Compositional modulation in ZnGa_2O_4 via $\text{Zn}^{2+}/\text{Ge}^{4+}$ co-doping to simultaneously lower sintering temperature and improve microwave dielectric properties

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Abstract: AB_2O_4 -type spinels with low relative permittivity (ϵ_r) and high quality factor ($Q \times f$) are crucial to high-speed signal propagation systems. In this work, $\text{Zn}^{2+}/\text{Ge}^{4+}$ co-doping to substitute Ga^{3+} in ZnGa_2O_4 was designed to lower the sintering temperature and adjust the thermal stability of resonance frequency simultaneously. $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$) ceramics were synthesised by the conventional solid-state method. $\text{Zn}^{2+}/\text{Ge}^{4+}$ co-substitution induced minimal variation in the macroscopical spinel structure, which effectively lowered the sintering temperature from 1385 to 1250 °C. All compositions crystallized in a normal spinel structure and exhibited dense microstructures and excellent microwave dielectric properties. The compositional dependent quality factor was related to the microstructural variation, being confirmed by Raman features. A composition with $x = 0.3$ shows the best dielectric properties with $\epsilon_r \approx 10.09$, $Q \times f \approx 112,700$ THz, and $\tau_f \approx -75.6$ ppm/°C. The negative τ_f value was further adjusted to be near-zero through the formation of composite ceramics with TiO_2 .

Keywords: ceramics; spinel; composition modulation; dielectric properties

1 Introduction

Microwave dielectric ceramics can meet the ever-growing requirements of wireless communication as primary functional materials for dielectric resonators and filters. Radars, mobile networking (4G and 5G),

base stations, satellite transmission, and global positioning systems are only a few examples of applications where such dielectrics have been commercialized [1–3]. The last few decades have witnessed intensive development and commercialization of microwave dielectric ceramics and a lot of candidates with good dielectric performances (high relative permittivity ϵ_r , high quality factor $Q \times f$, tunable temperature coefficient of resonance frequency τ_f) have been explored [4–6]. Unfortunately, the undesirable incompatibility between these three merits, however, restricts the range of

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possibilities for practical applications [7]. As a consequence, there is still a high demand ongoing for novel microwave dielectrics with optimized performances for the above-mentioned merits.

AB₂O₄ spinel materials have received intense attention and are now considered as attractive microwave dielectric materials due to their high quality factors, e.g., (Mg,Zn)Al₂O₄ ($Q \times f \approx 85,100$ and $56,300$ GHz), Mg₂TiO₄ ($Q \times f \approx 150,000$ GHz), CoZnTiO₄ ($Q \times f \approx 97,500$ GHz), etc. [8–11]. Ga-based spinels particularly have also been reported as promising materials for millimeter-wave devices due to their low permittivities and high quality factors. For example, MgGa₂O₄ has a low ϵ_r of 9.5, a $Q \times f$ of 117,000 GHz, and a near-zero τ_f of -4.0 ppm/°C, while the isostructural ZnGa₂O₄ possesses a large negative τ_f of -27 ppm/°C, which would severely restrict its commercial potential [12].

Different attempts have been conducted to improve the thermal drift of τ_f for ZnGa₂O₄. Rutile TiO₂ (6.9 vol%) was proved to be effective to compensate for the τ_f of ZnGa₂O₄ to be 3 ppm/°C [13]. Furthermore, cation substitution in either A- or B-site was found to simultaneously improve the thermal stability and increase the quality factor of ZnGa₂O₄. Mn²⁺ substitution in ZnGa₂O₄ tuned the τ_f value to be -12 ppm/°C coupled by a twofold increase in $Q \times f$ value to 181,000 GHz, whereas Cu²⁺ substitution reduced the temperature stability of resonance frequency despite the obvious improvement in quality factor (by $\sim 65\%$ to 131,500 GHz) [14,15]. Such variations in dielectric performances should be strongly related to the cation distribution and occupation preference, which would determine the normal or inverse crystal structure of the spinel. Additionally, given that the ZnGa₂O₄ is a normal spinel while MgGa₂O₄ is a partial inverse spinel, the difference in dielectric properties between the two materials may be due to structural differences in the cation distribution in tetrahedra and octahedra sites. As a result, establishing a primary correlation between the cation distribution and dielectric properties in spinels is extremely important.

Keeping in view the above challenges, spinel ZnGa₂O₄ was selected as the parent material and Zn²⁺/Ge⁴⁺ co-substitution for Ga³⁺ was proposed to form solid solution of Zn_{1+x}Ga_{2-2x}Ge_xO₄ with an aim to study the correlation among cation occupation, crystal structure, and microwave dielectric properties.

2 Experimental

2.1 Ceramics fabrication

Analytically pure ZnO, Ga₂O₃, and GeO₂ (99.99%; Guo-Yao Co., Ltd., China) were used as raw materials to synthesize a series of nominal compositions of Zn_{1+x}Ga_{2-2x}Ge_xO₄ ($0.1 \leq x \leq 0.5$) ceramics by the conventional solid-state reaction method. The raw materials were mixed using a ball milling for 6 h with ZrO₂ balls as a grinding media at a speed of 300 rpm. The slurry was subsequently dried at 120 °C for 2 h followed by calcination at 1150 °C for 6 h. The calcined powders were re-milled, dried, and mixed with 5 wt% PVA, which was used as the binder. The mixed powders were then pressed into disks of 10 mm in diameter and 6 mm in height under a uniaxial pressure of 80 MPa. To extract the organic binder, the green samples were heated to 550 °C for 6 h at a rate of 1.5 °C/min, followed by calcination in a temperature range of 1250–1340 °C for 6 h.

2.2 Structural and dielectric measurements

The phase composition and purity were investigated by X-ray diffractometer (XRD; Cu K α 1, 1.54059 Å, Model X' Pert PRO, PANalytical, Almelo, the Netherlands). The crystal structure of all compositions was identified by the Rietveld refinement and Raman spectrometer (DXR; Thermo Fisher Scientific, USA). The bulk density of the sintered samples was measured by the Archimedes' principle. The microstructure of polished and thermally etched samples was observed using scanning electron microscopy (SEM; S4800, Hitachi, Tokyo, Japan). The etching temperature was 50 °C lower than the optimum sintering temperature. The microwave dielectric properties were measured using a network analyzer (N5230A, Agilent Co., Palo Alto, CA, USA) connected with a temperature chamber (Delta 9039, Delta Design, San Diego, CA, USA). τ_f values were calculated using the following equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 represent the resonant frequency at T_1 (25 °C) and T_2 (85 °C), respectively. The room-temperature infrared reflectivity spectra were measured by a Bruker IFS 66v FT-IR spectrometer (Bruker Optics, Ettlingen, Germany).

3 Results and discussion

Figure 1 shows the room-temperature XRD patterns of the $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$) ceramics calcined 1150°C . All the observed peaks were indexed with the PDF card No. 86-0415 and the crystal structure could be assigned to the cubic spinel ZnGa_2O_4 with space group $Fd\bar{3}m$. Furthermore, all compositions exhibited identical diffraction patterns with no evidence of the second phase, suggesting a single-phase solid solution formed in the whole compositional range. Another evidence that endorsed the formation of the solid solution was the slight shift to the lower angle of the diffraction peaks, as a representative in Fig. 1(b) for the enlarged profile of (311) peak (around $2\theta = 36^\circ$).

Fig. 1 (a) X-ray powder diffraction patterns of the $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$) ceramics fired at 1150°C and (b) amplified diffraction peak (311) around $2\theta = 36^\circ$.

The variation in ionic radius between Ga^{3+} and the doped $(\text{Zn}_{0.5}\text{Ge}_{0.5})^{3+}$ was responsible for the peak shift [16] as $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ previously reported to form spinel solid solutions for x ranging from 0 to 0.5 [17].

Rietveld refinement was conducted to further confirm the phase purity and crystal structure of the $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$) samples and a structural model was built based on the crystal structure data of ZnGa_2O_4 [18]. A perspective view of the spinel structure of ZnGa_2O_4 is shown in Fig. 2, with the characteristic feature of bivalent Zn^{2+} occupying the tetrahedral sites and trivalent Ga^{3+} in the octahedral sites, featuring a normal spinel structure. Especially, for Rietveld refinement the doped $(\text{Zn}_{0.5}\text{Ge}_{0.5})^{3+}$ was fixed in the octahedral interstices. As shown in Figs. 3(a)–3(e), good matching between the

Fig. 2 A perspective view of the crystal structure of spinel ZnGa_2O_4 .

Fig. 3 (a–e) Rietveld refinement patterns for $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$) ceramics (the red cross symbol represents the measured data while the solid line represents the calculated ones) and (f) variation of lattice parameters as a function of x value.

calculated and the observed profiles indicates the structural model's reliability and yields the accuracy of fit indicators (as shown in Table 1). The bond length of Zn–O1 initially decreased with x increasing from 0.1 to 0.3 and then increased for the remaining composition. On the other hand, the length of Ga–O1 and angle of Zn–O1–Ga decreased with increasing x , indicating the effects of cation substitution on bond features. The refined cell parameter a and cell volume V are plotted in Fig. 3(f) as a function of composition with $0.1 \leq x \leq 0.5$ and saw a linear increase with increasing x (from 0.1 to 0.5) which is also validated by Vegard's law [19]. These variations also proves the solid solution formation and can further be explained by the larger average ion radii of Zn^{2+} ($R = 0.74 \text{ \AA}$, CN = 6) and Ge^{4+} ($R = 0.53 \text{ \AA}$, CN = 6) (with an average radius of $0.635 \text{ \AA}$) than the Ga^{3+} ($R = 0.62 \text{ \AA}$, CN = 6) [16].

To investigate the influence of sintering temperature

on the densification of $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$) ceramics, the temperature dependence of the bulk density was plotted and is shown in Fig. S1 in the Electronic Supplementary Material (ESM). A tendency variation similar to bond length was observed for bulk density with increasing sintering temperature and showed an initial increase followed by a subsequent decrease. The optimum sintering temperature and the corresponding bulk density are shown in Fig. 4(a) as a function of composition (x value). The bulk density gradually increased from 5.82 to 5.96 g/cm^3 , as predicted from the calculated theoretical density. Notably, the optimum sintering temperature decreased significantly, although the relative density increased slightly from 94.5% at $x = 0.1$ to 97.2% at $x = 0.5$. Because of the low melt point of GeO_2 ($\sim 1115^\circ\text{C}$), the addition of Zn/Ge improved the sintering characteristic of $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$. Similar phenomena have previously

Table 1 Refined crystal structure parameters of $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$)

Value x	$a = b = c$ (Å)	Volume (Å ³)	Bond length (Å)	Angle (°)	R factor (%)		
			Ga–O1	Zn–O1–Ga	R_{wp}	R_{exp}	χ^2
0.1	8.33621(5)	579.3035(2)	2.0445(2)	121.86(2)	9.5	5.42	3.07
0.2	8.33814(3)	579.7052(6)	2.0306(5)	122.33(6)	13	5.47	5.65
0.3	8.34027(7)	580.1509(8)	2.0217(7)	122.83(2)	12.3	5.62	4.76
0.4	8.34265(5)	580.6463(4)	2.028(5)	123.23(8)	13.4	5.68	5.59
0.5	8.34595(1)	581.3366(5)	2.0034(1)	123.61(4)	12.6	5.25	5.73

Fig. 4 Compositional dependence of bulk density and microwave dielectric properties of $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$) ceramics sintered at their optimum temperature.

been reported in Zn_2GeO_4 systems [20].

Figure 4(b) shows the compositional variation in the dielectric permittivity of $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ with increasing x from 0.1 to 0.5. The relative permittivity increased linearly from 9.78 at $x = 0.1$ to 10.42 at $x = 0.5$. Based on the Clausius–Mossotti equation ($\epsilon = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D}$), the relative permittivity depends upon the total molecular polarizability (α) and unit cell volume (V) and is directly proportional to the polarizability density (α/V) [21,22]. The theoretical relative permittivity estimated by the Clausius–Mossotti equation was ~7.6% higher than the measured values, as shown in Fig. 4(b). After porosity corrected based on the Bosman and Having's equation $\epsilon_{\text{corr}} = \epsilon_r \times (1 + 1.5p)$ where p represents the fractional porosity, the deviation of the corrected permittivities from the estimated values was in the range of 3.6%–6.4% [23–26]. This result indicates that porosity (or density) has a direct influence on the permittivity of the material.

The τ_f values of the $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$) ceramics sintered at their relative optimum temperatures are shown in Fig. 4(c). The τ_f values decreased initially from -66.3 to -75.6 ppm/°C followed by an increase to -65.6 ppm/°C at $x = 0.5$. The Ga–O bond valence in the octahedron was calculated by the following equations [27]:

$$V_i = \sum_j v_{ij}, \quad v_{ij} = \exp\left(\frac{R_{ij} - d_{ij}}{b}\right) \quad (2)$$

where R_{ij} represents the bond valence parameter which has been summarized by Brown and Altermatt [28], d_{ij} is the length of a bond between atoms i and j , and b is a universal constant (0.37 Å). The variation in bond valence (x from 0.1 to 0.3) followed a pattern, opposite to τ_f value in which the bond valence initially increased followed by a decrease. The various bond valences correspond to the different atom interactions [29] and a higher valence means stronger interaction and higher band energy. In the present system, the increase in Ga–O bands resulted in the increasing resorting force, which recovered the titling of the octahedron, and thus a decrease in τ_f value.

In contrast to the permittivity, the quality factor exhibited an increasing trend with increasing Zn/Ge doping content (x value) from 0.1 to 0.3 and then declined. As reported by Kim *et al.* [30], Yin *et al.* [31],

and Li *et al.* [32], the quality factor can be intrinsically predicted by packing fraction. A higher packing fraction signifies a smaller space for ion vibration, which leads to lower dielectric losses. The calculated packing fraction for $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ shows a decrease with the variation of x . Intrinsically, the quality factors were expected to exhibit a decreasing trend. The observed deviation suggested that the intrinsic packing fraction was not the only dominant influencing factor but other extrinsic factors, e.g., pores, grain size, cation ordering, etc., also play a part [6,33–35].

To investigate the underlying factors influencing the quality factor, the grain morphology and size distribution were studied. As shown in Fig. 5, the polished and thermal etched surfaces for all compositions are shown. Dense microstructures consisted of uniform grains and defined grain boundaries and a few visible pores, were observed. All compositions exhibited similar grain size distribution with average grain size in the range of 4.6–5.2 μm (Fig. 5(f)). Along with the higher relative density (94%–98%), the extrinsic contribution from density, pores, and grain size on the quality factor can be ruled out in relation to their dependency on the quality factor.

Raman spectroscopy has been recognized to be an effective approach to correlate the lattice vibrational modes with dielectric properties, especially in those materials with cation ordering, e.g., $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ complex perovskite [36] and A_2MgTeO_6 ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) double perovskites [37]. To explore the structural correlation of the microwave dielectric properties for $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ spinel, Raman spectroscopy was utilized at room temperature for all compositions.

According to the space group theory, ZnGa_2O_4 is a cubic spinel with space group $Fd\bar{3}m$ and has 14 atoms in its primitive unit cell. The irreducible representations can be given as [38,39]:

$$\Gamma = A_{1g}(\text{R}) + E_g(\text{R}) + T_{1g} + 3T_{2g}(\text{R}) + 2A_{2u} + 2E_u + 5T_{1u}(\text{IR}) + 2T_{2u} \quad (3)$$

where R and IR represent the Raman and infrared active modes, respectively. Among them, T_{1g} , A_{2u} , E_u , and T_{2u} modes are silent [40,41]. Generally, five modes (E_g , $3T_{2g}$, A_{1g}) with the first-order could be detected in the spine structure. As shown in Fig. 6(a), similar Raman profiles were observed and after Gaussia–Lorentzian fitting (Figs. 6(a) and 6(d) as a representative) only three first-order modes could be recorded, which were

Fig. 5 Polished and etched microstructure of $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ceramics: (a) $x = 0.1$ sintered at 1340°C , (b) $x = 0.2$ sintered at 1310°C , (c) $x = 0.3$ sintered at 1280°C , (d) $x = 0.4$ sintered at 1260°C , and (e) $x = 0.5$ sintered at 1250°C .

positioned at 463 cm^{-1} (T_{2g}^1), 610 cm^{-1} (T_{2g}^2), and 712 cm^{-1} (A_{1g}) [42]. The T_{2g}^1 mode was related to the Zn–O symmetric bending vibrations. The A_{1g} mode and T_{2g}^2 modes were assigned to the symmetric and asymmetric stretching vibrations of ZnO_4 tetrahedron [40]. The relative intensity of T_{2g}^1 and T_{2g}^2 gradually decreased with the increasing Zn/Ge doping, as displayed in Fig. 6(a). A similar phenomenon has been observed in $\text{Mg}_2(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_4$, which is caused by the

different ion radius between Ti^{4+} and Sn^{4+} [43]. In this work, the effective ionic radius of $(\text{Zn}_{0.5}\text{Ge}_{0.5})^{3+}$ was larger than Ga^{3+} , which was responsible for the variation in the Raman intensity. Additionally, it should be noted that the characteristic mode (A_{1g}^* , $\sim 673\text{ cm}^{-1}$) for the direct recognition of an inverted spinel was silent for all $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ceramics, confirming a stable normal spinel structure [43].

Figure 6(d) shows the Raman shift and FWHM (full

Fig. 6 (a) Room temperature Raman spectra of the $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ($0.1 \leq x \leq 0.5$), (b, c) fitted results of $x = 0.1$ and 0.5 , respectively, and (d) change of Raman shift and FWHM as a function of x value.

width at half maximum) of A_{1g} mode as a function of x value. The A_{1g} mode had a blue shift while the FWHM gradually decreased to $x = 0.3$ initially followed by an increment to $x = 0.5$. The blue shift indicated the vibration phonon energy increased which limited the movement of the ions and decreased the polarizability. The FWHM was inversely correlated to the lifetime of phonon, and lower FWHM values mean the longer lifetime of phonon and less interaction with other phonons. These interactions can increase the intrinsic dielectric loss due to energy consumption. Thus, decreasing FWHM values are beneficial to improve the quality factor.

The fitted and measured values of IR reflectivity are shown in Fig. 7(a) while the real and imaginary parts of the complex permittivity are shown in Fig. 7(b). For ceramic with $x = 0.3$, there were 7 modes used and the detailed information on the fitted parameters is listed in Table 2. Out of those 7 modes, the modes at 303.46 and 424.26 cm^{-1} had a primary contribution to the dielectric properties. Based on the fitted parameters, the calculated permittivity in optical range (ϵ_∞) was 1.92 while in the microwave frequency range, the permittivity was 9.22. These values were significantly lower than the measured values ($\epsilon_r = 10.04$ for $x = 0.3$), which could be attributed to the extrinsic contributions stemming from the defects [44]. Compared to the total permittivity, the contributions of the optical permittivity were only 19.1%, suggesting that the primary contributions to the microwave dielectric properties were dominated by ionic polarization compared to electronic polarization [45]. On the other hand, the theoretical quality factor was fitted to be 153,000 GHz, which was much higher than the measured $Q \times f$ value (112,700 GHz). The deviation can be related to the processing parameters, e.g., the density, pore, and grain

size. However, the fitting results indicate that there is still a wide space for dielectric properties optimization in the $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ceramic system.

To further investigate the intrinsic dielectric properties of $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ceramics, the IR reflectivity spectrum of $x = 0.3$ sample as a representative was fitted using a classical harmonic oscillator modeled as follows [46,47]:

$$R(\omega) = \left| \frac{\sqrt{\epsilon^*(\omega)} - 1}{\sqrt{\epsilon^*(\omega)} + 1} \right|^2 \quad (4)$$

$$\begin{aligned} \epsilon^*(\omega) &= \epsilon'(\omega) - i\epsilon''(\omega) \\ &= \epsilon_\infty + \sum_{j=1}^n \frac{S_j(\omega_j^2 - \omega^2)}{(\omega_j^2 - \omega^2)^2 + \omega^2\gamma_j^2} - \\ &\quad i \sum_{j=1}^n \frac{S_j\omega\gamma_j}{(\omega_j^2 - \omega^2)^2 + \omega^2\gamma_j^2} \end{aligned} \quad (5)$$

where n represents the order of transverse polar-phonon modes; ω_j , S_j , and γ_j are the frequency, strength, and damping constant of the j -th mode, respectively; and ϵ_∞ is the relative permittivity caused by electronic polarization. When $\omega \ll \omega_j$, Eqs. (6) and (7) are reasonable:

$$\epsilon'(\omega) = \epsilon_\infty + \sum_{j=1}^n \Delta\epsilon'_j = \epsilon_\infty + \sum_{j=1}^n \frac{\omega_{pj}^2}{\omega_{oj}^2} \quad (6)$$

$$\epsilon''(\omega) \approx \sum_{j=1}^n \frac{\omega_{pj}^2 \gamma_j}{\omega_{oj}^2 \omega} \quad (7)$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \sum_{j=1}^n \frac{S_j \omega \gamma_j}{\epsilon'(\omega) \omega_j^4} \quad (8)$$

Table 3 shows some spinel-type ceramics with their optimum sintering temperatures and microwave dielectric

Fig. 7 (a) Measured and calculated infrared reflectivity spectra and (b) real and imaginary parts of the complex responses obtained from the fitting of the IR reflectivity spectra.

Table 2 Phonon parameters obtained from the fitting of the infrared reflectivity spectra of the $x = 0.3$ ($\text{Zn}_{1.3}\text{Ga}_{1.4}\text{Ge}_{0.3}\text{O}_4$) ceramic

Mode	ω_b (cm^{-1})	ω_p (cm^{-1})	γ (cm^{-1})	$\Delta\epsilon$
1	170.75	193.68	8.5044	0.0498
2	295.9	184.81	17.352	0.0586
3	303.46	421.36	25.86	4.86
3	319.48	495.07	19.321	0.0605
4	385.02	850.98	28.244	0.0734
5	388	384.05	45.511	0.117
6	424.26	794.84	32.95	3.54
6	466.15	302.07	133.26	0.286
7	571.74	465.29	102.63	0.18
		$\epsilon_\infty = 1.92$	$\epsilon_r = 9.22$	

Table 3 Sintering temperature and microwave dielectric properties of some spinel-type ceramics

Composition	Sintering temperature ($^{\circ}\text{C}$)	Microwave dielectric properties			Ref.
		ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/ $^{\circ}\text{C}$)	
MgAl_2O_4	1600	7.8	85,100	-59.2	[8]
Mg_2TiO_4	1450	14	150,000	-50	[10]
CoZnTiO_4	1200	17.31	97,571	-36.4	[11]
ZnGa_2O_4	1385	10.4	94,600	-27	[12]
MgGa_2O_4	1410	9.54	117,000	-4	[48]
$\text{Li}_2\text{ZnTi}_3\text{O}_8$	1075	26.8	83,000	-12.4	[49]
$\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$	1250–1340	9.78–10.42	94,500–112,700	(-75.6)–(-66.3)	This work

Table 4 Microwave dielectric properties of $(1-y)\text{Zn}_{1.3}\text{Ga}_{1.4}\text{Ge}_{0.3}\text{O}_4-y\text{TiO}_2$ ceramics sintered at their optimum sintering temperature

y	Sintering temperature ($^{\circ}\text{C}$)	Microwave dielectric property		
		ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/ $^{\circ}\text{C}$)
0.1	1260	11.3	109,400	-52.3
0.2	1260	12.8	105,900	-25.8
0.3	1270	14.7	101,800	+6.1
0.4	1270	17.7	97,200	+42.5

properties. Compared with the parent ZnGa_2O_4 , the $Q \times f$ value increased by 19.1% after Zn/Ge co-doping, whereas the temperature stability of the resonance declined. Commonly, the listed spinels possess low relative permittivity and high quality factor, rendering their potential applications in high-speed signal propagation fields. However, the negative τ_f values signify minor thermal drift of resonance frequency, which largely imposes a limit to their commercial promotion. To adjust the τ_f values of the present spinels, we have adopted TiO_2 as an τ_f compensator to form composite ceramics with $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$. As represent, a series of compositions of $(1-x)\text{Zn}_{1.3}\text{Ga}_{1.4}\text{Ge}_{0.3}\text{O}_4$ ($x = 0.3$)- $x\text{TiO}_2$ ($x = 0.1, 0.2, 0.3, 0.4$) are arranged.

Figure 8 shows the XRD, SEM, and EDS recorded on the representative $0.7\text{Zn}_{1.3}\text{Ga}_{1.4}\text{Ge}_{0.3}\text{O}_4-0.3\text{TiO}_2$ composite fired at 1270°C for 6 h. XRD profiles demonstrate only the diffraction peaks from the spinel phase and rutile (JCPDS#01-1292), with no other phase detected, suggesting no chemical reaction occurred between them. SEM images featured distinct grains with different sizes, morphologies, and elemental contrasts. Upon conducting EDS analysis on different grains, the small bright grains (marked with #) were rich in Ti and Zn/Ge/Ga were not identified. As a result, it was concluded that the marked grains were TiO_2 . These results provide evidence for the chemical compatibility between TiO_2 and $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$, which is a prerequisite for property modulation.

As expected, TiO_2 successfully tuned the negative τ_f value of the representative $x = 0.3$ sample to close to zero (+6.1 ppm/ $^{\circ}\text{C}$) when adding 30 mol% TiO_2 . Meanwhile, with the increasing TiO_2 content, the relative permittivity gradually increased to 17.7 while the quality factor decreased to 97,200 GHz, which was reasonable in consideration of the high relative permittivity and low quality factor of TiO_2 ceramic ($\epsilon_r \approx 105$ and $Q \times f \approx 46,000$ GHz) [50].

Fig. 8 (a) XRD patterns and (b) SEM of $0.7\text{Zn}_{1.3}\text{Ga}_{1.4}\text{Ge}_{0.3}\text{O}_4-0.3\text{TiO}_2$ ceramic sintered at $1270\text{ }^\circ\text{C}$ for 6 h (the EDS analysis of TiO_2 is shown in the inset).

4 Conclusions

In summary, lowered sintering temperature and improved dielectric properties are simultaneously achieved by introducing $\text{Zn}^{2+}/\text{Ge}^{4+}$ to substitute Ga^{3+} in the ZnGa_2O_4 system. Solid solutions with a normal spinel structure were successfully synthesized in the whole composition range with $0.1 \leq x \leq 0.5$. Combined microwave dielectric properties with $\epsilon_r \approx 10.09$, $Q \times f \approx 112,700\text{ GHz}$, and $\tau_f \approx -75.6\text{ ppm}/^\circ\text{C}$ were obtained in a composition with $x = 0.3$ when sintered at $1280\text{ }^\circ\text{C}$. The thermal stability of resonance frequency was achieved through the formation of ceramic composite with TiO_2 . A near-zero τ_f value was achieved in $x = 0.3$ sample with 30 mol% TiO_2 and achieved dielectric values of $\epsilon_r \approx 14.7$ and $Q \times f \approx 101,800\text{ GHz}$. All the merits demonstrated that the $\text{Zn}_{1+x}\text{Ga}_{2-2x}\text{Ge}_x\text{O}_4$ ceramic is a promising candidate for high-speed signal propagation applications.

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Electronic Supplementary Material

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