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Low temperature sintering and microwave dielectric properties of $CoTiNb_2O_8$ ceramics with CuO addition

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Abstract

Low-fired CuO-doped $CoTiNb_2O_8$ microwave dielectric ceramics were synthesized via a conventional solid-state reaction method and the effects of CuO additives on their sintering behavior, phase composition, microstructure and microwave dielectric properties were investigated systematically. The addition of CuO to $CoTiNb_2O_8$ successfully lowered the sintering temperature from 1250 to 950 °C. Liquid phase $CuNb_2O_6$ was formed due to the chemical reaction between CuO and matrix for the CuO-containing samples; meanwhile, (Co, Cu)$TiNb_2O_8$ solid solution was detected by XRD and EDS analysis. Both of them promoted the densification of $CoTiNb_2O_8$ ceramics. The addition of CuO did not induce apparent degradation in microwave properties but tailored the τ_f values toward zero direction. With 2 wt% CuO, $CoTiNb_2O_8$ ceramics sintered at 950 °C reached the maximum relative density of 98.21% and possessed optimum microwave dielectric properties with ε_r of 61.45, a high $Q \times f$ of 15,938 GHz, and a τ_f of 42.12 ppm/°C, making them a promising candidate for LTCC applications.

Keywords: LTCC; Microwave dielectric properties; $CoTiNb_2O_8$; CuO

1. Introduction

With the rapid development of wireless communication industry, low-temperature cofired ceramic (LTCC) technology has been extensively investigated for miniaturization and integration of components [1,2]. Considering its high conductivity and low cost, Ag (melting point 960 °C) is widely used as the metallic electrode in a compact multiplayer ceramic structure [3,4]. Hence, promising candidate ceramics are required to have low sintering temperature (<960 °C) and good chemical compatibility with Ag electrode. In addition, high dielectric constant ($\varepsilon_r > 20$, to reduce the size of resonators), excellent quality factor ($Q \times f > 10{,}000$ GHz, to minimize dielectric loss), and near zero temperature coefficient of resonant frequency ($\tau_f \sim 0$ ppm/°C, to ensure temperature stability of the microwave components at high frequencies) are also the key characteristic properties for practical applications [5]. The important low-temperature firing ceramics so far studied include $(Bi_{1-x}Ce_x)VO_4$ system, $NaAgMoO_4$ system and Li_2WO_4 system [6–8]. The development of new LTCC materials is still a critical requirement for the multiplayer devices.

Rutile TiO_2 which possessed high dielectric constant (105) and high quality factor (9200 at 5 GHz) had been most popularly used as dielectric of resonator since 1960s. However, the large τ_f value (+465 ppm/°C) and high sintering temperature (1500 °C) limited its practical applications [9]. Recently, many rutile-type dielectric ceramics with better characteristics have been developed [10,11]. Baumgarte et al. demonstrated that $CoTiNb_2O_8$ ceramics were also crystallized in rutile structure [12]. Moreover, the $CoTiNb_2O_8$ ceramics exhibited a medium ε_r of 64 and a high $Q \times f$ of 65,300 GHz after sintering at 1120 °C [13]. So it is of great significance for LTCC if we can decrease their sintering temperature to 950 °C. Several methods have been attempted over past decades to lower the sintering temperature of host materials: (1) chemical processing for smaller particle sizes of starting materials by sol–gel and co-precipitation methods, (2) adding low melting

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point materials, such as glass (lithium borosilicate and lithium magnesium zinc borosilicate), oxides (B_2O_3, CuO and V_2O_5) and fluorides (LiF, CaF_2 and MgF_2) [14].

Traditionally, adding sintering aids had been known to be the most effective and convenient way to carry out, and CuO was usually introduced to develop low-fired dielectric materials for LTCC applications. For instance, CuO addition to $BiNbO_4$ ceramics significantly reduced the sintering temperature to 950 °C without deterioration of the microwave dielectric properties [15]. Besides, Kim et al. [16] found the microwave dielectric characteristics of 5 wt% CuO-doped $ZnNb_2O_6$ ceramics sintered at 900 °C to be $\varepsilon_r=22.1$, $Q\times f=59{,}500$ GHz, and $\tau_f=-66$ ppm/°C. By the addition of 3.2 wt% CuO to $7NiNb_2O_6$–$9TiO_2$ ceramics, the sintering temperature was effectively decreased to 935 °C and the system had an ε_r of 60.5, a $Q\times f$ of 10,039 GHz, and a τ_f of 62 ppm/°C [17]. Nevertheless, no investigations on the low-sintered $CoTiNb_2O_8$ ceramics have been reported so far.

Thus, CuO was chosen to lower the sintering temperature of $CoTiNb_2O_8$ ceramics in the present work. Subsequently, the influence of CuO additions on the sintering behavior, phase composition and microwave dielectric properties of $CoTiNb_2O_8$ ceramics was investigated systematically.

2. Experimental

$CoTiNb_2O_8$ ceramics were synthesized by conventional solid state route. CoO (99.9%), Nb_2O_5 (99.99%), TiO_2 (99.9%) and CuO (99.9%) were adopted as raw chemicals. Firstly, stoichiometric proportions of the above oxides were milled in alcohol medium and calcined at 1100 °C in air to obtain $CoTiNb_2O_8$. Different weight percentages of CuO were then added to the as-prepared powders. After remilling and sieving, the CuO-containing powders together with the organic binder (5 wt% polyvinyl alcohol) were pressed into cylinders of 10 mm in diameter and 6 mm in thickness under the pressure of 150 MPa. Finally, the green bodies were sintered in the temperature range of 850–1300 °C for 4 h followed by natural cooling.

The relative densities of the sintered samples were identified by the Archimedes method. The crystal structure was investigated by X-ray diffraction (XRD, Rigaku, DMAX-RB, Japan) with CuKα radiation. Scanning electron microscopy (SEM; JSM-6480LV) and energy dispersive spectroscopy (EDS) were utilized to observe the surface morphology and chemical composition of the ceramics, respectively. The microwave dielectric properties of the samples were conducted with a HP8720ES network analyzer. The dielectric constant was measured using the Hakki–Coleman post-resonator method [18] by exciting the TE_{011} resonant mode of the DR using the electric probe of an antenna as suggested by Courtney [19]. All measurements were made in the frequency range of 3–8 GHz at room temperature. The unloaded quality factors were measured using the $TE_{01\delta}$ mode in the cavity method [20]. The temperature coefficients of the resonant frequencies of the TE_{011} mode were obtained in the temperature range from 25 °C to 80 °C. The τ_f values were defined by the following relationship:

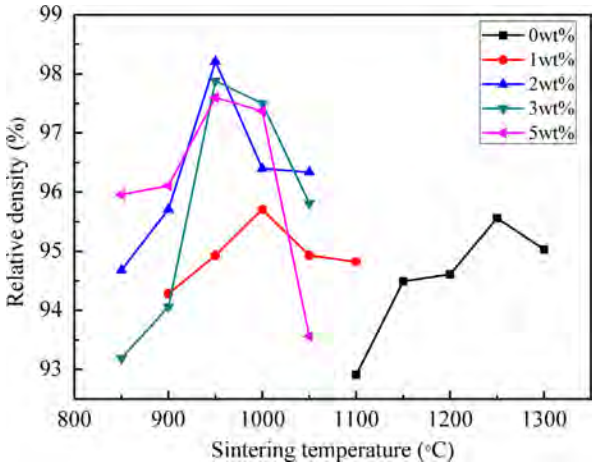


Fig. 1. Relative densities of $CoTiNb_2O_8$ ceramics with different CuO additions as a function of sintering temperature.

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

where f_1 and f_2 were the resonant frequency at T_1 and T_2, respectively.

3. Results and discussion

The relative densities of $CoTiNb_2O_8$ ceramics with CuO additions as a function of sintering temperature are shown in Fig. 1. For pure $CoTiNb_2O_8$ ceramics, the relative density reached its saturated value at 1250 °C. But when 1 wt% CuO was added, the densities of the samples remained relatively low, which indicated that 1 wt% CuO was not enough to densify the ceramics efficiently at low sintering temperatures. Further increasing CuO content, the optimized sintering temperature was significantly lowered to 950 °C. However, the densities started to decrease as the CuO content was greater than 2 wt%. By firing at 950 °C, the maximum relative density of about 98.21% was obtained in 2 wt% CuO-doped samples. All these results revealed that low-temperature sinterable $CoTiNb_2O_8$ ceramics were possible by CuO doping.

Fig. 2 depicts the XRD patterns of the CuO-added $CoTiNb_2O_8$ ceramics. Without CuO addition, the pattern could be indexed as the tetragonal rutile structure $CoTiNb_2O_8$ (JCPDS No. 52-1875) with space group *P42/mnm*. Besides the main phase $CoTiNb_2O_8$, a small amount of second phase $CuNb_2O_6$ (JCPDS No. 20-0361) was detected for the CuO-containing samples. Thus, it could be considered that CuO reacted with the matrix material during a sintering process. It was noticeable that the (1 1 0) diffraction peak shifted towards higher 2θ angles with CuO content ranging from 1 wt% to 3 wt%. This is clearly shown in inset of Fig. 2. Such a kind of peak shift indicated a decrease in unit cell volume due to the smaller Cu^{2+} ions (0.73 Å, CN=6) substitution for larger Co^{2+} ions (0.745 Å, CN=6) at A-site [21]. With CuO addition up to 5 wt%, the (1 1 0) peak shifted toward lower angles distinctly as compared to other CuO-modified samples.

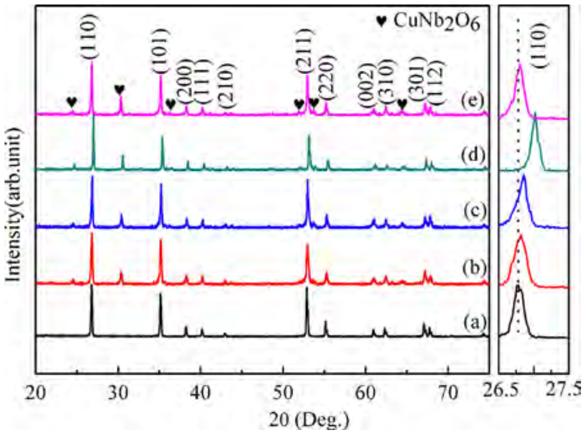


Fig. 2. XRD patterns of $CoTiNb_2O_8$ ceramics added with various amounts of CuO additions (a) pure $CoTiNb_2O_8$ ceramic, at 1250 °C, (b) 1 wt%, at 950 °C, (c) 2 wt%, at 950 °C, (d) 3 wt%, at 950 °C, and (e) 5 wt%, at 950 °C.

One possible assumption was that liquid-phase formation required a relatively long time. Before Cu^{2+} could diffuse into $CoTiNb_2O_8$ lattice, the sintering process was stopped.

Fig. 3 illustrates the SEM photographs of $CoTiNb_2O_8$ ceramics with different CuO additions sintered at 950 °C. The microstructure of un-doped sample was also given here for comparison. After sintering at 1250 °C, pure $CoTiNb_2O_8$ ceramic exhibited dense microstructure with closely packed polygonal grains having 8–12 μm size [Fig. 3(a)]. From Fig. 3 (b), it was seen that a small amount of porosity was developed after the addition of 1 wt% CuO. This might be a result of insufficient liquid phase. Moreover, some lath-like grains were embedded in a matrix of polygonal grains, resulting in abnormal grain growth. When the CuO content increased to 2 wt%, the sample was well-sintered. And it consisted of two types of polygonal grains with main average sizes of ~5 μm and ~1 μm, as seen in Fig. 3(c). Probably because of the increasing liquid phase content, micropores appeared again in 3 wt% CuO doped sample [Fig. 3(d)], whereas for ceramic with 5 wt% CuO addition, superfluous liquid phase separated out and accumulated at the surface. Combining with the relative densities in Fig. 1, it was regarded that proper amount of CuO addition was beneficial to achieve a fully-densified specimen at lower temperatures. However, excessive CuO additive would result in a porous structure. That was because a large amount of liquid phase formed unduly thick film at some specific grain boundaries, which in turn hindered mass transportation [22].

In order to identify the composition of the matrix, smaller grains and liquid phase, EDS analysis is performed on 2 wt% CuO-doped specimen sintered at 950 °C. And the quantitative results are shown in the inset of Fig. 3. For the matrix [marked A in Fig. 3(c)], the molar ratio of Co:Ti:Nb was about 1:1:2, indicating that it was composed of $CoTiNb_2O_8$ phase. In boundary, the ratio of (Co+Cu), Ti and Nb for the smaller grain (see spot B) was approximately 1:1:2, which implied the formation of tetragonal structured (Co, Cu)$TiNb_2O_8$ solid solution. Additionally, only three elements (Nb, O and Cu) were detected for the liquid phase [such as spot C in Fig. 3(c)]. Moreover, Cu and Nb ions with a molar ratio of 1:2 suggested that this was the $CuNb_2O_6$ phase.

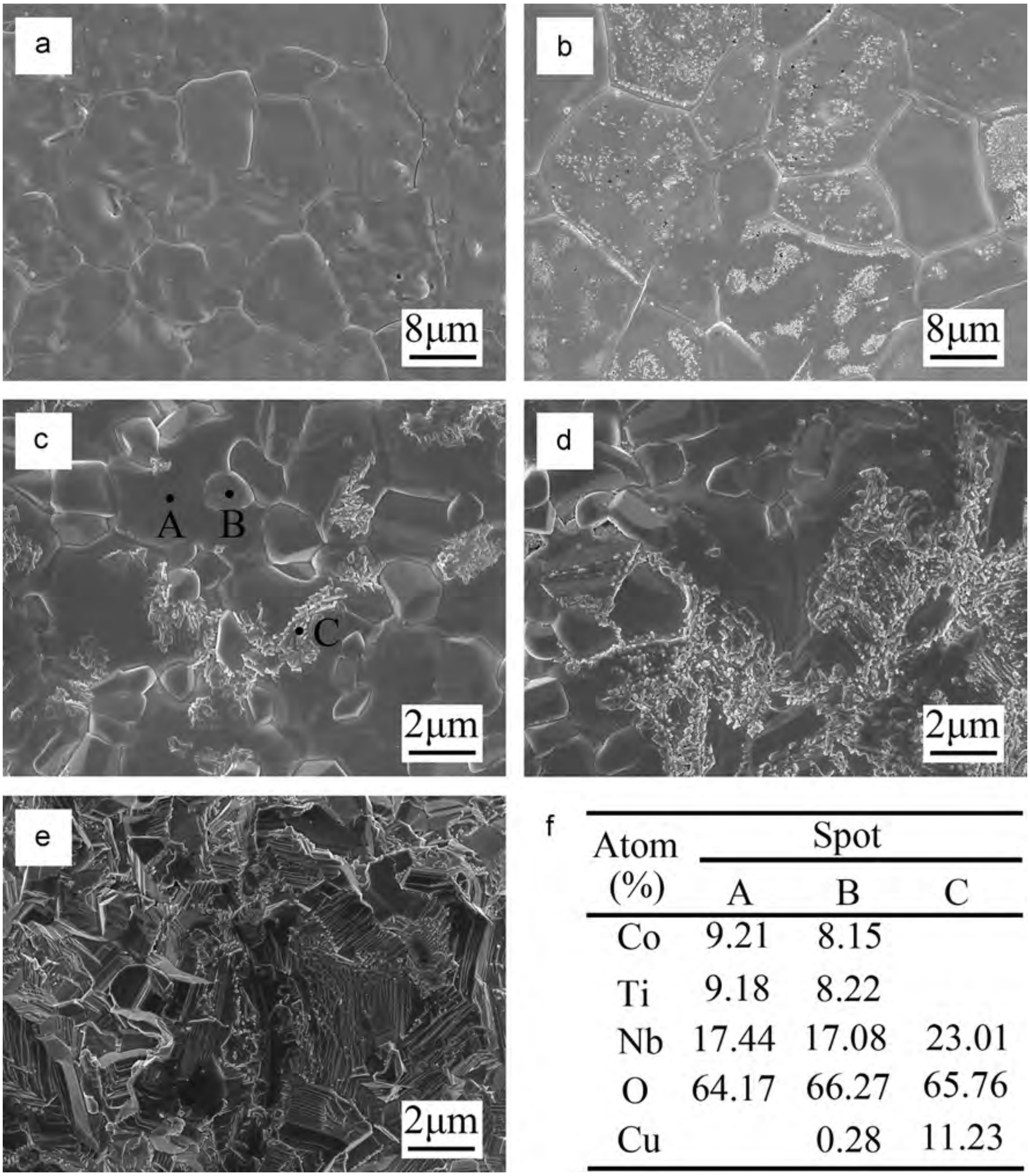
In summary, the low-temperature sintering mechanism of CuO-doped $CoTiNb_2O_8$ ceramics could be elucidated by the following two aspects: (i) when CuO was introduced into this system, chemical reaction between dopant and $CoTiNb_2O_8$ occurred according to Eq. (2). The generated $CuNb_2O_6$ existed in the form of liquid phase at high temperature. In the presence of a liquid phase, particle rearrangement became easier and mass transport by grain-boundary diffusion took place much faster, leading to enhanced densification kinetics [23]; and (ii) Cu^{2+} ion in $CuNb_2O_6$ was preferably incorporated into the Co-site because of its similar ionic radius to Co^{2+}, forming a limited solid solution as described in Eq. (3). This would certainly help to lower the sintering temperature of host samples since $CuTiNb_2O_8$ ceramics could be well densified at just 960 °C [24]. The substitution of smaller Cu^{2+} for Co^{2+} caused weakening of cobalt bond strength, thereby reducing the intrinsic sintering temperature and facilitating the diffusion process. A similar analysis was reported by Xu et al. for MgO–LiF co-doped Li_2TiO_3 ceramics [25]. On the other hand, the grains comprised of (Co, Cu)$TiNb_2O_8$ solid solution were quite small as compared to the matrix grains [Fig. 3(c)]. During the sintering process, the smaller grains would tend to fill the voids between the matrix grains and hence gave rise to a packing structure.

$$CuO + CoTiNb_2O_8 \rightarrow CuNb_2O_6 \tag{2}$$

$$Cu^{2+} + CoTiNb_2O_8 \rightarrow (Cu,\ Co)Nb_2O_6 \tag{3}$$

The microwave dielectric properties of $CoTiNb_2O_8$ ceramics doped with CuO additions sintered at various temperatures are demonstrated in Figs. 4–6. As shown in Fig. 4, the relationship between ε_r values and sintering temperatures displayed a similar trend to that between relative densities and sintering temperatures. This phenomenon could be attributed primarily to that higher density for samples meant there were more dipoles per unit volume, which indicated that the ceramics were more liable to be polarized. As a result, the samples exhibited higher ε_r values. From Fig. 4, it was seen that the dielectric constants had a trend of decreasing at higher CuO-doping levels (>2 wt%). This was ascribed to the comparative lower permittivity of the $CuNb_2O_6$ (~16.1) compared to that of $CoTiNb_2O_8$ (~64) [26,27].

Fig. 5 depicts the $Q \times f$ values of CuO-doped $CoTiNb_2O_8$ ceramics as a function of sintering temperature. Generally, the factors affecting the $Q \times f$ values of microwave dielectric ceramics were divided into intrinsic dielectric loss and extrinsic loss. The intrinsic loss was mainly caused by lattice variation modes, while the extrinsic loss was dominated by secondary phase, oxygen vacancies, grains sizes, densification and lattice defects [28]. In the present work, the $Q \times f$ values of all compositions gradually increased with increasing sintering temperature and saturated at their respective optimal sintering temperatures. Owing to the emergence of $CuNb_2O_6$ phase ($Q \times f$~7100 GHz), the $Q \times f$ values of CuO-doped samples were degraded even though the sintering behavior was greatly



Atom (%)	Spot A	B	C
Co	9.21	8.15	
Ti	9.18	8.22	
Nb	17.44	17.08	23.01
O	64.17	66.27	65.76
Cu		0.28	11.23

Fig. 3. Scanning electron microscopic micrographs of $CoTiNb_2O_8$ ceramics with CuO additions: (a) pure $CoTiNb_2O_8$ ceramic, at 1250 °C, (b) 1 wt%, at 950 °C, (c) 2 wt%, at 950 °C, (d) 3 wt%, at 950 °C, (e) 5 wt%, at 950 °C, and (f) EDS analysis of matrix, smaller grains and liquid phase formed in the specimen with 2 wt% CuO addition.

improved [26]. With the CuO content ranging from 1 wt% to 2 wt%, $Q\times f$ values were found to increase up to 15,938 GHz, possibly depending on improved densification. However, further increasing CuO content resulted in decreased $Q\times f$. This was associated mostly with the excess second phase as well as the lattice defects produced in crystal growth. Obviously, the sintering temperature and loss factor of pure $CoTiNb_2O_8$ ceramics in our study exhibited some differences from the measurements in Ref. [13]. It was inferred that the differences had been made were from the starting raw chemicals.

The τ_f values of $CoTiNb_2O_8$ ceramics with different CuO additions are illustrated in Fig. 6. It is well known that τ_f largely depends on the composition, the amount of additives, and the second phases present in ceramics [29]. As CuO was added to $CoTiNb_2O_8$ ceramics, τ_f decreased almost linearly to 24.18 ppm/°C. Two explanations for this variation were proposed here. One was that $CuNb_2O_6$ had a negative τ_f of -45 ppm/°C [26]. It was reasonably believed that the τ_f values of the samples were adjusted to small positive values [30]. The other was that τ_f values were closely related to the degree of

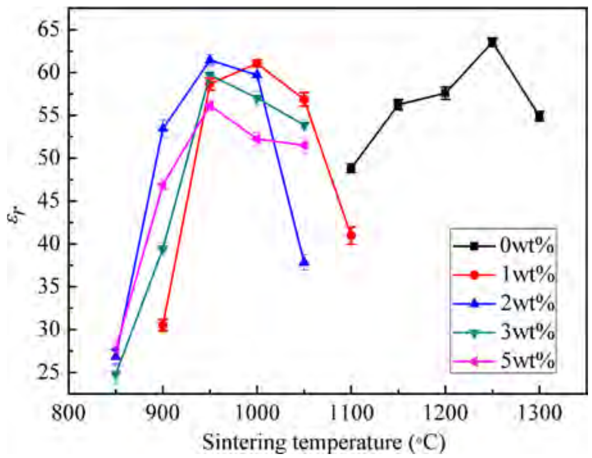


Fig. 4. Dielectric constants of $CoTiNb_2O_8$ ceramics with different CuO additions as a function of sintering temperature.

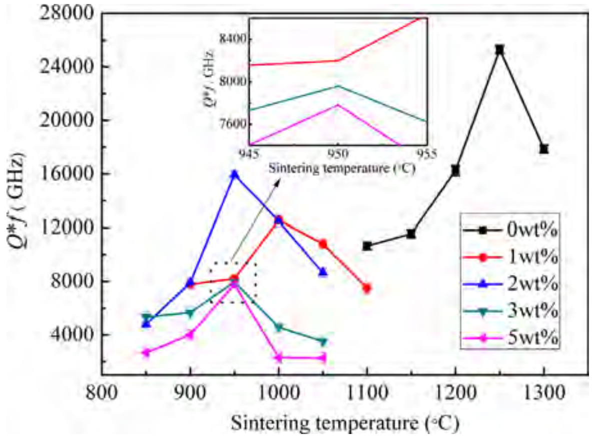


Fig. 5. Quality factors of $CoTiNb_2O_8$ ceramics with different CuO additions as a function of sintering temperature. Inset shows a magnified view of quality factors for $CoTiNb_2O_8$ ceramics sintered at 950 °C.

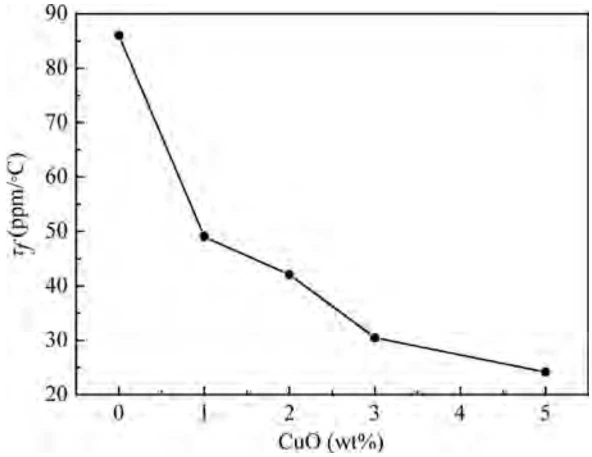


Fig. 6. Temperature coefficients of resonant frequency of $CoTiNb_2O_8$ ceramics as a function of CuO addition.

tilting and distortion of the octahedron in compounds [31]. The replacement of Co^{2+} by Cu^{2+} would inevitably influence the cation-oxygen bond length in present work. Increasing CuO amount probably led to an increase in the NbO_6 octahedral distortion, which indirectly declined the τ_f values to some extent. It is of particular note that near-zero τ_f may be readily achieved for this material by controlling the amount of CuO additions.

4. Conclusion

The effects of CuO additions on the sintering characteristics, microstructure and microwave dielectric properties of $CoTiNb_2O_8$ ceramics had been investigated. It was found that the addition of 2 wt% CuO to $CoTiNb_2O_8$ ceramics reduced the sintering temperature to 950 °C. The reduction in sintering temperature was attributed to the liquid phase effect. The proposed low-temperature sintering mechanism suggested that the substitution of Cu for Co in $CoTiNb_2O_8$ also assisted the densification behavior. The addition of CuO to the $CoTiNb_2O_8$ ceramics induced a limited degradation in ε_r and $Q \times f$ values. Typically, 2 wt% CuO-doped $CoTiNb_2O_8$ ceramics exhibited a well-sintered microstructure with microwave dielectric properties of $\varepsilon_r = 61.45$, $Q \times f = 15{,}938$ GHz, and $\tau_f = 42.12$ ppm/°C at $T_s = 950$ °C.

Acknowledgments

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