ELSEVIER

Ceramics International 30 (2004) 2067–2073

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Low temperature sintering and microwave dielectric properties of $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics using copper oxide additions

Cheng-Shing Hsu [a], Cheng-Liang Huang [a,*], Jing-Fang Tseng [a], Cheng-Chi You [b]

[a] *Department of Electrical Engineering, National Cheng Kung University,1 University Road, Tainan 70101, Taiwan*
[b] *Department of Electrical Engineering, NanKai College, Nantou, Taiwan*

Received 9 September 2002; received in revised form 2 October 2003; accepted 15 October 2003
Available online 2 July 2004

Abstract

The microwave dielectric properties and the microstructures of $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics with CuO addition prepared with conventional solid-state route have been investigated. Doping with CuO (up to 1 wt.%) can effectively promote the densification and remain comparable dielectric properties of $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics. It is found that $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics can be sintered at 1400 °C due to the sintering aid effect resulted from CuO as addition observed by scanning electron microscopy. The dielectric constant as well as the $Q \times f$ value decreases with increasing CuO content. At 1460 °C, $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics with 0.25 wt.% CuO addition possess a dielectric constant (ε_r) of 35.2, a $Q \times f$ value of 24 000 (at 8 GHz) and a temperature coefficient of resonant frequency (τ_f) of −13.5 ppm/°C.

Keywords: Microwave dielectric properties; $LaAlO_3$–$SrTiO_3$ ceramics; Sintering aid

1. Introduction

Recently, many researches have been focusing on developing dielectric materials with high quality factor ($Q \times f$), high dielectric constant (ε_r) and zero temperature coefficient of resonant frequency (τ_f) for use as dielectric resonators and microwave device substrate. High dielectric constant material can effectively reduce the size of resonators since the wavelength (λ) in dielectrics is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength (λ_0) in vacuum ($\lambda = \lambda_0/\sqrt{\varepsilon_r}$). The inverse of the dielectric loss ($Q = 1/\tan\delta$) is required to be high for achieving prominent frequency selectivity and stability in microwave transmitter components. And small temperature coefficient of the resonant frequency is required to ensure the stability of the microwave components at different working temperatures. Several compounds such as $(Zr,Sn)TiO_4$, $Ba(Mg_{1/3}Ta_{1/3})O_3$ and $(Mg,Ca)TiO_3$ have therefore been developed [1–3]. Rare-earth aluminates, $LaAlO_3$ have been widely used as substrates for superconducting microwave devices since they provide a high quality factor, excellent lattice matching and a good matching for thermal expansion. It also possesses suitable microwave dielectric properties ($\varepsilon_r \sim 23$, $Q \times f \sim 65\,000$, $\tau_f \sim -44$ ppm/°C) [4] for applications in dielectric resonators. The crystal structure of $LaAlO_3$ exhibits rhombohedral symmetry. A phase transition of $LaAlO_3$ occurs at ~800 K from the high temperature cubic phase (space group *Pm3m*) to the rhombohedral phase (space group $R\bar{3}c$) [5]. To compensate the τ_f value, $SrTiO_3$ ($\varepsilon_r > 200$, $Q \times f < 1000$, $\tau_f > 1100$ ppm/°C) with positive τ_f value has been introduced to form the solid solution $(1-x)LaAlO_3$–$xSrTiO_3$. With $x = 0.5$, $(1-x)LaAlO_3$–$xSrTiO_3$ gave a dielectric constant ε_r of 35, a $Q \times f$ value of 28 000, and a τ_f value of −18 ppm/°C [6]. By prolonging its sintering time to 12–24 h, a $Q \times f$ value of 54 000 and a ε_r value of 33 were also reported [5]. However, they required high sintering temperatures (1550–1650 °C).

Chemical processing and small particle sizes of the starting materials are generally advantageous to reduce the sintering temperature of dielectric materials [7–10]. However, they required a flexible procedure, which was not only expensive but also time consuming. The liquid phase sintering by adding glass or other low melting point material was found to effectively lower the firing tempera-

* Corresponding author. Tel.: +886-6-2757575x62390; fax: +886-6-2345482.
E-mail address: huangcl@mail.ncku.edu.tw (C.-L. Huang).

0272-8842/$30.00 © 2003 Elsevier Ltd and Techna S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2003.10.016

ture of ceramics [8,9]. The microwave dielectric properties of dielectric resonators were also deeply affected by the liquid sintering temperature due to the development of microstructure at low sintering temperature or the reaction between host material and addition. In this paper, CuO was chosen as a sintering aid to lower the sintering temperature of $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics. The crystalline phases, the microstructures and the microwave dielectric properties of CuO-doped $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics were investigated.

2. Experimental procedures

Samples of $0.5LaAlO_3$–$0.5SrTiO_3$ were synthesized by conventional solid state method. The starting materials were mixed according to a stoichiometric ratio. A small amount of CuO (0.25–1 wt.%) was added as a sintering aid. High purity oxide powders (>99.9%) La_2O_3, Al_2O_3, $SrCO_3$, 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 1150 °C for 2 h. The calcined powder was ground and sieved through 100-mesh screen. Phase formation of $0.5LaAlO_3$–$0.5SrTiO_3$ 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. These pellets were sintered at temperatures 1340–1460 °C for 2 h in air.

The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III. V) spectra were collected using Cu K_α radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2θ range of 20–60°. The microstructural observations and the analysis of sintered surfaces were performed by a scanning electron microscopy (SEM, Philips XL-40FEG) and an energy dispersive X-ray spectrometer (EDS), respectively.

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 [11] dielectric resonator method as modified and improved by Courtney [12]. 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 to +80 °C. The τ_f value (ppm/°C) can be calculated by noting the change 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

Fig. 1 shows the X-ray diffraction patterns of 0.25 wt.% CuO-doped $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics at different sintering temperatures (1340–1460 °C). All of the XRD profiles of the ceramics samples can be indexed by pseudo-cubic unit cell of the perovskite structure. The X-ray diffraction patterns of the $0.5LaAlO_3$–$0.5SrTiO_3$ solid solution have not

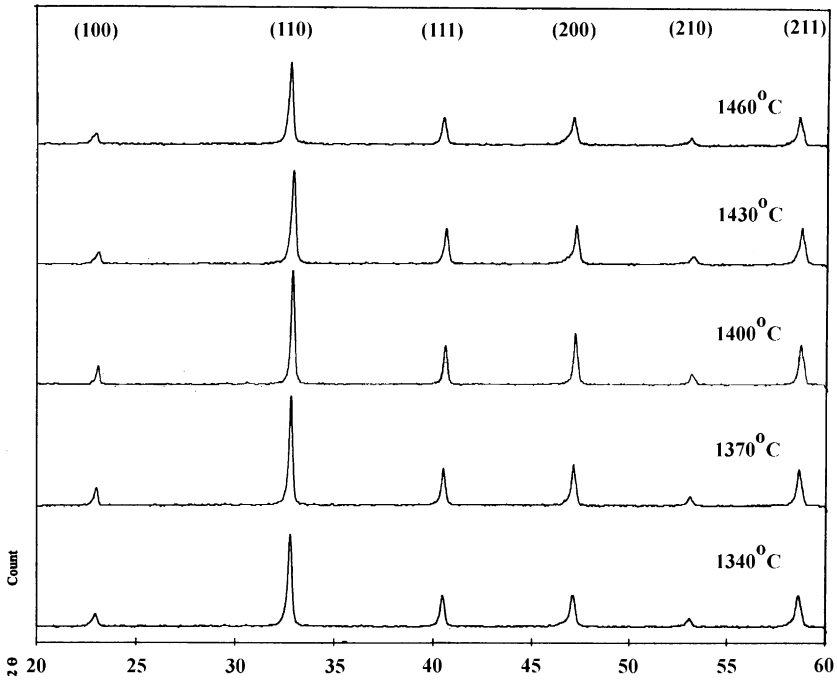


Fig. 1. X-ray diffraction patterns of 0.25 w.t% CuO-doped 0.5LaAlO3–0.5SrTiO3 ceramics at different sintering temperatures.

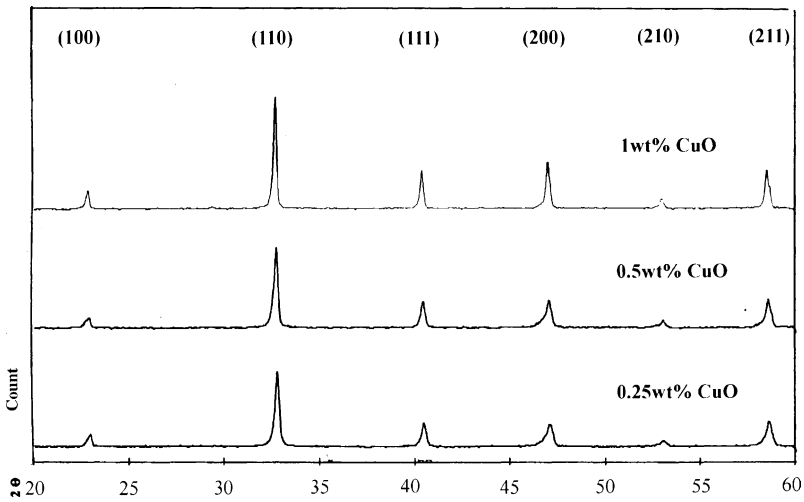
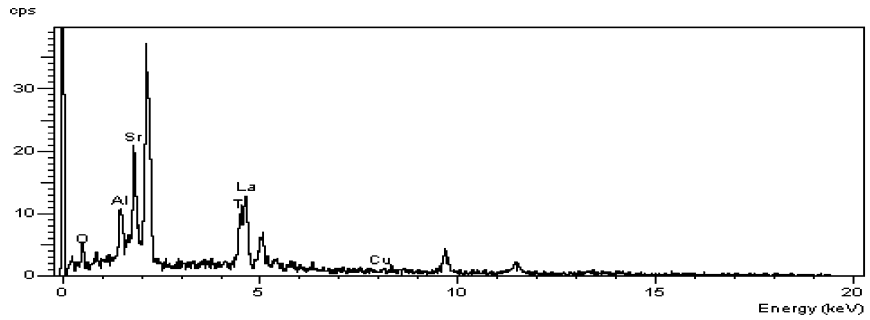
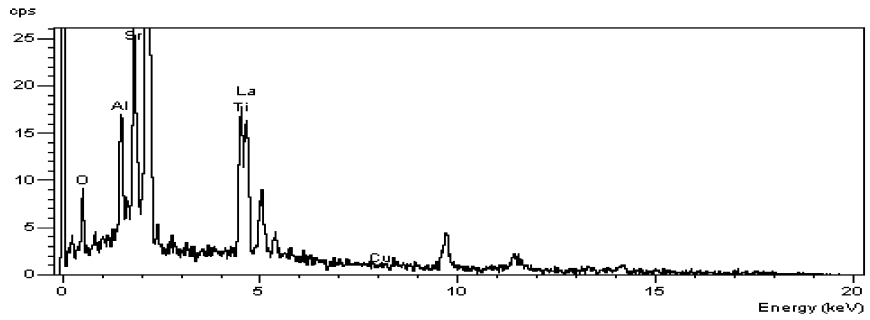


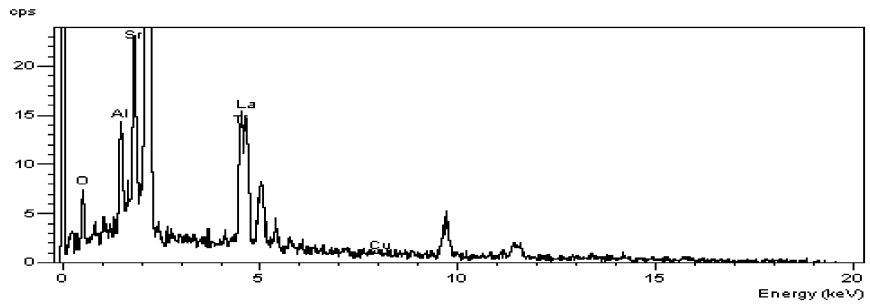
Fig. 2. X-ray diffraction patterns of 0.5LaAlO3–0.5SrTiO3 ceramics with different amount of CuO addition sintered at 1460 °C.



(a) atomic% : La:15.58, Al:11.5, Sr:17.21, Ti:16.9, O:38.73, Cu:0



(b) atomic% : La:14.32, Al:10.35, Sr:15.65, Ti:13.96, O:45.77, Cu:0



(c) atomic% : La:15.37, Al:10.15, Sr:15.7, Ti:15.29, O:42.97, Cu:0.51

Fig. 3. EDS spectra of 0.5LaAlO3–0.5SrTiO3 ceramics with (a) 0.25 wt.% (b) 0.5 wt.% and (c) 1 wt% CuO additions at 1460 °C.

significant change with 0.25 wt.% CuO addition at sintering temperatures of 1340–1460 °C. Second phase was not observed at the level of 0.25 wt.% CuO addition since detection of a minor phase by X-ray is extremely difficult.

The X-ray diffraction patterns of $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics with different amount of CuO addition sintered at 1460 °C are illustrated in Fig. 2. Identical XRD patterns were observed for the ceramics in spite of the amount of CuO additions.

Fig. 3 shows the EDS spectra of $0.5LaAlO_3$–$0.5SrTiO_3$ ceramics with CuO additions (0.25–1 wt.%) at 1460 °C for 2 h. It revealed that the surfaces of the CuO-doped 0.5LaAlO3–0.5SrTiO3 ceramics have the same ions La, Al, Sr, Ti and O. However, the ion Cu was also detected for specimen with 1 wt.% CuO addition. In fact, a small amount of CuO addition (0.25–0.5 wt.%) was difficult to detect. With 1 wt.% CuO addition, a Cu atomic percentage of 0.51 was obtained for 0.5LaAlO3–0.5SrTiO3 ceramics sintered at 1460 °C.

The surface microstructural photographs of CuO-doped 0.5LaAlO3–0.5SrTiO3 at sintering temperature 1460 °C are demonstrated in Fig. 4. The grain size increased with the increase of sintering temperature as well as amount of CuO addition. At the level of 0.25–0.5 wt.% CuO additions, porous specimens were observed at the sintering temperatures of 1340 and 1370 °C. However, the sample with 1 wt.% CuO addition was dense at 1370 °C. It provided the evidence of densification enhanced by sintering aid.

The density of the CuO-doped 0.5LaAlO3–0.5SrTiO3 ceramics at differential sintering temperatures is shown in Fig. 5. It indicated that densities of 5.27–5.57 g/cm^3 were obtained for CuO-doped 0.5LaAlO3–0.5SrTiO3 ceramics at sintering temperatures from 1340 to 1460 °C. The density increased with increasing sintering temperature due to enlarged grain size as observed in Fig. 4, and was also affected by the CuO addition and slightly increased with increasing CuO content. Higher CuO doping level formed, which would enhance the densification resulted in a higher ceramic density. Moreover, the density also related to the porosity and increased with the decrease of porosity.

Fig. 6 demonstrates the dielectric constant of 0.5LaAlO3–0.5SrTiO3 ceramics with different amount of CuO additions as a function of their sintering temperatures. The relationships between ε_r values and sintering temperatures revealed the same trend with those between densities and sintering temperatures since higher density means lower porosity. The

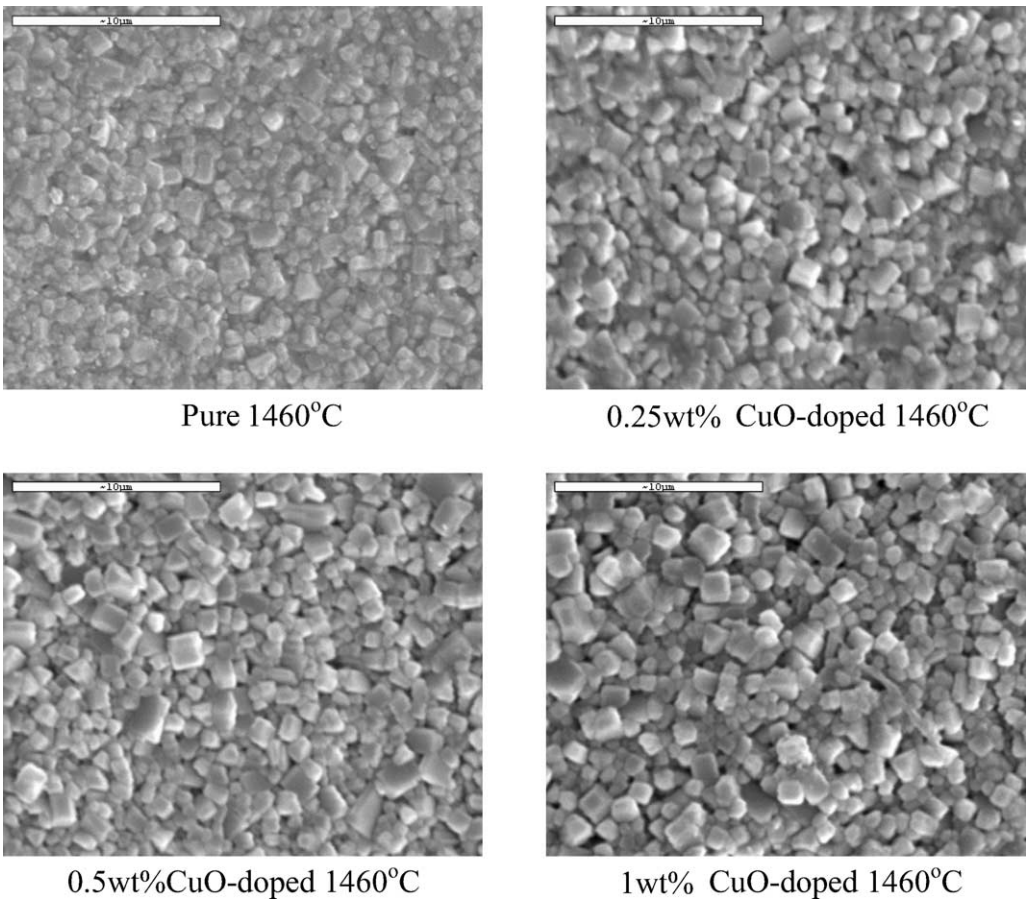


Fig. 4. SEM photographs of 0.5LaAlO3–0.5SrTiO3 ceramics with (a) 0.25 wt.% (b) 0.5 wt.% and (c) 1 wt.% CuO additions at different sintering temperatures.

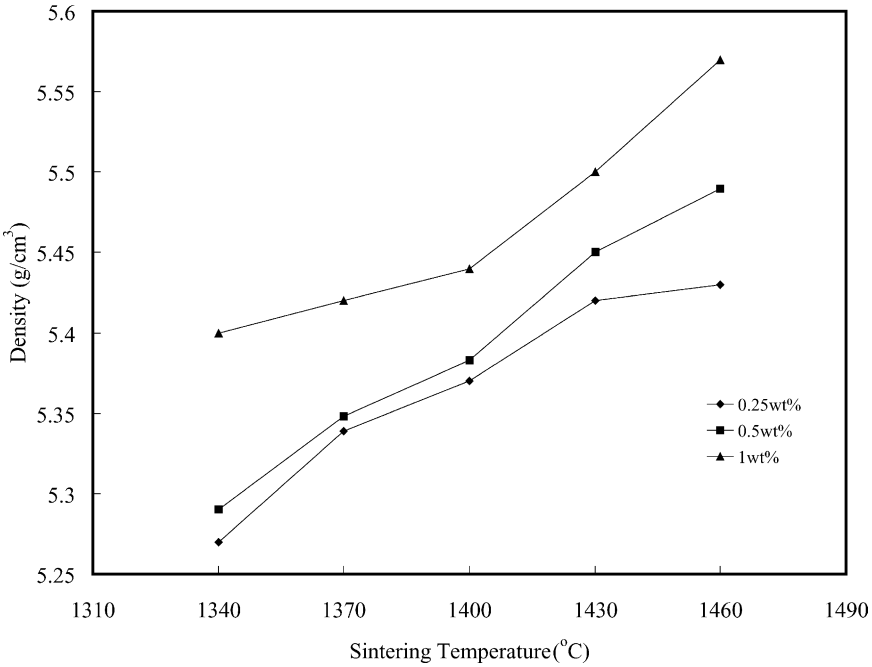


Fig. 5. Dependence of sintering temperature of 0.5LaAlO3–0.5SrTiO3 ceramics on density with various CuO additions.

dielectric constant slightly increased with increasing sintering temperature. It varied from 35 to 35.2 as the sintering temperature increased from 1340 to 1430 °C. The increase of ε_r value could be explained owing to higher densities. However, the dielectric constant decreased with increasing CuO content, and it was not consistent with the variation of density. The decrease in dielectric constant might be attributed to low ε_r value of CuO.

Fig. 7 shows the $Q \times f$ value of 0.5LaAlO3–0.5SrTiO3 ceramics with various CuO additions at different sintering temperatures. The microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pores and the second phases. Relative density also plays an important role in controlling the dielectric loss and has been shown for other microwave dielectric materials. At low level of CuO additions (0.25–1 wt.%), the $Q \times f$ values

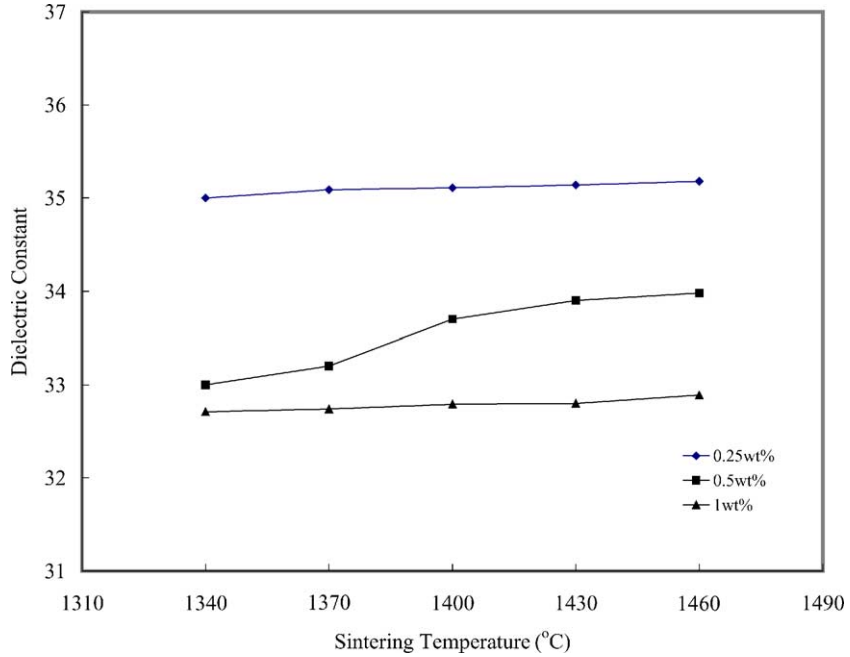


Fig. 6. Dependence of sintering temperature of 0.5LaAlO3–0.5SrTiO3 ceramics on dielectric constant with various CuO additions (note: $\varepsilon_r = 34.7$ for pure 0.5LaAlO3–0.5SrTiO3 at 1460 °C).

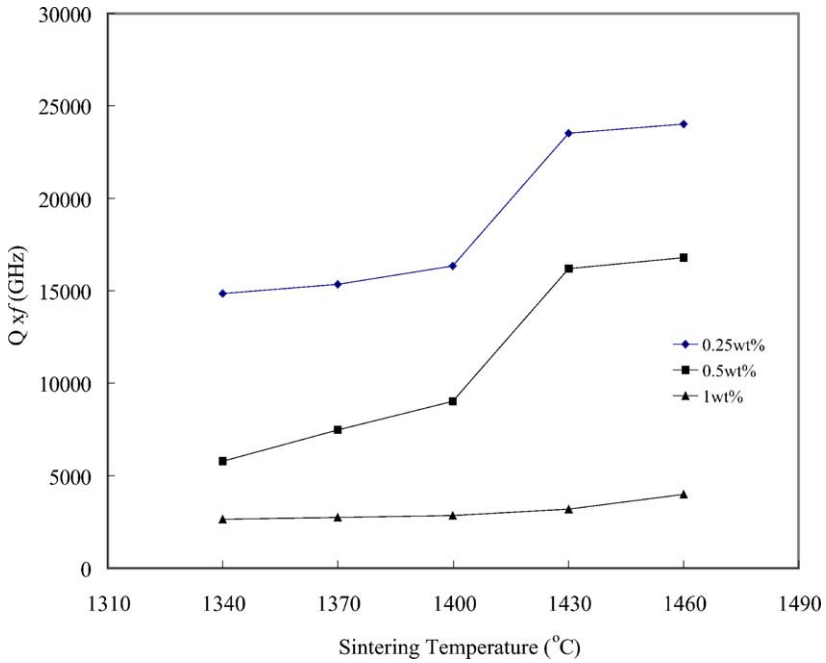


Fig. 7. Dependence of sintering temperature of 0.5LaAlO3–0.5SrTiO3 ceramics on quality factor value ($Q \times f$) with various CuO additions (note: $Q \times f = 16\,500$ for pure $0.5LaAlO_3$–$0.5SrTiO_3$ at 1460 °C).

of 0.5LaAlO3–0.5SrTiO3 ceramics increased with increasing sintering temperature. With 0.25 wt.% CuO addition, the $Q \times f$ value increased from 15 000 to 24 000 GHz as the sintering temperature increased from 1340 to 1460 °C for 2 h. It was consistent with the variation of density. However, higher $Q \times f$ values were observed at 0.25 wt.% CuO doping level. Conversely, higher CuO content would degrade the $Q \times f$ value of 0.5LaAlO3–0.5SrTiO3 ceramics. It was due to that addition of flux to lower the sintering temperature is normally accompanied by an increase in the dielectric loss. That would explain the decrease in $Q \times f$ values for 0.5LaAlO3–0.5SrTiO3 ceramics with more CuO additions.

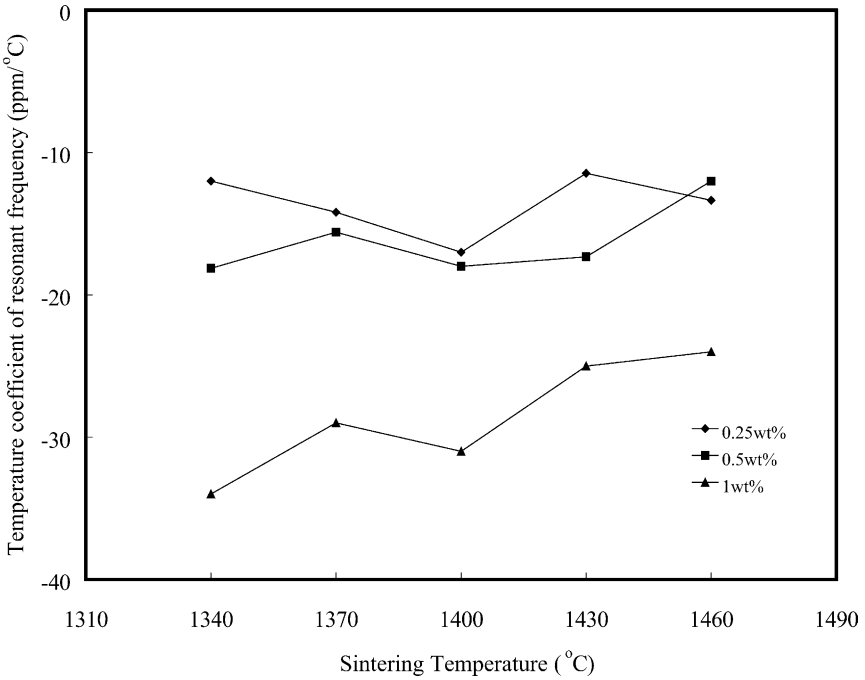


Fig. 8. Dependence of sintering temperature of 0.5LaAlO3–0.5SrTiO3 ceramics on τ_f value with various CuO additions (note: $\tau_f = -15$ ppm/°C for pure 0.5LaAlO3–0.5SrTiO3 at 1460 °C).

The temperature coefficients of resonant frequency (τ_f) of CuO-doped 0.5LaAlO3–0.5SrTiO3 ceramics at different sintering temperatures are illustrated in Fig. 8. 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 CuO content would shift the τ_f value to more negative. The variation of τ_f value might be a result from CuO addition. Significant change was not observed in the τ_f value with fixed CuO addition at different sintering temperatures.

4. Conclusion

The dielectric properties of CuO-doped 0.5LaAlO3–0.5SrTiO3 ceramics were investigated. 0.5LaAlO3–0.5Sr TiO3 ceramics exhibited perovskite structure with pseudocubic unit cell. A tremendous sintering temperature reduction (100–200 °C) can be achieved by adding CuO to the 0.5LaAlO3–0.5SrTiO3 ceramics. With 0.25 wt.% CuO addition, a dielectric constant of 35.2, a $Q \times f$ value of 24 000 GHz and a τ_f value of −13.5 ppm/°C were obtained for 0.5LaAlO3–0.5SrTiO3 ceramics sintered at 1460 °C for 2 h.

Acknowledgements

This work was supported by the National Science Council of the Republic of China under grant NSC90-2213-E-006-061.

References

[1] S. Nomura, K. Toyama, K. Kaneta, Jpn. J. Appl. Phys. 21 (1982) L624.
[2] G. Wolfram, H.E. Gobel, Mater. Res. Bull. 16 (1981) 1455.
[3] I. Burn, US Patent 4,845,062 (1989).
[4] S.Y. Cho, I.T. Kim, K.S. Hong, J. Mater. Res. 14 (1999) 114.
[5] P.H. Sun, T. Nakamura, Y.J. Shan, Y. Inaguma, M. Itoh, Jpn. J. Appl. Phys. 37 (1998) 5625.
[6] S.Y. Cho, K.S. Hong, K.H. Ko, Mater. Res. Bull. 34 (1999) 511.
[7] T. Kakada, S.F. Wang, Syoshikawa, S.T. Jang, R.E. Newnham, J. Am. Ceram. Soc. 77 (1994) 1909.
[8] T. Kakada, S.F. Wang, Syoshikawa, S.T. Jang, R.E. Newnham, J. Am. Ceram. Soc. 77 (1994) 2485.
[9] S.I. Hirno, Takashi, Hayashi, A. Hattori, J. Am. Ceram. Soc. 74 (1991) 1320.
[10] V. Tolmer, G. Desgardin, J. Am. Ceram. Soc. 80 (1997) 1981.
[11] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theor. Technol. 8 (1960) 402.
[12] W.E. Courtney, IEEE Trans. Microwave Theor. Technol. 18 (1970) 476.