Synthesis and characterization of CuO/ZnO-doped (Zr$_{0.8}$Sn$_{0.2}$)TiO$_4$ microwave ceramics

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Abstract. The (Zr$_{0.8}$Sn$_{0.2}$)TiO$_4$ material (ZST), has been prepared by solid state reaction and characterized. The samples were sintered in the temperature range of 1050–1300 °C for 2 h. The effects of sintering parameters like sintering temperature and CuO addition (1-3 wt. %) on structural and dielectric properties were investigated. Bulk density increases from 4.4 to 5.2 g/cm$^3$ with the increase of sintering temperature and adding elements. The effect of CuO addition is to lower the sintering temperature in order to obtain well sintered samples with high value of bulk density. The material exhibits a dielectric constant of 38.2 and high values of the $Q_f$ product, greater than 60000, at microwave frequencies. The dielectric properties make the ZST material very attractive for microwave applications such as dielectric resonators, filters, dielectric antennas, substrates for hybrid microwave integrated circuits, etc.

1. Introduction
The growing diffusion of personal computers and satellite communication systems and the constant need for miniaturization provide a continuous driving force for the discovery and development of new materials to perform the same or improved functions with decreased size and weight [1,2]. Dielectric resonators (DRs) occupy a prominent position in the development of miniaturization of microwave components because of its advantage of compactness and ease of matching to the microwave integrated circuit [3,4]. For a material to be used as a dielectric resonator, it must have high dielectric constant ($e_r > 25$), very high quality factor ($Q > 3000$ at 10 GHz) and very low dependence of resonant frequency on temperature ($\Delta f < \pm 10$ ppm °C$^{-1}$). The development of materials based on the ZrO$_2$–SnO$_2$–TiO$_2$ ternary system was motivated by the achievement of very low loss and high dielectric constant and a controlled temperature coefficient of the permittivity [4,5]. Remarkable temperature stability can be achieved by using the compound (Zr$_{0.8}$Sn$_{0.2}$)TiO$_4$ [6,7]. The resonators made of ZST exhibit an almost zero temperature coefficient of the resonant frequency. Therefore, the ZST materials
have been successfully applied for microwave devices like low phase-noise dielectric resonator oscillators (DRO), duplexers, filters, frequency discriminators, etc. [8,9]. But the high sintering temperature of this composition makes it difficult to reach a sufficiently dense structure. Three methods have been used to deal with this problem; 1- using glass additives, 2- chemical processing such as sol-gel method or co-precipitation and 3-using sintering aids as liquid flux [10,11]. The first method was found to effectively lower the firing temperature. However, it decreased the microwave dielectric properties of ZST ceramic. The wet chemical process often required a complicated procedure that would increase the cost and time in fabricating the samples. The third method, used in present research, is expected to be able to reduce sintering temperature and keeps the dielectric properties in desired range by adding combination of two or more oxides. The preparation of ZST materials at low sintering temperatures without additives is difficult. The La$_2$O$_3$ addition promotes the grain growth. ZnO, increase the sinterability, but no mechanisms have been proposed for the improved densification kinetics or for their effect on the dielectric loss [12-18].

Aiming at the improvement of low-loss dielectric material with a small temperature coefficient of resonant frequency, the dielectric properties of Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ ceramics at microwave frequency have been studied. Small amounts of ZnO and CuO additions were added to obtain well-sintered ceramic samples. Consequently, they showed excellent characteristics at microwave frequencies. The effects of additions on the microwave dielectric properties and the microstructures of Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ ceramics were also investigated in this article.

2. Experiments

Samples of Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ were synthesized by conventional solid-state methods from high-purity oxide powders of ZrO$_2$, SnO$_2$, and TiO$_2$. The starting materials were mixed according to the desired stoichiometry of Zr$_{0.8}$Sn$_{0.2}$TiO$_4$. Then 1 wt% ZnO and various amount of CuO (1–3 wt %) were added as sintering aids. The powders were ground in distilled water for 8 h in a ball mill with agate balls. All mixtures were dried and calcined at 1100°C for 3 h. The calcined powders were then remilled for 10 h with PVA solution as a binder. Pellets 13 mm in diameter and 6 mm thick were formed by uniaxial pressing. After debinding, these pellets were sintered at temperatures of 1050–1300°C for 2 h. The heating rate and the cooling rate were both kept at 5°C/min.

The phase compositions were identified by X-rays diffraction analysis using copper target. The bulk densities of the sintered pellets were measured by Archimedes method. The transmission coefficients versus frequency were measured by Vector Network Analyser. The dielectric constant has been measured by transmission method as proposed by William Courtney [12], which is a modified version of Hakki and Coleman method [13] using a Vector Network Analyser (HP8720A). Here the sample is kept between two copper plates and the microwave is inductively coupled to the samples through the antenna connected to the analyzer by the coaxial cables. The dielectric constant was calculated from the sample dimensions and the resonant frequency of TE$_{011}$ mode, which can be easily distinguished from high-frequency modes. The quality factor was measured by reflection method. The temperature coefficient of resonant frequency at microwave frequency was measured in the temperature range of 25–80°C.

3. Results and Discussion

3.1. Structural and dielectric properties

It is identified from XRD patterns (which are not shown here) that Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ exhibits an orthorhombic-type crystal structure. On the contrary when additives such as La, Fe, or Bi are used, some second phases were formed, due to the size difference between the substitution ions and the ions in Zr$_{0.8}$Sn$_{0.2}$TiO$_4$. Although ZnO is well known to form boundary phases such as Zn$_2$TiO$_4$, the second phase was not observed at the 1-3 wt% level of CuO addition, due to the fact that detection of a minor phase by XRD is extremely difficult. It must be mentioned that above 1400 °C, ZrTiO$_4$ displays a structure with a random distribution of Zr$^{4+}$ and Ti$^{4+}$ cations and addition of Sn$^{4+}$ would stabilize this
disordered structure. Disorder-order transformation in ZST can be affected by these changes. It has been proved that change in structure from disorder to order state, is accompanied by reduction in unit cell volume. As these two have been increased with CuO addition, it can be concluded that adding CuO, would not accelerate the disorder-order transformation.

The plots of bulk densities of 1 wt% ZnO-doped Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ ceramics with different amounts of CuO addition versus sintering temperature are illustrated in Fig. 1. As shown in Fig. 1(a), the Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ ceramics were dense at 1250°C and possessed densities higher than 95%. Initially, the density increased with increasing sintering temperature and seemed to saturate at 1250°C. After reaching the maximum at 1250°C, it decreased slightly owing to the appearance of open pores. It seemed that CuO did attribute to the densification of Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ ceramics. The maximum relative density was found to be 96.5% with 3 wt% CuO addition at 1250°C. It is difficult to synthesize ceramics with ultrahigh relative density by the conventional solid-state method unless it is augmented by other methods, such as chemical processing.

Figure 1(b) shows the dielectric constants of 1 wt% ZnO-doped Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ ceramics with different amounts of CuO addition as functions of their sintering temperatures. As can be seen, the addition as well as the sintering temperature did not significantly affect the dielectric constant. The $\varepsilon_r$ values of the well-sintered Zr$_{0.8}$Sn$_{0.2}$TiO$_4$ ceramics ranged from 36.2 to 38.2. As dielectric constant of the material is related to dielectric constant of each phase present in the sample and its volume fraction, and porosity is regarded as a separate phase with dielectric constant of 1, increase in density caused by CuO addition, raised the dielectric constant. Another effect is the increase of the c-axis length which is correlated to increase in ionic polarization and can lead to higher dielectric constant.

![Figure 1](image.png)

Fig. 1. (a) The relative densities and (b) dielectric constant of ZST ceramics with different amounts of CuO addition versus sintering temperature

### 3.2. Microwave properties

The variation of transmission coefficients with frequency for samples prepared at 1250 °C are shown in Fig. 2. The sample contains 1wt% CuO exhibits the largest linewidth in compare to the other samples. The maximum transmission coefficient is belonging to resonant frequency of 11.2 GHz. There are another two resonant peaks which might be attributed to the others excitation modes in microwave region. The transmission coefficients of the other excitation modes are more than -20 dB at 8.7GHz and -9 dB at 12.2 GHz respectively. The resonant frequency and transmission coefficient can be easily engineered by adding the additional amount of CuO in the component. It reveals that the sample with 2 wt% CuO provides transmission coefficient value of -33.62 dB at 13.8 GHz. In this material no secondary peaks were found. The largest transmission coefficient along with resonant frequency could be achieved with incorporation of 3 wt% CuO in the microstructure. It is clearly observed that the originated linewidth is negligible. Consequently, it can be concluded that with
controlling of CuO additive, the manipulation of high $Q_f$ is plausible. The results regarding to the $Q_f$ values will be explained in this section.

![Fig. 2. Transmission coefficient versus frequency of ZST doped with (a) 1 wt% CuO, (b) 2 wt% CuO, (c) 3wt% CuO, and (d) variation of resonant values with amount of CuO](image)

The resonant frequency is known to be related to the length and diameter of cylindrical samples along with dielectric constants. In this research, we treat the dimension as a constant due to the same values of length and diameter in all prepared samples. Consequently the position of resonant frequency is due to the variation of dielectric constants with adding elements. Figure 2(d) clearly reveals the relevant data.

The $Q_f$ values of 1 wt% ZnO-doped $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ ceramics with various amounts of CuO addition, as functions of their sintering temperatures, are shown in Fig. 3. The relationships between $Q_f$ values and sintering temperatures reveal the same trend as those between densities and sintering temperatures. Relative density plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials. With 3 wt% CuO addition, the $Q_f$ value of $\text{Zr}_{0.8}\text{Sn}_{0.2}\text{TiO}_4$ ceramics increased from 29,000 at 1050°C to 61,000 at 1250°C and then decreased with further increase in the sintering temperature. However, the $Q_f$ values decreased with the increase of CuO addition at fixed sintering temperature. It has been reported [6,7] that the microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pores, the second phases, the impurities, or...
the lattice defect. Because the second phase was not observed, the degradation in $Q_f$ value might be due to impurities. One can generally state that to obtain a maximum quality factor, it is necessary to produce a perfect single phase material devoid of doping or impurity. For a perfect crystal, the quality factor would be limited only to intrinsic lattice dampening, which depends on crystal structure. However, when densification requires the use of additives, it is important to identify the mechanism involved. Second phases usually increase dielectric losses and oxygen vacancies are important factors on dielectric loss for ZST ceramic. In this research no secondary phase containing Cu or Zn was detected.

The temperature coefficient of resonant frequency is known to be related to the composition and the second phase of the material. Because $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics are temperature stable, and CuO addition did not cause an observable second phase, the $\Delta_f$ values did not change much and ranged from -3.2 to -1.2 ppm/°C in the experiment (Fig. 3(b)). With 3wt% CuO addition, the 1 wt% ZnO-doped $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics sintered at 1250°C had excellent microwave dielectric properties with an $\varepsilon_r$ value of 38.2, a $Q_f$ value of 61,000, and a $\Delta_f$ value of -1.2 ppm/°C.

Fig. 3. (a) The $Q_f$ values and (b) $\Delta_f$ of $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics with various amounts of CuO addition given as a function of sintering temperature.

4. Conclusions
The effect of CuO addition on the microwave dielectric properties and the microstructures of 1 wt% ZnO-doped $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics were investigated. $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics with ZnO and CuO additions can be well sintered to approach 96.5% theoretical density at 1250°C. The $Q_f$ value of $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics can be promoted to be as high as 61,000 at this sintering temperature. The reduction of the dielectric loss of $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics with CuO addition was mainly attributed to enhanced densification. $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics with 1 wt% ZnO and 3 wt% CuO additions sintered at 1250°C exhibited an $\varepsilon_r$ of 37.8, a $Q_f$ value of 61,000, and a $\Delta_f$ value of -1.2 ppm/°C. Compared to other additions, $Zr_{0.8}Sn_{0.2}TiO_4$ ceramics with CuO added exhibited enhanced $Q_f$ values without significantly changing the dielectric constant or temperature coefficient.

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