Structure, Raman spectra and microwave dielectric properties of novel garnet-type Ca$_3$MZrGe$_3$O$_{12}$ (M = Co, Zn) ceramics

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ABSTRACT
Two novel garnet-type ceramics Ca$_3$MZrGe$_3$O$_{12}$ (M = Co and Zn) with pure phase were prepared through a solid-state reaction method. Structure–property relationships were studied by the Rietveld refinement and Raman spectra. The appearance of two weak symmetric stretching vibrational peaks in Ca$_3$ZnZrGe$_3$O$_{12}$ might be due to the lower ordering. Higher Q × f value in Co-analogue was related to the larger packing fraction and the lower FWHM of A$_1g$ mode. The smaller oxygen bond valence in Ca$_3$CoZrGe$_3$O$_{12}$ indicates a smaller τ$_f$ value. At the optimized sintering temperature of 1280 °C, Ca$_3$CoZrGe$_3$O$_{12}$ shows desirable microwave dielectric properties with ε$_f$ of 10.37, Q × f value of 60.100 GHz, and τ$_f$ value of −28.5 ppm/°C. The Ca$_3$ZnZrGe$_3$O$_{12}$ ceramic sintered at 1200 °C has the best microwave dielectric properties with ε$_f$ of 10.48, Q × f value of 49.700 GHz, and τ$_f$ value of −35.8 ppm/°C.

1. Introduction
The rapid growth of communication technologies, specifically in the upgrade from 4 G to 5 G and beyond, has facilitated the need for novel, high-performance microwave dielectric materials. In order to meet the requirement of 5 G communications, microwave dielectric ceramics with low permittivity (ε$_r$) and high-quality factor (Q × f) is one of the research emphases, since low ε$_r$ can provide high-speed signal transmission and high Q × f usually ensure good frequency selectivity. Additionally, these dielectrics should possess a near-zero temperature coefficient of resonant frequency (τ$_f$) for satisfactory thermal stability [1–4].

Owing to the high chemical and physical stabilities, garnet-type AB$_2$CO$_3$O$_{12}$ materials are well-known materials for lasers, phosphors, and dielectrics [5]. In recent years, different kinds of low ε$_r$ ceramics with garnet structure have been developed, such as vanadates Ca$_3$Al$_2$(VO)$_6$A ($A$ = Mg and Zn), lanumates Y$_3$MgAl$_2$SiO$_{12}$ and Y$_3$MgAl$_2$O$_{12}$, ferrate Gd$_3$Fe$_2$O$_{12}$ and tellurate Ca$_3$Te$_2$Zn$_2$O$_{12}$ [6–10]. However, large negative τ$_f$ for vanadates and high densification temperature for aluminates are unfavorable in commercialization, and tellurate and tungstate are unacceptable for their low-quality factor. Germanates is one of the new developing low ionic polarizability of Ge and the strong covalent bond in GeO$_4$ tetrahedrons [11,12]. Recently, garnet-type Ge-based microwave dielectrics such as Ca$_3$Al$_2$Ge$_3$O$_{12}$, Ca$_3$Y$_2$Ge$_3$O$_{12}$ and Ca$_3$ZrGe$_3$O$_{12}$ have achieved great attentions because of their high-quality factors [13–15]. All of them possessed a high-quality factor (>75,000 GHz) but sintered above 1320 °C. Geller et al. firstly reported the synthesis of garnet structured Ca$_3$CoZrGe$_3$O$_{12}$ in 1960 [16]. However, the microwave dielectric properties of Ca$_3$CoZrGe$_3$O$_{12}$ have remained unclear. Furthermore, considering the low melting point ZnO could lower the sintering temperature and also Zn$^{2+}$ exhibits similar ionic radius to that of Co$^{2+}$ in Ca$_3$CoZrGe$_3$O$_{12}$, it is reasonable to investigate the microwave dielectric properties of Ca$_3$MZrGe$_3$O$_{12}$ (M = Co, Zn) (CCZGO and CZZGO) ceramics. Therefore, the structural characteristics, microstructures and Raman spectra of CCZGO and CZZGO are studied in this work.

2. Experimental procedures
Ca$_3$M$_2$ZrGe$_3$O$_{12}$ (M = Co and Zn) ceramics were synthesized through a conventional solid-state method using CaCO$_3$ (99.99%), Co$_2$O$_3$ (99.9%), ZnO (99.9%) and GeO$_2$ (99.9%) as raw materials. The reagents were ball-milled using zirconia balls in alcohol for 5 h. After being dried, the CCZGO and CZZGO mixed powder were calcined at 1150 °C and 1080 °C for 4 h, respectively. After that, the calcined samples were ball-milled...
and dried again, followed by pressing into cylindrical pellets with 10 mm in diameter and approximately 6.5 mm in height. Finally, CCZGO and CZZGO were sintered in the range of 1220–1300°C and 1180–1220°C, respectively.

The crystalline structures of the synthesized compounds were identified by using an X-ray diffractometer (XRD; X’Pert PRO, PANalytical, Almelo, Holland). The bulk densities of the sintered samples were measured by Archimedes’ method. The ceramics were polished and etched 35°C below sintering temperature for 30 min. The microstructure analysis was performed using Hitachi S4800 scanning electron microscope. The chemical compositions and valent states were tested by an X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, Waltham, USA). Raman measurements were performed using a Raman spectrometer (DXR, Thermo Fisher Scientific, Waltham, USA) with a 532 nm laser from 50 to 1000 cm⁻¹ in a spectral resolution of 3.5 cm⁻¹.

A network analyzer (N5230A, Agilent, Palo Alto, USA) was employed to measure the relative permittivity ($\varepsilon_r$) and quality factor ($Q \times f$). The temperature coefficient of resonant frequency ($\tau_f$) values was calculated as follows:

$$\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}}$$

where $f_{25}$ and $f_{85}$ represent the resonant frequencies at 25°C and 85°C, respectively.

3. Results and discussions

Figure 1 (a) and (b) shows the normalized XRD patterns of CCZGO and CZZGO ceramics sintered at 1220–1300°C and 1180–1220°C, respectively. The patterns could be indexed to the cubic garnet structure in the $Ia3d$ space group, which is similar to that of $Ca_3Sn_2SiGa_2O_{12}$ (JCPDS no. 01–081-2356). The bulk densities of CCZGO and CZZGO ceramics at various sintering temperatures are shown in Figure 1 (c) and (d). The density of CCZGO ceramics firstly increases to the maximum value of 4.49 g/cm³ at 1280°C and then decreases with the increasing temperature. The bulk density of CZZGO ceramics increases from 4.47 g/cm³ to the maximum of 4.55 g/cm³ as the sintering temperature from 1180°C to 1200°C. In order to
investigate the crystal structure in detail, the Rietveld refinement of XRD data of CCZGO and CZZGO ceramics was carried out using Fullprof software. The refinement plots of CCZGO and CZZGO ceramics at optimized temperatures are exhibited in Figure 2 (a) and (b). The calculated patterns are consistent with the observed data. The refined crystallographic parameters are given in (table 1) and (table 2). The cell parameter of CCZGO is a = 12.5199 (2) Å and V = 1962.468 (5) Å³, with good reliability factors $R_{wp} = 4.32\%$, $R_p = 3.20\%$ and $\chi^2 = 3.08$. The cell parameters of CZZGO is $a = 12.5541 (3)$ Å and $V = 1978.594 (7)$ Å³, with acceptable reliability factors $R_{wp} = 3.35\%$, $R_p = 2.37\%$ and $\chi^2 = 3.58$. As shown in Figure 2 (c), the 24$c$ dodecahedral site and 24$d$ tetrahedral site are fully occupied by Ca atoms and Ge atoms, respectively. Co (Zn) and Zr are located at the 16$a$ octahedral site with 1:1 ratio.

XPS was carried out to clarify the electronic states of the CCZGO. The peaks corresponding to the primary elements are shown in Figure 3 (a). By using the Gaussian–Lorentzian fitting method, the Co spectra in Figure 3 (b) can be fitted with two Co 2p peaks and two shake-up satellites (identified as Sat). The binding energies at 780.09 eV and 797.08 eV are ascribed to Co (2p$_{3/2}$) and Co (2p$_{1/2}$), respectively. The results indicate that the oxidation state of cobalt species in CCZGO is Co$^{3+}$ [17–19].

SEM images of CCZGO and CZZGO ceramics sintered at 1280 °C and 1200 °C are shown in Figure 4.
Well-densified microstructure can be obtained for the ceramics, smaller and uniform polygonal grains (average size ~ 1.46 μm, as shown in Figure 4 (c)) are noticed for CCZGO, whereas CZZGO shows larger grain size (average size ~ 1.67 μm, as shown in Figure 4 (d)).

Figure 5 (a) and (b) shows the Raman spectra of CCZGO and CZZGO ceramics from 100 to 1000 cm⁻¹, respectively. By using the Gaussian function, 11 and 12 Raman-active bands could be deconvoluted for CCZGO and CZZGO, respectively (see Figure 6 (a) and (b)). According to Factor group analysis, the total irreducible representation of the O₁₀ʰ group is given as [20]:

\[
\Gamma = 3A₁g + 14F₂g + 5A₂g + 14F₁g + 8E_g + 5A₂u + 5A₁u + 18E_u + 16F₂u
\]

where A₁g, E_g, and F₂g modes are Raman-active modes of the garnets. However, not all vibrational
modes could be observed in these ceramics due to the overlapping or coupling of bands. The Raman vibrational modes of observed peaks in CCZGO and CZZGO ceramics are listed in Table 3. The Raman spectrum of Co-analogue is analogous to the Zn-analogue spectrum. However, a significant difference is that two weak symmetric stretching vibrational peaks (shouldered peaks of band 9 and 12) in the Zn-analogue are absent in the Co-analogue. The local- and long-range symmetry has an impact on the activities of vibrational modes. According to Wang's work, the local symmetry would be changed and some inactive Raman modes may be activated when the ceramics became more disordered [21].

The microwave dielectric properties of CCZGO and CZZGO as the function of sintering temperature are shown in Figure 7. The \( \varepsilon_r \) of both analogues increases firstly and then decreases similar to the trend of density, and the maximums of CCZGO and CZZGO are 10.48 ± 0.1 and 10.26 ± 0.1, respectively. A close relationship between relative permittivity and density in the ceramics can be observed since \( \varepsilon_r \) of the samples do not continue to increase due to the lower densities. For the single cubic CCZGO and CZZGO garnets, the theoretical permittivity \( \varepsilon_{\text{theo}} \) can be predicted by the Clausius–Mossotti equation (see Eq. (3)) and Shannon's additive rule (see Eq. (4)) [22,23]:

Table 3. The vibration modes of activated Raman peaks in CCZGO and CZZGO ceramics (trans–translation, rot–rotatory, bend–bending, str–stretching).

| Band | CCZGO | CZZGO |
|------|-------|-------|
| 1    | 172   | 174   |
| 2    | F_{2g} | E_g   |
| 3    | 257   | Ca^{2+}\text{trans} |
| 4    | 301   | E_g + F_{2g} |
| 5    | 359   | [GeO_4]_\text{trans} + [GeO_4]_\text{rot} |
| 6    | 378   | F_{2g} |
| 7    | 483   | [GeO_4]_\text{band} |
| 8    | 677   | F_{2g} |
| 9    | 731   | [GeO_4]_\text{band} |
| 10   | 799   | A_{1g} |
| 11   | 817   | F_{2g} |
| 12   | 849   | A_{1g} |

Figure 5. The Raman spectra of (a) CCZGO and (b) CZZGO ceramics from 100 to 1000 cm\(^{-1}\).

Figure 6. Deconvoluted Raman spectra of (a) CCZGO and (b) CZZGO ceramics.
Figure 7. The relative density and microwave dielectric properties of (a)-(d) CCZGO and (e)-(h) CZZGO ceramics sintered at various temperatures:

$$\varepsilon_{\text{theo}} = \frac{3V_m + 8\alpha_{\text{theo}}}{3V_m - 4\alpha_{\text{theo}}}$$

(3)

where $V_m$ and $\alpha_{\text{theo}}$ are the molar volume and the sum polarizability of constituent ions, respectively.

$$\alpha_{\text{theo}} = 3\alpha(\text{Ca}^{2+}) + 2\alpha(M^{2+}) + \alpha(\text{Zr}^{4+}) + 2\alpha(\text{Ge}^{4+}) + 12\alpha(O^{2-})$$

(4)

where $\alpha(\text{Ca}^{2+})$, $\alpha(M^{2+})$, $\alpha(\text{Zr}^{4+})$, $\alpha(\text{Ge}^{4+})$ and $\alpha(O^{2-})$ are the polarizability of $\text{Ca}^{2+}$, $M^{2+}$, $\text{Zr}^{4+}$, $\text{Ge}^{4+}$ and $O^{2-}$, respectively. The calculated $\varepsilon_{\text{theo}}$ of CCZGO and CZZGO ceramics sintered at the optimized temperature are 9.56 ± 0.1 and 9.59 ± 0.1, respectively. Inspection from Figure 7 (c) and (g), the variation in $Q \times f$ values as a function of sintering temperature is similar to that of the density. This phenomenon indicates the densification contributes to the improvement of $Q \times f$ values. On the whole, comparing the $Q \times f$ values of CCZGO and CZZGO ceramics, the former has higher values. It is well known that the intrinsic factors such as crystal structure and packing fraction are often used to correlate the dielectric loss. Therefore, packing fraction is used to understand the difference in $Q \times f$ values, and it can be expressed by the follows [24]:

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

(5)

where $Z$ is 8 for garnet. As given in Table 4, the packing fractions of optimized sintered CCZGO and CZZGO ceramics are 62.43% and 62.14%, respectively. The increase in packing fraction would result in the decrease of intrinsic losses because of the space for lattice vibrations decrease [24]. Furthermore, it is proved that the damping behavior and degree of ordering in the crystal structure are closely related to the full width at half maximum (FWHM) in Raman spectra. As shown in Table 4, CCZGO shows the smaller FWHM and the higher $Q \times f$ value compared to CZZGO. The narrower Raman peak (namely smaller FWHM) usually implies a weaker damping behavior and a higher degree of ordering, which results in the decrease of inherent dielectric loss [25]. Actually, the higher degree of ordering obtained in CCZGO could be also manifested by the less activated Raman modes mentioned above.

As shown in Figure 7 (d) and (h), the $\tau_\ell$ value fluctuated around $-29$ ppm/°C for CCZGO ceramics, whereas the entire $\tau_\ell$ value obtained by CZZGO ceramics is around $-36$ ppm/°C. Park et al. suggested that a close correlation between $\tau_\ell$ and bond valence of B-site in the

Table 4. Microwave dielectric properties, packing fraction, FWHM of $\alpha_y$ peak at band 10 and oxygen bond valence of $\text{Ca}_x\text{CoZrGe}_3\text{O}_{12}$ and $\text{Ca}_x\text{ZnZrGe}_3\text{O}_{12}$ ceramics.

| Compounds         | S.T. (°C) | $\varepsilon$ | $\varepsilon_{\text{theo}}$ | $Q \times f$ (GHz) | $\tau_\ell$ (ppm/°C) | $f$ (%) | FWHM (cm$^{-1}$) | $V_0$ (eV) |
|-------------------|-----------|---------------|----------------------------|-------------------|----------------------|--------|----------------|------------|
| $\text{Ca}_x\text{CoZrGe}_3\text{O}_{12}$ | 1280      | 10.37 ± 0.1   | 9.56 ± 0.1                 | 60,100 ± 300      | -28.5 ± 1.2          | 62.43  | 14.69          | 1.7992     |
| $\text{Ca}_x\text{ZnZrGe}_3\text{O}_{12}$ | 1200      | 10.48 ± 0.1   | 9.59 ± 0.1                 | 49,700 ± 300      | -35.8 ± 1.1          | 62.14  | 58.31          | 2.0199     |
tilted octahedra of ABO$_3$ perovskite [26]. In addition, it has been reported that the $\tau_f$ is strongly dependent on the bond valence and the degree of distortion of polyhedral in ABO$_4$ scheelite [27]. However, the link between octahedral distortions and $\tau_f$ value in other complicated crystal systems might be not applicable anymore. For ideal cubic garnet $A_3B_2C_3O_{12}$ without structural distortion, the bond valence of dodecahedral, octahedral and tetrahedral site cations should be considered. Then the investigation on the relationship between oxygen bond valence and $\tau_f$ would be reasonable [28]. As shown in table 4, the larger $V_o$ obtained for CZZGO ceramic shows the larger $\tau_f$ value in the negative direction. The higher oxygen bond valence corresponds to the stronger average bond strength in the polyhedra, which would lead to a stronger restoring force for recovering the tilting of polyhedra, thereupon deterioration of the $\tau_f$ value happens [28]. Despite the $Q \times f$ values obtained in Ca$_3$Y$_2$Ge$_3$O$_{12}$ and Ca$_2$ZrGe$_3$O$_{12}$ ceramics are relatively higher than that of Ca$_3$MzrGe$_3$O$_{12}$ (M = Zn and Co), but the latter two can offer advantages over the formers especially in the lower sintering temperatures and smaller $\tau_f$ values [14,15].

4. Conclusions
Two novel Ca$_3$MzrGe$_3$O$_{12}$ (M = Co and Zn) ceramics with pure garnet phase were successfully prepared by solid-state reaction process. The differences in
microwave dielectric properties of CCZGO and CZZGO are closely related to the octahedral cations. The increase of packing fraction and the decrease of FWHM enhance $Q \times f$ value by the substitution of $\text{Zn}^{2+}$ by $\text{Co}^{2+}$. The smaller oxygen bond valence in CCZGO indicates a smaller $\tau_r$ value. CCZGO ceramic exhibits a low $\varepsilon_r$ of 10.37, a $Q \times f$ value of 60,100 GHz, and a $\tau_r$ value of $-28.5$ ppm/°C at 1280 °C whereas $\varepsilon_r = 10.48$, $Q \times f = 49,700$ GHz and $\tau_r = -35.8$ ppm/°C of CZZGO ceramic were obtained at 1200 °C.

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Disclosure statement

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