Structural Elucidation, Electronic and Microwave Dielectric Properties of Ca(Sn$_x$Ti$_{1-x}$)O$_3$, (0 ≤ x ≤ 0.8) Lead-Free Ceramics

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ABSTRACT: The lead-free Ca(Sn$_x$Ti$_{1-x}$)O$_3$, (0 ≤ x ≤ 0.8) sample has been successfully prepared through the ball milling process, sintered at 1200 °C for 3 h. The structural, morphological, vibrational, and microwave dielectric properties of synthesized samples were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and impedance analysis. All the samples have an orthorhombic phase structure with a space group of $Pbnm$ formation, and the crystalline size and strain changes with respect to Sn$^{4+}$ doping were observed in the XRD analysis. From a morphological point of view, on increasing the content “x”, the grain size reduces from 3.29 to 1.37 μm. The existence of vibrations and the bridging stretching mode of Ti−O−Ti and Ti−O−Sn both are associated with the broadband in the region below 800 cm$^{-1}$ verified by FT-IR. The variation in electrons hopping off the host compound with respect to Sn$^{4+}$ ions was analyzed in AC conductivity. The changes of dielectric properties such as complex permittivity, modulus spectroscopy, and dielectric loss at room temperature with a different frequency range of 1.00−2.00 GHz are discussed.

INTRODUCTION

The ceramic microwave dielectric plays a significance role in the development of the Global Positioning Systems, modern transport system, and satellite for broadcasting. Titanate-based compounds with a perovskite structure have been determined as one of the notable diverse categories of the materials, having novel and tremendous applications such as photocatalysis, thermoelectric, ferroelectrics, and batteries. Ferroelectric materials are utilized in the industry as a ferroelectric memory gear and dynamic random-access memory, which were mostly made from lead. With the increasing demand of nanotechnologies, nanoelectronics, and microelectronics, it was necessary to develop new lead-free ferroelectrics. Among those, the oxide, that belongs to the ABO$_3$ family, was the most suitable candidate because of its ferroelectric and reputed piezoelectric properties.

Calcium titanate is remarkably known as a chemical-resistive n-type semiconductor and thermal-resistive element and exhibits optical, electrical, and thermal properties. These optimum dielectric properties of calcium titanate reveal a wide range of applications in the sensors, capacitor, and microwave communication system. CaTiO$_3$ can occur in a crystalline or may be in amorphous form; the stable cubic phase is above 1370 °C, while the stable tetragonal and orthorhombic phase is above 1250 and 1213 °C, respectively.

The sintering temperature can influence the phase of CaTiO$_3$, the average crystallite size, morphology, and particle size, and the dielectric constant of CaTiO$_3$ (CTO) escalated remarkably with raising the sintering temperature. Low-loss microwave-based (MW) ceramics such as CaTiO$_3$ have been recommended as a dielectric resonator in MW ICs (integrated circuits). The researcher has examined to enhance the effectiveness of this ceramic material by coupling Fe and by doping Mn.

Calcium titanate shows a high dielectric constant ($\varepsilon_r$) of 170 and an average quality factor of 3600 GHz and is usually recommended for stimulating material for microwave applications. The $\varepsilon_r$ of CaTiO$_3$ is considered to be the

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function of temperature, and it has been investigated that the $\epsilon_r$ is increases as the temperature drops and saturates at low temperature, as can be noticed. This response could be considered as a “fingerprint” of emerging ferroelectricity. The dielectric constant of CaTiO$_3$ is higher than that of TiO$_2$ at low temperature.\(^{16}\) Many researchers already have publicized the effect of Sn$^{4+}$ on the relationship between the structural, dielectric properties, and microstructure development of milled powders.\(^{18}\) Lattice parameters were calculated using the least-square refinement method such that $\sum \Delta d (\Delta d = \langle d_{\text{obs}} - d_{\text{calc}} \rangle) $, which should be minimum. It can also be seen that the lattice parameters and lattice volume increased with increasing the Sn content at the B site of Ca(Sn$_{\text{x}}$Ti$_{1-x}$)$_3$O$_9$ ($0 \leq x \leq 0.8$), solid solution as shown in Table 2. The increase in the lattice parameters and lattice volume should be attributed to the fact that the ionic radius of the substituted Sn$^{4+}$ ion (0.69 Å) is larger than that of the Ti$^{4+}$ ion (0.64 Å).\(^{22}\)

Table 1. Indexed Pattern for the Ca(Sn$_{\text{x}}$Ti$_{1-x}$)$_3$O$_9$ at $\lambda = 0.15418$ nm

| $2\theta_{\text{exp}}$ | $2\theta_{\text{calc}}$ | $I_{\text{exp}}$ | $h$ | $k$ | $l$ | $d_{\text{exp}}$ | $d_{\text{calc}}$ |
|----------------------|----------------------|--------------|-----|-----|-----|--------------|--------------|
| 23.25                | 23.30                | 582.84       | 0   | 0   | 2   | 3.82134      | 3.81377      |
| 29.85                | 29.92                | 593.44       | 1   | 1   | 1   | 2.98913      | 2.98334      |
| 33.15                | 33.19                | 1110.92      | 2   | 0   | 0   | 2.69891      | 2.69608      |
| 42.75                | 42.97                | 627.95       | 1   | 1   | 3   | 2.11248      | 2.10210      |
| 47.55                | 47.61                | 918.72       | 2   | 2   | 0   | 1.90972      | 1.90783      |
| 59.11                | 59.32                | 747.24       | 3   | 1   | 2   | 1.56092      | 1.55587      |
| 69.45                | 69.55                | 674.18       | 0   | 4   | 0   | 1.35183      | 1.34993      |

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The crystallite size ($D$) of Ca(Sn$_{\text{x}}$Ti$_{1-x}$)$_3$O$_9$ ($0 \leq x \leq 0.8$) ceramics was calculated using a well-known Debye–Scherrer equation\(^{23}\)

$$D = \frac{K\lambda}{\beta \cos \theta}$$

(1)

where $D$, $K$, $\lambda$, $\beta$, and $\theta$ denoted the crystal size, constant (0.89), X-ray wavelength, full width at half maximum (fwhm) of the most concentrated peak, and Bragg angle, respectively. This technique is used to study XRD data, where the crystal size is associated with the expansion of the strong diffraction peak.

Mathematically, the dislocation density ($\delta$) and micro strain ($\varepsilon$) were calculated by using these equations\(^{24}\)

$$\delta = \frac{1}{D^2}$$

(2)
The size and strain of Tin-doped calcium titanate samples were determined using the Williamson–Hall technique from the broadening of the XRD peaks.

\[
\beta \cos \theta = k \lambda D + 4 \varepsilon \sin \theta
\]

where \( \beta \) is the fwhm in radian by fitting the prominent peaks, \( \theta \) is the diffraction angle in radian, \( k \) is the shape factor value 0.94, \( \lambda \) is the XRD wavelength (\( \lambda = 0.15418 \) nm), and \( D \) is the effective crystalline size. Figure 3 shows that the Tin-doped calcium titanate samples, the slope of the linear data-plotted fit against \( 4 \sin \theta / \beta \cos \theta \), contribute the information about the inverse of intercept, and the lattice strain yields the value of the crystalline size \( (D_{\text{Hall}}) \).

**Table 3. Calculated Average Crystallite Size (D), Dislocation density(\( \delta \)), Micro Strain (\( \varepsilon \)), and Lattice Strain (\( \eta \)) of Ca(Sn\( \text{Ti}_{1-x} \))O\text{3} \((0 \leq x \leq 0.8)\)**

| composition | D (nm) | \( \delta \) (nm\(^{-1}\)) | \( s \times 10^{-5} \) | \( \eta \times 10^{-3} \) |
|-------------|--------|-----------------|-----------------|-----------------|
| 0.0         | 440.389| 13.75           | 5.1562          | 2.1055          | 0.7784          |
| 0.2         | 378.469| 18.66           | 8.2651          | 2.4703          | 0.9057          |
| 0.4         | 331.456| 19.29           | 9.1022          | 2.8207          | 1.0342          |
| 0.6         | 343.345| 21.25           | 8.4828          | 2.7229          | 0.9984          |
| 0.8         | 413.925| 24.87           | 5.8365          | 2.2587          | 0.8281          |

The behavior of the crystallite size is presented in Figure 2. The crystallite size depends on the lattice strain and radius of the substituted ions. It has been observed that the average crystallite size generally decreases with the increasing Sn\(^{4+} \) content \( (x) \); this may be attributed toward growth of the crystal restricted by the substitution element with ionic radii \( R_{\text{Sn}} \) greater than \( R_{\text{Ti}} \).

**Figure 2.** Crystallite size of Ca(Sn\( \text{Ti}_{1-x} \))O\text{3} \((0 \leq x \leq 0.8)\) ceramics at 1200 °C.

The particle size and lattice strain of Tin-doped calcium titanate samples were determined using the Williamson–Hall technique from the broadening of the XRD peaks.

The vibrational modes of pure CaTiO\text{3} and Sn-doped CaTiO\text{3} were examined through Fourier transform infrared spectros-
copy (FTIR) as depicted in Figure 5. The spectra of both pure and Sn-doped CaTiO₃ represent a common peak at 3440 cm⁻¹, which can be estimated as the stretching mode of the water/hydroxyl group presumably adsorbed at the surface. In addition, the bending mode of the hydroxyl group could be ascribed to the small peak positioned at 1437 cm⁻¹. In the wavenumber range of 500–600 cm⁻¹, stretching and bridging vibrational modes of Ti–O and Ti–O–Ti are particularly evident. The stretching mode of vibrations and the bridging stretching mode of Ti–O–Ti and Ti–O–Sn both are associated with the broadband in the region below 800 cm⁻¹. In the FTIR spectra of Sn-doped CaTiO₃ ceramics, no extra peak for Sn–O/Sn–Ti–O vibrational modes is detected, which could be explained by trace substitution of Sn with Ti.

**Dielectric Spectroscopy.** The dielectric reaction in a solid material can be described by expressing the relative dielectric permittivity as a complex quantity made up of real and imaginary components

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' \]

where \( \varepsilon' \) and \( \varepsilon'' \) denote the real and imaginary part of the dielectric permittivity, respectively. It represents the quantity of stored energy in dielectric materials as polarization and energy loss occurs when the external field is applied. The real and imaginary part of the dielectric permittivity can be calculated from complex impedance data by using these equations

\[ \varepsilon' = \frac{Z''}{\omega C_0(Z''^2 + Z'^2)} \]

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Figure 6a illustrates the frequency dependence of the real component of dielectric permittivity, measured at 1.00–2.00 GHz for CST ceramics sintered at 1200 °C. It is clearly observed that \( \varepsilon' \) increases slowly with a rise in the frequency and the increasing of the content \( x \), and it reaches a saturation limit at \( f \sim 1.8 \) GHz. On further increasing the frequency, there is a rapid decrease in the real permittivity. As a result, the dipoles fail to maintain the accurate oscillatory field when the permittivity decreases with the increasing frequency.

The imaginary part of dielectric permittivity, as a function of the frequency range from 1.00 to 2.00 GHz for CST \( (x = 0.0, 0.2, 0.4, 0.6, 0.8) \) ceramics sintered at 1200 °C, is represented graphically in Figure 6b. The \( \varepsilon'' \) values increase with increasing the frequency up to 1.8 GHz and the decrease in permittivity at the higher-frequency region \( (f > 1.8 \) GHz). These developments of the curves are usual conducts for most of the dielectric ceramics due to the existence of strong dielectric relaxation as the rotation of the dipoles becomes deficient to align with the oscillatory AC electric field with the growing frequency. The imaginary part of dielectric permittivity, as a function of the frequency range from 1.00 to 2.00 GHz for CST ceramics sintered at 1200 °C, is represented graphically in Figure 6b. The \( \varepsilon'' \) values increase with increasing the frequency up to 1.8 GHz and the decrease in permittivity at the higher-frequency region \( (f > 1.8 \) GHz). These developments of the curves are usual conducts for most of the dielectric ceramics due to the existence of strong dielectric relaxation as the rotation of the dipoles becomes deficient to align with the oscillatory AC electric field with the growing frequency.35

**Complex Impedance Spectroscopy.** Currently, the complex impedance spectroscopy (CIS) mechanism is generally used to investigate the structural properties and bonding of the various types of materials, comprising the ionic insulator and ferroelectric and linked ceramics under various experimental conditions.36

\[ Z^* = Z' - jZ'' = \frac{1}{j\omega C_0 e^*} \]

where \( J = \sqrt{-1} \), \( C_0 \) is the geometrical capacitance, \( e^* \) is the complex permittivity, and \( \omega = 2\pi f \) is the angular frequency.

The deviation in impedance \( Z' \) of Ca(SnₓTi₁₋ₓ)O₃ \( (0 \leq x \leq 0.8) \) ceramics as a function of the frequency \( (1.00–2.00 \) GHz) is shown in Figure 7a. Initially, it has been investigated that the magnitude of \( Z' \) increases with increasing the frequency and

\[ 1.00–2.00 \] GHz for CST ceramics sintered at 1200 °C. It is clearly observed that \( \varepsilon' \) increases slowly with a rise in the frequency and the increasing of the content \( x \), and it reaches a saturation limit at \( f \sim 1.8 \) GHz. On further increasing the frequency, there is a rapid decrease in the real permittivity. As a result, the dipoles fail to maintain the accurate oscillatory field when the permittivity decreases with the increasing frequency.34

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concentration of Sn$^{4+}$ ($0 \leq x \leq 0.8$) in the frequency ranges $1.00-1.6$ GHz; thereafter, it appears to slightly decrease in the high-frequency region ($f > 1.6$ GHz). It is simply possible because rising temperatures and frequencies cause the release of space charge polarization.\(^{37}\) From this behavior, we can also conclude that the conduction mechanism is directly related to frequency. As the frequencies increase from 1.00 to 1.6 GHz, the magnitude of $Z'$ decreases with the increases in concentration Sn ($0 \leq x \leq 0.8$).

Figure 7b demonstrate the reciprocal dependence of the frequency of the hypothetical component $Z''$ (also called loss spectrum) of Ca($Sn_x Ti_{1-x})O_3$, ($x = 0.0, 0.2, 0.4, 0.6, 0.8$). The magnitude of $Z''$ decreases by increasing the frequencies (1.00–1.8 GHz) and also the concentration of Sn contents at room temperature. When the frequencies increase from 1.8–2.00 GHz, the $Z''$ spectrum sharply increases at concentration Sn ($x = 0.0, 0.2, 0.4, 0.6, 0.8$). It demonstrates that with the addition of the Sn concentration, the magnitude of $Z''$ decreases, and all the peaks move toward the higher-frequency region. At higher frequencies, the contribution from the grain predominates attributable to the absence of the space charge effects of the various compositions.\(^{38}\)

Analysis of Complex Modulus. The complex modulus formalism is a technique which plays a significant role in studying the electrical relaxation process in ionic conducting materials.\(^{39}\) This particular technique is used for the easy suppressing of electrode polarization effects.
The complex modulus can be stated quantitatively using the following formula:

\[ M^* = M' + iM'' \]  

The following formulae were used to determine the real and imaginary components of the complex electrical modulus:

\[ M' = -\omega C Z'' \]  

\[ M'' = \omega C Z' \]  

Figure 8a shows the real part of the modulus \( M' \) as a function of frequencies (1.00–2.00 GHz) of \( \text{Ca(} \text{Sn}_x\text{Ti}_{1-x})_3 \) (0 ≤ \( x \) ≤ 0.8). It was observed that for all samples, the real part of the electrical modulus \( M' \) decreases, with the increasing of the concentration \( \text{Sn}^{4+} \) and frequencies at room temperature. The mobility of long-distance charges is demonstrated in the low-frequency range. Similarly, the high-frequency region indicates the mobility of short-distance charges because of the potential well limitation. It could be described through a conduction phenomenon resulted by charge carrier’s long-range mobility.

Figure 8b illustrates the frequency dependence of the imaginary part of the modulus \( M'' \) of \( \text{Ca(} \text{Sn}_x\text{Ti}_{1-x})_3 \) (0 ≤ \( x \) ≤ 0.8) at room temperature. It has been reported that the hypothetical modulus \( M'' \) decreases with the increasing frequency, but it reaches the maximum and then increases along with concentration \( \text{Sn}^{4+} \). This may be explained as the frequency region below the maximum peak classifies within the range charge carriers owing to extended range hopping. However, because charge carriers are mobile over short distances, they are restricted to potential wells in the frequency region above the peak maximum. The specific region wherever the exact maximum peak arises is basically the sign of the transition from long-range to short-range mobility as frequency increases.

Tangent Loss. The power dissipation (dielectric loss) of commercial capacitors could be calculated through the given expressions:

\[ \tan(\delta) = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = \frac{Z''}{Z'} \]
In Figure 9, the dielectric loss (tan $\delta$) values for all the sintered samples of Ca(Sn$_x$Ti$_{1-x}$)O$_3$, ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) ceramics are the highest at 2.00 GHz and the lowest at 1.00 GHz. The tan $\delta$ values are found to increase with the increasing frequency (upto $1.7 \times 10^9$ Hz) and the increase in the concentration Sn ($0.0 \leq x \leq 0.8$). The frequency further increases ($f > 1.7$ GHz), and the dielectric loss abruptly decreases. The tan $\delta$ value decreases with an increase in the frequency because the charge carrier growth does not align with the frequency of the applied field beyond a definite frequency range. It is important to note that DC conductivity and electrode polarization of the samples primarily cause the low values of tan $\delta$ at a lower-frequency range. On the other hand, the large value of tan $\delta$ characterizes decent microwave (MW)-absorbing characteristics of the material. This particular arrangement of frequency dependency with the losses of “tan $\delta$” is generally interrelated with conduction losses. Therefore, the curves presented in Figure 9 actually signify the main dielectric relaxation related to the dipolar polarization.

AC Conductivity. Figure 10 shows the mechanism of electrical conduction and helps in understanding the activities of charge carriers, the field effect of the mobile charges, and actual functions of the domain structure. The variation of AC conductivity with the frequency (1.00–2.00 GHz) could clarify the frequency dependence of AC conductivity, which can be describe through the given equation

$$\sigma_{ac} = \varepsilon_r \varepsilon_0 \omega^2 \tan \delta$$

(14)

where $\varepsilon_r$ corresponds to the dielectric constant, $\varepsilon_0$ is the permittivity of the free space ($8.85 \times 10^{-14}$ F/cm), tan $\delta$ = dielectric loss, and $\omega^2$ is angular frequency (i.e., $\omega = 2\pi f$).

Figure 10 clearly shows that at the lower-frequency region, the magnitude of conductivity gets to zero. When the concentration of the Sn content ($0.0 \leq x \leq 0.8$) and the frequency (upto 1.8 GHz) increase, then the AC conductivity value grows gradually until it reaches a definite value. However, when the frequencies are greater ($f > 1.8$ GHz), than the conductivity abruptly decreases. At higher frequencies, the curves merge with each other. Consequently, the conduction of charge carriers, the field effect of the mobile charges, and actual functions of the domain structure. The variation of AC conductivity with the frequency (1.00–2.00 GHz) could clarify the frequency dependence of AC conductivity, which can be describe through the given equation

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mechanism in the material increases with the frequency. It is because of the increase in the motion of charge carriers which are thermally activated due to the rise in temperature.\textsuperscript{47} In every sample, we can also note the shifting of the peak toward the high-frequency region. The value of conductivity is high for the \((x = 0.6)\) sample as compared to others. Conversely, due to large impudence, the values of AC conductivity are relatively low for the \((x = 0)\) sample.\textsuperscript{38}

**CONCLUSIONS**

In the present study, the Ca\((Sn_{t-\delta})O_3\) \((0 \leq x \leq 0.8)\) lead-free ceramics were successfully prepared via a ball milling process sintered at 1200 °C. When Sn\textsuperscript{4+} ions are doped in CaTiO\textsubscript{3} ceramics, the average crystallite size, dislocation density, lattice parameter, unit cell volume, lattice strain, and micro-strain value change. The phase analysis confirmed the formation of the orthorhombic structure with \(Pbnm\) symmetry. The average crystallite size also decreased from 440.389 to 331.456 nm (CST). The surface morphology reveals the formation of grains with different sizes (small and large) and shapes (spherical, oval, and irregular with low porosity). The grain size sub-microns in size that decreased from 3.29 to 1.37 \(\mu\)m.

We obtained excellent microwave dielectric properties in this study for the application of the microwave wireless communication system. The dielectric loss (\(\tan \delta\)) increases with increasing of the Sn\textsuperscript{4+} concentration. These lead-free ceramic materials are a suitable candidate for the application in Global Positioning Systems and communication antennas.

**MATERIALS AND METHODS**

The ceramic samples with an ostensible composition Ca\((Sn_{t-\delta})O_3\) were prepared through the ball milling method. Therefore, as to prepare the samples of Ca\((Sn_{t-\delta})O_3\), suitable quantities of chemical-agent grade raw materials of CaCO\textsubscript{3} (SIGMA-ALDRICH) with purity \(\geq 99.9\%\), TiO\textsubscript{2} (SIGMA-ALDRICH) with purity \(\geq 99.5\%\), and SnO\textsubscript{2} (UNICHEM) with purity \(\geq 99.9\%\) were computed to the relevant stoichiometric molar ratios. As subjected to milling, the powder was ball milled horizontally in a polycrystalline container for a maximum of 24 h using distilled water and zirconia balls. Once the milling step was completed, the samples were then put to the drying method at 90 °C for 24 h, and then, they were ground. After grinding, the powder was calcined at a temperature of 950 °C for the compositions with \(0 \leq x \leq 0.8\) for 3 h, by keeping cooling and heatings constant at a rate of 5 °C/min. Then, the weighing range from 0.5 to 0.7 g, diameter of about 13 mm, and also the thickness of 4–5 mm pellets of the calcined fine powders were determined, with the 80 MPa pressure using a stainless-steel dye. Sintering was carried out at 1200 °C for 3 h after the calcined pellets were put on a ceramic foil, with the cooling/heating temperatures kept at the same rate of 5 °C/min.

**Characterization of CaTiO\textsubscript{3} and Sn-Doped CaTiO\textsubscript{3}**

The phase formation of sintering and milling samples was performed through an X-ray diffractometer (JDX-3532, JEOL, Japan) with Cu-\(K\alpha\) radiations of wavelength \(\lambda = 0.1540598\) nm, functioned at 45 kV and 40 mA used to identify the phases. Primarily, the step size 0.05 (°C), the scan rate 0.5 (°C/min), and the scan range 10.020–70.020 °C were assumed. A scanning electron microscopy instrument (SEM) (JSM-5910, JEOL Japan) was used to analyze the microstructures. The samples were refined and thermally etched for 1 h at temperatures of 10% less than their sintering temperatures as a special condition for SEM. Microwave (MW) dielectric properties of the sintered sample were measured using an impedance analyzer (Agilent-E4991A, from 1 MHz to 3 GHz).

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**Author Contributions**

This work was carried out in collaboration among all authors. A.Z. prepared samples and wrote the original draft of the article. S.U. supervised this research. N.M., V.T., and A.A. did the final writing review, corrections, and editing. A.A., M.A., and K.U. helped in Methodology and measurements. F.S. and M.M. prepared content analysis and graphical arrangements. K.B. and R.U. helped in Software and Validation. K.A. helped in formal analysis and provided funding acquisition. All authors read and approved the final article.

**Notes**

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