Crystal Structure, Infrared Spectra, and Microwave Dielectric Properties of Ce$_2$(Zr$_{0.94}$Sn$_{0.06}$)$_3$(MoO$_4$)$_9$ Ceramics With Low Sintering Temperature

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Ce$_2$(Zr$_{0.94}$Sn$_{0.06}$)$_3$(MoO$_4$)$_9$ (CZSM) ceramics were synthesized via a traditional solid-state method. The effects of Sn-substitution on phase composition, microstructure, and microwave dielectric properties as a function of sintering temperature were discussed. The XRD results indicated that all the samples exhibited a single phase. The chemical bonds of CZSM ceramics were calculated based on P-V-L theory, which could be used to evaluate the relationship between structure and microwave dielectric properties. The tendency of dielectric constant was depended on the theoretical dielectric polarizability and bond ionicity. Moreover, the improvement of $Q$-$f$ value was ascribed to the increase of packing fraction. The reduced $\tau_f$ value could be explained by decrease of the bond energy, enhanced the co-efficient of thermal expansion and increase of bond valence ($V_{Zr(Sn)}$). The complex permittivity values were obtained from infrared reflectivity spectra. The dielectric permittivity and loss were 10.92 and $3.08 \times 10^{-4}$, respectively, which agreed well with the measured value. Typically, the optimal microwave dielectric properties of $\varepsilon_r = 10.35$, $Q$-$f = 59,660$ GHz (at 9.70 GHz), and $\tau_f = -7.52$ ppm/°C were achieved in CZSM ceramics sintered at 800°C for 6 h.

Keywords: Ce$_2$(Zr$_{0.94}$Sn$_{0.06}$)$_3$(MoO$_4$)$_9$, low-temperature sintering, microwave dielectric properties, chemical bonds theory of complex crystals, infrared spectra

INTRODUCTION

Owing to the characteristics of light weight, low cost, and high performance, the microwave dielectric ceramics have been widely used as filters, waveguides, resonators, substrates, and waveguides (Cava, 2001; Reaney and Iddles, 2006; Li et al., 2018; Chen et al., 2019; Cheng et al., 2019; Wu et al., 2019). Currently, 5th generation mobile communication systems have received increasing attention (Zhou et al., 2017; Pang and Zhou, 2019; Bafrooei et al., 2020; Lin et al., 2020). To meet the microwave devices applied at millimeter wave, new materials and technologies are required. As a new ceramic fabrication technology, the low temperature co-firing ceramics (LTCC) technology have been intensively studied, it provide the platform for fabrication of three-dimensional ceramic modules (Yu et al., 2015; Sebastian et al., 2016; Guo et al., 2019; Hsiang et al., 2019; Song et al., 2020). Materials in this discipline require a low sintering temperature to co-fire with electrode material and suitable properties: a low dielectric constant ($\varepsilon_r$) to avoid the signal delay, a high quality factor
(Qf) for better selectivity at higher frequencies and a near-zero temperature coefficient of resonant frequency (τf) for the frequency stability (Song et al., 2018; Lin et al., 2020). Therefore, it is essential to develop the microwave materials with low permittivity and high Qf value.

Recently, Mo-based dielectric ceramics have been widely reported owing to low sintering temperature (<960°C) and good microwave dielectric properties (Choi et al., 2007; Pang et al., 2011; Surjith and Ratheesh, 2013; Zhang et al., 2015, 2019; Liu and Zuo, 2017, 2018; Tao et al., 2019; Xing et al., 2019; Zhang and Wu, 2019; Zheng et al., 2020). Among these excellent materials, the Ce₂Zr₃(MoO₄)₉ ceramic was regarded as candidate for LTCC materials applications due to low sintering temperature and near-zero τf value (Tao et al., 2019). However, the Ce₂Zr₃(MoO₄)₉ ceramics exhibited a higher dielectric losses, some strategies should be adopted in this paper. A large of studies for improving microwave dielectric properties have been carried out via Sn⁴⁺ ions substitution (Yang et al., 2009; Ma et al., 2013; Li et al., 2019).

For instance, when x value increased from 0.0 to 0.6, the quality factor of Ca₅(Sn₁₋ₓSiₓ)O₃ (x = 0.5–1.0) ceramics increased from 16,000 to 63,000 GHz (Ma et al., 2013). The optimal microwave dielectric properties of Mg₂(Ti₀.₅Sn₀.₅)O₄ ceramics with εr = 12.18, Qf = 170,130 GHz, and τf = −53.1 ppm/K°C (Li et al., 2019). Thus, Sn⁴⁺ substitution was taken to improve Qf value of Ce₂Zr₃(MoO₄)₉ ceramics in this work. The Ce₂(Zr₀.₉₄Sn₀.₀₆)₃(MoO₄)₉ (CZSM) ceramics were successfully prepared. The phase composition, sintering characteristics, microstructure, and dielectric properties of CZSM ceramics were investigated scientifically. Infrared reflectivity spectra (IR) and chemical bonds theory of complex crystals were adopted as useful tools to analyze the effect of intrinsic factor on microwave dielectric properties of CZSM ceramics.

RESULTS AND DISCUSSION

Figure 1 presented the XRD patterns of CZSM ceramics sintered between 650–850°C. It was observed that all of diffraction patterns match well with the Pr₂Zr₃(MoO₄)₉ (PDF#51-1851) phase, with no secondary phase detected. It indicated that all of sintered samples formed single phase solid solution, which belongs to trigonal system with R-3c (167) space group. To determine its structure, refinement of the XRD data were conducted using FullProf program with Rietveld’s method. The Nd₂Zr₃(MoO₄)₉ (ICSD File No. 92600) was used as starting

EXPERIMENTAL

The reagent grade CeO₂ (99.9%, Macklin, China), ZrO₂ (99.99%, Macklin, China), SnO₂ (99.95%, Aladdin, China), and MoO₃ (99.95%, Aladdin, China) powders were used to fabricate CZSM ceramics by the traditional solid-state method. Based on the chemical formula, the raw materials were mixed by zirconia balls for 24 h with absolute ethanol as media. After drying at a temperature 80°C, the slurries were calcined at 700°C for 2 h. Then, the pre-sintered powders were crushed and re-milled for 24 h. Subsequently, 12 wt.% PVA added to the mixture, and the powders were pressed into pellets (10 mm in diameter and 6 mm in height). Finally, all the samples were sintered at 650–850°C for 6 h in air.

XRD was applied to examine the phase compositions of the sintered samples with Cu Kα radiation (D8 Advance, Bruker Co., Germany). The structure parameters and cell volume were obtained from refinement of XRD data using FullProf program. The microstructures of sintered samples were observed using SEM (FEI Co., United States) coupled with EDS. The εr value at microwave frequencies (13–15 GHz) and the Qf value at microwave frequencies (9–11 GHz) were measured using the network analyzer (N5234A, Agilent Co., USA) (Hakki and Coleman, 1960; Courtney, 1970). The τf value was calculated using Equation (1):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \times 10^6(\text{ppm}/\text{°C})$$

(1)

where $f_1$ and $f_2$ are the resonant frequencies at the measuring temperatures $T_1$ (25°C) and $T_2$ (85°C), respectively. The apparent density was measured via the Archimedes method, and the theoretical density can be obtained through Equation (2).

$$\rho_{\text{theory}} = \frac{Z A}{V_c N_A}$$

(2)

where $A$, $Z$, and $N_A$ are the atomic weight, number of atom in unit cell and volume of unit cell, respectively. The relative density was calculated by Equation (3):

$$\rho_{\text{relative}} = \frac{\rho_{\text{apparent}}}{\rho_{\text{theory}}} \times 100\%$$

(3)
structural model. The refinement pattern of samples sintered at range of 650–850°C, as shown in Figure 2. The main crystallographic parameters and reliability factors of $R_{wp}$, $R_p$, and $\chi^2$ for samples are summarized in Table 1. The $R_{wp}$, $R_p$, and $\chi^2$ values were found to be in the range of 9.5–10.9, 7.2–8.6%, and 1.8–2.5, respectively. The value $\chi^2$ were smaller to ensure the reliability of refinement. With the increasing sintering temperature, the $a$ and $b$ gradually increased from 9.8251 to 9.8269 Å, and $c$ increased from 58.8278 to 58.8434 Å, which resulted in $V_m$ increased from 4918.02 Å³ at 650°C to 4921.14 Å³ at 800°C. Figure 3 presented crystal structure of CZSM ceramics. It can be seen that the Ce, Zr(1), Zr(2), Mo(1), and Mo(2) atoms are nearest neighbors to 9, 6, 6, 4, and 4 oxygen atoms, respectively. The [CeO$_9$] occupying the large cavities of the structure, the [CeO$_9$] and [ZrO$_6$] were connected by [MoO$_4$] at the structure.

Figure 4 illustrated the curves of the apparent and relative density of CZSM samples sintered at 650–850°C. The apparent densities increased from 3.50 g/cm$^3$ to the maximum value of 3.90 g/cm$^3$ with increasing sintering temperature. The relative density have same tendency as apparent density, a high relative density (>94%) was achieved at 750–850°C. Typical SEM images
TABLE 1 | The refinement parameters, theoretical densities and relative densities of Ce₂(Zr₀.₉₄Sn₀.₀₆)₃(MoO₄)₉ ceramics fired at 650–800°C.

| S.T. | a = b (Å) | c (Å) | α = β (°) | γ (°) | Vₘ (Å³) | Rₛ (%) | Rₚ (%) | χ²  |
|------|-----------|-------|------------|------|---------|--------|--------|-----|
| 650  | 9.825 (1) | 58.827 (8) | 90         | 120  | 4918.0 (2) | 8.60   | 10.90  | 2.51 |
| 700  | 9.826 (6) | 58.844 (3) | 90         | 120  | 4920.8 (4) | 7.24   | 9.55   | 1.85 |
| 750  | 9.826 (9) | 58.840 (3) | 90         | 120  | 4920.7 (4) | 8.31   | 10.40  | 2.18 |
| 800  | 9.827 (7) | 58.840 (3) | 90         | 120  | 4921.7 (3) | 8.35   | 10.90  | 2.36 |
| 850  | 9.827 (0) | 58.843 (4) | 90         | 120  | 4921.1 (4) | 7.64   | 9.91   | 2.04 |

S.T., Sintering Temperature.  
Rₛ, reliability factor of patterns.  
Rₚ, the reliability factor of weighted patterns.  
χ², goodness of fit indicator = (Rₚ/Rₑₓₚ)².

FIGURE 3 | The schematic of the crystal structure for Ce₂(Zr₀.₉₄Sn₀.₀₆)₃(MoO₄)₉ ceramics.

FIGURE 4 | Apparent and relative density of Ce₂(Zr₀.₉₄Sn₀.₀₆)₃(MoO₄)₉ ceramics as a function of sintering temperature.

of CZSM ceramics sintered at different temperature were shown in Figures 5A–E. Grain boundaries were evident in all the samples, indicating that crystalline grains grew well in these samples. Moreover, the grain size increased from 1.93 to 3.19 μm and the pores gradually decreased with the increase of sintering temperature. The result of EDS about grain from samples sintered at 800°C was presented in Figure 5F. The ratio of Ce, Zr, Sn, Mo, and O atom were 3.93, 6.56, 0.34, 18.50, and 70.67%, respectively, which was corresponded to theoretical composition of CZSM ceramic.

The curves of microwave dielectric properties for CZSM samples were shown in Figure 6. The dielectric constant (εᵣ) increased and reached maximum value of 10.47 as the temperature shifted from 650 to 750°C, and then kept stable with further increasing sintering temperature. In addition, the tendency of the εᵣ value was corresponded to the density when sintering temperature at 650–800°C, suggesting that dielectric constant was closely related to the density in lower temperature. As we all know, apart from the extrinsic factors like density and phase composition, the εᵣ also affected by the intrinsic factors such as polarizability and bond ionicity (Bi et al., 2018; Manan et al., 2018; Zhang et al., 2019). The XRD result suggesting the single phase ceramics was formed. Thus, the εᵣ value of CZSM ceramics were mainly determined by polarizability and bond ionicity when the sample was compact. The theoretical dielectric polarizability (αₑₓₑₑ) and observed
dielectric polarizability ($\alpha_{\text{obs}}$) were calculated through Equations (4) and (5), respectively.

$$\alpha_{\text{theo}}(\text{Ce}^{3+}) = 6.15 \text{ Å}^3, \alpha(\text{Zr}^{4+}) = 3.25 \text{ Å}^3, \alpha(\text{Sn}^{4+}) = 2.83 \text{ Å}^3, \alpha(\text{O}^{2+}) = 2.01 \text{ Å}^3$$ was reported by Shannon et al. and $\alpha(\text{Mo}^{6+}) = 3.28 \text{ Å}^3$ is calculated by Choi et al. (Shannon, 1993; Choi et al., 2007). Moreover, $V_m$ is the molar volume and $b$ is a constant value ($4\pi/3$), respectively. The results were listed in Table S1.

The $\varepsilon_r$ value (123.85 $\text{ Å}^3$) lower than the Ce$_2$Zr$_3$(MoO$_4$)$_9$ ceramics (123.93 $\text{ Å}^3$), which could be attributed to the smaller polarizability of Sn$^{4+}$: $\alpha(\text{Sn}^{4+}) = 2.83 \text{ Å}^3 < \alpha(\text{Zr}^{4+}) = 3.25 \text{ Å}^3$ (Tao et al., 2019). Besides, the tendency of $\varepsilon_r$ value was similar to the $\alpha_{\text{theo}}$ value and $\alpha_{\text{obs}}$ value, indicating that the reduced $\varepsilon_r$ value was strongly dependent on the decrease of polarizability.

Moreover, the quality factor ($Q\cdot f$) increased from 24,410 to 59,660 GHz, and then declined slightly with further increasing sintering temperature, the maximum of the $Q\cdot f$ was 59,660 GHz at 800°C. In general, the dielectric losses are composed of intrinsic losses (lattice vibration) and extrinsic losses (grain size and impure phase). The grain size showed upward tendency with increasing sintering temperature, it was similar to the variation of $Q\cdot f$ value. Therefore, the increased grain size was important for improvement of the $Q\cdot f$ value (Yang et al., 2002, 2019; Ichinose and Shimada, 2006). In order to investigate the effect of the intrinsic factors, the packing fraction has been calculated by Equation (6).

$$\text{packing fraction(\%)} = \frac{\text{volume of the atoms in the cell}}{\text{volume of unit cell}} \times Z \quad (6)$$

where $Z$ is the number of molecules per cell. Kim et al. reported the effective ionic size (Kim et al., 2010). The results indicated that the smaller ions size of Sn$^{4+}$ (0.69 Å) substitution to Zr$^{4+}$ (0.72 Å) lead to the higher packing fraction (47.84 > 47.74%). Thus, the improvement of $Q\cdot f$ value was ascribed to the increase of packing fraction. Furthermore, it suggested that the
Sn$^{4+}$ ions substitution could improve the quality factor of Ce$_2$Zr$_3$(MoO$_4$)$_9$ ceramics.

The temperature co-efficient of resonant frequency ($\tau_f$) of CZSM ceramics sintered at different temperatures from 650 to 850°C was shown in Figure 6. It can be seen that the saturation value of $\tau_f = -7.52$ ppm/°C was obtained when sintered at 800°C and kept stable at 700–850°C. The temperature coefficient of resonant frequency was associated with bond valence (Yoon et al., 2003; Cai et al., 2015). Therefore, the bond valence of $[\text{Zr(Sn)}\text{O}_6]$ octahedra can be obtained by Equations (7) and (8).

$$V_i = \sum_j v_{ij}$$

(7)

$$v_{ij} = \exp \left[ \frac{(R_{ij} - d_{ij})}{b} \right]$$

(8)

where $V_{ij}$ represent the sum of all the bond valences, $R_{ij}$ is the bond valence parameter, $d_{ij}$ is the length of the bond between atoms $i$ and $j$, and $b$ is an constant equal to 0.37. The results of bond valence were listed in Table S1. The bond valence ($V_{\text{Zr(Sn)}}$) increased from 8.92 to 9.17 with the Sn$^{4+}$ substitution, and the $\tau_f$ value correlated to the change of bond valence ($V_{\text{Zr(Sn)}}$) (Tao et al., 2019). It indicated that the decline of $\tau_f$ value was related to the increase of bond valence ($V_{\text{Zr(Sn)}}$).

Figure 7 showed the microwave dielectric properties of Mo-based dielectric ceramics with low dielectric constant, and the parameters were summarized in Table S2 (Choi et al., 2007; Pang et al., 2011; Surjith and Ratheesh, 2013; Zhang et al., 2015, 2019; Liu and Zuo, 2017, 2018; Tao et al., 2019; Xing et al., 2019; Zhang and Wu, 2019; Zheng et al., 2020). The CZSM ceramics possessed excellent microwave dielectric properties and low sintering temperature in this system. It suggests that they have potential for exploitation in LTCC technology. Certainly, it is necessary to study the relationship between structure and microwave dielectric properties. Thus, the bond ionicity, lattice energy, bond energy, and coefficients of thermal expansion were calculated to investigate the relationships between chemical bond and dielectric properties of the CZSM ceramic. Based on P-V-L theory, the complex crystals CZSM were decomposed into the sum of binary crystals as Equation (9) (Xue and Zhang, 1996; Wu et al., 1998; Yang et al., 2019):

$$\text{Ce}_2\text{(Zr}_{0.94}\text{Sn}_{0.06})_3\text{(MoO}_{4})_9=\text{Ce}_2\text{Zr/}\text{Sn(1)}\text{Zr/}\text{Sn(2)}_2\text{Mo(1) }_c\text{Mo(2)}_3$$

(9)

$$\text{O(1)}_b\text{O(2)}_b\text{O(3)}_b\text{O(4)}_b\text{O(5)}_b\text{O(6)}_b=\text{Ce}_2\text{O}_3\text{O(1)}_b\text{+Ce}_2\text{O}_3\text{O(2)}_b\text{+Ce}_2\text{O}_3\text{O(6)}_b$$

$$+\text{Zr/Sn(1)}\text{O(4)}_b\text{+Zr/Sn(2)}\text{O(5)}_b\text{+Zr/Sn(2)}\text{O(5)}_b$$

$$+\text{Mo(1)}_b\text{O(1)}_b\text{+Mo(1)}_b\text{O(2)}_b\text{+Mo(1)}_b\text{O(3)}_b$$

$$+\text{Mo(1)}_b\text{O(3)}_b\text{+Mo(2)}_b\text{O(5)}_b\text{+Mo(2)}_b\text{O(6)}_b$$

Equation (10) indicated that the dielectric constant can be predicted by bond ionicity (Batsanov, 1982).

$$\varepsilon_r = \frac{n^2 - 1}{1 - f_i} + \frac{1}{C}$$

(10)

where $n$ is the refractive index. The bond ionicity were calculated using the Equations (11)–(13) (Xue and Zhang, 1996; Wu et al., 1998).

$$f_i = \frac{(C^i)^2}{(E^i_h)^2 + (C^i)^2}$$

(11)

$$E^i_h = \frac{39.74}{(d_{ij})^{3.48}}$$

(12)

$$C^i = 14.4b^{1/2} exp(-k_0^{1/2}) \left[ \frac{(Z_{A}^{i})^{*}}{r_0} - \frac{(Z_{B}^{i})^{*}}{r_0} \right]$$

(13)

$$k_0^{1/2} = \frac{4k_f^1}{\pi \alpha B}$$

(14)

$$r_0^{1/2} = \frac{1}{2} d_{ij}^{1/2}$$

(15)

where $E^i_h$ is the average energy gap, and it can be separated into homopolar $E^h_i$ and heteropolar $c_{ij}$ parts. The $k_0^{1/2}$ is Thomas-Fermi prescreening factor, and it was calculated through Equations (14) and (15) (Levine, 1973). The $f_i$ value of CZSM ceramics were shown in Figure 8, and the results were listed in Table 2. Decreasing sequence of $f_i$ was $f_i$ (Ce-O)$>$ $f_i$ (Zr/Sn-O)$>$ $f_i$ (Mo-O), the largest $f_i$ value of 85.64% was obtained in Ce-O bond. Besides, the average of $f_i$ (Ce-O) value decreased from 85.18 to 85.14% with the Sn$^{4+}$ doped shifted from 0 to 0.06. The tendency of the $\varepsilon_r$ value was consisted with the variation of $f_i$ (Ce-O) value. It indicated that the reduced $\varepsilon_r$ value was mainly dominated by the degreese bond ionicity of Ce-O bond.

The dielectric loss can be control by the binding ability between cation and oxygen ion, high binding energy corresponds to low intrinsic loss. Thus, lattice energy of CZSM ceramics can be calculated by Equations (16)–(18) (Xue and Zhang, 1996; Wu et al., 1998).

$$U = \sum_{i} \left( U_{bi}^{\mu} + U_{bi}^{\nu} \right)$$

(16)

$$U_{bi}^{\mu} = 1270 \frac{(m + n)Z_{bi}^{\mu}Z_{bi}^{\mu}}{d_{ij}} \left(1 - \frac{0.4}{d_{ij}} U_{bi}^{\mu} \right)$$

(17)

$$U_{bi}^{\nu} = 2100m \frac{(Z_{bi}^{\mu})^{1.64}}{(d_{ij})^{0.75}} U_{bi}^{\mu}$$

(18)
where the lattice energy $U_{b}$ can be separated into covalent $U_{bc}$ and ionic $U_{bi}$ parts. According to Figure 9, the sequence of $U$ (Mo-O) > $U$ (Zr/Sn-O) > $U$ (Ce-O) suggested that Mo-O bond play a vital role in enhancing the stability of ionic crystals.

What's more, the $\tau_f$ should be considered for realistic application of microwave dielectric ceramic. High bond energy could lead to a small absolute $\tau_f$ value. Hence, the bond energy can be obtained by Equations (19)–(21) (Sanderson, 1968, 1971, 1983):

$$E^\mu_b = t_c E^\mu_c + t_i E^\mu_i$$

$$E^\mu_i = \frac{33200}{d^\mu}$$

where $E^\mu_c$ and $E^\mu_i$ represent the covalent and ionic bond energy, respectively.
where $r_{cA}$ and $r_{cB}$ are the covalent radii of atom A and atom B; $t_i$ and $t_c$ are ionic and covalent proportional coefficient of an individual bond $\mu$. The bond energy $E_{A-A}$ and $E_{B-B}$ can be referred to handbook (Luo, 2007). What's more, $S_A$ and $S_B$ are the electronegativities of A and B atoms. Figure 10 illustrated bond energy of different bond type for Ce$_2$(Zr$_{0.94}$Sn$_{0.06}$)$_3$(MoO$_4$)$_9$ ceramics. The bond energy of Mo-O bond was larger than others, it suggested that Mo-O bond provided major contribution to the structural stability of CZSM ceramics. Compared with the Ce$_2$Zr$_3$(MoO$_4$)$_9$ ceramic, the bond energy of Mo-O bond declined from 574.8383 to 568.7162 KJ/mol. Meanwhile, the $\tau_f$ value was positively correlated with the change of bond energy ($E_{Mo-O}$). It suggested that the downward trend $\tau_f$ value could be explained by the decrease of bond energy ($E_{Mo-O}$).

The $\tau_f$ value was negatively related to the coefficients of thermal expansion, which can be obtained via Equation (22). Thus, the coefficients of thermal expansion were calculated based on P-V-L theory (Hakki and Coleman, 1960; Courtney, 1970; Xing et al., 2019).

$$\tau_f = -\left(\frac{r_c}{2} + \alpha\right)$$  (22)

where $\tau_f$ is temperature coefficient of the dielectric constant. The average values of Ce-O, Mo-O, and Zr/Sn-O bond were 10.0908 × 10$^{-6}$ K$^{-1}$, −0.3333 × 10$^{-6}$ K$^{-1}$ and 3.3463 × 10$^{-6}$ K$^{-1}$, respectively. In addition, The Mo-O bonds had a positive effect on $\tau_f$ value due to $\alpha_{Mo-O}$ value was negative. The $\alpha_{Mo-O}$ value increased from −0.3575 × 10$^{-6}$ K$^{-1}$ to −0.3333 × 10$^{-6}$ K$^{-1}$ because of the Sn$^{4+}$ substitution for Zr$^{4+}$. The higher $\alpha_{Mo-O}$ value result in large absolute value. Hence, the reduced $\tau_f$ value was associated with enhanced the thermal expansion coefficient ($\alpha_{Mo-O}$).

IR reflectivity spectra of CZSM ceramics was exhibited in Figure 11. Based on the classical harmonic oscillator model, the infrared spectra were fitted with 24 internal modes, which were listed in Table 3 (Petzelt and Kamba, 2003). $\varepsilon^* (\omega)$ (the complex dielectric permittivity) and $R (\omega)$ (the complex reflectivity) were calculated by Equations (23) and (24) (Wakino et al., 1986; Li et al., 2016; Tang et al., 2019; Guo et al., 2020).
TABLE 3 | Phonon parameters obtained from the fitting of the infrared spectra of Ce$_2$(Zr$_{0.94}$Sn$_{0.06}$)$_3$(MoO$_4$)$_9$ ceramic sintered at 800°C.

| Mode | $\omega_{po}$ | $\omega_{pj}$ | $\gamma_j$ | $\Delta \varepsilon_j$ |
|------|---------------|---------------|------------|---------------------|
| 1    | 56.63         | 31.15         | 4.545      | 0.3030              |
| 2    | 73.45         | 53.33         | 29.307     | 0.5270              |
| 3    | 117.86        | 137.00        | 22.011     | 2.7700              |
| 4    | 156.39        | 65.61         | 6.926      | 0.0853              |
| 5    | 214.31        | 111.57        | 25.332     | 0.2710              |
| 6    | 273.66        | 86.48         | 11.651     | 0.0879              |
| 7    | 306.77        | 96.06         | 7.964      | 0.0338              |
| 8    | 350.69        | 44.43         | 24.191     | 0.0280              |
| 9    | 424.12        | 161.49        | 24.722     | 0.1450              |
| 10   | 589.11        | 376.94        | 175.040    | 0.4020              |
| 11   | 678.33        | 280.36        | 51.634     | 0.1710              |
| 12   | 697.73        | 203.30        | 12.768     | 0.0849              |
| 13   | 734.27        | 377.97        | 21.214     | 0.2650              |
| 14   | 774.94        | 168.59        | 21.578     | 0.0473              |
| 15   | 809.94        | 197.95        | 19.772     | 0.0597              |
| 16   | 884.55        | 333.41        | 10.980     | 0.1420              |
| 17   | 896.15        | 84.03         | 18.700     | 0.0422              |
| 18   | 914.91        | 81.92         | 21.151     | 0.0080              |
| 19   | 954.88        | 142.99        | 10.245     | 0.0224              |

Furthermore, the tan $\delta$ (dielectric loss tangent) can be obtained through Equation (25).

$$\varepsilon'(\omega) = \varepsilon_{\infty} + \sum_{j=1}^{n} \frac{\omega_{pj}^2}{\omega_{pj}^2 - \omega^2 - j\gamma_j \omega}$$  \hspace{1cm} (23)

$$R(\omega) = \left| \frac{1 - \sqrt{\varepsilon'\varepsilon''}}{1 + \sqrt{\varepsilon'\varepsilon''}} \right|^2$$  \hspace{1cm} (24)

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\sum_{j=1}^{n} \Delta \varepsilon_j \gamma_j \omega}{\varepsilon_{\infty} + \sum_{j=1}^{n} \Delta \varepsilon_j}$$  \hspace{1cm} (25)

where $\varepsilon_{\infty}$ is dielectric constant by electronic polarization, $n$ is the number of transverse phonon modes, $\omega_{pj}$, $\omega_{pj}$, and $\gamma_j$ are plasma frequency, transverse frequency and damping factors of the j-th Lorentz oscillator, respectively.

Figure 12 presented the complex permittivity of CZSM ceramics sintered at 800°C. The extrapolated dielectric permittivity and loss were $10.92$ and $3.08 \times 10^{-4}$, respectively. It can be seen that the calculated permittivity was slightly higher than the measured permittivity, the measured and calculated dielectric losses of CZSM ceramic were comparable with the same order of magnitude. Therefore, the major dielectric contribution of the CZSM ceramics was in microwave region, and related to the absorptions of phonon oscillation.

CONCLUSION

Ce$_2$(Zr$_{0.94}$Sn$_{0.06}$)$_3$(MoO$_4$)$_9$ (CZSM) microwave dielectric ceramics were successfully prepared. The XRD patterns demonstrated that all samples displayed a single phase. The SEM results indicated that nearly compact structure can be obtained sintered at 750–850°C. Subsequently, the dependence of microwave dielectric properties on intrinsic factors was evaluated based on P-V-L theory. The decrease of dielectric constant was mainly dominated by the decline of polarizability and bond ionicity of Ce-O bond. The improvement of quality factor was dependent on enhanced packing fraction. In addition, the reduced temperature coefficient of resonant frequency was related to the increase of thermal expansion coefficient and decrease of bond energy ($E_{Mo-O}$). The complex permittivity values were obtained by infrared spectra, which agreed well with the measured value. The CZSM ceramic sintered at 800°C exhibited an optimum microwave dielectric properties of $\varepsilon_r = 10.35$, $Qf = 59,660$ GHz (at 9.70 GHz) and $\tau_f = -7.52$ ppm/$^\circ$C.
AUTHOR CONTRIBUTIONS

HT: methodology, investigation, data curation, visualization, writing-original draft, and writing-review and editing. XL: investigation, validation, methodology, software and formal analysis. YY: software, validation, writing-review and editing. HW and ZZ: conceptualization, resources, writing-review and editing, project administration, supervision, and funding acquisition.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats.2020.00145/full#supplementary-material
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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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