Effect of CuO on the sintering and cryogenic microwave characteristics of (Zr$_{0.8}$Sn$_{0.2}$)TiO$_4$ ceramics

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Received 12 April 2007; received in revised form 20 June 2007; accepted 25 July 2007
Available online 5 September 2007

Abstract

The effect of CuO on the sintering temperature, microstructure and microwave dielectric properties of (Zr$_{0.8}$Sn$_{0.2}$)TiO$_4$ (ZST) modified with 1 wt% of ZnO has been investigated. Microwave dielectric properties of ZST ceramics are measured from cryogenic to room temperatures (15–290 K). Crystallite sizes of sintered ZST ceramics as derived from XRD are in the 30–50 nm range. The addition of CuO effectively reduced the sintering temperature to 1300$^\circ$C, possibly due to liquid-phase effects. Addition of CuO did not cause any secondary phases up to 1.5 wt% of CuO. The dielectric constant ($\varepsilon_r$) and temperature coefficient of resonant frequency ($\tau_f$) of ZST ceramics do not significantly vary with temperature, whereas the unloaded quality factor ($Q_u$) changes noticeably. It is found that the $Q_u$ factor of the sample without CuO decreased with increase in temperature, whereas the samples with addition of CuO up to 1.0 wt% showed less dependence on temperature. The $Q_u$ factor of CuO-free ZST is 15,000 and that of ZST with 0.5 wt% of CuO is 11,800 at 15 K. The $Q_u$ factor while measured at room temperature ranged between 2900 and 7000. Efforts were made to understand whether the increase in $Q_u$ factor at both cryogenic and room temperatures is the result of intrinsic or extrinsic factors.

1. Introduction

Modern technology is demanding smart materials and/or materials with advanced properties to incorporate more and more functions in electronic devices. Among the different categories of electronic materials, dielectric materials are prominent, especially in RF and microwave devices and circuits. In order to add more and more functions, additional circuits are necessary. However, the industry prefers to have miniaturized circuits with improved and added functions. As a result, the device size may become bigger, which could be avoided only by using dielectric materials with high permittivity or using multilayer technology. Typically, the loss tangent of high-permittivity materials is higher.

The desired properties of materials for high-frequency applications are high dielectric constant ($\varepsilon_r > 20$), low dielectric loss ($Q = 1/(\tan \delta > 5000$ at 10 GHz) and a zero or near-zero temperature coefficient of resonant frequency ($\tau_f$ ppm/$^\circ$C). Ba(Mg$_{0.33}$Ta$_{0.66}$)O$_3$ BMT (permittivity $\varepsilon_r \sim 24$) is one of the popular dielectric materials, which satisfies these requisites. Zirconium tin titanate (Zr$_{0.8}$Sn$_{0.2}$)TiO$_4$ (ZST) ceramics exhibits higher permittivity than BMT and is tipped as a commercial dielectric material for microwave devices due to its satisfactory dielectric properties at high frequencies [1]. The base material of ZST is ZrTiO$_4$, whose crystal structure is $\alpha$-PbO type structure and belongs to the Pbnm space group. Ti and Zr ions are ordered in the low-temperature phase and disordered in the high-temperature phase. When 20 mol% Zr ions are replaced by Sn ions, a temperature-stable ZST is obtained. The dielectric constant of ZST is 38, the $Q \times f$ is in the range of 35,000–50,000 GHz and the temperature coefficient of frequency is near to 0 ppm/$^\circ$C. The ZST is ideal for
a variety of high-frequency applications ranging from mobile phones to GPS. One of the advantages of ZST is that it could be fabricated as thin films, the backbone of all electronic industry [2–5]. Dedicated research is essential to overcome the poor sinterability of pure ZST (sintering temperature is \(\sim 1600^\circ\)C). Addition of trace additives to the ZST system to lower the sintering temperature without causing significant loss of the required dielectric properties is reported [6–8]. ZST ceramics is generally produced by the ZST system to lower the sintering temperature without CuO–Cu2O–TiO2 at 1070°C. A liquid-phase effect is believed to be the cause also added to achieve better sinterability and lower levels of CuO, i.e., in addition to 1 wt% ZnO, CuO is added to improve electromagnetic properties of ZST with different doping suitable additives cannot be found.

In this paper, we have synthesized and studied the electromagnetic properties of ZST with different doping levels of CuO, i.e., in addition to 1 wt% ZnO, CuO is also added to achieve better sinterability and lower loss. A liquid-phase effect is believed to be the cause of increased sinterability brought in by the eutectic of CuO–Cu2O–TiO2 at 1070°C [11]. The microwave properties were investigated as a function of temperature to understand the feasibility of using the material in cryogenic and low-temperature devices. During the last one decade, more and more devices started using the low-temperature electronic devices since the high-temperature superconductors allowed for significant reduction of losses and noise in microwave filters and oscillators. Successful design and manufacture of low-loss devices at cryogenic temperatures require careful choice of dielectric materials for their construction. Low-loss materials can be used in conjunction with the high Q factor superconducting systems to reduce the overall loss of the device.

2. Experimental procedure

Samples of (Zr0.8Sn0.2)TiO4 were synthesized by the conventional solid-state method from individual high-purity oxide powders ZrO2, SnO2, TiO2, ZnO and CuO (99.9%) of Sigma Aldrich, USA. The starting materials were mixed according to the desired stoichiometry of (Zr0.8Sn0.2)TiO4 ceramics, with addition of 1 wt% ZnO as sintering aid. A planetary ball mill with zirconia balls (Retsch, PM100) was used to mix and to reduce the particle size of the powders. The powder was mixed using distilled water and was calcined at 1300°C for 1 min. The calcined powders were again ball milled at higher speeds. The powder was divided into two batches; the first batch of powder was remilled with different amounts (0.5–1.5 wt%) of CuO additions for 1 h each. Pellets of 12 mm diameter were formed by uniaxial pressing. They were sintered at temperatures of 1300–1400°C for different durations. The phase purity of the calcined powders and pellets was identified by an X-ray diffractometer (Philips PW 1830). The microstructure of the sintered (Zr0.8Sn0.2)TiO4 ceramics was observed by scanning electron microscopy (Philips XL 30 ESEM). The finished cylindrical resonators used for cryogenic microwave measurements are of 10.5 mm diameter and 5.5 mm height.

A TE012 mode post-dielectric resonator [12] loaded with the dielectric under test was used for microwave characterization. The experimental technique used for the microwave characterization is thoroughly discussed elsewhere [13]. The experimental system consists of a network analyzer (HP 8722C), a closed-cycle refrigerator (APD DE-204), a temperature controller (LTC-10), a vacuum dewar, a PC and the TE012 mode dielectric resonator. The resonator containing the dielectric material was cooled from room temperature to approximately 13 K. The TE011 mode resonance was identified around 5 GHz. The \(S_{21}\), \(S_{11}\) and \(S_{22}\) parameters around the resonance were measured at the lowest temperature. The multi-frequency measurement and data-processing technique (TMQF) [14] was used to eliminate all kinds of parasitic losses and to precisely compute coupling coefficients \(k_1\) and \(k_2\). The unloaded \(Q\) factor was calculated using [15]

\[
Q_0(T) = Q_L(T)[1 + k_1(T) + k_2(T)],
\]

where \(Q_L\) is the loaded \(Q\) factor.

The \(S_{21}\) parameter was measured as a function of temperature from 15 to 290 K. The coupling coefficient for each measurement temperature was calculated using a simplified TMQF [14], and hence the unloaded \(Q\) factor. The perpendicular component of the real part of relative permittivity and loss tangent (\(\tan\delta\)) of ZST was computed from the measured resonant frequency and unloaded \(Q\) factor, respectively.

3. Results and discussion

The XRD patterns of the ZST ceramics sintered at 1300°C for 3.5 h with different amounts of CuO and the sample doped only with 1 wt% of ZnO sintered at 1400°C for 3 h are shown in Fig. 1. The average crystallite size of the sintered ZST ceramics was calculated from the Williamson–Hall plot (\(\beta \cos \theta vs. \sin \theta\)) and ranged between 30 and 50 nm. It is observed that all samples exhibited orthorhombic, \(\alpha\)-PbO2 crystal structure. Although ZnO is well known to form boundary phases such as Zn2TiO4 [16], a secondary phase was not observed at the 0.5–1.5 wt% level of CuO addition, due to the fact that detection of a minor phase by XRD is extremely difficult. Because the ionic radius of Cu2+ (0.73 nm) is comparable to that of Zr4+ (0.72 nm), Sn4+ (0.69 nm) and Ti4+ (0.605 nm) [17], Cu2+ ion could completely substitute for the tetravalent elements of ZST ceramics. Furthermore, the total charges of two Cu2+ ions are equal to the valency of the ions in ZST, and hence will not result in charge distortion.
Therefore, it is believed that CuO is dissolved in ZST ceramics [11].

Fig. 2(a) shows the variation in density as a function of wt% of CuO addition. The samples are sintered at different sintering temperatures for a constant sintering duration. In the case of CuO-free samples, it is observed that the densities of the samples increased with increase in sintering temperature, while the densities of the samples with CuO decreased with increase in sintering temperature. The densities of the samples are higher when doped with 1.0 wt% of CuO irrespective of the sintering temperature. The variation in density as a function of wt% of CuO sintered at 1300°C for different sintering durations is plotted in Fig. 2(b). It is observed that the density of the samples increased as the sintering duration increased up to 3.5 h, but started decreasing further. The density is increased with increase in concentration of CuO up to 1 wt%, and above that it is decreased. The maximum density of 96.6% of theoretical density (TD) is observed for the sample doped with 1 wt% of CuO and sintered for 3.5 h at 1300 °C. ZST ceramics without the addition of CuO showed better densification at 1400 °C and the density is 96.3% of TD when sintered for 3 h. The decrease in density after longer sintering durations can be attributed to the evaporation of CuO, the liquid-phase effect and to possible secondary phases, which are difficult to observe from XRD patterns. The increase in density is attributed to the reduction in porosity and uniform grain growth. It is observed that the addition of CuO reduced the sintering temperature of the ZST ceramics without enhancing the grain growth.

The microstructures of the CuO-free ZST ceramics and that added with different amounts of CuO, sintered at 1400 °C for 3 h and 1300 °C for 3.5 h, respectively, are shown in Fig. 3(a–d). It is observed that the grain size is higher and uniform up to 1.0 wt% addition of CuO and above that the grain size started decreasing. The sample without the addition of CuO showed higher average uniform grain size of 10 μm and the sample doped with different concentrations of CuO at 0.5, 1.0 and 1.5 wt% showed 9, 8 and 5 μm, respectively. The variation in grain size for the samples with and without CuO can be attributed partly to the differences in their sintering temperatures. It is well known that the higher the sintering temperature, the higher the grain size. The decrease in density and grain size with 1.5 wt% addition of CuO can be attributed to the liquid-phase effect, which is clearly observed from the microstructure of the sample.
Variation in the resonant frequency of the ZST ceramics doped with different concentrations of CuO and without CuO, measured as a function of temperature, is shown in Fig. 4(a). It is observed that there is difference in the resonant frequencies of the ZST ceramics prepared as dielectric resonators with and without the addition of CuO, the dimensions being kept constant. The difference in the resonant frequency is due to the difference in the real part of the permittivity of the sample and slight difference in the sample dimensions. In order to obtain the highest accuracy in the permittivity, we have accounted the exact dimensions of each sample separately.

The variation in dielectric constant as a function of temperature for the ZST ceramics is plotted in Fig. 4(b). It is observed that the decrease in dielectric constant with increase in temperature over the wide range of temperature is quite small. The sample without CuO showed the higher dielectric constant of 37.88 at 15 K and 37.62 at room temperature. ZST ceramics doped with CuO showed lower values compared with the undoped sample. There is not much variation in dielectric constant with the variation in wt% of CuO at cryogenic temperatures. For samples with CuO added in the range of 0.5–1.5 wt%, the variation in dielectric constant is between 34.89 and 35.15 at 15 K, and between 34.63 and 34.94 at 290 K. There is a slight variation in dielectric constant measured at ambient conditions for the samples doped with and without CuO and are tabulated in Table 1. The set-up used for cryogenic measurements and that for measurement at ambient are different.

The unloaded $Q$ factor of the ZST ceramics measured as a function of temperature is shown in Fig. 5(a). It is found that the unloaded $Q$ factor decreased with increase in temperature. In the case of ZST without CuO, the unloaded $Q$ factor is higher compared with CuO-added samples at cryogenic temperatures, but decreased drastically with increase in temperature compared with other samples. The maximum unloaded quality factor ($Q_u$) of pure ZST is 15,000 at 15 K and 3180 at 290 K. In the case of CuO-added samples, even though the unloaded $Q_u$ factors are lower compared with the pure sample at 15 K, the reduction in the unloaded $Q_u$ factor with increase in temperature is lower, resulting in the modified sample giving higher $Q_u$ value towards room temperature. The sample doped with 0.5 wt% of CuO showed higher value of $Q_u$ compared with 1.0 and 1.5 wt% of concentrations. The $Q_u$ for this sample ranged between 11,800 at 15 K and 7886 at 290 K. The maximum values of $Q_u$ among the
CuO-added resonators ranged between 11,800–6510 at 15 K and 7886–2660 at 290 K. $Q_u$ of the ZST ceramics measured at ambient conditions at a resonant frequency of 6.44 GHz increased with increase in concentration of CuO up to 1 wt% and decreased with further increase in wt% of CuO. The difference between ambient measurement and measurement in the controlled environment of a cryogenic system is attributed to humidity, and hence for further discussion only the data obtained with the cryogenic set-up are used. The increase in $Q_u$ factor at room temperature is generally attributed to the uniform grain growth, increase in grain size, enhanced density and also to the reduction in oxygen vacancies [18]. The resonant frequency of the samples measured at room temperature is 6.44 GHz. However, in the present case, with addition of CuO, the grain size is in fact decreasing. The reduction in $Q_u$ factor with increase in wt% of CuO can be attributed to the

![Fig. 4. (a) Variation in the resonant frequency of the ZST ceramics without CuO and doped with different concentrations of CuO measured as a function of temperature. (b) Variation in dielectric constant of the ZST ceramics as a function of temperature.](image)

![Table 1](image)

| Sample name                  | $\varepsilon$ | Unloaded $Q$ factor | $\tau_r$ (ppm/°C) |
|------------------------------|---------------|--------------------|-------------------|
| 1 wt% ZnO + ZST              | 37.62         | 4600               | 3.1               |
| 1 wt% ZnO + ZST + 0.5 wt% CuO| 34.74         | 5780               | 1.68              |
| 1 wt% ZnO + ZST + 1.0 wt% CuO| 34.69         | 7000               | 1.36              |
| 1 wt% ZnO + ZST + 1.5 wt% CuO| 35.11         | 2900               | 1.72              |

![Fig. 5. (a) The unloaded $Q$ factor of the ZST ceramics measured as a function of temperature. (b) The variation in $Q_u/C_f$ of the ZST ceramics as a function of temperature. (c) The variation in loss tangent of the ZST ceramics as a function of temperature.](image)
decrease in density, presence of liquid phase and smaller grain size. The maximum contrast in $Q_u$ value is exhibited between the sample without CuO and the sample with 0.5 wt% of CuO. Addition of CuO modified the microstructure and microwave dielectric properties along with reduction in sintering temperature. The modification in microstructure and sintering temperature shows that CuO influences the recrystallization process and thereby the extrinsic loss mechanisms commonly found in ceramics. However, the drastic variation between the sample without CuO and the sample with 0.5 wt% of CuO shows that the CuO in limited quantities must be influencing the very intrinsic loss mechanism in ZST, that is, it must be getting into the lattice of ZST and modifying its lattice dynamics. The decrease in $\varepsilon$ while $Q_u$ value increases shows that the polarizable lattice modes are getting confined to their harmonic limits. Under such conditions, the unharmonicity associated with those modes will be less, resulting in lower values of dielectric loss and thereby higher $Q_u$ values. At the same time, within the harmonic limits, the polarizability also will be less, and hence the resulting dielectric constant also will be less.

The product of the quality factor and resonant frequency is considered as a tool for evaluating the quality of dielectric materials. Fig. 5(b) shows the $Q_u \times f_0$ of the resonator loaded with ZST sample under test. The results substantiate that the dielectric properties are improved as a result of the 0.5% and 1% CuO doping.

The variation in loss tangent as a function of temperature is plotted in Fig. 5(c). It is observed that as the temperature increases the loss tangent of the samples increases. For the sample without CuO, the loss is higher compared with CuO-added samples. The loss tangent of the ZST ceramics increased with increase in the concentration of CuO. This shows that with additional CuO, the extrinsic losses must be increasing. In other words, the intrinsic losses could be influenced only to a limited extent. Attempt to influence it further by adding more CuO unleashes more extrinsic factors associated with the recrystallization process, giving rise to increase in total loss. The sample doped with 0.5 wt% of CuO showed low loss tangent and is almost stable with increase in temperature. The observed increase in $\tan \delta$ for the sample with 1.5 wt% of CuO with increase in temperature can be attributed primarily to the extrinsic losses. From the SEM micrographs, it is clear that, for this sample, there is the presence of liquid-phase sintering and it exhibits smaller grain sizes and gave lower density. As is known, smaller grain sizes increase the grain boundary areas, which are sources of many extrinsic loss-inducing centers. For most of the measurement temperatures, loss exhibited by this sample is higher than the loss of the CuO-free sample, and the slopes of their temperature dependence are different. In addition to the higher loss tangent, the slope of the $\tan \delta$ vs. temperature graph for the 1.5 wt% of CuO sample is also different from those of the other two CuO-added samples. This indicates that the origin of the loss in this sample differs from other cases. The difference in the microstructure for this case is quite drastic and the increased loss could therefore be attributed to it.

The difference in slope of the $Q_u$ vs. temperature response of the CuO-free sample in comparison with the CuO-added samples shows that CuO doping brings in a fundamental difference in the loss mechanism of the ZST system. Again, it could be attributed to a moderation in the anharmonicity of lattice modes because that will result in both a reduction in loss as well as a reduction in temperature dependence, which is indeed observed.

In general, the microwave dielectric loss can be attributed to both the intrinsic and extrinsic losses. The intrinsic losses are due to the anharmonic forces that mediate the interaction between crystal lattice modes and the applied electromagnetic field, which leads to damping of the optical phonons. On the other hand, the extrinsic losses are caused by the extended dislocations, grain boundaries, porosity, oxygen vacancies and secondary phases [18]. These losses are caused mainly by the dipole relaxation of the defect-oriented polarizations concentrated at the interfaces [19]. The unharmonicity terms in the potential energy when a pair of atoms is at mean separation decrease with decrease in temperature, which is in agreement with the second law of thermodynamics. The frequency dependence of dielectric loss tangent is given by [20]

$$\tan \delta = \frac{\omega_T}{\omega_{T,1}^2},$$

where $\omega_T$ is the resonant frequency of the transverse optical mode lattice vibration and $\gamma$ is its damping constant. The damping constant $\gamma$ is proportional to temperature, and hence the intrinsic losses increase with temperature. The specimen with large grain size is expected to have a high $Q$ value because the grain growth decreases the grain boundary area [21]. Yet, in this case, it could be seen that the CuO-free sample got the highest grain size, but the highest loss and temperature dependence also. This again strengthens the assumption that the difference between the CuO-free sample and the rest of the samples are primarily intrinsic in origin. The observation that the slope of $Q_u$ vs. temperature behavior of the CuO-free sample is drastically moderated with CuO addition leads to the assumption that $\gamma$ got reduced with CuO addition. A lower $\gamma$ value leads to higher $Q_u$ value and lower temperature dependence. The addition of CuO tailored the microwave dielectric properties of ZST ceramics at room temperature to make it suitable for dielectric resonator applications.

The temperature coefficient of resonant frequency is known to be related to the composition and secondary phases in the material. From the measured resonant frequency of the ZST dielectric resonator, we have calculated the $\tau_f$ using the equation:

$$\tau_f = \frac{f_0 - f_{0T}}{f_0} \frac{1}{\Delta T},$$

where $f_0$ and $f_{0T}$ are the resonant frequency at room temperature and at temperature $T$, respectively. It is found
that there is no significant difference in the $\tau_f$ of the four materials studied. The $\tau_f$ values of the samples at ambient temperature are tabulated in Table 1.

The $\tau_f$ as a function of temperature is calculated using the measured frequency at room temperature and is shown in Fig. 6(a). The temperature coefficient of permittivity is also calculated as a function of temperature using the permittivity data and is shown in Fig. 6(b). There is no significant variation in $\tau_f$ and $\tau_z$ observed especially in the temperature range from 15 to 250 K. The 1 wt% CuO doping exhibited lowest temperature coefficient of frequency as well as dielectric constant. Negligible difference between the $\tau_f$ (or $\tau_z$) of the four materials shows that, without affecting the stability of the resonating structure, the performance of the device loaded with ZST can be improved.

4. Conclusions

The dielectric properties of ZST at microwave frequencies were thoroughly investigated at both cryogenic and room temperatures. It is found that as temperature increases the dielectric constant of ZST ceramics is not affected much, whereas the $Q_u$ factor of pure ZST ceramics decreased compared with the CuO-added samples. The addition of CuO changes the real part of complex permittivity significantly. The addition of CuO tailored the microwave dielectric properties of ZST ceramics, particularly near room temperature. The improvement in $Q_u$ factor at cryogenic temperatures is attributed primarily to reduction in intrinsic losses. The moderation in the loss and temperature dependence of loss factor with CuO addition in ZST is also attributed to the CuO influencing the intrinsic loss mechanism of ZST. The difference with variation in CuO doping concentration is attributed to extrinsic factors. The ZST ceramics doped with ZnO and CuO resulted in a high permittivity dielectric with reasonably stable performance with temperature, which promises it as a potential entrant in the field of devices for microwave communication.

Acknowledgments

M.V.J. acknowledges the financial support obtained under the ARC Discovery Project scheme. The authors acknowledge financial support from ISRO and DLRL for the work.

D.P. acknowledges a SRF from ISRO and G.L.N. acknowledges a fellowship from DLRL.

Facilities provided by the ISRO, UGC, UGC-SAP, UGC-UPE, DST-FIST and DLRL of India are gratefully acknowledged.

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