Journal of the Korean Ceramic Society
Vol. 41, No. 1, pp. 9~12, 2004.

Effect of $CuO-V_2O_5$ Addition on Microwave Dielectric Properties of $(Pb_{0.45}Ca_{0.55})[(Fe_{0.5}Nb_{0.5})_{0.9}Sn_{0.1}]O_3$ Ceramics

Jong-Yoon Ha,* Ji-Won Choi,* Ki Hyun Yoon,** Doo-Jin Choi,** Seok-Jin Yoon,†,* and Hyun-Jai Kim***

**Thin Film Materials Research Center, KIST, Seoul 136-791, Korea*
***Department of Ceramic Engineering, Yonsei University, Seoul 120-749, Korea*
(Received October 11, 2003; Accepted December 16, 2003)

ABSTRACT

The effect of x wt% CuO - y wt% V_2O_5 content on the microwave dielectric properties of $(Pb_{0.45}Ca_{0.55})[(Fe_{0.5}Nb_{0.5})_{0.9}Sn_{0.1}]O_3$ (PCFNS) ceramics was investigated. In order to decrease the sintering temperature and use as a Low Temperature Co-firing Ceramics (LTCC), $CuO-V_2O_5$ are added in the PCFNS. The bulk density, dielectric constant (ε_r) and quality factor($Q \cdot f_0$) increased with increase in CuO content within a limited value. The microwave properties were degraded with increases in V_2O_5 content. The temperature coefficient of the resonant frequency (τ_f) of PCFNS was shifted to positive value abruptly with increasing the V_2O_5 content, while the τ_f was slightly shifted to positive value with increasing the CuO content. The optimized microwave properties, $\varepsilon_r = 88$, $Q \cdot f_0 = 6100$ (GHz), and $\tau_f = 18$ ppm/°C, were obtained in $(Pb_{0.45}Ca_{0.55})[(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}]O_3$ with 0.2 wt% CuO 0.05 wt% V_2O_5 and sintered at 1000°C for 3 h. The relationship between the microstructure and microwave dielectric properties of ceramics was studied by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

Key words : Microwave, Dielectric, LTCC, Additive, $CuO-V_2O_5$

1. Introduction

Recently, the development of microwave dielectric resonators for communication systems such as Personal Communication System (PCS), cellular phone, and IMT-2000 etc. has been advancing rapidly. The microwave dielectric materials require a high dielectric constant (ε_r) to reduce the size of resonator, high quality factor ($Q \cdot f_0$) value for stable resonator frequency, and a stable temperature coefficient of the resonant frequency ($\tau_f \leq |10|$ ppm/°C) for the temperature-stable circuits. In order to miniaturize resonator devices such as band-pass filters, antenna and duplexers, the multilayer microwave devices have been investigated. For the fabrication of multilayer microwave devices, microwave materials must be co-fired with conductors such as Ag, Cu, Pd, and Pt. There have been many investigations to find the sintering additives did not degrade the microwave dielectric properties. Many researchers have also studied on the reduction of sintering temperature for the co-firing with Ag or Cu. Kucheiko *et al.*[1] reported the microwave dielectric properties of (Pb,Ca)(Fe,Nb,Sn)O_3 ceramics. The dielectric constant value (e_r) was 86, the quality factor ($Q \cdot f_0$) was 7900 GHz and the temperature coefficients of the resonant frequency (τ_f) was 0 ppm/ but the sintering temperature of this ceramic was some high as 1165°C. This paper reports the microwave dielectric properties of $(Pb_{0.45}Ca_{0.55})[(Fe_{1/2}Nb_{1/2})_{0.9}\ Sn_{0.1}]O_3$ (PCFNS) prepared with addition of x wt% CuO – y wt%V_2O_5 as sintering additives. The relationship between the physical properties and microwave dielectric properties of ceramics are also examined.

†Corresponding author : Seok-Jin Yoon
E-mail : sjyoon@kist.re.kr
Tel : +82-2-958-5550 Fax : +82-2-958-6720

2. Experimental Procedure

The powders of PCFNS were prepared using high-purity PbO (High Purity Chemical Ltd., 99.9%), $CaCO_3$, Nb_2O_5, SnO_2, V_2O_5 (all Aldrich, 99.9%), Fe_2O_3, CuO (Aldrich, 99+%). The starting materials were mixed according to the desired stoichiometry, $(Pb_{0.45}Ca_{0.55})[(Fe_{1/2}Nb_{1/2})_{0.9}\ Sn_{0.1}]O_3$, and ground in ethanol for 24 h in a ball-mill. The mixtures were dried and calcined in an alumina crucible at 900°C for 4 h in air. Calcined powder was re-milled with the additives of x wt% CuO – y wt% V_2O_5 for 24 h. This powder was ground with 5 wt% Poly-Vinyl Alcohol (PVA) and then sieved with 60 mesh. Pellets with 12 mm diameter and 5~6 mm thickness were pressed by uniaxial pressing at 800 Kg/cm^2. The sintering temperature was 1000°C for 3 h in air. The bulk density was measured by the Archimedes method. The microwave dielectric properties were measured by the dielectric rod resonator method[2] using a network analyzer (HP8720C). The temperature coefficient of resonant frequency (τ_f) at microwave frequencies was measured in the temperature range of 20 to 80. Sintered pellets were exam-

ined by powdered XRD (X-Ray Diffraction, D/MAX 2500, Rigaku) analysis with CuKα radiation and SEM (Scanning Electron Microscope, S-4200, Hitachi). The samples were prepared without thermal etching to investigate liquid phases in the grain boundaries.

3. Results and Discussion

Fig. 1 shows the XRD patterns of PCFNS with additives, 0.1 wt% CuO and y wt% V_2O_5 (0.1 – 0.3 wt%), sintered at

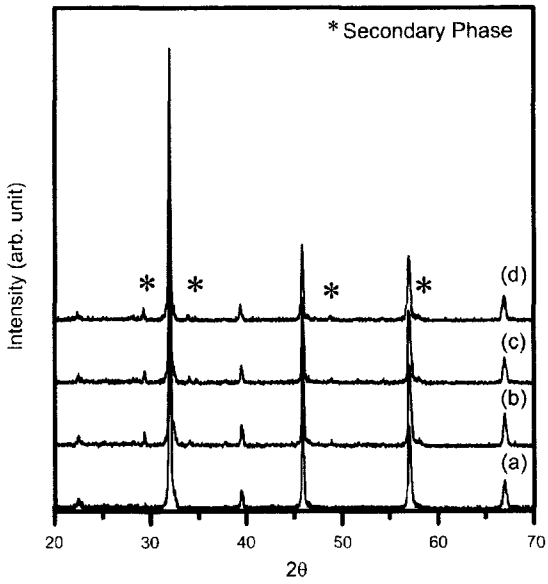

Fig. 1. XRD pattern of PCFNS sintered at 1000°C for 3 h with contents of 0.1 wt% CuO – x wt% V_2O_5 : (a) PCFNS [Sintered at 1165°C for 3 h], (b) 0.1, (c) 0.2, and (d) 0.3.

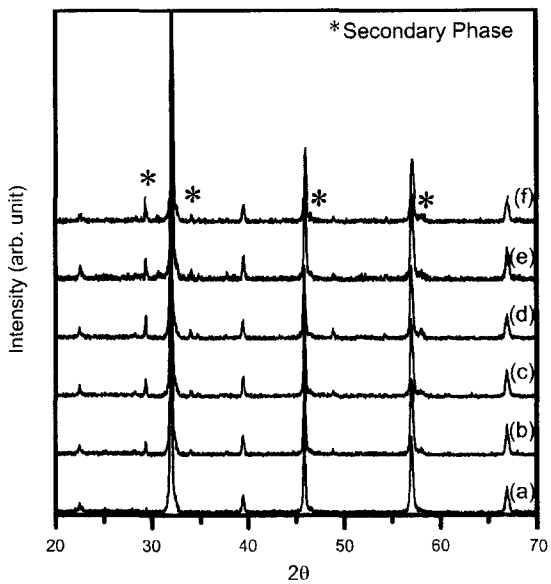

Fig. 2. XRD pattern of PCFNS sintered at 1000°C for 3 h with contents of x wt% CuO – 0.05 wt% V_2O_5 : (a) PCFNS [Sintered at 1165°C for 3 h], (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, and (f) 0.5.

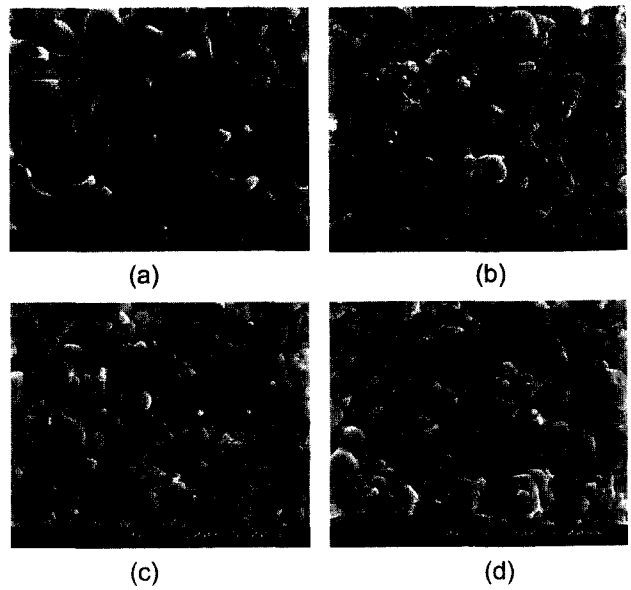

Fig. 3. SEM photographs of PCFNS sintered at 1000°C for 3 h with contents of 0.1 wt% CuO – x wt% V_2O_5 : (a) PCFNS [Sintered at 1165°C for 3 h], (b) 0.1, (c) 0.2, and (d) 0.3.

1000°C for 3 h. The XRD peaks were indexed based on the $CaTiO_3$-type orthorhombic perovskite structure. The secondary phase was not found in pure PCFNS (Fig. 1(a)) sintered at 1165°C for 3 h. With increasing the V_2O_5 content, the secondary phases were formed slightly. The XRD patterns of PCFNS ceramics with x CuO (0.1 – 0.5 wt%) – 0.05 wt% V_2O_5 sintered at 1000°C for 3 h were shown in Fig. 2. With increasing the CuO content, the secondary phases increased slightly.

Fig. 3 illustrates the SEM photographs of the PCFNS with 0.1 wt% CuO and different amounts (0.1 – 0.3 wt%) of V_2O_5 sintered at 1000°C for 3 h. As shown in Fig. 3(a), no secondary phase was detected in PCFNS ceramics sintered at 1165°C for 3 h. With increasing the V_2O_5 content, secondary phases slightly increased but abnormal grain growth was not found because liquid phase inhibited grain growth due to a higher surface energy.[3] However, the grains show irregular variations.

Fig. 4 shows the SEM photographs of the PCFNS with various (0.1 – 0.5 wt%) CuO – 0.05 wt% V_2O_5 sintered at 1000°C for 3 h. With increasing the CuO content, secondary phases also increased. The grain growth of the PCFNS ceramics slightly increased with increasing the CuO addition up to 0.3 wt% since the liquid phase facilitated densification of the ceramics, and secondary phases slightly increased with more addition of CuO. Fig. 4 shows a heterogeneous microstructure formed during the sintering because of an inhomogeneous liquid-phase distribution.[4]

The density of PCFNS ceramics with x (0.1 – 0.5 wt%) CuO y (0.05 – 0.3 wt%) V_2O_5 sintered at 1000°C for 3 h was shown in Fig. 5. The bulk density increased up to 0.3 wt% CuO content, and then decreased. However, the bulk den-

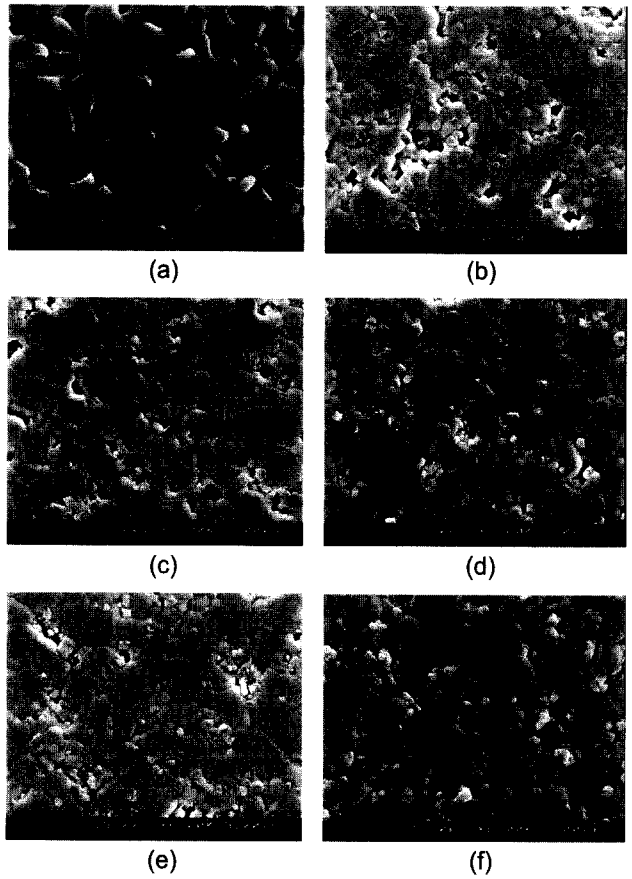

Fig. 4. SEM photographs of PCFNS sintered at 1000°C for 3 h with contents of x wt% CuO – 0.05 wt% V_2O_5 : (a) PCFNS [Sintered at 1165°C for 3 h], (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, and (f) 0.5.

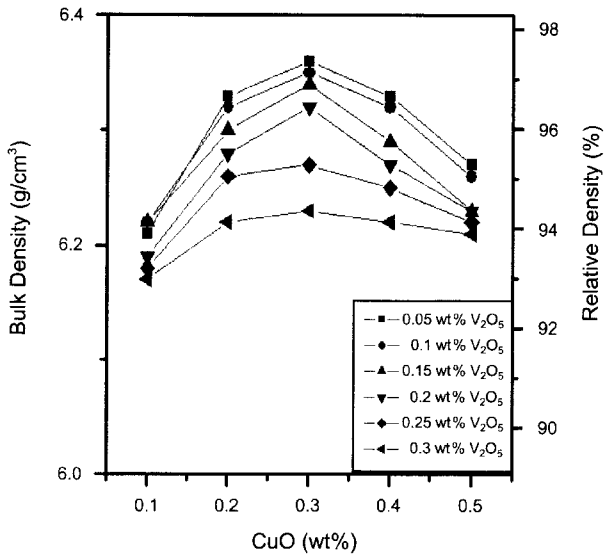

Fig. 5. Bulk density of PCFNS sintered at 1000°C for 3 h with contents of x wt% CuO – y wt% V_2O_5.

sity over 93% of theoretical density of PCFNS (6.521 g/cm^3)[1] were obtained regardless the CuO and V_2O_5 contents. In the case of liquid phase sintering, sintering additives decrease

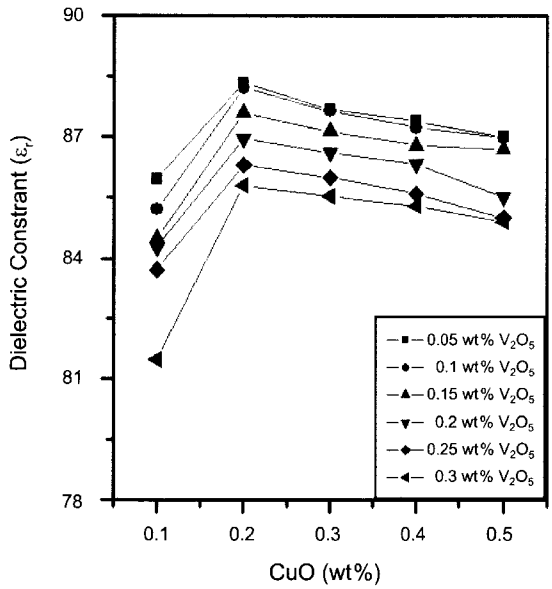

Fig. 6. Dielectric constant of PCFNS sintered at 1000°C for 3 h with contents of CuO – V_2O_5 [wt%].

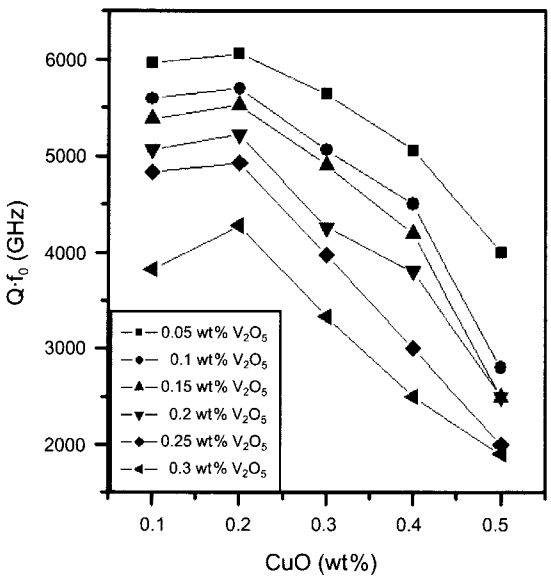

Fig. 7. Unloaded quality factor value of PCFNS sintered at 1000°C for 3 h with contents of CuO – V_2O_5 [wt%].

the sintering temperature and increase the bulk density within a limited content. When the amount of sintering additive is excessive, the bulk density is decreased. Therefore, the decrease of bulk density was attributed to the excessive CuO content. As increasing the V_2O_5 content, the sintered density of specimens were decreased.

Fig. 6 shows the relative permittivity of PCFNS with additives sintered at 1000°C for 3 h. The relative permittivity of PCFNS increased with an increase of CuO content up to 0.2 wt% and then slightly decreased. For the additions of V_2O_5, the dielectric constants were also decreased. The relative permittivity also showed the similar tendency of the sintered density. The present results are in accordance with

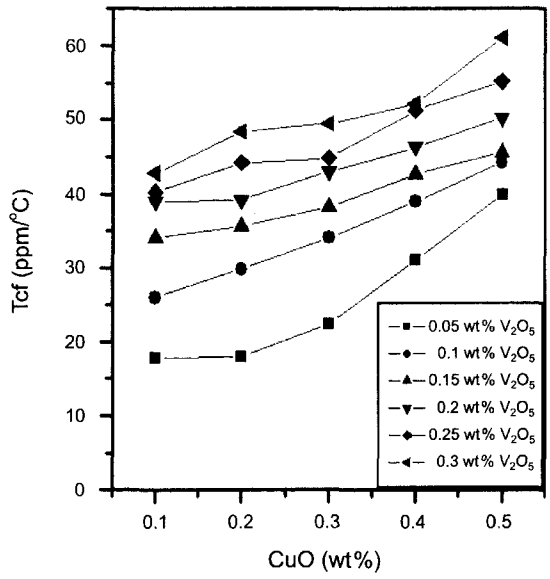

Fig. 8. τ_f value of PCFNS sintered at 1000°C for 3 h with contents of CuO - V_2O_5 [wt%].

the report by Kingery *et al.*[5] The decrease of the dielectric constant was due to the secondary phases and pores remained at grain boundary. The maximum dielectric constant of 88 was obtained at 0.2 wt% CuO 0.05 wt% V_2O_5.

The quality factor ($Q \cdot f_0$) value of PCFNS with additives sintered at 1000°C was shown in Fig. 7. As the V_2O_5 content increased regardless CuO content, the $Q \cdot f_0$ value decreased abruptly due to the increased secondary phases and pores. The microwave dielectric losses were affected by impurities, secondary phases, and oxygen vacancy etc.[6] The maximum $Q \cdot f_0$ value was 6100 GHz at 0.2 wt% CuO 0.05 wt% V_2O_5.

Fig. 8 shows the t_f of PCFNS with *x* wt% CuO *y* wt% V_2O_5 sintered at 1000°C for 3 h. The temperature coefficient of resonance frequency was related to that of the main ceramics and secondary phase of materials. With increasing V_2O_5 contents, the τ_f was shift to positive abruptly. The τ_f slightly shifted to positive with addition of the CuO. According to the Cheng-Fu Yangs report,[7] the τ_f was shifted to positive by CuO – V_2O_5 mixtures. The optimized microwave properties, $\varepsilon_r = 88$, $Q \cdot f_0 = 6100$ (GHz), and $\tau_f = 18$ ppm/°C, was obtained at PCFNS with 0.2 wt% CuO 0.05 wt% V_2O_5.

4. Conclusion

The effect of sintering additives, CuO – V_2O_5, on sintering behavior and dielectric properties of $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ (PCFNS) sintered at 1000°C for 3 h was investigated. The bulk density increased with increasing the CuO content to 0.2 wt%, and the dielectric constant and $Q \cdot f_0$ value increased with increase of CuO content up to 0.3 wt%. The optimized microwave properties, $\varepsilon_r = 88$, $Q \cdot f_0 = 6100$ (GHz), and $\tau_f = 18$ ppm/°C, were obtained in $(Pb_{0.45}Ca_{0.55})\{(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}\}O_3$ with 0.2 wt% CuO 0.05 wt% V_2O_5 at 1000°C for 3 h.

REFERENCES

1. S. Kucheiko, J. W. Choi, H. J. Kim, S. J. Yoon, and H. J. Jung, "Microwave Characteristics of (Pb,Ca)(Fe,Nb,Sn)O_3 Dielectric Materials," *J. Am. Ceram. Soc.*, **80** 2937-40 (1997).
2. Y. Kobayashi and M. Katoh, "Microwave Measurement of Dielectric Properties of Low-loss Materials by the Dielectric Rod Resonator Method," *IRE Trans. Microwave Theory Tech.*, **33** 586-92 (1985).
3. C.-L. Huang, M.-H. Weng, C.-C. Wu, and C.-C. Wei, "Microwave Dielectric Properties and Microstructures of V_2O_5-Modified $Zr_{0.8}Sn_{0.2}TiO_4$ Ceramics," *Jpn. J. Appl. Phys.*, **40** 698-702 (2001).
4. C.-H. Wang, "Microstructure and Characteristics of Ba(Ti,Zr)O_3 Ceramics with Addition of Glass Frit," *Jpn. J. Appl. Phys.*, **41** 5317-22 (2002).
5. W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, "Introduction to Ceramics, 2nd Ed.," 949-50. Wiley, New York (1976).
6. D. M. Iddles, A. J. Bell, and A. J. Moulson, "Relationships between Dopants, Microstructure and the Microwave Dielectric Properties of ZrO_2-TiO_2-SnO_2 Ceramics," *J. Mater. Sci.*, **27** 6303-10 (1992).
7. C.-F. Yang, "Improvement of Quality Value and shift of τ_f Value of $BiNbO_4$ Ceramics with Addition of CuO-V_2O_5 Mixtures," *Jpn. J. Appl. Phys.*, **38** 6797-800 (1999).