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Microwave Dielectric Properties of Low Temperature Fired $(Pb_{0.45}Ca_{0.55})[(Fe_{0.5}Nb_{0.5})_{0.9}Sn_{0.1}]O_3$ Ceramics with Various Additives

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

Thin Film Technology Research Center, KIST, Seoul 136-791, Korea
**Department of Ceramic Engineering, Yonsei University, Seoul 120-749, Korea*
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ABSTRACTS

The effect of CuO, B_2O_3, V_2O_5 and CuO-Bi_2O_3 additives on microwave dielectric properties of $(Pb_{0.45}Ca_{0.55})[(Fe_{0.5}Nb_{0.5})_{0.9}Sn_{0.1}]O_3$ (PCFNS) were investigated. The PCFNS ceramics were sintered at 1165°C. To decrease the sintering temperature for using as a low-temperature co-firing ceramics (LTCC), CuO, B_2O_3, V_2O_5 and CuO-Bi_2O_3 were added to the PCFNS. As the content of CuO increased, the sintered density and dielectric constant increased and the temperature coefficient of resonance frequency (τ_f) shifted to the positive value. When the CuO-Bi_2O_3 were added, dielectric properties were ε_r of 83, $Q \cdot f_0$ of 6085 GHz, and τ_f of 8 ppm/°C at a sintering temperature of 1000°C. The relationship between the microstructure and properties of ceramics was studied by X-ray diffraction and scanning electron microscopy.

Key words : Microwave, Dielectric property, Low- temperature sintering

1. Introduction

Recently, multilayer microwave devices have been extensively used in bandpass filters, antenna and duplexers. Low-temperature-firing microwave dielectric materials require high dielectric constants (ε_r), high quality factor values ($Q \cdot f_0$), and stable temperature coefficient of the resonant frequency ($\tau_f \leq |10|$ ppm/°C), and low sintering tem- perature to use with low-melting-point conductors in fabrication of multilayer microwave devices. In general, three methods are used to reduce the sintering temperature of ceramics such as low-melting glass addition,[1,2] chemical processing,[3] and using starting materials with smaller particle size.[4] The first method was found to effectively decrease the firing temperature in spite of decreasing the microwave dielectric properties of dielectric ceramics. It has been investigated to find the sintering additives minimizing the microwave dielectric properties. The microwave dielectric properties of (Pb,Ca) $(Fe,Nb,Sn)O_3$ ceramics were reported by Kucheiko *et al.*[5,6] The dielectric constant value (ε_r) was 85.9-89.9, the quality factor ($Q \cdot f_0$) was 7510-8600 GHz and temperature coefficients of the resonant frequency (τ_f) was 0-9 ppm/°C but sintering temperature of this ceramic is over 1165°C. This paper reports the sintering characteristics and microwave dielectric properties on $(Pb_{0.45}Ca_{0.55})[(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}]O_3$ added with CuO, B_2O_3, V_2O_5 and CuO-Bi_2O_3 as sintering additives to decrease the sintering temperature, and the relationship between the physical properties and microwave dielectric properties of ceramics.

†Corresponding author : mickey71@kist.re.kr

2. Experimental Procedure

The powders were prepared using high-purity PbO (High Purity Chemical Ltd., 99.9%), $CaCO_3$, Nb_2O_5, SnO_2, Bi_2O_3 (all Aldrich, 99.9%), Fe_2O_3, CuO, V_2O_5, B_2O_3 (all 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 distilled water for 24 h in a ball mill with zirconia balls. The mixtures were dried and calcined in an alumina crucible at 900°C for 4 h in air, then milled again with the additives of CuO, B_2O_3, V_2O_5, and CuO-Bi_2O_3, from 0.1 wt% to 1 wt% for 24 h. This powder was ground with 5 wt% polyvinyl alcohol (PVA) to form the desired shape. Pellets with 12 mm diameter and 5~6 mm thick were pressed uniaxially at 800 kg/cm^2. The sintering temperature was 1000°C for 3 h. The bulk density was measured by the Archimedes method. The microwave dielectric properties were measured by the dielectric rod resonator method[7] (Hakki-Coleman method) interfaced with a network analyzer (HP 8720C). As not all specimens were available in equal size, the properties were measured at different frequencies. For the presentation of loss quality data, the following general relation observed in a narrow frequency range was utilized: $Q \cdot f_0$ = constant. The temperature coefficient of resonant frequency (τ_f) at microwave frequencies was measured in the temperature range of 20 to 80°C. Sintered pellets were examined by powder X-ray diffraction (XRD, Philips PW 1820) analysis with Cu$K\alpha$ radiation. In order to investigate the microstructures of ceramics using a scanning electron microscope (SEM, JXA-8600, Jeol), the samples were prepared by polishing with SiC paper and thermal etching at 920°C for 15 min.

Table 1. Dielectric Properties of PCFNS with Various Additives (Sintering Condition : 1000°C, 3 h)

Additive (wt%)		Density (g/cm^3)	ε_r	Q · f (GHz)	τ_f (°C/ppm)
B_2O_3	0.3	5.32	64.29	5281	50.5
	0.4	6.19	56.29	5786	27.8
	0.5	6.17	53.84	5428	26.0
	1.0	5.70	58.83	5072	
V_2O_5	0.3	5.50	67.30	4583	50.0
	0.4	5.50	64.96	4120	57.0
	0.5	5.65	68.32	4077	49.9
	1.0	5.64	65.19	3172	
CuO	0.2	5.69	75.56	3122	17.5
	0.3	5.98	80.41	2965	18.1
	0.4	6.06	82.76	4041	21.9
	0.5	6.10	82.55	2016	31.9
CuO (0.2 wt%)-Bi_2O_3	0.1	6.08	82.88	6085	8.3
	0.2	5.98	81.24	4434	4.6
	0.3	5.63	74.15	4042	17.9

3. Results and Discussion

It was reported that, $(Pb_{0.45}Ca_{0.55})[(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}]O_3$ (PCFNS) was sintered at 1165°C as mentioned. Addition of CuO, B_2O_3, V_2O_5, and CuO-Bi_2O_3 has influenced on decrease of sintering temperature to 1000°C. Table 1 summarizes the microwave dielectric properties of PCFNS, as functions of species and amount of various additives. All specimens sintered well. Fig. 1 shows the XRD patterns of PCFNS with various additives. The diffraction peaks were indexed based on the $CaTiO_3$-type orthorhombic perovskite structure. The PCFNS added with B_2O_3 or V_2O_5 (Fig. 1(a)-(d)) had a large amount of the secondary phase, pyrochlore phase. But the PCFNS added with 0.2 wt% CuO (Fig. 1(e)) was found to be a orthorhombic perovskite structure with a small amount of the pyrochlore phase. As increasing CuO contents over 0.2 wt% (Fig. 1(f)-(h)) the amounts of the pyrochlore phase ($CuNbO_3$) were substantial. The PCFNS added with 0.2 wt% CuO and 0.2 wt% Bi_2O_3 (Fig. 1(i)) was found to be a orthorhombic perovskite structure with a small amount of the pyrochlore phase and the amounts of the $BiNbO_4$ phase were increased with Bi_2O_3 content (Fig. 1(j)).

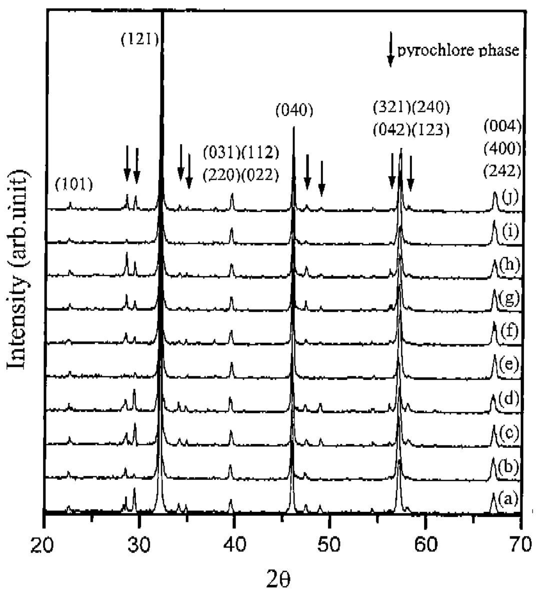

Fig. 1. XRD patterns of PCFNS with additives of B_2O_3 : (a) 0.3, (b) 0.4, V_2O_5 : (c) 0.3, (d) 0.4, CuO (e) 0.2, (f) 0.3, (g) 0.4, (h) 0.5 and CuO-Bi_2O_3 : (i) 0.2-0.2, (j) 0.2-0.3 (wt%).

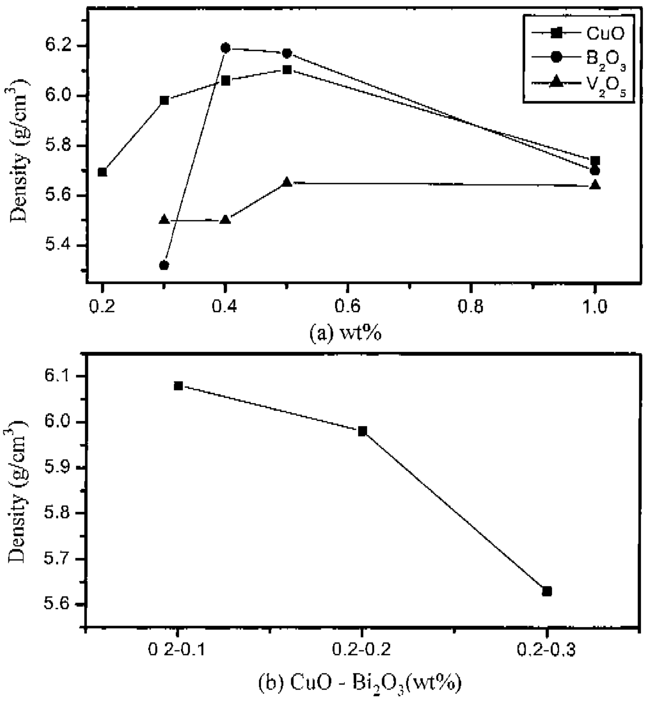

Fig. 2. Bulk density of PCFNS with additives of (a) CuO, B_2O_3, V_2O_5 and (b) CuO-Bi_2O_3 (wt%).

Fig. 2 shows the bulk density of PCFNS with various additives. The density of CuO-added PCFNS ceramics increased with increasing CuO to 0.5 wt% and then decreased. In case of liquid phase sintering, sintering additives decrease the sintering temperature and increase the bulk density within a limited content. When sintering additives are excessive, the bulk density is decreased. As adding the B_2O_3 and V_2O_5 in PCFNS, the sintered density also increased within a limited content and then decreased. When CuO and Bi_2O_3 were added together, these formed $Bi_xCu_yO_4$, which transformed to a liquid phase below 600°C.[8] The CuO content fixed 0.2 wt% and various content of Bi_2O_3 were added in PCFNS. As increasing Bi_2O_3 content with fixed CuO content (0.2 wt%), the sintered density decreased from 6.08 to 5.63 g/cm^3. The bulk density of the sintered ceramics ranged between 87.2% and 93.6% of the

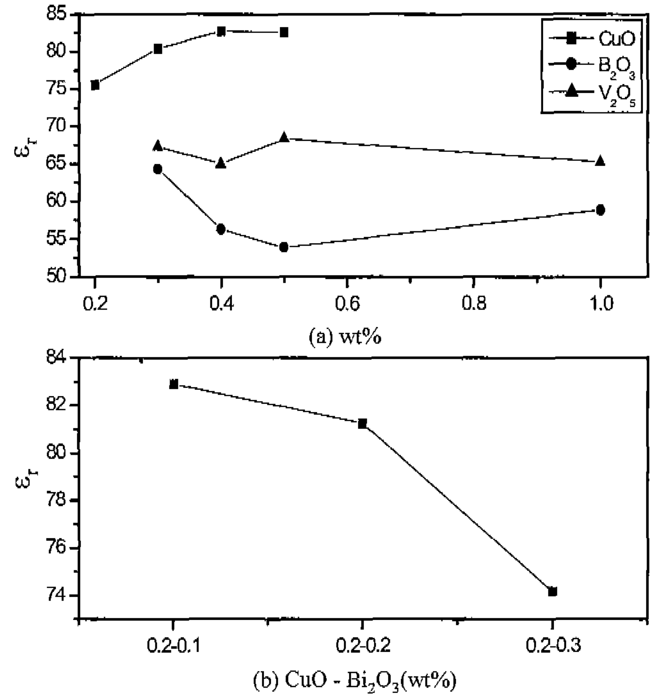

Fig. 3. Dielectric constant of PCFNS with additives of (a) CuO, B_2O_3 and V_2O_5 and (b) CuO-Bi_2O_3 (wt%).

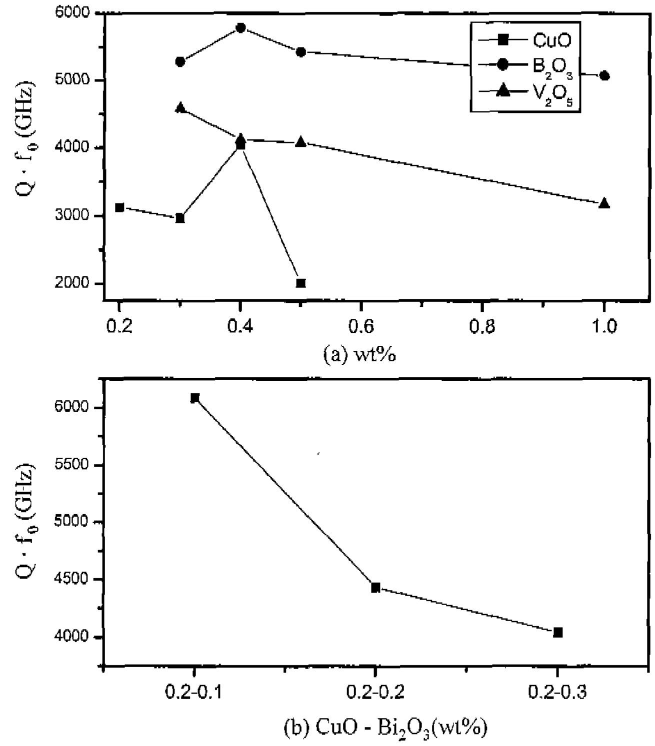

Fig. 4. Unloaded quality factor value of PCFNS with additives of (a) CuO, B_2O_3, V_2O_5 and (b) CuO-Bi_2O_3 (wt%).

X-ray density of PCFNS.

Fig. 3 shows the dielectric constant of PCFNS with various additives. The dielectric constant (ε_r) also shows the same tendency of the bulk density. This result shows the correlation between the bulk density and the dielectric constant. As increasing the bulk density, the dielectric constant increased. Addition of CuO did not degrade the dielectric constant in comparison with one of PCFNS, but additions of B_2O_3 or V_2O_5 degraded the dielectric constant. Fig. 4 shows the $Q \cdot f_0$ value of PCFNS with various additives. When B_2O_3 increased from 0.3 wt% to 0.4 wt%, the $Q \cdot f_0$ value is increased due to decreasing the secondary phase. As increasing V_2O_5 or CuO-Bi_2O_3, the $Q \cdot f_0$ values decreased continuously. As increasing V_2O_5 contents from 0.3 wt% to 1 wt%, the $Q \cdot f_0$ value is decreased slowly due to increasing the secondary phase slightly. As increasing CuO content, the $Q \cdot f_0$ value increased to CuO addition of 0.4 wt%, and then abruptly decreased over 0.5 wt% CuO contents. As the content of CuO addition is less then 0.4 wt%, the increase of the $Q \cdot f_0$ value was caused by the increase of densities and grain growth. As the density and grain size increase, the pores and grain boundary area decreased, thus reducing the dielectric losses. As the content of CuO addition is over 0.5 wt%, the $Q \cdot f_0$ value was decreased due to secondary phase. The secondary phase in grain boundary affected increasing the dielectric losses.

Fig. 5 shows the microstructure of PCFNS with various additives. Showing the microstructure of 0.2 wt% CuO contents, the grain did not grow, but as increasing CuO from 0.2 to 0.4 wt%, grain size increased from 0.5 to 2.0 mm. An increase of sintered density had resulted from the increase of grain size.[9] When 0.5 wt% CuO added, the number and size of secondary phase increased. Thus, the $Q \cdot f_0$ value was decreased by the secondary phase.[10] As the increasing Bi_2O_3 contents from 0.1 to 0.3 wt% co-doped with 0.2 wt% CuO, however, the $Q \cdot f_0$ value was decreased from 6085 to 4042 GHz. This resulted from the secondary phase also.

Fig. 6 shows the τ_f values of PCFNS ceramics with various additives. As increasing CuO content, the τ_f values also increased continuously. But in case of B_2O_3, the τ_f values decreased with increasing B_2O_3 content. As increasing the Bi_2O_3 content with fixing CuO content (0.2 wt%), the τ_f value decreased from +8 to +4 ppm/°C with increasing Bi_2O_3 content form 0.1 to 0.2 wt% and then abruptly increased over 0.2 wt% Bi_2O_3 content.

Excellent microwave dielectric properties, with a low sintering temperature of 1000°C, were realized by adding 0.2 wt% of CuO and 0.1 wt% of Bi_2O_3 in $(Pb_{0.45}Ca_{0.55})[(Fe_{1/2}Nb_{1/2})_{0.9}Sn_{0.1}]O_3$ and the dielectric constant, the $Q \cdot f_0$ value and the τ_f value were 83, 6085 GHz and 8 ppm/°C, respectively.

4. Conclusion

The effect of sintering additives (CuO, B_2O_3, V_2O_5 and CuO-Bi_2O_3) 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) was investigated. Additives of B_2O_3 and V_2O_5 degraded the microwave

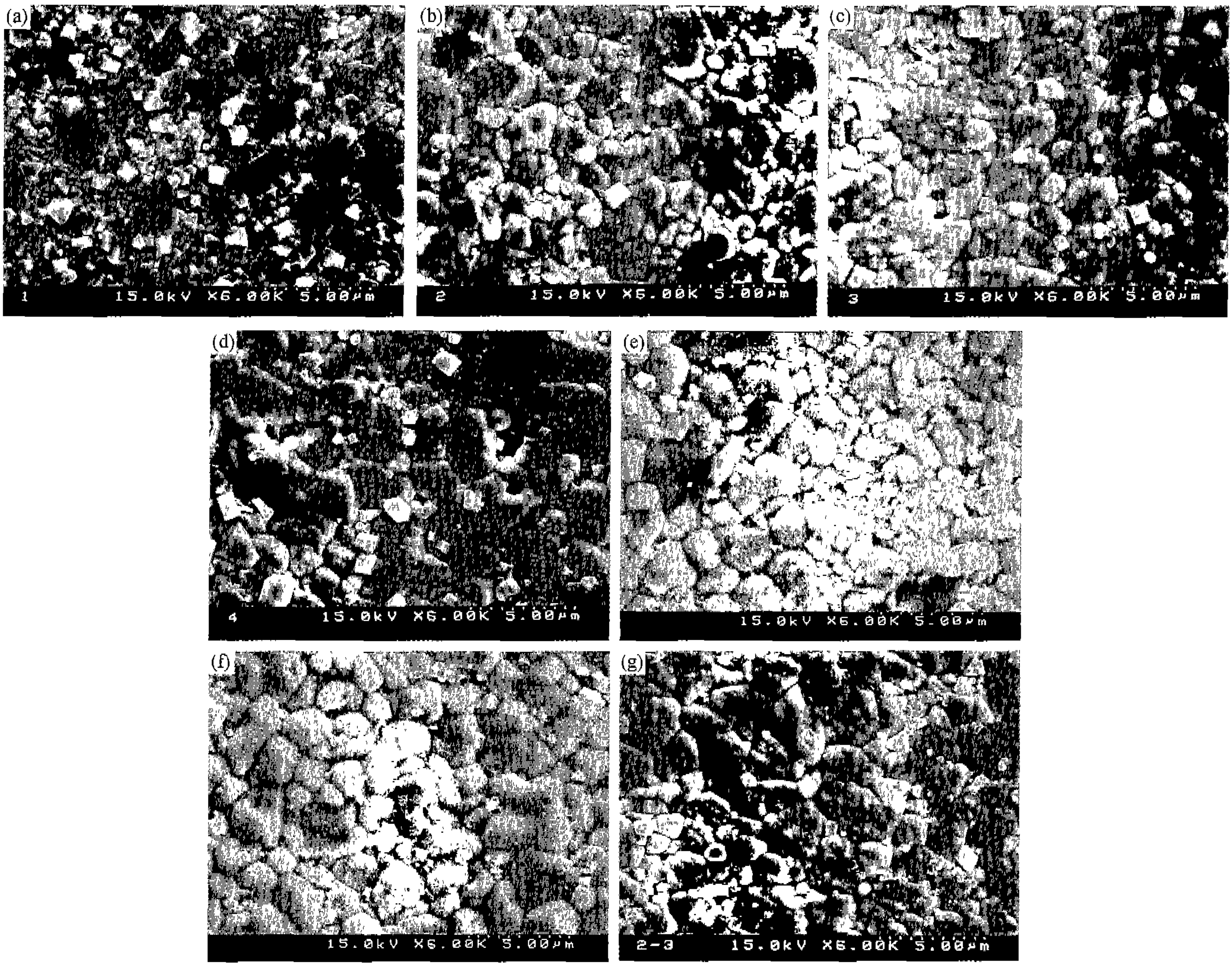

Fig. 5. SEM photographs of PCFNS with additives of CuO : (a) 0.2, (b) 0.3, (c) 0.4, (d) 0.5 and CuO-Bi_2O_3 : (e) 0.2-0.1, (f) 0.2-0.2, (g) 0.2-0.3 (wt%).

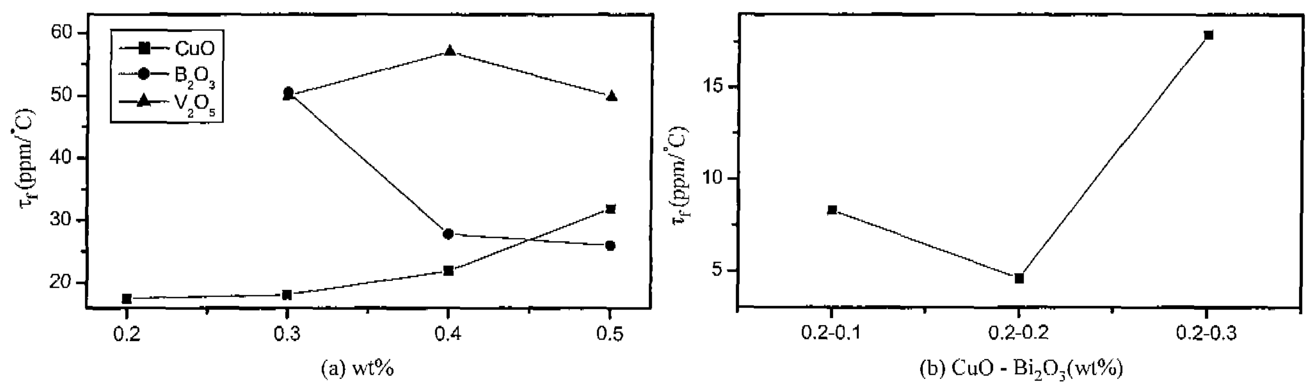

Fig. 6. t_f value of PCFNS with additives of (a) CuO, B_2O_3, V_2O_5 and (b) CuO-Bi_2O_3 (wt%).

dielectric properties of PCFNS. As increasing CuO additive content, the grain size, bulk density, dielectric constant (ε_r), $Q \cdot f_0$ value, and the temperature coefficient of resonant frequency (τ_f) increased within a limited CuO content. As increasing Bi_2O_3 with fixing CuO content (0.2 wt%), the grain size increased abnormally, and the bulk density, ε_r, $Q \cdot f_0$ value decreased. When the 0.2 wt% CuO and 0.1 wt% Bi_2O_3 was added to PCFNS, the τ_f value was 8 ppm/ and the dielectric constant and the $Q \cdot f_0$ value were 83 and 6085 GHz, respectively.

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