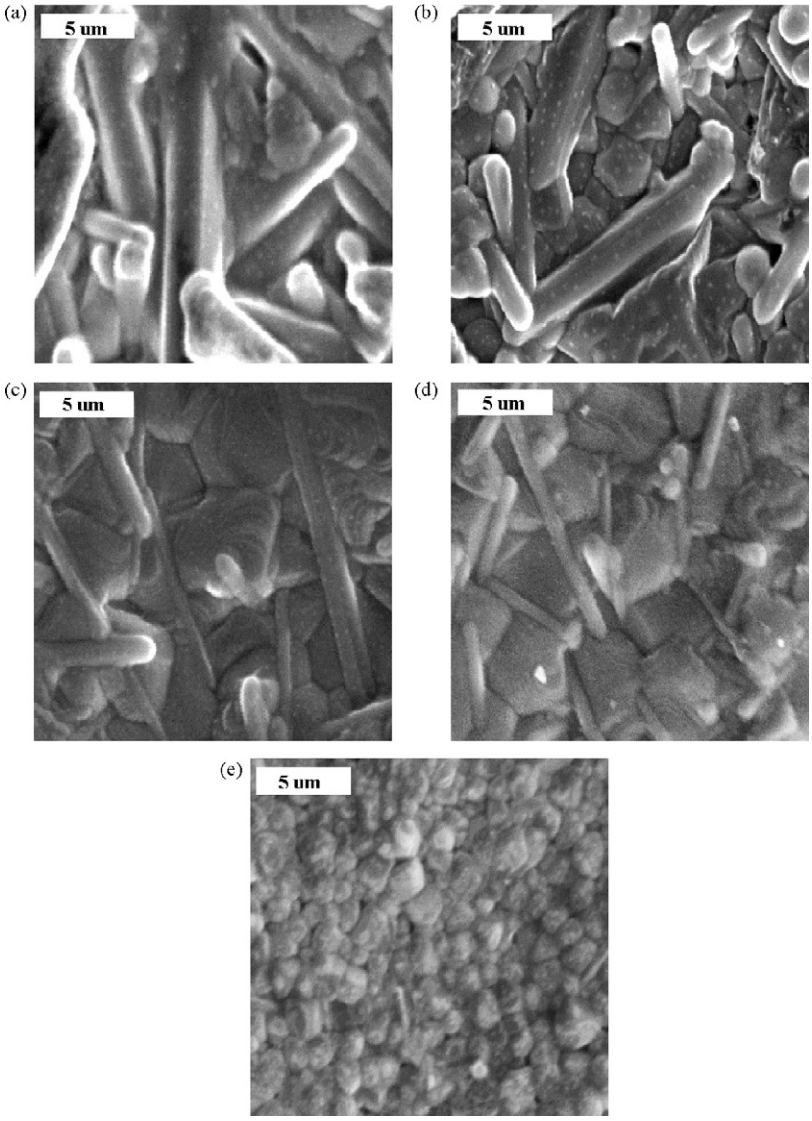

Fig. 2. SEM photographs of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)$ $Ca_{0.6}La_{0.8/3}TiO_3$ ceramics (a) $x=0.4$, (b) $x=0.5$, (c) $x=0.6$, (d) $x=0.7$ and (e) $x=0.8$ with 1 wt.% CuO additions sintered at 1450 °C for 5 h.

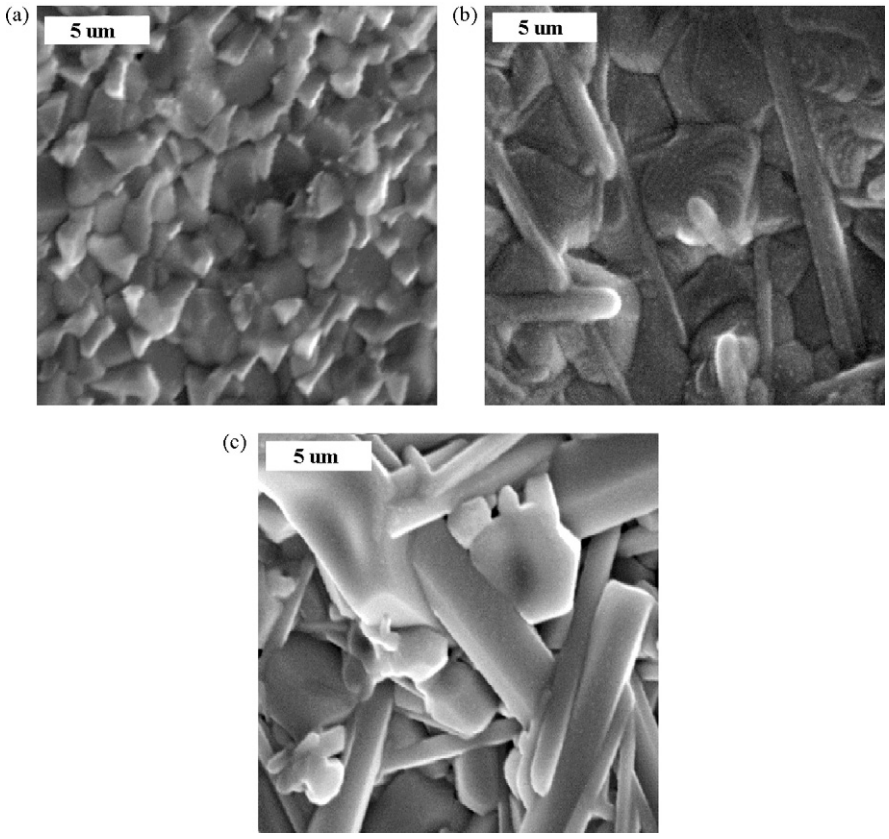

Fig. 3. SEM photographs of $0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics sintered at (a) 1400 °C, (b) 1450 °C and (c) 1500 °C with 1 wt.% CuO additions for 5 h.

in resonant frequency (Δf),

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

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

X-ray diffraction patterns of 1 wt.% CuO-doped $0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics at different sintering temperatures (1400–1500 °C) are shown in Fig. 1. All the peaks were indexed based on the cubic perovskite unit cell. All the peaks were indexed based on the cubic perovskite unit cell. The figure reveals that a series of extra peaks were present at the 1/2(1 1 1)(2θ = 19.56°), 1/2(2 1 0) (2θ = 25.309°), 1/2(3 0 0) (2θ = 34.5°) and 1/2(3 1 1) (2θ = 37.98°) positions. The X-ray diffraction patterns of the $0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ solid solution have not significant change with 1 wt.% CuO addition at sintering temperatures of 1400–1500 °C. Second phase was not observed at the level of 1 wt.% CuO addition since that detection of a minor phase by X-ray is extremely difficult. Fig. 1 XRD patterns of $La(Mg_{1/2}Ti_{1/2})O_3$–$Ca_{0.6}La_{0.8/3}TiO_3$ ceramic systems form solid solution, and all peaks match with $La(Mg_1Ti_{1/2})O_3$–$Ca_{0.6}La_{0.8/3}TiO_3$ compound.

The SEM photographs of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics sintered at 1450 °C for different x value are illustrated in Fig. 2. For all compositions, low level porosity and densed ceramic could be observed. The grain size was increased as increasing the $Ca_{0.6}La_{0.8/3}TiO_3$ content.

The SEM photographs of $0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ ceramics sintered at various temperatures for 5 h are illustrated in Fig. 3. For all compositions, low level porosity and densed ceramic could be observed in the figure. The degree of the grain growth increased with the increase of sintering temperature. No pores were observed at a temperature of 1450 °C for 4 h due to grain growth [see Fig. 3(b)]. In addition, uniform grain morphology was produced at 1450 °C with sintering for 4 h. However, degradation in grain uniformity and abnormal grain growth started to appear for$0.6La(Mg_{1/2}Ti_{1/2})O_3$–$0.4Ca_{0.6}La_{0.8/3}TiO_3$ specimens at sintering temperatures higher than 1450 [see Fig. 3(c)], which could damage

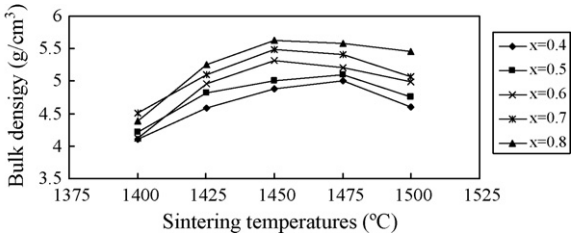

Fig. 4. Bulk density of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics system sintered at different temperatures with 1 wt.% CuO addition.

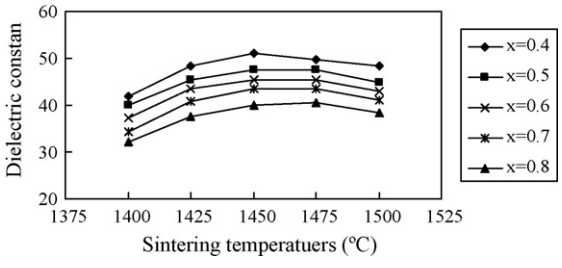

Fig. 5. ε_r value of $xLa(Mg_{1/2}Ti_{1/2})O_3$–$(1-x)Ca_{0.6}La_{0.8/3}TiO_3$ ceramics system sintered at different temperatures with 1 wt.% CuO addition.

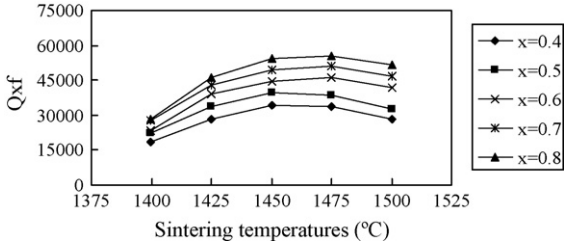

Fig. 6. $Q \times f$ value of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics system sintered at different temperatures with various 1 wt.% CuO addition.

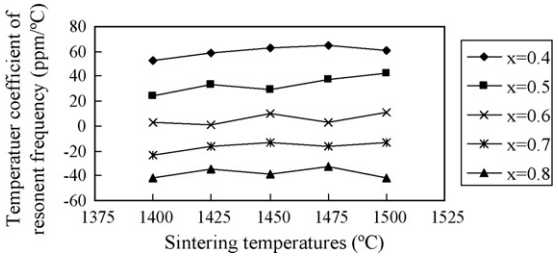

Fig. 7. Temperature coefficient value of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics system sintered at different temperatures with 0.5 wt.% CuO addition.

their microwave dielectric properties. The inhomogeneous rod-like grains were identified, in all samples at 1500 °C. It is possible to evaluate the effect of grain orientation on the XRD patterns as can see from Fig. 1.

The relative densities of the CuO-doped $0.6\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-0.4\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics at differential sintering temperature as shown in Fig. 4. It indicated that densities of 4.11–5.31 (g/cm^3) were obtained for CuO-doped $0.6\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-0.4\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics at sintering temperatures from 1400 to 1500 °C. The density increased with increasing sintering temperature due to enlarged grain size as observed in Fig. 3, and was also affected by the composition and decreased with increasing x value. It suggested that more $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ content and sintering at higher temperatures (above 1475 °C owing to the over-sintering) would degrade the bulk density of the ceramics.

The dielectric properties of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ with 1 wt.% CuO addition are illustrated in Fig. 5. As the x value increased from 0.4 to 0.8, the dielectric constants decreased from 51.1 to 3.2. The dielectric constants slightly decreased with increasing sintering temperature. The decrease of ε_r value with increasing sintering temperature could be explained owing to the over-sintering of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$. With 1 wt.% CuO addition, a ε_r value of 45.5 was obtained for $0.6\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-0.4\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics sintered at 1450 °C.

Fig. 6 shows the $Q \times f$ values of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics with 1 wt.% CuO additions at different sintering temperatures as functions of the x value and with different x value had a maximum value at 1500 °C. The $Q \times f$ value increase with the increase of $\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$ content and sintering temperature. It was expected since that the quality factor of $\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3$ is much higher than that of $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ and the bulk density increased with increasing sintering temperature due to the ceramics being denser. Many factors could affect the microwave dielectric loss of dielectric resonators such as the lattice vibration modes, the pores and the secondary phases. Generally, a larger grain size, i.e., a smaller grain boundary, indicates a reduction in lattice imperfection and the dielectric loss was thus reduced. It seems that the dielectric loss of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics system was dominated by the bulk density and the grain size.

The temperature coefficients of resonant frequency (τ_f) of CuO-doped $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\ \mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics at different sintering temperatures are illustrated in Fig. 7. The temperature coefficient of resonant frequency is well known related to the composition, the additives and the second phase of the material. It seemed that higher $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ content would shift the τ_f value to more positive. It varied from −41.8 to 62.8 ppm/°C as the amount of $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ addition increased from 0.4 to 0.8 sintered at 1450 °C. In general, the temperature coefficient of resonant frequency was found to be related to the composition and the existing phase in ceramics.

4. Conclusion

The microstructure and microwave dielectric properties of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics were investigated. $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics exhibited perovskite structure. The relative permittivity (ε_r) and the temperature coefficient of resonant frequency (τ_f) of $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics increased with an increase of $\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$, but the $Q \times f$ value decreased. With 1 wt.% CuO addition, a dielectric constant of 45.5, a $Q \times f$ value of 44,600 (GHz) and a τ_f value of 2 ppm/°C were obtained for $0.6\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-0.4\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramics at 1450 °C for 4 h. Their excellent dielectric properties make the $x\mathrm{La}(\mathrm{Mg}_{1/2}\mathrm{Ti}_{1/2})\mathrm{O}_3-(1-x)\mathrm{Ca}_{0.6}\mathrm{La}_{0.8/3}\mathrm{TiO}_3$ ceramic capable in the application of microwave devices.

References

[1] C.-L. Huang, Y.-B. Chen, C.-F. Tasi, J. Alloys Compd. 460 (2008) 675–679.
[2] C.-L. Huang, Y.-B. Chen, C.-F. Tasi, J. Alloys Compd. 454 (2008) 454–459.
[3] C.-L. Huang, C.-F. Tasi, Y.-B. Chen, Y.-C. Cheng, J. Alloys Compd. 453 (2008) 337–340.
[4] S.-Y. Cho, C.-H. Kim, D.-W. Kim, Mater. Res. Soc. 14 (1999) 2484.
[5] C.-L. Huang, J.-T. Tsai, Y.-B. Chen, Mater. Res. Bull. 36 (2001) 54.
[6] N. Santha, I.N. Jawahar, P. Mohanan, M.T. Sebastian, Mater. Lett. 54 (2002) 318.
[7] W.S. Kim, K.H. Yoon, E.S. Kim, J. Am. Ceram. Soc. 83 (2000) 2327.
[8] V.M. Ferreir, F. Azough, R. Freer, L. Baptista, J. Mater. Res. 12 (1997) 3293.
[9] D. Lee, S. Yoon, J. Mater. Sci. Lett. 19 (2000) 131.
[10] C. Yang, Y. Chen, W. Tzou, S. Chang, Mater. Lett. 57 (2003) 2945.
[11] S.G. Lu, K.W. Kwok, H.L.W. Chan, C.L. Choy, Mater. Sci. Eng. B 99 (2003) 491.
[12] K.P. Surendran, P. Mohanan, M.T. Sebastian, J. Solid-State Chem. 177 (2004) 4031.
[13] B.W. Hakki, P.D. Coleman, IEEE Trans. Microw. Theory Tech. 8 (1960) 402.
[14] W.E. Courtney, IEEE Trans. Microw. Theory Tech. 18 (1970) 476.