Journal of the Korean Ceramic Society
Vol. 41, No. 8, pp. 633~636, 2004.

Note

Microwave Dielectric Properties of $CaTi_{0.5}Fe_{0.25}Nb_{0.25}O_3$ Ceramics with CuO Addition

Kui Won Kang,† Hyo Tae Kim, Joon-Cheol Hwang, Joong-Hee Nam, and Dong-Hun Yeo

Korea Institute of Ceramic Engineering and Technology, Seoul 153-801, Korea
(Received May 19, 2004; Accepted July 28, 2004)

ABSTRACT

The sintering behavior, microstructure and microwave dielectric properties of $CaTi_{0.5}Fe_{0.25}Nb_{0.25}O_3$ with CuO have been investigated. Among the range of additions, 3 wt% CuO was observed to perform most satisfactory for acting as a sintering aid. The dielectric properties were found to strongly depend on the sintered densities. The dielectric constant increased with sintering temperatures, while the $Q \times f_0$ value affected by second phase. For $CaTi_{0.5}Fe_{0.25}Nb_{0.25}O_3$ with 3 wt% CuO sintered at 1000°C for 2 h, the dielectric properties with an ε_r value of 56, a $Q \times f_0$ value of 3,500 GHz and a τ_f value of 10 ppm/°C were obtained and suggested for practical applications.

Key words : $CaTi_{0.5}Fe_{0.25}Nb_{0.25}O_3$, Microwave dielectric properties, CuO, Sintering aid

1. Introduction

Complex perovskite dielectrics represented by A(B',B")O_3 are known as low-loss dielectric ceramics at microwave frequencies.[1,2] Many case of studies reported the Ba-based (A=Ba) or Sr-based (A=Sr) complex perovskite ceramics, however only few studies reported the dielectric properties of Ca-based perovskite ceramics.[3-6] Orthorhombic symmetry of $CaTiO_3$ and monoclinically deformed $Ca(Fe_{0.5}Nb_{0.5})O_3$ were in complete solubility for the perovskite series $CaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ ceramics.[7] Kagata and Kato[8] characterized the dielectric properties at microwave frequencies and crystal structure of $Ca(B^{3+}{}_{0.5}B^{5+}{}_{0.5})O_3$ (B^{3+}: Al, Cr, Mn, Fe; B^{5+}: Nb, Ta), and determind that $Ca(Fe_{0.5}Nb_{0.5})O_3$ has an ε_r of 40, and a $Q \times f_0$ of 20,000 GHz. However, its τ_f factor is relatively negative (−76 ppm/°C).

Kucheiko *et al.*[9] have reported that $CaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$, in particular, exhibits a control of τ_f value. The effects of ZnO additive on the microstructure and microwave dielectric properties were demonstrated and the addition of 1 wt% ZnO in $CaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ (x=0.54) sintered at 1500°C for 10 h has a $Q \times f_0$ value of 3,87 0GHz, ε_r=59.9, and τ_f=0 ppm/°C.

The aim of this study is to reduce the sintering temperature of $CaTi_{1-x}(Fe_{0.5}Nb_{0.5})_xO_3$ using CuO which was chosen as liquid phase sintering aid. Kim *et al.*[10] proposed CuO-doped Ag(Nb,Ta)O_3 composite ceramics for LTCC application. It also reported that CuO lead to a low temperature sintering in $ZnNb_2O_6$[11] and TiO_2.[12] In the present work, the effect of CuO additions on the microstructure, sintering characteristics and microwave dielectric properties of the $CaTi_{0.5}Fe_{0.25}Nb_{0.25}O_3$ (CTFN) system were investigated.

†Corresponding author : Kui Won Kang
E-mail : kkuiw@ihanyang.ac.kr
Tel : +82-2-3282-7776 Fax : +82-2-3282-2460

2. Experimental Procedure

$CaTiO_3$-$Ca(Fe_{0.5}Nb_{0.5})O_3$ dielectrics were synthesized via the solid state reaction route with reagent grade $CaTiO_3$, $CaCO_3$, Fe_2O_3, and Nb_2O_5 powders (High Purity Chemetals, Sakato, Japan). The raw materials were weighed in the appropriate molar ratio and ball milled with ZrO_2 balls for 24 h in water, then calcined at 1150°C for 4 h. The calcined powders were ground for 24 h again with the addition of 0.5~5 wt% CuO in water. The dried powders were mixed with 2 wt% solution of PVA and pressed into pellets under 1000 kg/cm^2 by uniaxial pressing with 10 mm diameter and 1.2 or 4.8 mm thickness for the low-frequency and resonant post-measurement technique. The pellets were sintered at 950~1050°C for 2 h in air.

Phase identification and unit-cell parameters of the sintered specimens were performed using X-Ray Diffraction (XRD; M03XHF, Mac-Sci. Co. Ltd., Japan) analysis with Cu Kα radiation. Field Emission Scanning Electron Microscopy (FE-SEM; JSM-6700F, Jeol, Tokyo, Japan) work was carried out to investigate the microstructure of CTFN ceramics.

Dielectric properties in the microwave range were measured using a network analyzer (Model 8720ES, Agilent Technologies, Palo Alto, CA) in the s_{21} transmission mode. The sintered specimens were lapped and polished to cylindrical-shape dielectric resonators. The dielectric constant was measured by the resonant post method[13] using silver coated copper plates and the value was calculated from TE_{011} resonance mode values. The temperature coefficient of resonant frequency was measured by open cavity method using an copper at the temperature range of 25°C to 80°C.

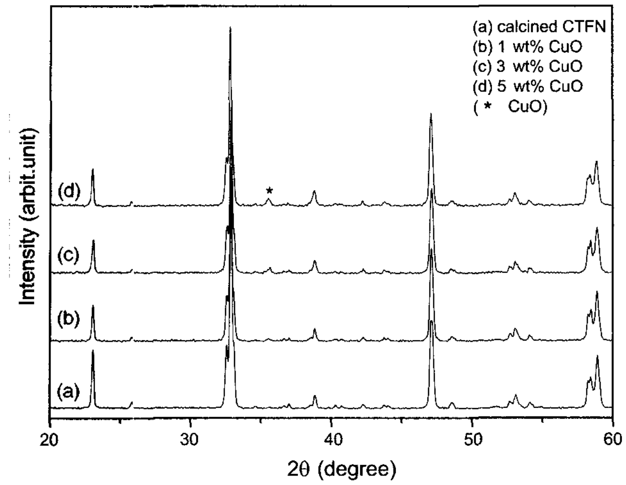

Fig. 1. X-ray diffraction patterns of CTFN ceramics with contents of CuO sintered at 1000°C for 2 h; (a) calcined CTFN, (b) 1, (c) 3, and (d) 5 wt%.

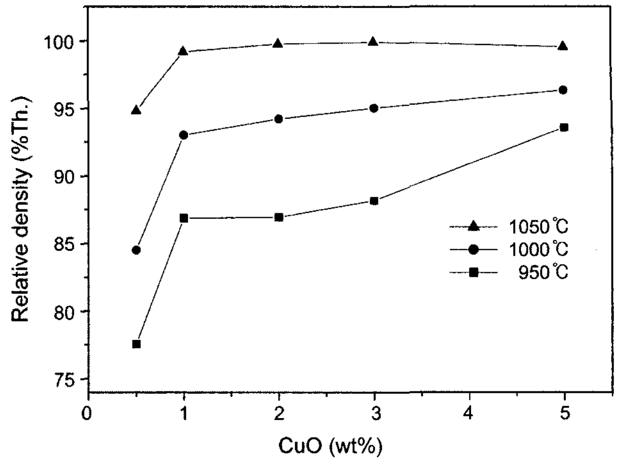

Fig. 2. Relative density of CTFN ceramics doped with the addition of CuO.

3. Results and Discussion

Fig. 1 demonstrates the X-ray diffraction patterns of the CTFN ceramics with various CuO additions sintered at 1000°C for 2 h. The diffraction patterns are indexed based on the orthorhombic perovskite structure. As the increasing CuO contents, the secondary phase are increased slightly.

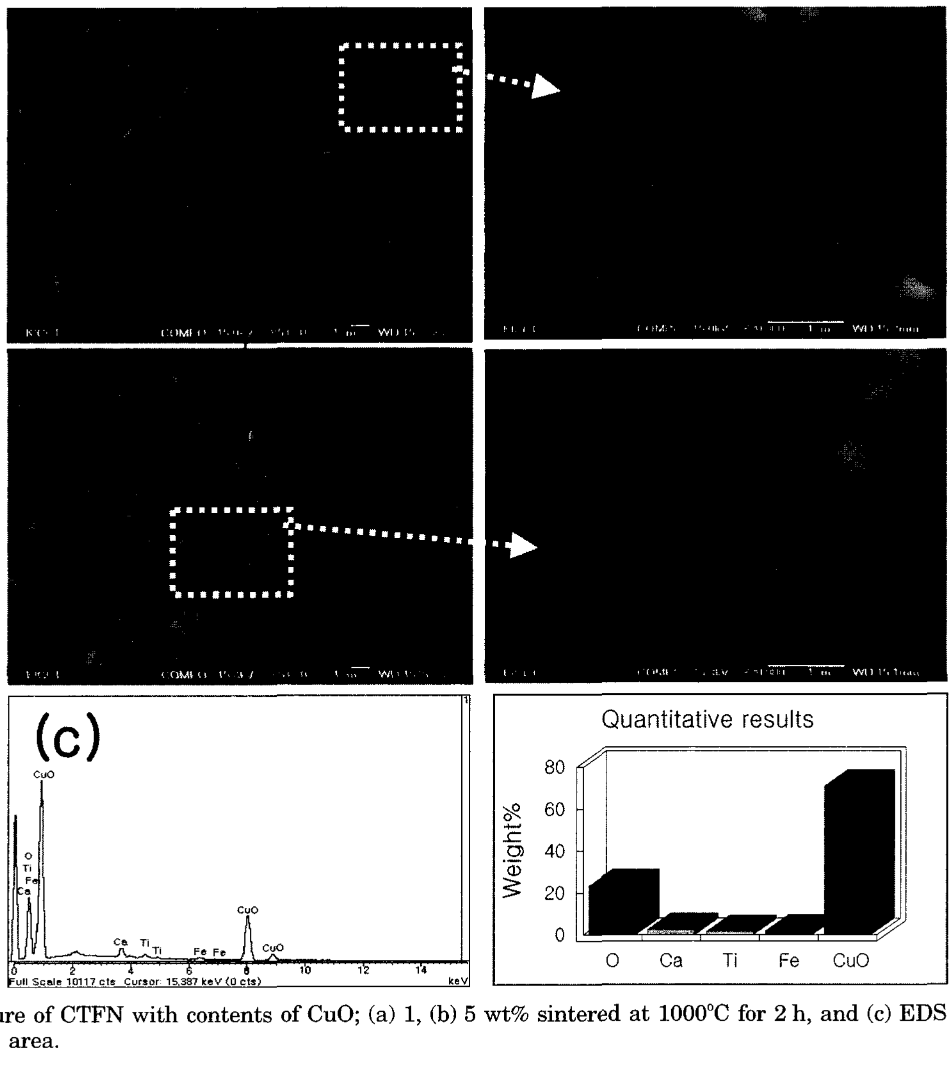

Fig. 3. Microstructure of CTFN with contents of CuO; (a) 1, (b) 5 wt% sintered at 1000°C for 2 h, and (c) EDS elemental mapping of the select area.

The second phases are confirmed as CuO (JCPDS; 45-0937) which allows the formation in triple junction at the sintering temperature.

Fig. 2 shows the relative density of the CTFN ceramics with various CuO amounts and sintering temperatures. By increasing the contents of CuO to 1 wt%, the relative density was abruptly increased and then slightly increased with further CuO additions. The sinterability of pellets also depended on the sintering temperature. For CTFN with 3 wt% CuO sintering at 1000°C for 2 h, samples are well sintered over 95% of theoretical density of CTFN. Therefore, these results indicate that successful reductions in the sintering temperature of CTFN are possible with CuO additions.

Microstructure of CTFN with CuO additions are shown in Fig. 3. The second phases are confirmed as CuO phase by using energy-dispersive spectroscopy, Fig. 3(c). It is obvious that the reaction of low-fired CTFN ceramics with 1, 5 wt% CuO shows the second phase in the triple junction. As CuO additions increase, the amounts of second phases are increased slightly.

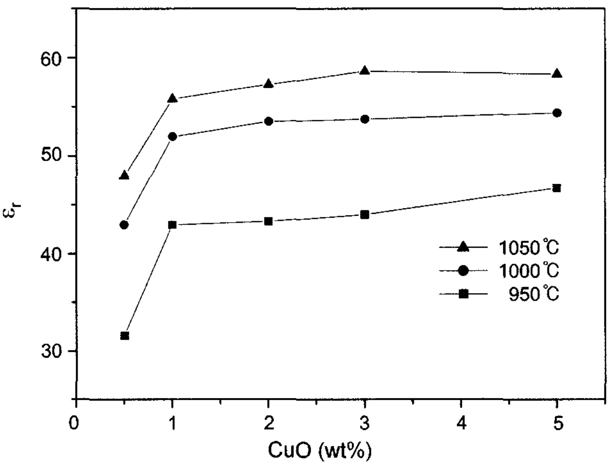

Fig. 4. Dielectric constant of CTFN ceramics with the addition of CuO.

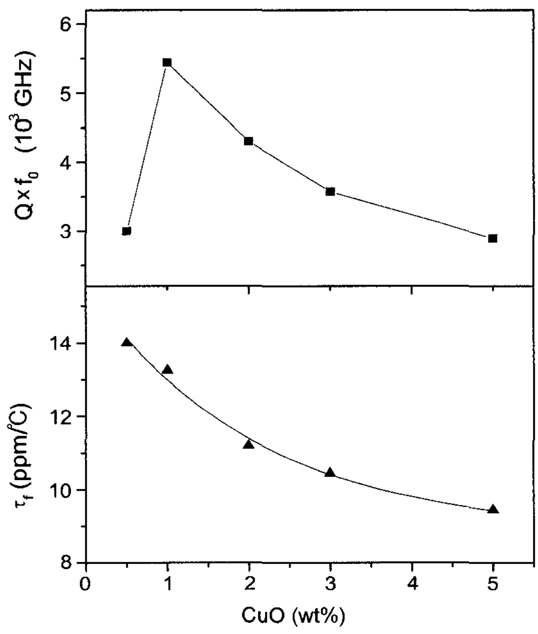

Fig. 5. Microwave dielectric properties of CTFN ceramics sintered at 1000°C for 2 h with contents of CuO (wt%).

Fig. 4 shows the dielectric constants of CTFN ceramics with CuO additions as a function of sintering temperatures. The relationship between ε_r values and sintering temperatures shows the similar trend as the relationship between densities and sintering temperatures.

The quality factors ($Q \times f_0$) and the temperature coefficient of resonance frequency (τ_f) of the CTFN with CuO additives sintered at 1000°C for 2 h are shown in Fig. 5. As the CuO content increased to 1 wt%, the $Q \times f_0$ value increased abruptly due to the densification and then decreased due to the increase of second phase. There are many reports that the microwave losses are affected by impurity, secondary phase and oxygen vacancy etc.[14,15]

4. Conclusions

The effect of sintering additives, 0.5~5 wt% CuO, on sintering behavior and dielectric properties of CTFN ceramics sintered at 1000°C for 2 h was investigated. CuO additions not only enhanced the densification of CTFN ceramics but also reduced the sintering temperature at 1000°C for 2 h. Dielectric constant was controlled by the additive content, sintering temperature and relative density. The quality factor was correlated to the densification of CTFN ceramics under 1 wt% CuO addition, and then controlled by second phase. CTFN ceramics with 3 wt% CuO sintered at 1000°C for 2 h shows the useful microwave dielectric properties : ε_r =56, $Q \times f_0$=3,500 GHz and τ_f value of 1 0ppm/°C.

REFERENCES

1. S. Kawashima, M. Nishida, I. Ueda, and H. Ouchi, "$Ba(Zn_{1/3}Ta_{2/3})O_3$ Ceramics with Low Dielectric Loss at Microwave Frequencies," *J. Am. Ceram. Soc.*, **66** [6] 421-23 (1983).
2. M. Takata and K. Kageyama, "Microwave Characteristics of $A(B^{3+}_{1/2}B^{5+}_{1/2})O_3$ Ceramics (A=Ba, Ca, Sr; Ba^{3+}=Na, Nd, Sm, Yb; B^{5+}=Nb, Ta)," *J. Am. Ceram. Soc.*, **72** [10] 1955-59 (1989).
3. S. Kucheiko, J. W. Choi, H. J. Kim, and H. J. Jung, "Microwave Dielectric Properties of $CaTiO_3$-$Ca(Al_{1/2}Ta_{1/2})O_3$ Ceramics," *J. Am. Ceram. Soc.*, **79** [10] 2739-43 (1996).
4. S. Kucheiko and D. H. Yeo, "Microwave Dielectric Properties of $CaTiO_3$-$CaAl_{1/2}Nb_{1/2}O_3$ Ceramics Doped with Li_3NbO_4," *J. Am. Ceram. Soc.*, **85** [5] 1327-29 (2002).
5. C. L. Huang, H. L. Chen, and C. C. Wu, "Improved High Q Value of $CaTiO_3$-$Ca(Mg_{1/3}Nb_{2/3})O_3$ Solid Solution with Near Zero Temperature Coefficient of Resonant Frequency," *Mater. Res. Bull.*, **36** [9] 1645-52 (2001).
6. T. Lowe, F. Azough, and R. Freer, "The Microstructure and Microwave Dielectric Properties of Ceramics in the System $CaTiO_3$-$Li_{0.5}Nd_{0.5}TiO_3$," *J. Kor. Ceram. Soc.*, **40** [4] 328-32 (2003).

7. A. R. Chakhmouradian and R. H. Mitchell, "A Structural Study of the Perovskite Series $CaTi_{1-2x}Fe_xNb_xO_3$," *J. Solid State Chem.*, **138** 272-77 (1998).
8. H. Kagata and J. Kato, "Dielectric Properties of Ca-Based Complex Perovskite Microwave Frequencies," *Jpn. J. Appl. Phys.*, **33** 5463-65 (1994).
9. S. Kucheiko, H. J. Kim, S. J. Yoon, and H. J. Jung, "Effect of ZnO Additive on Microstructure and Microwave Dielectric Properties of $CaTi_{1-x}(Fe_{0.5}Nb_{0.5})O_3$ Ceramics," *Jpn. J. Appl. Phys.*, **36** 198-202 (1997).
10. H. T. Kim, T. Shrout, C. Randall, and M. Lanagan, "Low-Temperature Sintering and Dielectric Properties of Ag $(Nb,Ta)O_3$ Composite Ceramics," *J. Am. Ceram. Soc.*, **85** [11] 2738-44 (2002).
11. D. W. Kim, T. G. Kim, and K. S. Hong, "Influence of Copper (II) Oxide Additions to Zinc Niobate Microwave Ceramics on Sintering Temperature and Dielectric Properties," *J. Am. Ceram. Soc.*, **84** [6] 1286-90 (2001).
12. D. W. Kim, K. H. Ko, and K. S. Hong, "Low Firing of CuO-Doped Anatase," *Mater. Res. Bull.*, **34** [5] 771-81 (1999).
13. B. W. Hakki and P. D. Coleman, "A Dielectric Resonator Method of Measurement Inductive Capacities in the Millimeter Range," *IRE Trans. Microwave Theory Tech.*, [8] 402-10 (1960).
14. W. S. Kim, T. H. Kim, E. S. Kim, and K. H. Yoon, "Microwave Dielectric Properties and Far Infrared Reflectivity Spectra of the $(Zr_{0.8}Sn_{0.2})TiO_4$ Ceramics with Additives," *Jpn. J. Appl. Phys.*, **37** 5367-71 (1998).
15. P. Liu, E. S. Kim, and K. H. Yoon, "Low-Temperature Sintering and Microwave Dielectric Properties of $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ Ceramics," *Jpn. J. Appl. Phys.*, **40** 5769-73 (2001).