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Research Article

Interlocking layered $\text{Li}_2\text{Si}_2\text{O}_5$: A novel low-permittivity microwave dielectric ceramic with superior dielectric and mechanical properties

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Abstract: Achieving low relative permittivity (ϵ_r) together with high mechanical reliability remains a key challenge for low-temperature co-fired ceramic (LTCC) substrates used in high-frequency communication and electronic packaging. Herein, single-phase $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics with a stable crystal framework and an interlocked layered microstructure are developed as low-permittivity LTCC substrate candidates. Their microwave and terahertz dielectric properties and mechanical performance are systematically investigated for the first time. The $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic sintered at 960 °C exhibits a low ϵ_r (4.86 ± 0.01), high quality factor ($Q \times f = 105,420 \pm 366$ GHz at 19.5 GHz and 175,131 GHz at 1 THz), and a moderate temperature coefficient of resonant frequency ($\tau_f = -24.84 \pm 1.0$ ppm/°C). Meanwhile, it achieves a hardness of 8.34 ± 0.05 GPa, a flexural strength of 320.72 ± 5.0 MPa, and a fracture toughness of 2.49 ± 0.06 $\text{MPa} \cdot \text{m}^{1/2}$, demonstrating its robust mechanical reliability. Furthermore, based on the P-V-L theory, the structure–property relationship between chemical bonding parameters and dielectric response is established. The ionicity of Li-O bonds is found to primarily govern ϵ_r , whereas the covalent character of Si-O bonds plays a dominant role in reducing intrinsic dielectric loss and regulating temperature stability, providing a theoretical basis for performance optimization. To further assess practical applicability, a 2.45 GHz microstrip patch antenna is designed using $\text{Li}_2\text{Si}_2\text{O}_5$ +1 wt% LiF ceramic as the substrate. The simulated antenna possesses a high radiation efficiency of 90.64%, a gain of 5.60 dBi, and good impedance matching. These results confirm that $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics offer a promising combination of low ϵ_r , low loss, and mechanical robustness for high-frequency electronic packaging and Internet of Things (IoT) devices.

Keywords: $\text{Li}_2\text{Si}_2\text{O}_5$, interlocking layered structure, microwave dielectric ceramics, low-permittivity, high flexural strength, microstrip patch antenna.

1 Introduction

The widespread deployment of 5G and the emergence of 6G technologies are driving microwave electronic components toward higher frequencies, miniaturization, multifunctional integration, and improved reliability [1-4]. These trends impose increasingly stringent demands on microwave dielectric ceramics for passive devices. Low-temperature co-fired ceramic (LTCC) technology, which enables low-temperature sintering, multilayer integration, and compatibility with Ag or Cu electrodes, has become a key platform for advanced microwave components [5-8].

For LTCC applications, microwave dielectric ceramics generally require a low permittivity (ϵ_r), an ultralow dielectric loss ($\tan\delta$) or a high-quality factor ($Q \times f$), and a near-zero temperature coefficient of resonant frequency (τ_f). These properties are essential for reducing signal delay, enhancing frequency selectivity, and maintaining thermal stability [9,10]. Additionally, practical LTCC materials should possess a low sintering temperature, high mechanical reliability, and a coefficient of thermal expansion compatible with those of electrodes [11,12]. However, dielectric performance, densification behavior, mechanical strength, and thermal matching are strongly coupled, making their simultaneous optimization highly challenging [5]. Therefore, developing new low- ϵ_r LTCC ceramics with well-balanced comprehensive properties remains a key issue for next-generation communication systems.

Silicate-based microwave dielectric ceramics are attractive candidates because their highly covalent $[\text{SiO}_4]$ tetrahedral frameworks generally exhibit low ϵ_r and $\tan\delta$ [13]. Meanwhile, their structural diversity, chemical stability, and environmental friendliness further support them as suitable for high-frequency applications. Depending on the connectivity of $[\text{SiO}_4]$ tetrahedra, silicates can be classified into isolated, chain, ring, and layered structures. Among them, isolated and chain silicates, such as Mg_2SiO_4 , Zn_2SiO_4 , $\text{CaMgSi}_2\text{O}_6$, and MgSiO_3 , have been widely investigated owing to their low ϵ_r and high $Q \times f$ values [14-17]. Nevertheless, most conventional silicate ceramics require high sintering temperatures ($> 1300\text{ }^\circ\text{C}$), large negative τ_f values, and difficulty in obtaining single-phase compositions. Although ionic substitution, sintering aids, and compositional regulation have been

employed to improve densification and dielectric properties, achieving an optimal balance among these multidimensional requirements remains a formidable challenge. Recently, Li-containing silicates, including Li_2MSiO_4 ($M = \text{Mg, Zn, Ca, Sr}$) and Li_2SiO_3 , have emerged as promising candidates for overcoming these limitations [18-22]. The incorporation of Li can markedly reduce the sintering temperatures of silicate ceramics by 200–500 °C compared with conventional systems, and enables densification without glass additives. Sintering temperatures and microwave dielectric properties of representative silicate-based ceramics are summarized in Table S1. Moreover, analyses based on the Phillips-Van Vechten-Levine (P-V-L) theory suggest that Si–O bonds dominate the dielectric response of silicate ceramics [21]. Therefore, Li-based silicates containing abundant $[\text{SiO}_4]$ structural units offer an appealing platform for designing low- ϵ_r , low-loss LTCC microwave dielectric ceramics.

In this context, $\text{Li}_2\text{Si}_2\text{O}_5$ may be expected to be a promising LTCC candidate because of its layered structure, high fraction of $[\text{SiO}_4]$ tetrahedra, and the presence of the low-melting-point Li element. Moreover, $\text{Li}_2\text{Si}_2\text{O}_5$ is well known for forming interlocking rod-like or needle-like microstructures, which can effectively enhance mechanical strength and fracture toughness, thereby improving ceramic processability and device reliability [23,24]. Despite these advantages, previous studies on $\text{Li}_2\text{Si}_2\text{O}_5$ have mainly focused on glass-ceramics and dental restorative materials. In these applications, $\text{Li}_2\text{Si}_2\text{O}_5$ is typically introduced as a crystalline precipitate, glass powders, whiskers, or fiber reinforcement, where the research focus is mainly related to crystallization behavior, mechanical strengthening mechanisms, biocompatibility, and phase evolution in glass matrices [25-28]. However, the intrinsic microwave dielectric response of $\text{Li}_2\text{Si}_2\text{O}_5$ as a microwave dielectric ceramic remains largely unexplored. Meanwhile, the relationship between its layered crystal structure, chemical bonding characteristics, and microwave dielectric performance has not yet been systematically established. Another critical challenge is the preparation of high-purity $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. Existing synthesis routes, including sol-gel, combustion synthesis, and conventional reaction sintering methods, often suffer from incomplete phase transformation and the formation of secondary phases such as

Li_2SiO_3 and SiO_2 . This difficulty may be associated with the multistep reaction process between Li_2CO_3 and SiO_2 , where limited diffusion kinetics, local compositional fluctuation, and the formation of a $\text{Li}_2\text{Si}_2\text{O}_5$ phase layer can hinder the complete consumption of the intermediate phase during sintering [29,30]. The residual secondary phases are undesirable for LTCC applications because they may deteriorate dielectric performance and structural reliability. For instance, Li_2SiO_3 exhibits a relatively low $Q \times f$ value (30,500 GHz) and a large negative τ_f (-40.95 ppm/ $^{\circ}\text{C}$), while residual SiO_2 may increase dielectric loss and weaken mechanical reliability [21]. Therefore, developing an effective synthesis strategy to achieve single-phase $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics is essential for revealing their intrinsic structure-property relationships.

Herein, single-phase $\text{Li}_2\text{Si}_2\text{O}_5$ microwave dielectric ceramics were successfully prepared through a two-step solid-state reaction strategy combined with an appropriate excess SiO_2 addition. This synthesis design promotes the complete reaction between Li_2SiO_3 and SiO_2 by improving interfacial contact, maintaining sufficient reactive SiO_2 during the reaction, and reducing diffusion-related limitations. Based on the obtained single-phase ceramics, the crystal structure, microwave dielectric properties, and mechanical performance were systematically investigated. Furthermore, the intrinsic structure-property relationship was elucidated by correlating chemical bonding characteristics, layered crystal topology, and microstructural features with the dielectric properties. The combined effects of the rigid Si–O framework and the layered structure on dielectric polarizability and loss suppression were revealed. Owing to their low ϵ_r , high mechanical strength, lightweight characteristics, and interlocking rod-like microstructure, $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics are promising LTCC materials for advanced communication applications.

2 Experimental

2.1 Material synthesis

Three different synthesis strategies were investigated to obtain high-purity $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. The detailed experimental procedures of Schemes I and II are provided in the Electronic

Supplementary Material (ESM). Among them, scheme III was prepared via a two-step solid-state reaction route combined with a slight SiO₂ compensation method. First, high-purity Li₂CO₃ (99.5%, Macklin) and SiO₂ (99.99%, Macklin) powders were weighed according to the stoichiometric ratio and ball-milled at 300 rpm for 4 h using zirconia balls with anhydrous ethanol as the milling medium. The resulting slurry was dried at 80 °C to remove the solvent, and subsequently calcined at 800 °C for 3 h to obtain single-phase Li₂SiO₃ powder. The as-prepared Li₂SiO₃ powder was then mixed with SiO₂ in a non-stoichiometric ratio containing 2 wt% excess SiO₂, followed by the same ball-milling and drying procedures. The mixed powders were calcined at 900 °C for 6 h. After calcination, the powders were crushed, ground, and re-milled under identical conditions. A 5 wt% polyvinyl alcohol (PVA) solution was added as a binder for granulation. Granules with particle sizes in the range of 80–120 mesh were selected and uniaxially pressed at 200 MPa into cylindrical green bodies (10 mm in diameter and 6 mm in height). The green bodies were heated at 550 °C for 2 h to remove the binder, and then sintered at 940–1020 °C for 4 h to obtain dense Li₂Si₂O₅ ceramic samples.

2.2 Material characterizations

Phase composition was characterized by X-ray diffractometer (XRD, SmartLab 9 kW, Rigaku, Japan). Rietveld refinement was performed using the FullProf software, and the corresponding electron density Fourier maps were visualized with the GFourier 04.06 program. Raman spectra were obtained using a confocal micro-Raman spectrometer (inVia, Renishaw, UK) with a 532 nm excitation laser. Surface morphology of ceramics was observed through scanning electron microscopy (SEM, Gemini 300, Zeiss, Germany). Before SEM observation, the ceramics were polished, cleaned, and thermally etched at a temperature 50 °C below their respective sintering temperature for 30 min. Nano Measure 1.2 software was used to measure the grain dimensions from SEM images, and more than 100 grains were statistically analyzed for each sample. High-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were acquired using a transmission electron microscope (JEM-F200, JEOL, Japan). Additionally, single-crystal electron

diffraction simulations were conducted using SingleCrystal software. Geometric phase analysis (GPA) was carried out using Strain++ software.

The ε_r and $Q \times f$ of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics in the microwave frequency range were measured with an Agilent vector network analyzer (870ES, Agilent, USA) based on the Hakki-Coleman method, and the τ_f was determined between 25 °C and 85 °C in a temperature chamber, with the calculation formula as follows:

$$\tau_f = \frac{(f_{85} - f_{25})}{(85 - 25)f_{25}} \times 10^6 \quad (1)$$

where f_{25} and f_{85} are the resonant frequencies at temperatures of 25 °C and 85 °C, respectively. The time-domain spectrum (TDS) of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics was measured using a terahertz time-domain spectrometer system (Z3, Zomega Terahertz Corp., USA). The TDS signals were then converted into frequency-domain spectra (FDS) via fast Fourier transform (FFT) to obtain the amplitude and phase information. The optical parameters can be calculated using the following equations [31,32]:

$$\varphi_s - \varphi_r = \frac{(n-1)\omega d}{c} + \arctan \frac{k(-n^2 + 1 - k^2)}{n(n+1)^2 + (n+2)k^2} \quad (2)$$

$$A_s / A_r = \frac{4\sqrt{(n^2 + k^2)}}{(n+1)^2 + k^2} e^{-k\omega d/c} \quad (3)$$

where φ_s and φ_r represent the phase information of the sample and reference signals, respectively, while A_s and A_r denote their corresponding amplitudes. n and k correspond to the real and imaginary parts of the refractive index. d , c , and ω are the sample thickness, the speed of light in vacuum, and the angular frequency, respectively. Furthermore, the complex permittivity and dielectric loss of the ceramics can be calculated as follows:

$$\varepsilon' = n^2 - k^2 \quad (4)$$

$$\varepsilon'' = 2nk \quad (5)$$

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{2nk}{n^2 - k^2} \quad (6)$$

where ε' and ε'' are the real part (the relative dielectric constant) and the imaginary part of the complex permittivity, respectively, while $\tan\delta$ is the dielectric loss tangent. The linear coefficient of thermal expansion (CTE) was measured using a dilatometer (DIL 402SE, Netzsch, Germany). The load-displacement curves were measured using a nanoindenter (G200, Keysight, USA) operated in static indentation mode with a load of 50 mN. Three-point bending tests were performed on bar-shaped specimens (30 mm × 3 mm × 4 mm) with a support span of 20 mm and a displacement rate of 0.2 mm min⁻¹. Fracture toughness was evaluated by the single-edge notched beam (SENB) method. The specimen dimensions were 20 mm × 2 mm × 4 mm, with a notch width of approximately 0.2 mm and a notch depth of approximately 1 mm. The span length was 16 mm, and the loading rate was 0.05 mm min⁻¹. The fracture toughness K_{IC} was calculated according to Eqs. (7) and (8) [33]:

$$K_{IC} = \frac{FL}{bt^2} f\left(\frac{a}{t}\right) \quad (7)$$

$$f\left(\frac{a}{t}\right) = \frac{3\left(\frac{a}{t}\right)^{0.5} \left\{ 1.99 - \frac{a}{t} \left(1 - \frac{a}{t}\right) \left[2.15 - 3.93 \frac{a}{t} + 2.7 \left(\frac{a}{t}\right)^2 \right] \right\}}{2 \left(1 + 2 \frac{a}{t}\right) \left(1 - \frac{a}{t}\right)^{\frac{3}{2}}} \quad (8)$$

where F is the maximum fracture force in terms of Newton, L is the length of the span in millimeters, a is the formed crack length on the samples in mm, b is the thickness of the sample, and t is the width of the samples in millimeters. At least three parallel samples were tested for each condition, and the mechanical properties are presented as the mean value $\pm$ standard deviation. Additionally, the microstrip patch antenna was simulated using Ansys HFSS finite element simulation software, specifically employing the time-domain solver.

3 Results and discussion

To clarify the influence of different synthesis strategies on the phase evolution of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic, the powders prepared by the three strategies were systematically analyzed by thermal analysis, XRD, and Rietveld refinement. The detailed optimization process and phase evolution behavior are presented in EMS (Figs. S1-S6). The results reveal that the $\text{Li}_2\text{Si}_2\text{O}_5$ phase occurs at approximately

900 °C through a continuous reaction pathway involving Li_2CO_3 decomposition, formation of the Li_2SiO_3 intermediate phase, and subsequent reaction between Li_2SiO_3 and SiO_2 (Eqs. S1-S3), rather than a direct one-step reaction. For Scheme I, the coupled multi-step reactions resulted in insufficient interaction between Li_2SiO_3 and SiO_2 , leading to residual Li_2SiO_3 . Although Scheme II improved reaction homogeneity by pre-forming the Li_2SiO_3 intermediate, a small amount of Li_2SiO_3 remained under stoichiometric conditions, indicating that solid-state diffusion still limited the complete conversion.

Based on these results, a modified two-step synthesis strategy (Scheme III) was developed by introducing a slight excess of SiO_2 in the second reaction step. The additional SiO_2 promoted the complete conversion of Li_2SiO_3 by maintaining sufficient reactant availability during the reaction process. The effect of excess SiO_2 content was further investigated (Fig. S6). An excess of 1 wt% SiO_2 was insufficient to eliminate residual Li_2SiO_3 , whereas 2-3 wt% excess SiO_2 obtained high-purity $\text{Li}_2\text{Si}_2\text{O}_5$. Further increasing the SiO_2 content to 4 wt% led to residual SiO_2 . Therefore, 2 wt% excess SiO_2 was selected as the optimal composition. In conclusion, only Scheme III, based on a two-step, non-stoichiometric method, can produce single-phase $\text{Li}_2\text{Si}_2\text{O}_5$, whereas Schemes I and II both have residual Li_2SiO_3 phases. Therefore, all samples investigated in this work were prepared using Scheme III. As shown in Figure 1(a), all diffraction peaks of the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at various temperatures can be well indexed to orthorhombic $\text{Li}_2\text{Si}_2\text{O}_5$ with the $Ccc2$ space group (PDF#82-2396), and no detectable secondary phases are observed, indicating that single-phase $\text{Li}_2\text{Si}_2\text{O}_5$ remains stable in the sintering temperature range of 940–1020 °C. The enlarged view of the strongest diffraction peaks (Fig. 1(b)) reveals that the peak position initially shifts toward lower diffraction angles with increasing temperature, followed by a slight shift toward higher angles at 1020 °C, implying a subtle variation in the lattice parameters during sintering. Meanwhile, the (040) peak intensity gradually increases with increasing sintering temperature, which may be related to the rod-like grain morphology of $\text{Li}_2\text{Si}_2\text{O}_5$ (discussed below) and the abnormal grain growth at elevated temperatures. Although the ceramics

were finely ground before XRD measurement to reduce preferred orientation, residual orientation effects may not be completely excluded.

Rietveld refinement was further performed using FullProf to clarify the effect of sintering temperature on lattice parameters of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics (Figs. 1(c), (d), Fig. S7, and Table S2). The low reliability factors (R_{wp} and $R_p < 10\%$) and acceptable goodness-of-fit values ($\chi^2 = 1.87\text{--}2.77$), together with the excellent agreement between calculated and experimental patterns, particularly in the 2θ range of $23^\circ\text{--}26^\circ$ (Fig. 1(d)), demonstrate the reliability of the refinement results. The refined crystal structure of the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic sintered at 960°C is illustrated in Fig. 1(e). In this structure, both Li and Si atoms occupy the $8d$ Wyckoff sites, coordinating with four adjacent O atoms to form $[\text{LiO}_4]$ and $[\text{SiO}_4]$ tetrahedra, respectively. The O atoms exhibit three distinct coordination environments, with O1 and O3 occupying the $8d$ sites and O2 located at $4c$ sites (Table S3). The $[\text{LiO}_4]$ and $[\text{SiO}_4]$ tetrahedra are connected through corner-sharing oxygen atoms, constructing a three-dimensional framework with layered features. This structure belongs to the C-type $\text{Li}_2\text{Si}_2\text{O}_5$ polymorph, characterized by $\text{K}4\text{--}4 = \text{L}_2\text{T}_2$ clusters, in which two $[\text{LiO}_4]$ (L) and two $[\text{SiO}_4]$ (T) tetrahedra are arranged in an L-T-L-T sequence to form four-membered rings [34,35]. Noticeable tetrahedral distortions are observed in the refined structure, mainly arising from Li-site displacement (Fig. 1(e)). Structural refinement and comparison with the ideal model reveal that the Li displacement increases with sintering temperature (Table S4), indicating thermally activated rearrangement of Li ions and then modification of the local coordination environment. The Li displacement occurs predominantly along the crystallographic z direction, which may be associated with the layer structure of $\text{Li}_2\text{Si}_2\text{O}_5$, where Li^+ exhibits preferential mobility along the dimensional direction among corrugated $[\text{SiO}_4]$ layers [36,37]. Meanwhile, anisotropic variations in Li–O bond lengths induce distortion of the $[\text{LiO}_4]$ tetrahedra, as evidenced by the variation in the $\angle\text{O1(3)–Li–O2}$ bond angles. The adjacent $[\text{SiO}_4]$ tetrahedra undergo cooperative rotations to accommodate the local Li-site perturbation, whereas the relatively small variation in the $\angle\text{O2(2)–Si–O3}$ bond angle reflects the intrinsic rigidity of the silicate

framework. These results demonstrate that the $\text{Li}_2\text{Si}_2\text{O}_5$ lattice achieves a balance between local structural adaptability and overall framework stability. Additionally, Fig. 1(f) displays the two-dimensional Fourier electron density map of the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic sintered at 960 °C, which visually reveals the chemical bonding characteristics of the crystal structure. Densely packed, nearly circular contours are observed around Si atoms, while slight nonspherical distortions appear at O atoms due to the directional Si–O bonding in $[\text{SiO}_4]$ tetrahedra. By contrast, the electron density around Li atoms is much weaker and more diffuse, reflecting its lower valence electron configuration [38]. Moreover, continuous electron density distribution between Si and O atoms demonstrates significant electron sharing, confirming the strong covalent contribution of the Si–O framework. Conversely, the lack of electron density overlap between Li and O atoms suggests that Li–O interactions are predominantly ionic. Thus, the coexistence of a covalently bonded Si–O network and ionically incorporated Li^+ ions contributes to the structural stability of the $\text{Li}_2\text{Si}_2\text{O}_5$ framework.

The Raman spectra and corresponding peak-fitting results further verify the structural stability of the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics, as shown in Figs. 1(g), (h), and Fig. S8. The nearly identical spectral profiles and the absence of anomalous peaks indicate that no phase transitions occur during sintering. The variations in peak intensity can be related to differences in crystallinity and grain size at different sintering temperatures. According to group theory, orthorhombic $\text{Li}_2\text{Si}_2\text{O}_5$ with the $Ccc2$ space group (point group $mm2$) has 54 theoretical vibrational modes [39]. However, only 25 experimentally distinguishable modes can be resolved after Gaussian-Lorentzian deconvolution, which is likely due to the limited spectral resolution and the overlap of closely spaced vibrational modes [40,41]. The modes in the 150–1200 cm^{-1} range can be categorized into lattice, bending, and stretching vibrations. Among them, the dominant mode at 1107 cm^{-1} is attributed to the symmetric stretching vibration of Si–O–Si bonds in the $[\text{SiO}_4]$ tetrahedra, which is crucial for the rigidity of the silicate framework [42]. Importantly, the full width at half maximum (FWHM) of this mode is strongly correlated with the $Q \times f$ values of the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics, as detailed in Fig. 4(c).

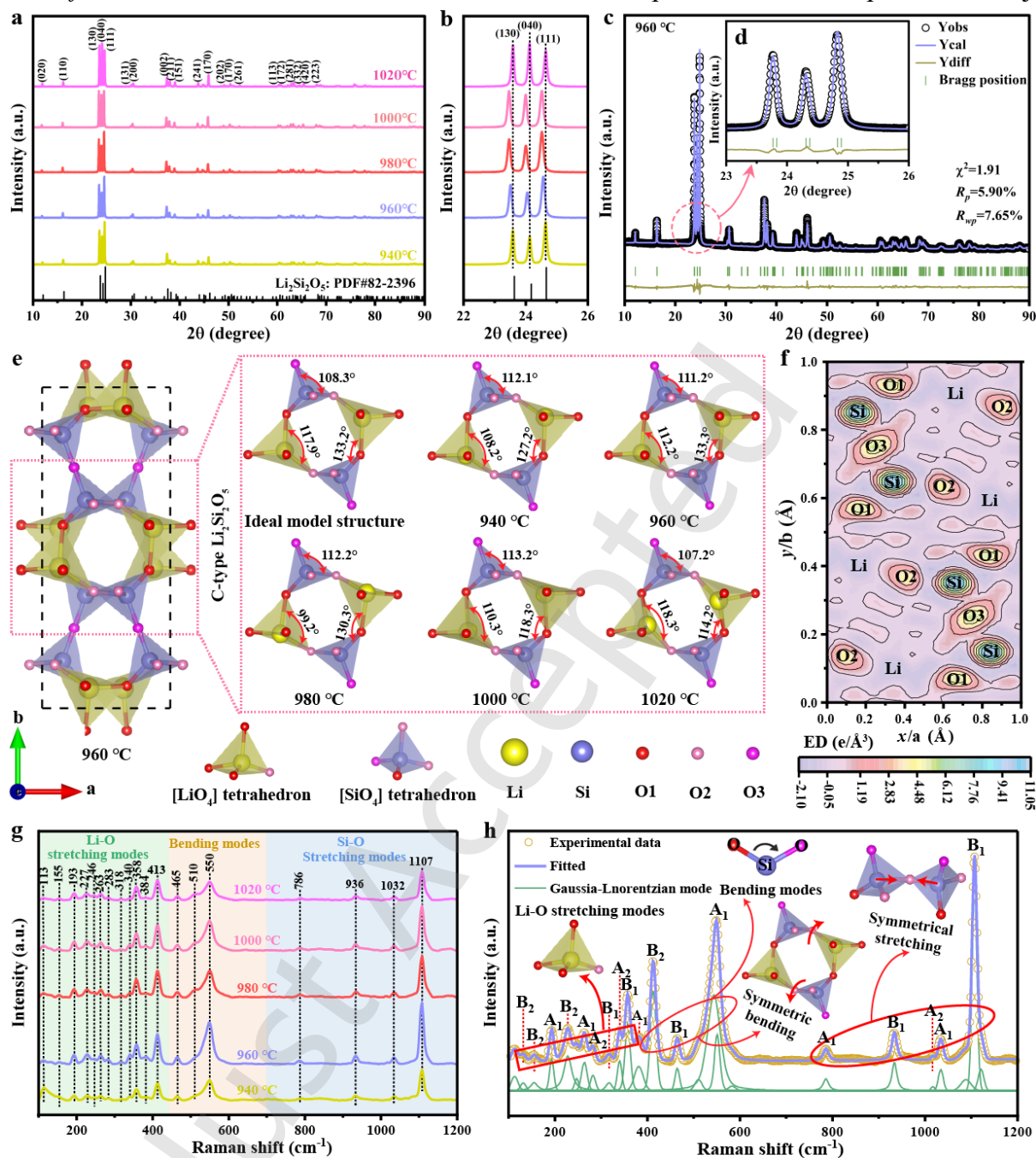


Fig.1 Structural characterization of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. (a) XRD patterns. (b) Magnified view of the 22°–26° region. (c) Rietveld refinement pattern. (d) Enlarged view of the 23°–26° region. (e) Crystal structure, highlighting the characteristic four-membered ring units. (f) 2D Fourier electron density map. (g) Raman spectra and (h) Deconvoluted Raman spectrum.

The crystal structures of the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at 960 °C and 1020 °C were further examined by selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). As shown in Figure 2(a), the SAED pattern of the sample sintered at 960 °C

along the $[010]$ zone axis exhibits sharp and well-defined diffraction spots that can be indexed to the (002) , (201) , and $(20\bar{1})$ planes of orthorhombic structure, in good agreement with the simulated pattern (Fig. 2(b)). The corresponding HRTEM image (Fig. 2(c)) shows clear lattice fringes with an interplanar spacing of $2.39 \text{ \AA}$, corresponding to the (002) plane and consistent with the calculated crystallographic value. Fast Fourier transform (FFT) analysis of the selected region (marked by the square) confirms a diffraction pattern (Fig. 2(d₁)), while the inverse FFT (IFFT) image displays highly uniform lattice fringes without obvious dislocations or lattice distortion (Fig. 2(d₂)), indicating good local crystallinity and structural integrity within the analyzed region. Moreover, geometric phase analysis (GPA) mapping (Fig. 2(e)) reveals a relatively homogeneous local strain distribution within the analyzed region, suggesting a relatively uniform lattice environment. Such a structural characteristic is beneficial for suppressing dielectric loss and enhancing the mechanical reliability of the ceramic [43,44].

In contrast, the sample sintered at 1020°C shows different local structural features. The SAED pattern along the $[\bar{1}\bar{3}8]$ zone axis displays diffraction spots indexed to the $(1\bar{3}\bar{1})$, $(3\bar{1}0)$, and (221) planes (Fig. 2(f)). The simulated pattern further validated the reliability of these indexing results (Fig. 2(g)). The HRTEM image (Fig. 2(h)) displays lattice fringes with a d -spacing of $2.32 \text{ \AA}$ for the (221) plane, while visible lattice distortions are also observed in the selected region. This is further supported by the FFT and IFFT results (Figs. 2(i₁) and 2(i₂)), where locally fluctuating and nonuniform lattice fringes can be clearly distinguished. In addition, GPA mapping (Fig. 2(j)) reveals a spatially inhomogeneous axial and shear strain distribution within the analyzed region, demonstrating the presence of local lattice distortion in the high-temperature sintered sample. Such local structural heterogeneity may originate from microstructural evolution during high-temperature sintering, including abnormal grain growth and the generation of defects. Furthermore, local strain is associated with the formation of crystal defects, such as dislocations. These defect-induced structural distortions can generate defect-related polarization and enhance phonon scattering, thereby contributing to an

increase in extrinsic dielectric loss at high sintering temperatures [43,45,46]. It should be noted that the GPA results are discussed as a qualitative assessment of the local strain distribution within each sample rather than direct quantitative comparisons.

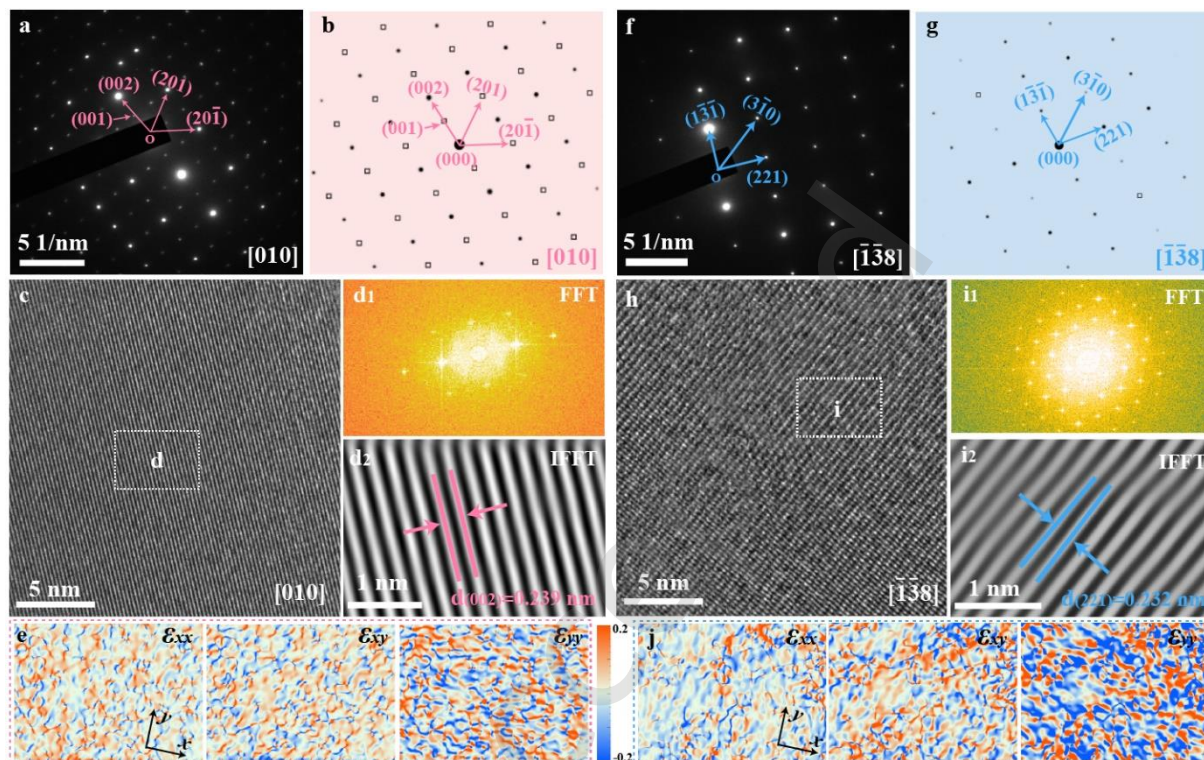


Fig.2 Structural analysis of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. SAED patterns of samples sintered at (a) 960 °C ([010] zone axis) and (f) 1020 °C ($[\bar{1}\bar{3}8]$ zone axis). (b, g) Simulated diffraction patterns for the orthorhombic *Ccc2* structure along the corresponding zone axes. HRTEM images of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic sintered at (c) 960 °C and (h) 1020 °C. (d₁, d₂, i₁, i₂) Corresponding FFT and IFFT patterns for the regions marked in (c) and (h), respectively. GPA strain maps for samples sintered at (e) 960 °C and (j) 1020 °C.

Figure 3(a-e) shows the SEM micrographs of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at 940–1020 °C after surface polishing and thermal etching. All samples exhibited rod-like grains with distinct layered features. At low sintering temperatures (≤ 960 °C), the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics present relatively uniform, dense microstructures with no obvious pores, as shown in Figs. 3(a, b). However, further increasing the sintering temperature (980–1020 °C) causes the rod-like grains to grow abnormally, reducing microstructural uniformity and forming larger gaps in some grains (Fig. 3(c-e)). Meanwhile, Fig. 3(f)

presents the violin plots of grain dimensions for $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at various temperatures.

The width of the shaded regions reflects the kernel density distribution of grain dimensions within different size ranges. With increasing sintering temperature, the width of rod-like grains increased from $1.12 \pm 0.1 \mu\text{m}$ to $5.38 \pm 0.2 \mu\text{m}$, while the length showed more pronounced growth. This demonstrates that grain growth in $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics is highly sensitive to sintering temperature, with the tendency for abnormal grain growth progressively intensifying at higher temperatures. Notably, small grains were observed on the sample surfaces. Generally, possible reasons for small grain formation include insufficient sintering temperature or time, excessive cooling rate, compositional inhomogeneity, or anisotropic crystal growth. However, EDS analysis (Fig. S9) confirmed identical atomic ratios in both large and small grains, ruling out compositional inhomogeneity as the underlying cause [41,47]. At 1020 °C, a noticeable molten phase appeared at grain boundaries, leading to a reduction in bulk density.

To further elucidate the layered structure, cross-sectional SEM images of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at different temperatures are presented in Fig. S10. The ceramics exhibit an interlocked layered structure composed of interconnected $\text{Li}_2\text{Si}_2\text{O}_5$ crystal networks. This unique structure is expected to enhance mechanical performance and inhibit crack propagation, thereby achieving a synergistic improvement in strength and toughness. Based on combined surface and cross-sectional observations, Fig. 3(g) proposes a three-stage formation mechanism for rod-like layered $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics: (i) Nucleation: Li_2SiO_3 initially forms from Li_2CO_3 and SiO_2 precursors, then rapidly reacts with residual SiO_2 to generate nanoscale $\text{Li}_2\text{Si}_2\text{O}_5$ nuclei; (ii) Grain growth: Nanoscale nuclei gradually grow into submicron rod-like grains; and (iii) Oriented self-assembly: Rod-like grains undergo oriented self-assembly to further form an interconnected layered structure, ultimately yielding microscale rod-like morphologies with layered characteristics.

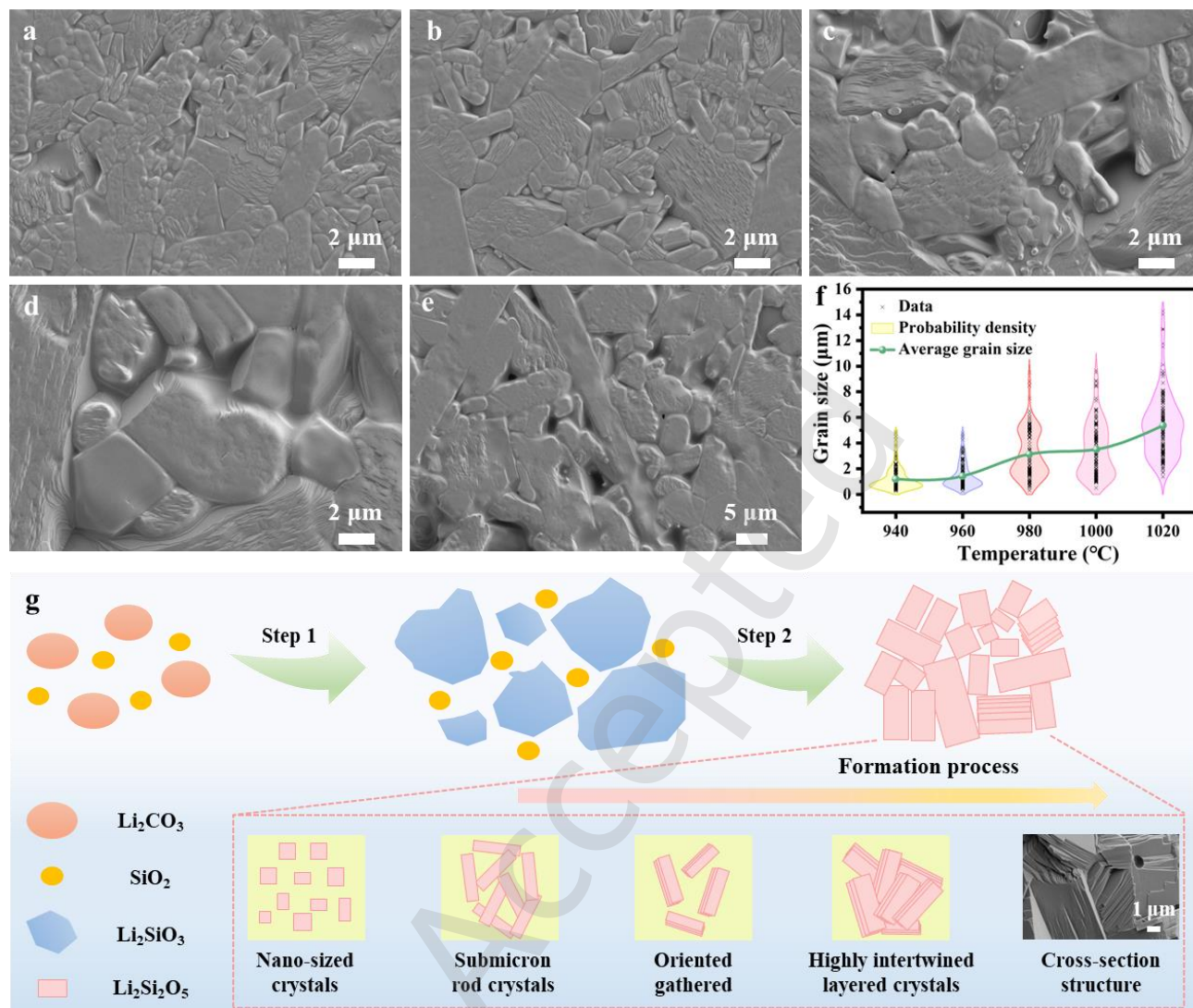


Fig.3 Local morphologies and formation process of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. SEM images of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics at various temperatures: (a) 940 °C, (b) 960 °C, (c) 980 °C, (d) 1000 °C, and (e) 1020 °C. (f) The grain size distribution of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. (g) The formation process of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic during sintering.

It is well known that microwave dielectric properties are collectively determined by intrinsic factors (ionic polarizability, lattice energy, and packing fraction) and extrinsic factors (porosity, grain size, and secondary phases) [5,48,49]. To clarify the effect of sintering temperature on the dielectric properties of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics, Figure 4 shows the evolution of microwave and terahertz dielectric properties as a function of sintering temperature. Densification behavior is a key extrinsic factor affecting dielectric performance. As illustrated in Fig. 4(a), the bulk density increased from $2.35 \pm$

0.01 g/cm³ to 2.38 ± 0.01 g/cm³, accompanied by an increase in relative density from 96.22% to 97.47%

when the sintering temperature increased from 940 °C to 960 °C. This densification process is mainly attributed to grain growth, gradual pore elimination, and improved microstructural uniformity during sintering. However, further increasing the sintering temperature to 1020 °C resulted in abnormal grain growth and the formation of closed pores, which restricted further densification and decreased the bulk density and relative density to 2.32 ± 0.01 g/cm³ and 94.78%, respectively. The ϵ_r exhibits only a slight variation over the entire sintering range, but follows a trend highly consistent with that of the relative density (Fig. 4(b)). Specifically, ϵ_r increases from 4.80 ± 0.02 to 4.86 ± 0.01 as the temperature rises from 940 °C to 960 °C, and then decreases to 4.72 ± 0.02 at 1020 °C. This behavior confirms that porosity is the dominant extrinsic factor influencing ϵ_r . To eliminate the porosity effect, the corrected dielectric constant (ϵ_{corr}) was calculated using the Bosman and Havinga correction equation [50]:

$$\epsilon_{corr} = \epsilon_r (1 + 1.5P) \quad (9)$$

where P is the porosity fraction. As depicted in Fig. 4(b), ϵ_{corr} is consistently higher than ϵ_r over the entire sintering temperature range, indicating the dielectric-dilution effect of pores. The smallest deviation between ϵ_{corr} and ϵ_r , approximately 3.73%, is observed for the sample sintered at 960 °C, corresponding to its lowest porosity and highest relative density. To further evaluate the contribution of intrinsic factors, the theoretical dielectric constant (ϵ_{theo}) was calculated using the Clausius-Mossotti equation [51]:

$$\epsilon_{theo} = \frac{3V_m + 8\pi\alpha}{3V_m - 4\pi\alpha} \quad (10)$$

where V_m is the unit cell volume, and α represents the total ionic polarizability per chemical formula unit. For Li₂Si₂O₅ ceramics, α_{theo} can be estimated according to the additive ionic polarizability rule:

$$\alpha_{theo} (Li_2Si_2O_5) = 2\alpha(Li^+) + 2\alpha(Si^{4+}) + 5\alpha(O^{2-}) \quad (11)$$

where $\alpha(Li^+) = 1.20 \text{ \AA}^3$, $\alpha(Si^{4+}) = 0.87 \text{ \AA}^3$, and $\alpha(O^{2-}) = 2.01 \text{ \AA}^3$ [52]. The ϵ_{theo} values fluctuate only slightly within the range of 5.20–5.23 for ceramics sintered between 940 and 1020 °C, and are slightly

higher than both ϵ_r and ϵ_{corr} . This discrepancy is mainly attributed to the "Compression" effect of Li^+ ions, which reduces the observed molecular polarizability ($13.93\text{--}14.00 \text{ \AA}^3$) by approximately 13–18% (Table 1) relative to the theoretical value of $14.19 \text{ \AA}^3$ calculated using the oxide additivity rule. Thus, the ϵ_{theo} is enhanced by 2.53–3.45% compared to the ϵ_{corr} due to Shannon's overestimation of the Li^+ polarizability. Similar deviations have also been reported in $(\text{Ce}_{1-x}\text{Ca}_x)(\text{Nb}_{1-x}\text{W}_x)\text{O}_4$ ceramics [53]. The nearly constant ϵ_{theo} values indicated that the intrinsic polarizability per unit volume is essentially unchanged at 940–1020 °C, which is consistent with the stable orthorhombic $\text{Li}_2\text{Si}_2\text{O}_5$ structure revealed by XRD, Raman, and TEM analyses. These results further demonstrate that the variation in ϵ_r value with sintering temperature is governed mainly by densification behavior rather than ion polarizability.

Table 1 Dielectric constant (ϵ_r), theoretical permittivity (ϵ_{theo}), porosity-corrected permittivity (ϵ_{corr}), deviation between ϵ_{theo} and ϵ_{corr} (Δ), observed molecular polarizability (α_{obs}), effective Li^+ polarizability (α_{Li^+}), and the deviation from Shannon ionic polarizability (Δ_{Li^+}) for $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at various temperatures

<i>S.T.</i> (°C)	ϵ_r	ϵ_{theo}	ϵ_{corr}	Δ (%)	α_{obs}	α_{Li^+}	Δ_{Li^+} (%)
940	4.80 ± 0.02	5.2294	5.075	2.95	13.971	1.090	9.14
960	4.86 ± 0.01	5.2016	5.045	3.02	13.964	1.087	9.40
980	4.79 ± 0.03	5.2015	5.070	2.53	14.001	1.106	7.86
1000	4.72 ± 0.01	5.2006	5.021	3.45	13.931	1.071	10.79
1020	4.71 ± 0.02	5.2322	5.075	3.00	13.967	1.089	9.29

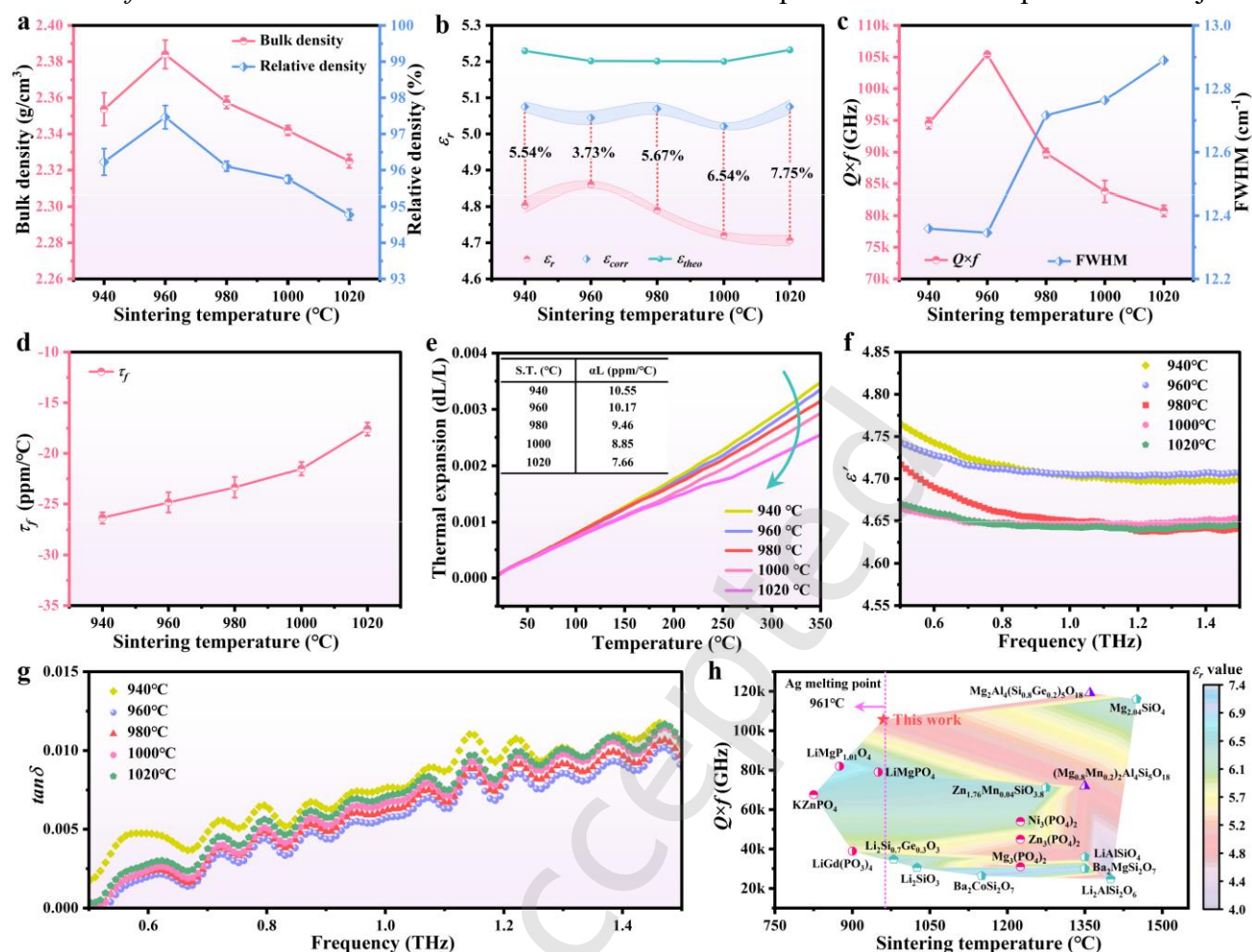


Fig.4 Microwave and terahertz dielectric properties of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic. (a) Bulk density and relative density. (b) ϵ_r , ϵ_{corr} , and ϵ_{theo} . (c) $Q \times f$ value and FWHM of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics with rising sintering temperature. (d) Curves of τ_f variation with sintering temperature. (e) The thermal expansion behavior of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. (f) The ϵ' and (g) $\tan \delta$ in the terahertz band of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. (h) Comparison of the properties of low ϵ_r microwave dielectric ceramics ($\epsilon_r < 8$).

Fig. 4(c) displays the correlation between the $Q \times f$ values and the FWHM of the characteristic Raman peaks for $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at various temperatures. As aforementioned, the strong Raman vibration peak at 1107 cm⁻¹ corresponds to Si–O stretching vibrations in the $[\text{SiO}_4]$ -based framework and is closely related to the rigidity of the silicate tetrahedral network. Therefore, the FWHM of this vibrational mode was selected as a sensitive structural descriptor to establish the relationship between local structure and microwave dielectric loss. Notably, the $Q \times f$ values exhibit a

significant negative correlation with the FWHM of the peak at 1107 cm^{-1} , first increasing and then decreasing as the sintering temperature increases, reaching a maximum of $105,420 \pm 366\text{ GHz}$ for the sample sintered at $960\text{ }^{\circ}\text{C}$. This variation trend can be explained by lattice-vibrational damping theory, in which the relationships among FWHM, $\tan\delta$, and the damping coefficient (γ) can be expressed as [22,54]:

$$FWHM = \frac{\gamma\sqrt{\gamma^2 + 4\omega_0^2}}{2\omega_0} \quad (12)$$

$$\tan\delta \approx \frac{\gamma\omega_0}{\omega_T^2} \quad (13)$$

A lower FWHM corresponds to a sharper vibration peak, indicating a smaller lattice damping coefficient, weaker phonon scattering, and reduced microwave dielectric loss. Additionally, a low FWHM value signifies a higher degree of local structural order and fewer lattice defects. Therefore, the lowest FWHM value for the ceramic sintered at $960\text{ }^{\circ}\text{C}$ confirms suppressed lattice-vibrational damping, which contributes to its enhanced $Q \times f$ value. Packing fraction (P.F.) is another important intrinsic parameter affecting $Q \times f$ values, which can be calculated as [20]:

$$\text{Packing fraction} = \frac{\frac{4\pi}{3} \times (2r_{\text{Li}^+}^3 + 2r_{\text{Si}^{4+}}^3 + 2r_{\text{O}^{2-}}^3)}{V_{\text{cell}}} \times Z \quad (14)$$

where V_{cell} represents the unit cell volume obtained from Rietveld refinement. Z is 4 in $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic, and r denotes the ionic radius of each ion. Generally, a higher P.F. corresponds to a more densely packed crystal structure, which is beneficial for reducing energy dissipation associated with lattice vibrations and thus improving $Q \times f$. As listed in Table S5, the P.F. values of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics display a slight decrease followed by an increase with increasing sintering temperature, inconsistent with the variation trend of $Q \times f$. This discrepancy suggests that P.F. is not the dominant factor governing the $Q \times f$ values in $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. This can be attributed to the highly stable single-phase orthorhombic structure maintained throughout the entire sintering-temperature range. Only a slight

variation in unit-cell volume is observed, with a difference of merely $1.271 \text{ \AA}^3$ between the maximum and minimum values. Thus, the effect of P.F. on the $Q \times f$ value can be neglected. Similar to ϵ_r , the $Q \times f$ value is also affected by relative density, porosity, grain size, and microstructural uniformity. When the sintering temperature increased from $940 \text{ }^\circ\text{C}$ to $960 \text{ }^\circ\text{C}$, the small grains gradually grew and the residual pores were progressively eliminated, which promoted densification and improved microstructural homogeneity. The increased relative density and reduced porosity effectively decreased the scattering centers during microwave propagation, thereby reducing the extrinsic dielectric loss. Consequently, the $Q \times f$ value rose from $94,535 \pm 883 \text{ GHz}$ to $105,420 \pm 366 \text{ GHz}$. However, with a further increase in sintering temperature, the samples began to exhibit abnormal grain growth, accompanied by the formation of residual pores and deterioration of microstructural uniformity. Particularly for the sample sintered at $1020 \text{ }^\circ\text{C}$, the significant abnormal grain growth disrupted the microstructural homogeneity and enlarged gaps between grains, ultimately resulting in a decrease in the $Q \times f$ value. Meanwhile, the local distortion and inhomogeneous strain distribution revealed by HRTEM and GPA analyses further enhance dielectric loss. These synergistic effects cause a significant reduction in $Q \times f$ values to $80,764 \pm 879 \text{ GHz}$. In summary, the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic sintered at $960 \text{ }^\circ\text{C}$ achieves the optimal $Q \times f$ value due to the combination of minimum lattice damping, maximum densification, reduced porosity, and a relatively uniform microstructure.

Fig. 4(d) presents the τ_f values of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at various temperatures. As the sintering temperature increases from $940 \text{ }^\circ\text{C}$ to $1020 \text{ }^\circ\text{C}$, the τ_f value gradually shifts from -26.37 ± 0.54 to $-17.61 \pm 0.65 \text{ ppm/}^\circ\text{C}$, moving closer to zero and indicating improved resonant-frequency thermal stability. For microwave dielectric ceramics, τ_f is generally governed by the temperature coefficient of permittivity (τ_ϵ) and the linear thermal expansion coefficient (α_L), according to the following relationship [55]:

$$\tau_f = -\left(\frac{1}{2} \tau_\epsilon + \alpha_L\right) \quad (15)$$

The τ_c value is closely related to the structural characteristics, including the chemical bond strength, the distortion of the oxygen polyhedral, and temperature-induced polarization variation. Among them, the bond strength can be evaluated using the bond valence theory, as expressed in Eqs. (16) and (17) [56]:

$$V_i = \sum_j v_{ij} \quad (16)$$

$$v_{ij} = \exp\left(\frac{R_{ij} - d_{ij}}{b}\right) \quad (17)$$

where b is 0.37 Å, R_{ij} represents the bond valence parameter, and d_{ij} denotes the bond length. As shown in Table 2, as the sintering temperature increased from 940 °C to 980 °C, the bond valence values of V_{Li} and V_O gradually increased, while V_{Si} remained relatively high, indicating enhanced bonding strength between cations and oxygen anions and improved stability of the silicate framework. Stronger chemical bonding can effectively suppress thermally induced structural vibration, thereby contributing to the improvement of τ_f . However, when the sintering temperature was further increased to 1020 °C, the bond valence gradually decreased, which was inconsistent with the trend of τ_f . This phenomenon may be associated with the adjustment of the local Li-site environment, leading to the distortion of the polyhedral at elevated temperatures. To further clarify the influence of local structural distortion on τ_f , the average distortion degrees (δ) of the tetrahedra were calculated as follows [57]:

$$\delta = \frac{1}{n} \times \sum \left(\frac{d_i - d_{avg}}{d_{avg}} \right)^2 \quad (18)$$

where d_i is the bond length for a certain bond, and d_{avg} denotes the average bond length in a tetrahedron. Notably, the variation tendency of τ_f is opposite to that of oxygen tetrahedral distortion. With increasing sintering temperature, the $\delta[LiO_4]$ and $\delta[SiO_4]$ tetrahedra gradually decreased, indicating that the enhancement of local structural stability and an improvement in the τ_f value. In addition, to further evaluate the contribution of the coefficient of thermal expansion (α_L) to the τ_f variation, Fig. 4(e) displays the thermal expansion curves of $Li_2Si_2O_5$ ceramics measured from 20 to 350 °C, along

with the corresponding average coefficients of thermal expansion. For all samples, the thermal expansion strain increases progressively with increasing temperature, mainly due to the enhanced anharmonic lattice vibrations at elevated temperatures. These vibrations increase the average interatomic spacing, reflecting the intrinsic thermal expansion behavior of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. Notably, the α_L gradually decreases with increasing sintering temperature and remains within a relatively low range of 7.66–10.55 ppm/°C. According to Eq. (15), a reduced α_L can weaken the contribution of thermal expansion to the temperature-induced drift of resonant frequency, thereby facilitating the shift of τ_f toward zero. Thus, the improved τ_f value mainly originates from the enhanced bond valence, reduced tetrahedral distortion, and decreased coefficient of thermal expansion.

Table 2 Bond valence and the average tetrahedral distortion of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at different temperatures

<i>S.T.</i> (°C)	V_{Li} (v.u.)	V_{Si} (v.u.)	V_{O1} (v.u.)	V_{O2} (v.u.)	V_{O3} (v.u.)	V_{O} (v.u.)	$\delta[\text{LiO}_4] \times 10^{-4}$	$\delta[\text{SiO}_4] \times 10^{-4}$
940	1.378	3.504	2.087	1.702	2.057	1.949	129.488	36.737
960	1.303	3.656	1.974	1.868	2.211	2.018	128.720	25.345
980	1.382	3.621	2.044	1.808	2.301	2.051	123.399	31.297
1000	1.281	3.439	2.065	1.77	2.213	2.016	72.369	15.274
1020	1.291	3.397	1.973	1.676	2.078	1.909	67.439	11.526

To further assess the potential of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics for high-frequency applications, the optical and dielectric properties were characterized using terahertz time-domain spectroscopy (THz-TDS), as shown in Fig. S11, Figs. 4(f), and 4(g). All samples exhibit similar time-domain waveforms (Fig. S11(a)). With increasing sintering temperature, the main pulse shows a slight delay shift accompanied by an increase in amplitude, indicating subtle changes in the terahertz response of the ceramics (Fig. S11(b)). Correspondingly, the refractive index exhibits a slight decrease in the range of 0.5–0.8 THz, followed by a gradual increase from 0.8 to 1.5 THz (Fig. S11(c)). This weak frequency dependence reflects the dielectric dispersion of the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics in the terahertz frequencies. Meanwhile, the

extinction coefficient increases gradually within the 0.5-1.5 THz range (Fig. S11(d)), indicating enhanced absorption loss at higher frequencies. As shown in Fig. 4(f), the ϵ_r value shows a similar dispersive trend to the refractive index, which is related to the intrinsic dielectric dispersion caused by polarization processes under terahertz excitation. Given the small fluctuation amplitude ($< 2\%$), the dielectric properties at 1 THz were selected for comparison with the microwave dielectric data. As shown in Fig. S11(e), the ϵ_r values measured in the microwave and terahertz ranges show a consistent variation trend with sintering temperature. However, the ϵ_r values at 1 THz (4.64–4.73) are slightly lower than those in the microwave range (4.72–4.86). This reduction arises from the suppression of ionic and electronic relaxation polarization with increasing frequency, leading to a diminished contribution in the THz range [58]. Fig. 4(g) shows the dielectric loss of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics in the terahertz frequency range. The $\tan\delta$ values gradually increase with increasing frequency from 0.5 to 1.5 THz, indicating enhanced dielectric absorption loss at higher terahertz frequencies. The corresponding $Q \times f$ values were further estimated by fitting the dielectric loss curves using a classical dispersion model. Notably, the $Q \times f$ values of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics in both the microwave and terahertz ranges show a similar dependence on sintering temperature, with the maximum values obtained at 960 °C ($105,420 \pm 366$ GHz at 19.5 GHz and 175,131 GHz at 1 THz). To avoid the influence of frequency dependence inherent in the $Q \times f$ parameter, Fig. S11(f) and Table S5 further compare the dielectric loss tangent ($\tan\delta$) of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics in the microwave and terahertz frequency ranges. The results show that all ceramics exhibit higher dielectric losses at 1 THz than those measured in the microwave region, which can be mainly attributed to enhanced intrinsic lattice vibration responses and phonon-related absorption processes at terahertz frequencies. Nevertheless, $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics maintain stable and relatively low $\tan\delta$ values over the range of 0.5–1.5 THz, indicating that their low-loss dielectric characteristics can be extended into the terahertz region. Further analysis suggests that dielectric loss in terahertz frequencies is more strongly governed by intrinsic lattice vibration and phonon absorption mechanisms, whereas microwave dielectric loss is affected by both intrinsic damping and extrinsic

microstructural contributions, including porosity, abnormal grain growth, and defect-related scattering.

Therefore, $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics exhibit stable low-loss dielectric characteristics over a broad frequency range from microwave to terahertz frequencies, highlighting their potential for broadband high-frequency dielectric applications.

Fig. 4(h) compares representative microwave dielectric ceramic systems with $\epsilon_r < 8$, providing a general overview of the relationship between sintering temperature and dielectric properties among different low-permittivity materials. Considering the differences in measurement frequencies reported in various studies, these data are intended to reveal general performance trends rather than provide a strict quantitative comparison. Phosphates exhibit low sintering temperature ($< 1000\text{ }^\circ\text{C}$) but universally show $\epsilon_r > 5$, insufficient for terahertz applications requiring ultra-low permittivity. Conventional silicates and cordierite-based ceramics typically achieve low ϵ_r (4~5) and high $Q \times f$ values, yet their excessive sintering temperatures ($> 1200\text{ }^\circ\text{C}$) preclude co-firing with low melting point metal electrodes (such as Ag, Cu), severely limiting their practical deployment in LTCC technology. In contrast, Li-based silicates, particularly $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics developed in this work, demonstrate a favorable combination of low permittivity, high quality factor, and low-temperature sinterability. $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics sintered at $960\text{ }^\circ\text{C}$ exhibit excellent dielectric performance at microwave frequencies: $\epsilon_r = 4.86 \pm 0.01$, $Q \times f = 105,420 \pm 366\text{ GHz}$, $\tau_f = -24.84 \pm 1.0\text{ ppm}/^\circ\text{C}$, enabling potential compatibility with Ag electrodes co-firing and indicating their suitability for LTCC applications. More importantly, $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics have an exceptionally high $Q \times f$ value at THz frequencies (175,131 GHz at 1 THz), suggesting their potential advantages for high-frequency applications. These findings suggest that $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics can be an ideal candidate material for next-generation high-frequency electronic devices, including terahertz waveguides, antennas, and 6G communication devices.

Additionally, the P-V-L bond theory is widely recognized as a pivotal tool for elucidating the intrinsic structure-property relationship in microwave dielectric properties, where the ϵ_r , $Q \times f$ value,

and τ_f value are closely correlated with the ionicity (f_i), lattice energy (U), and bond energy (E) of chemical bonds, respectively [60]. According to crystallographic data and the complex chemical bond theory, $\text{Li}_2\text{Si}_2\text{O}_5$ complex crystals could be decomposed as follows:

$$\begin{aligned} \text{Li}_2\text{Si}_2\text{O}_5 = & \text{Li}_{1/2}\text{O1}(1)_{1/2} + \text{Li}_{1/2}\text{O1}(2)_{1/2} + \text{Li}_{1/2}\text{O1}(3)_{1/2} + \text{Li}_{1/2}\text{O2}_{2/3} + \text{Si}_{1/2}\text{O1}_{1/2} \\ & + \text{Si}_{1/2}\text{O2}(1)_{2/3} + \text{Si}_{1/2}\text{O2}(2)_{2/3} + \text{Si}_{1/2}\text{O3} \end{aligned} \quad (19)$$

Detailed calculations of intrinsic bond parameters and the corresponding performance correlation equations are provided in the ESM. Figures 5(a-c) reveal the contributions of various chemical bonds to f_i , U , and E in the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic sintered at 960 °C. The Si–O bonds make the dominant contribution to these parameters, which highlights the essential role of the rigid silicate network in maintaining the structural framework and governing the intrinsic dielectric response of $\text{Li}_2\text{Si}_2\text{O}_5$. Notably, although the Si–O3 bond contributes most significantly to the total ionicity, its variation with sintering temperature is relatively limited (Fig. 5(d)). In contrast, the ionic contribution associated with the Li–O1 bond f_i (Li–O1) exhibits a significant temperature sensitivity, indicating that the local Li-site bonding environment is more sensitive to structural evolution during sintering. This is consistent with the phenomenon that Li atoms deviate from the tetrahedral center position as the sintering temperature increases. This trend is consistent with the evolution of ϵ_r shown in Fig. 5(g), suggesting that the Li–O1 bond plays a key role in modulating the permittivity. The lattice energy analysis in Fig. 5(e) shows the following order of bond contributions: $U(\text{Si–O1}) > U(\text{Si–O2}) > U(\text{Si–O3}) > U(\text{Li–O1}) > U(\text{Li–O2})$. Among these bonds, $U(\text{Si–O2})$ displays the strongest correlation with the variation in $Q \times f$ (Fig. 5(h)), indicating that the Si–O2 bond is a critical structural unit for influencing the intrinsic dielectric loss. Meanwhile, Fig. 5(f) reveals that the Si–O3 bond possesses the highest bond energy (330 kJ/mol). Fig. 5(i) shows the variations in E_{total} , $E(\text{Si–O3})$, and τ_f with sintering temperature. Below 980 °C, E_{total} exhibits a positive correlation with τ_f . With increasing bond energy, especially $E(\text{Si–O3})$, the Si–O bonding is strengthened, enhancing the structural stability and promoting the shift of τ_f toward zero. However, when the sintering temperature is further increased, the E_{total} decreases

slightly, whereas τ_f continues to increase, indicating that bond energy is not the sole factor governing τ_f at higher sintering temperatures. Combined with the Rietveld refinement results and bond valence analysis, the displacement of Li atoms induced by high-temperature sintering is accompanied by reduced local tetrahedral distortion and a weakened "compressed" effect of the Li cation, both of which are favorable for the further improvement of τ_f . A similar phenomenon has also been reported in the $(\text{Ce}_{1-x}\text{Ca}_x)(\text{Nb}_{1-x}\text{W}_x)\text{O}_4$ ceramic [53]. Thus, the evolution of τ_f in $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics is due to the synergistic effects of chemical-bond characteristics, local structural distortion, and thermal-expansion behavior. Overall, the P-V-L analysis demonstrates that different chemical bonds play distinct roles in determining the microwave dielectric properties of $\text{Li}_2\text{Si}_2\text{O}_5$. The Li–O1 bond mainly influences ε_r through its contribution to lattice polarization, whereas the Si–O bonds, particularly Si–O2 and Si–O3, regulate $Q \times f$ and τ_f values by controlling framework rigidity, phonon behavior, and thermal stability. These findings offer structural guidance for the compositional design and performance optimization of LTCC materials.

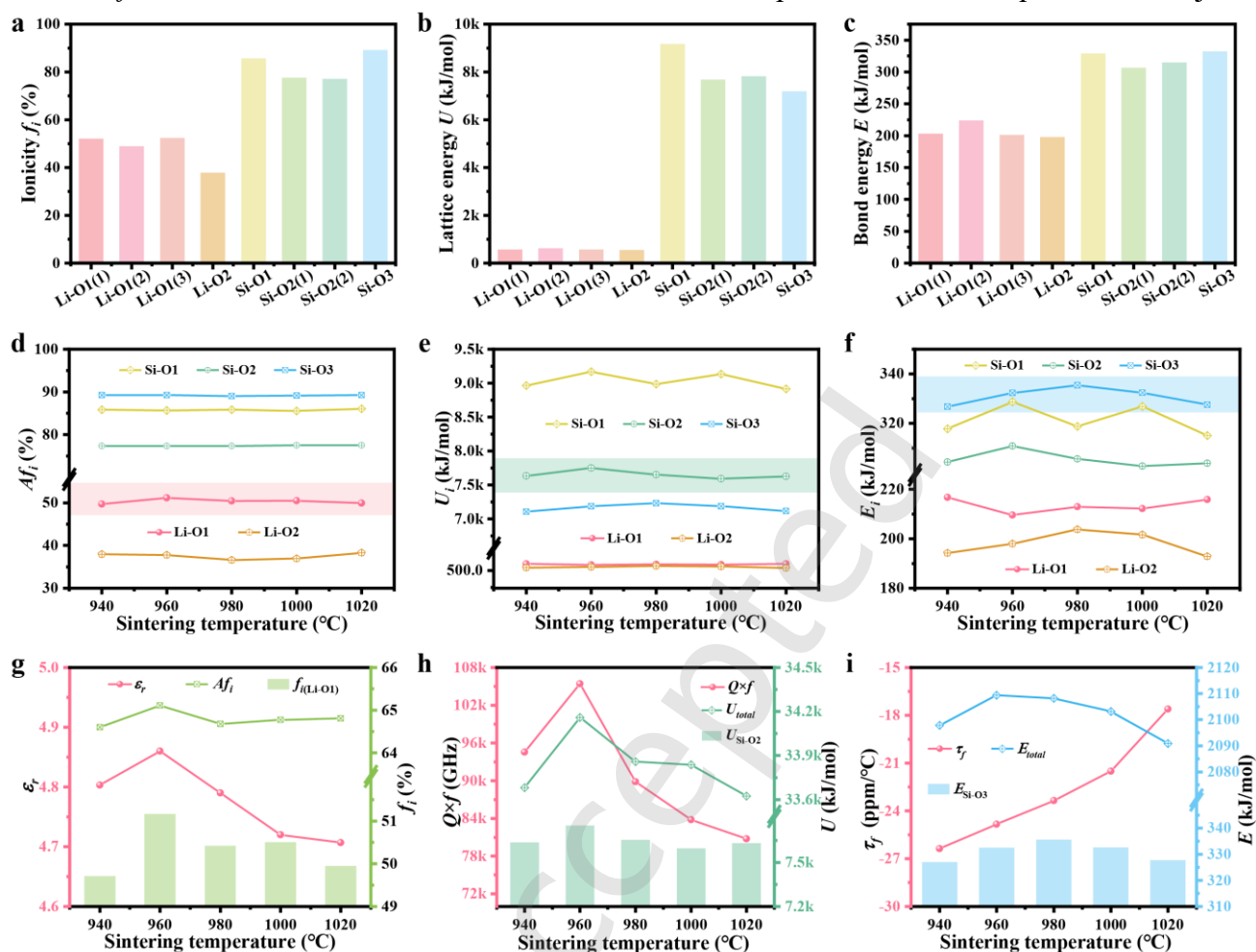


Fig.5 Structure-property relationship of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. Contributions of various chemical bonds in the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic sintered at 960°C to (a) ionicity (f_i), (b) lattice energy (U), and (c) bond energy (E). (d-f) Influence of sintering temperature on the f_i , U , and E of different chemical bonds. (g-i) Relationships between f_i , U , E , and microwave dielectric properties, highlighting the roles of Li-O and Si-O bonds in influencing ϵ_r , $Q \times f$, and τ_f values.

To further clarify the intrinsic structure-property relationship governing the microwave dielectric properties of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics, a schematic illustration of the proposed mechanism is presented in Fig. S12. As shown in Fig. S12, $\text{Li}_2\text{Si}_2\text{O}_5$ exhibits a highly polymerized Si-O covalent framework, where corner-sharing $[\text{SiO}_4]$ tetrahedra form corrugated $[\text{Si}_2\text{O}_5]^{2-}$ layers and Li^+ ions occupy the interlayer sites. This unique structural configuration integrates a rigid covalent network, layered

topology, and ordered microstructure, which collectively regulate dielectric polarization and dielectric loss.

From the perspective of dielectric polarization, the highly polymerized Si–O framework plays a dominant role in achieving a low ϵ_r . The strong covalent Si–O bonds and low ionic polarizability of Si^{4+} effectively suppress ionic displacement polarization under an external electric field. Meanwhile, the layered structure further limits local atomic displacement and polarization fluctuations. It should be noted that the layered structure alone is insufficient to achieve low ϵ_r ; rather, the combination of a rigid, low-polarizability covalent framework and a constrained crystal structure is essential for reducing dielectric polarization. In addition, the "compressed" effect of Li^+ ions may decrease the effective ionic polarizability, further contributing to a low ϵ_r according to the Clausius-Mossotti relationship.

The high $Q \times f$ value is attributed to the synergistic suppression of both intrinsic and extrinsic dielectric losses. Intrinsically, the rigid Si–O covalent framework provides high bond strength, large lattice energy, and excellent lattice rigidity, thereby suppressing anharmonic lattice vibrations and reducing phonon-related dielectric dissipation. Moreover, the relatively low distortion of the $[\text{SiO}_4]$ tetrahedra and the narrow Raman FWHM indicate a highly ordered local structure with reduced vibrational disorder, which is favorable for minimizing lattice scattering and intrinsic dielectric loss. Although the Raman FWHM is not a direct measure of phonon lifetime, a narrow FWHM provides strong evidence for suppressed anharmonic scattering. Extrinsically, the interlocked layered grain morphology promotes densification and reduces pores and structural defects, thereby decreasing extrinsic losses associated with defect relaxation and electromagnetic scattering.

Overall, the low ϵ_r and high $Q \times f$ in $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics rely on the synergistic optimization of three structural aspects: (i) a highly covalent and low-polarizability framework for suppressing dielectric polarization; (ii) a layered crystal topology for restricting atomic displacement and lattice vibration; and (iii) a highly ordered and dense microstructure for reducing both intrinsic and extrinsic dielectric

losses. This structure-property relationship provides useful guidance for designing low-loss layer silicate ceramics. Nevertheless, further atomic-scale investigations, including STEM-HAADF, synchrotron diffraction, and first-principles calculations, are required to validate the universality of this mechanism and provide deeper insight into polarization and lattice-vibration behavior.

With the rapid development of 5G and emerging 6G communication technologies, low- ϵ_r microwave dielectric ceramics are required to combine excellent dielectric performance with sufficient mechanical robustness for reliable high-frequency packing applications. Therefore, the flexural strength, fracture toughness, hardness, and elastic modulus of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics were systematically evaluated. As shown in Figure 6(d), all samples exhibit high flexural strengths of 249.63 ± 3.0 – 320.72 ± 5.0 MPa, with the strength initially increasing and then decreasing as the temperature increases. This trend is mainly associated with the microstructural changes induced by sintering. Enhanced densification and a homogeneous microstructure at 960 °C reduce defects and improve the load-bearing capability, whereas excessive sintering above 1000 °C promotes abnormal grain growth and pore formation, leading to stress concentration and strength degradation. The fracture-surface SEM images further support this interpretation (Figs. 6(a-c)). The sample sintered at 960 °C presents a dense and continuous interlocking layered grain microstructure with limited microcracks and minor grain pull-out features. This optimized microstructural configuration improves load-transfer efficiency and reduces stress concentration caused by residual pores, which is consistent with its maximum flexural strength (Fig. 6(a)). By contrast, the sample sintered at 1020 °C exhibits a loosened lamellar arrangement with increased pore defects, which provide preferential sites for crack initiation and propagation, leading to strength deterioration (Fig. 6(b)). Furthermore, the fracture surfaces reveal that the interlocking layered grains effectively alter crack propagation paths. For the sample sintered at 960 °C, the enhanced fracture toughness mainly originates from energy dissipation via grain pull-out (Fig. 6(a)). In contrast, the sample sintered at 1020 °C exhibits a higher density of cracks, which preferentially propagate along the layered grain interfaces and are accompanied by pronounced crack

deflection and branching. These crack propagation behaviors effectively extend the crack propagation path and enhance energy dissipation during fracture. However, the increased formation of pores and microcracks at the higher sintering temperature partially offsets the toughening effect, leading to a fracture toughness of $2.25 \pm 0.07 \text{ MPa}\cdot\text{m}^{1/2}$, which is slightly lower than that of the sample sintered at 960°C ($2.49 \pm 0.06 \text{ MPa}\cdot\text{m}^{1/2}$). Furthermore, Fig. 6(f) presents the load-displacement curves obtained from nanoindentation measurements across all samples, and the corresponding hardness and elastic modulus values calculated from these curves are shown in Fig. 6(g). Notably, the hardness and elastic modulus exhibit similar trends, both increasing initially and then decreasing with increasing sintering temperature. The maximum values were obtained for the sample sintered at 960°C , with a hardness of $8.34 \pm 0.05 \text{ GPa}$ and an elastic modulus of $118.13 \pm 1.0 \text{ GPa}$. This improvement can be attributed to the enhanced densification, homogeneous microstructure, and reduced porosity achieved at this temperature. However, further increases in sintering temperature induced abnormal grain growth, leading to the deterioration of the mechanical properties. Additionally, Fig. 6(h) compares the density and flexural strength of previously reported ceramics, glass-ceramics, and ceramic/glass composites. $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics achieve a low density of $2.38 \pm 0.01 \text{ g/cm}^3$ while maintaining superior mechanical strength, outperforming many reported lightweight ceramic systems. Moreover, compared with commercial LTCC substrates (Fig. 6(i)), $\text{Li}_2\text{Si}_2\text{O}_5$ simultaneously exhibits a low ϵ_r (< 5) and a high flexural strength ($> 230 \text{ MPa}$), demonstrating a favorable balance between dielectric and mechanical properties and indicating its potential as a lightweight dielectric candidate for high-frequency applications. The specific performances of the comparison systems are detailed in Table S6 and Table S7. Additionally, Table S8 summarizes the fracture toughness values reported in the literature for LTCC substrate materials and glass-ceramics, which generally fall within the range of $1\text{--}2 \text{ MPa}\cdot\text{m}^{1/2}$. In comparison, the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic developed in this work exhibits a fracture toughness exceeding $2 \text{ MPa}\cdot\text{m}^{1/2}$, indicating good resistance to crack propagation while maintaining high flexural strength. The enhanced fracture resistance is primarily attributed to the interlocking plate-like grain structure,

which promotes crack deflection and branching and thereby increases energy dissipation during fracture. Nevertheless, it should be noted that differences in testing methods may introduce variations in the measured fracture toughness values.

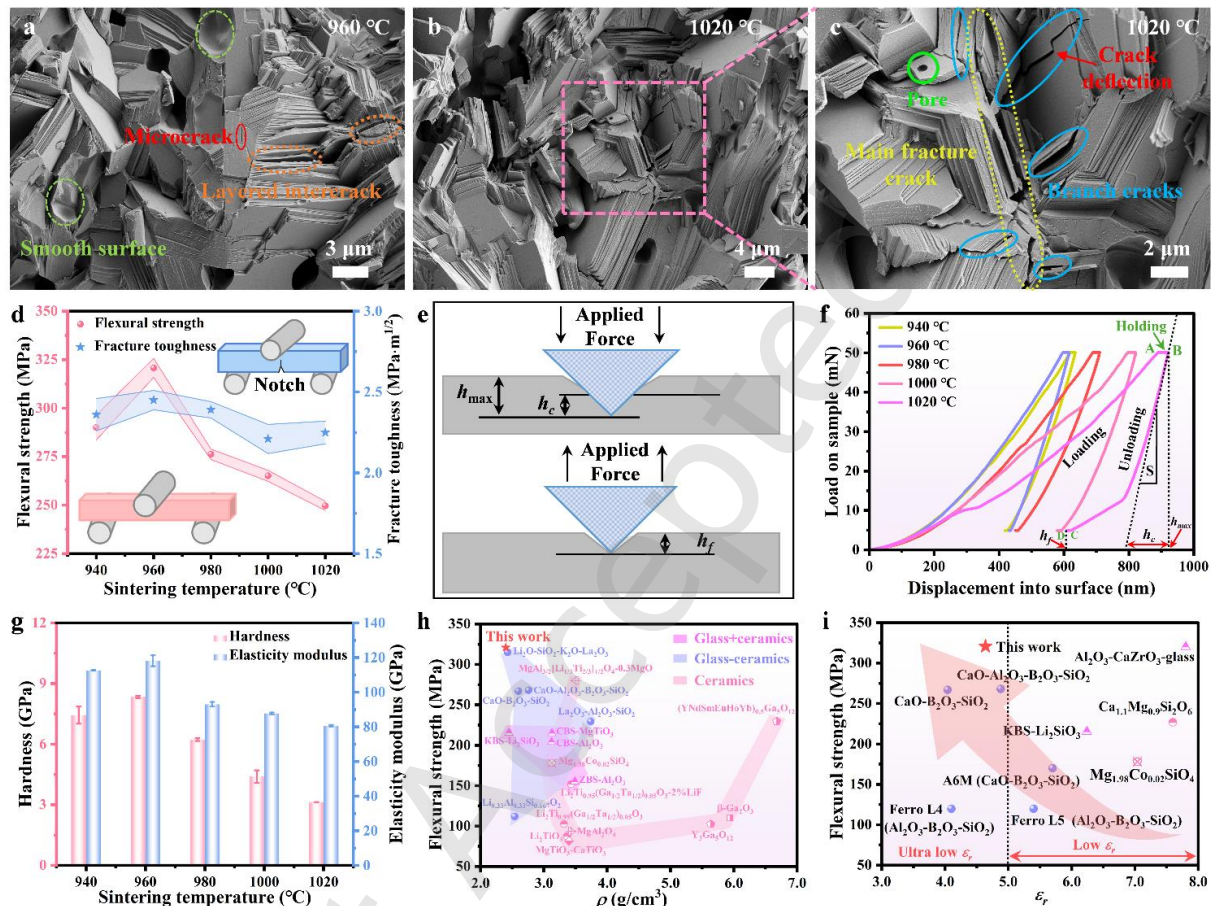


Fig.6 Analysis of the mechanical properties of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic. SEM images of the $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic fracture surface after a three-point bending test: (a) 960 °C, (b) 1020 °C, (c) magnified view of the crack in (b). (d) Flexural strength and fracture toughness. (e) Schematic diagram of the nanoindentation test. (f) Nanoindentation load-displacement curves. (g) Nano hardness and elastic modulus. (h) Comparison of density and flexural strength among glass-ceramics, ceramics, and glass/ceramic composite systems. (i) Comparison of flexural strength in low ϵ_r systems.

Overall, $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics exhibit excellent microwave dielectric properties, superior mechanical performance, light weight, and low cost. However, their relatively high sintering temperature limits practical applications. To meet the requirements of low-temperature co-firing and electrode compatibility in LTCC technology, a low-melting-point sintering additive of LiF was introduced to

reduce the densification temperature of $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. Fig. S13(a) presents the XRD pattern of the $\text{Li}_2\text{Si}_2\text{O}_5+1$ wt% LiF ceramic sintered at 900 °C for 4 h. The sample maintained the single-phase $\text{Li}_2\text{Si}_2\text{O}_5$ structure without detectable LiF-related secondary phases, indicating that the small amount of LiF did not alter the phase composition of the ceramic matrix. Instead, LiF mainly promoted densification through a liquid-phase-assisted sintering mechanism, facilitating particle rearrangement, mass transport, and grain boundary diffusion. As shown in Fig. S13(b), the $\text{Li}_2\text{Si}_2\text{O}_5+1$ wt% LiF ceramic exhibited a relatively dense microstructure after sintering at 900 °C, confirming the effectiveness of LiF in enhancing low-temperature densification. To evaluate its feasibility for LTCC applications, the $\text{Li}_2\text{Si}_2\text{O}_5-1$ wt% LiF ceramic was co-fired with Ag electrodes at 900 °C. As shown in Fig. S13(a), only the characteristic diffraction peaks of $\text{Li}_2\text{Si}_2\text{O}_5$ and Ag were observed in the co-fired sample, with no additional phases detected, demonstrating the excellent chemical compatibility between the ceramic matrix and Ag. Cross-sectional SEM images and EDS elemental mappings (Figs. S13(c-h)) revealed a continuous and well-bonded interface between the Ag electrode and ceramic substrate, without any obvious reaction layer. Moreover, Ag was mainly confined to the electrode region, and no noticeable Ag diffusion into the ceramic matrix was observed, further confirming the excellent co-firing compatibility of this ceramic system. The slight fluctuation of Si signals in the Ag region during line scanning (Fig. S13(i)) is attributed to the mechanical effects during sample preparation, where locally detached layered $\text{Li}_2\text{Si}_2\text{O}_5$ grains may have adhered to the Ag surface, rather than Ag diffusion into the ceramic.

Furthermore, the $\text{Li}_2\text{Si}_2\text{O}_5-1$ wt% LiF ceramic exhibited an ε_r of 4.72 and a $Q \times f$ of 94,600 GHz. Although these values decreased slightly compared with those of the pristine $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic, the dielectric properties remained suitable for microwave device applications. Considering its low sintering temperature of 900 °C, excellent Ag co-firing compatibility, and favorable microwave dielectric performance, the $\text{Li}_2\text{Si}_2\text{O}_5-1$ wt% LiF ceramic demonstrates significant potential for LTCC applications.

To further evaluate this potential, a 2.45 GHz microstrip patch antenna was designed using $\text{Li}_2\text{Si}_2\text{O}_5+1 \text{ wt\% LiF}$ ceramic ($\epsilon_r = 4.72$, $\tan\delta = 2.01 \times 10^{-4}$) as the substrate and Ag as both the radiating patch and microstrip feed line. The antenna geometry and dimensions are shown in Figure 7(a), while Figs. 7(b) and 7(c) present the simulated co-polarized and cross-polarized radiation patterns. As shown in Fig. 7(d), the antenna exhibits a return loss (S_{11}) of -41.24 dB, with a voltage standing wave ratio (VSWR) close to 1 at 2.45 GHz, demonstrating excellent impedance matching and low reflection loss. Furthermore, the antenna achieves a gain of 5.60 dBi and a radiation efficiency of 90.64% at 2.45 GHz (Fig. 7e), confirming efficient electromagnetic energy conversion and good radiation performance. These simulation results demonstrate the preliminary feasibility of $\text{Li}_2\text{Si}_2\text{O}_5+1 \text{ wt\% LiF}$ ceramics as microwave substrate candidates. However, further optimization of τ_f and experimental verification using fabricated antenna prototypes are required before practical LTCC applications.

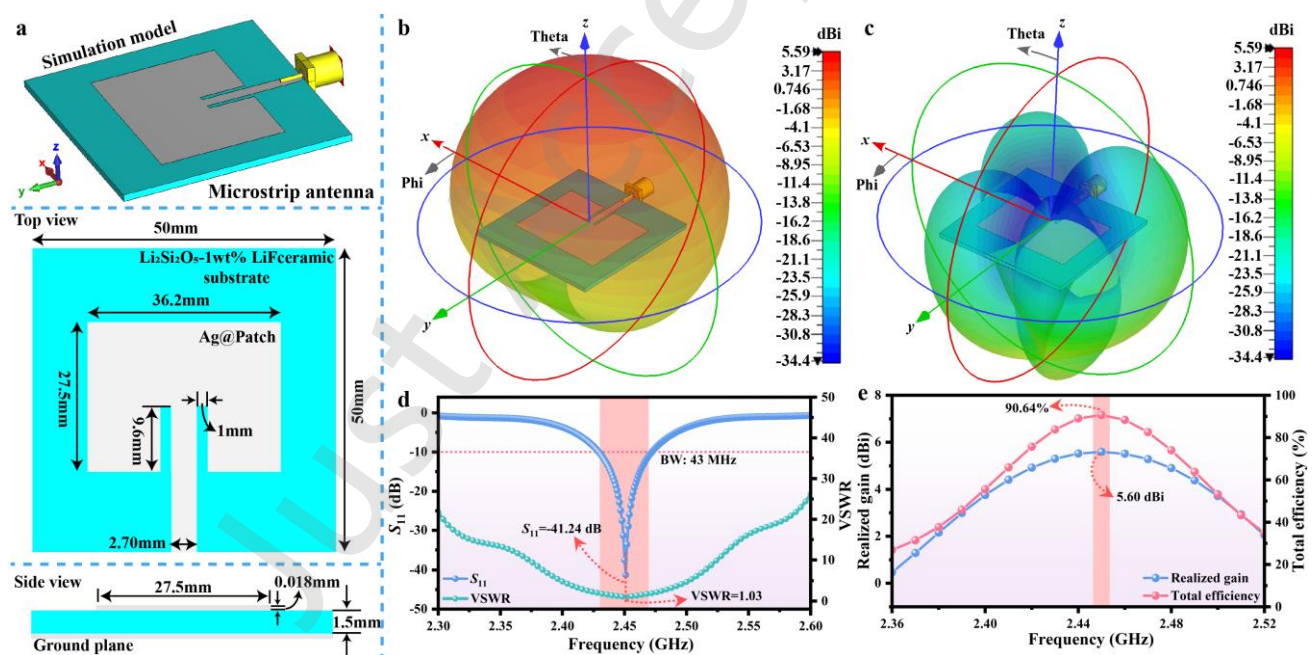


Fig.7 Simulation structure and results of a microstrip antenna. (a) Geometric structure of the rectangular microstrip antenna, including top and side views of the simulation model. 3D radiation patterns of co-polarization (b) and cross-polarization (c) at 2.45 GHz. (d) S_{11} and VSWR parameters. (e) Realized gain and radiation efficiency of the antenna.

4 Conclusions

In summary, single-phase $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics with an orthorhombic $Ccc2$ structure were successfully synthesized through an experimental design. The crystal structure consists of stable K4-4 clusters constructed from L-T-L-T rings, while the ceramics exhibit a unique interwoven layered microstructure. Benefiting from the synergistic contribution of this crystal structure and microstructural architecture, $\text{Li}_2\text{Si}_2\text{O}_5$ achieves an attractive balance between low permittivity and high mechanical performance. The optimized $\text{Li}_2\text{Si}_2\text{O}_5$ ceramic sintered at 960 °C exhibits excellent microwave and terahertz dielectric properties, including a low permittivity ($\epsilon_r = 4.86 \pm 0.01$), high $Q \times f$ values ($105,420 \pm 366$ GHz at 19.5 GHz and $175,131$ GHz at 1 THz), and a moderate $\tau_f = -24.84 \pm 1.0$ ppm/°C. Concurrently, it demonstrates superior mechanical properties, with a high nano-hardness of 8.34 ± 0.05 GPa, an elastic modulus of 118.13 ± 1.0 GPa, a flexural strength of 320.72 ± 5.0 MPa, and a fracture toughness of 2.49 ± 0.06 MPa·m^{1/2}. The ceramic also shows good thermal stability, with a relatively low CTE of 7.66–10.55 ppm/°C from 30 to 350 °C. Furthermore, the intrinsic structure–property relationship was established based on the P–V–L theory. The results suggest that Li–O bonds are mainly responsible for modulating ϵ_r , whereas the Si–O bond plays a dominant role in intrinsic dielectric loss and τ_f . This provides guidance for further optimizing $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics. To evaluate practical applicability, a 2.45 GHz microstrip patch antenna based on the $\text{Li}_2\text{Si}_2\text{O}_5 + 1$ wt% LiF ceramic was designed and simulated, achieving a radiation efficiency of 90.64%, a gain of 5.60 dBi, and good impedance matching. These results demonstrate that $\text{Li}_2\text{Si}_2\text{O}_5$ ceramics, featuring low cost, environmental compatibility, low density, excellent dielectric properties, and reliable mechanical performance, are promising substrate materials for high-frequency LTCC applications.

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Author contributions

Yanwei Huang: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Biao Yi:** Software, Software. **Xiuhong Yang:** Supervision, Resources. **Yingchun Zhang:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material (ESM)

Supplementary figures (Fig.S1-S13), tables (Table S1-S8), and P-V-L theory are available in the online version of this article.

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